Groundwater Quality – Measurement, Prediction and Protection

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CONTENTS

PREFACE

The surface layers of soil and the unsaturated and saturated zones of an aquifer have a considerable capacity for improving the quality of infiltrating water. As a consequence groundwater has long been used by water engineers as a good quality inexpensive source of supply and has accordingly been extensively developed. In recent years, however, an increasing number of cases of deterioration in quality have been reported. There are many reasons for this decline but common causes are badly located domestic and industrial waste disposal sites, certain modern agricultural practices, and over-pumping of resources. As groundwater in general moves very slowly, extensive pollution of an aquifer may develop and go unnoticed for many years. Once polluted it is always difficult and costly to rehabilitate a groundwater source. A growing awareness of these problems has led in recent years to an increasing number of field investigations and research studies into the natural and man-made changes that can occur in the quality of groundwater. Attention has particularly focused on man's activities that have caused or are likely to cause pollution and on ways in which these can be controlled so as to protect underground resources. In the United Kingdom the scientific investigations have been accompanied by appropriate and timely legislation in the form of the Deposit of Poisonous Wastes Act 1972 and the Control of Pollution Act 1974. These, together with previously existing legislation, should allow the authorities to protect adequately our valuable groundwater reserves. Within the European Economic Community a commission is drawing up proposals for a directive on the protection of underground water against pollution caused by the discharge of dangerous substances.

It was against this background that the Water Research Centre arranged the Groundwater Quality - Measurement, Prediction and Protection Conference at Reading in September 1976. Although the majority of participants were from the United Kingdom we were fortunate in having many overseas delegates and in all 20 countries were represented. The conference attracted groundwater scientists and engineers as expected, but it was encouraging that several engineers with waste disposal responsibilities, and agricultural scientists were also present.

The 44 papers and six discussions presented in this volume have been grouped into six sections. The first section contains papers that identify the principal groundwater quality problems facing the engineer or scientist. In the second section the physical, chemical and biological processes that govern the changes in groundwater quality are described. The type, method, frequency and cost of data that should be collected is discussed in the third section which leads into a description of field case studies in the fourth section. Models are being increasingly used to quantify changes in groundwater quality or to increase the understanding of a given system. The models used range from the relatively simple to the very complex. Although in many cases inadequate data would at present preclude the use of other than a simple model, it was considered necessary to bring these new techniques to the attention of the Conference. The fifth section therefore contained papers describing a range of groundwater quality models, modelling techniques and case histories. The measures that may be adopted to protect and rehabilitate aquifers are discussed in the sixth section. All the scientific and engineering depth of knowledge and experience goes for little if the administrators and legislative procedures are inadequate; these aspects are therefore also considered in this section.

Much remains to be done, but I believe that the assembly of papers and discussions presented in these Proceedings represents a step forward in understanding and controlling the factors which govern the quality of groundwater.

W. B. Wilkinson
Technical Editor.
Medmenham, September 1977

Session 1

GROUNDWATER QUALITY AND THE NEED TO MAKE PREDICTIONS

Chairman:

B. J. Hardcastle, BSc, ACGI, DIC, FICE,
FIWES, MIMechE,
Divisional Manager,
Thames Water Authority.

Presented Papers:

PAPER 1

UTILIZATION OF GROUND WATER IN BRITAIN

G. P. Jones

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1. INTRODUCTION

The subject matter of this paper provides little scope for originality in what is largely a documentary exercise, yet some such coverage is necessary to set the context for those topics to be covered in the Symposium. It seems all too obvious to make the point that the geological character of a country or area largely determines the type and pattern of its water-supply sources. Nevertheless, an understanding of the past, present and future utilization of ground water resources in Britain requires some appreciation of the distribution and nature of the relevant geological factors.

2. GEOLOGY

Britain is a small country of diverse geology, with representatives of all periods of geological time from before the Cambrian up to the Pleistocene. Within this incredibly long duration of more than 500 million years, deposition of sediment took place in a wide variety of fresh water and marine environments ranging from hot tropical swamps, deserts with salt pans, through marine seas to those associated with glacial conditions. Most of the resultant deposits were subsequently modified by a variety of geological processes. Moreover, the position of the country relative to geological events during this length of geological time has ensured that the strata have been variously affected by different degrees of folding and fracturing arising out of major and minor episodes of disturbance.

It means that in Britain we have a plethora of sedimentary rocks of different nature along with an interesting variety of rocks of igneous or metamorphic origin. One cannot do justice in a single map of the country as a whole to the complexity of geological units categorized either on the basis of lithological nature or geological time. Since the erstwhile Geological Survey was created for the explicit purpose of preparing a complete coverage of the country, we are fortunate in having relatively detailed maps on the scale of 1:10 000, 1:25 000 or 1:63 600 for most areas that are of economic significance. The fact that such a task is not yet complete indicates the enormity of the exercise which is the direct consequence of the non-uniform character of the ground conditions.

3. HYDROGEOLOGY

The acquisition of basic geological information and its translation into hydrogeologic form is an essential prerequisite to the proper utilization of ground water resources. Fundamental to this aim is the concept of relative permeability within any aquifer system with emphasis on those hydraulic properties and characteristics which significantly govern the quantity and quality of ground water. In strata where the flow pattern is dominantly interstitial, ground water velocities may range from 2 m/day to 2 m/year or less. Whereas in fractured strata, particularly where preferential solution has occurred, the dominantly fissure flow regime may allow flow rates to exceed 2000 m/day. Generally in Britain, the uppermost 100 metres of the saturated aquifer is the most productive, with increasing risks of lower permeability and poorer quality as one goes deeper.

It is the particular character of the ground conditions that determines which of the manyfold functions of an aquifer system may be operating. One would therefore expect the relative importance of intake area, conduit, reservoir and treatment plant to change from aquifer to aquifer, or even from one part of an aquifer to another part. Some or all of these functions are fulfilled in the many geological units in Britain that may be regarded as aquifers. These are arranged in Table 1 in order of relative importance, along with some indication of their characteristics. It is of interest, and pertinent to the subject matter of this Symposium to note that one of the three major British aquifers, the Coal Measures, is not commonly used for potable supply purposes.

Taken together, it is estimated that these aquifers underlie more than 2×10^5 km^2 (7.5×10^4 ml^2) of the country, with the important qualification that a significantly large part is overlain by materials (consolidated or unconsolidated) that behave as aquicludes in restricting replenishment or water movement. Furthermore, a large proportion of the aquifers beneath cover are occupied by saline water.

The diversity of geological units and their structural complexities provide us, in Britain, with a legacy of hydrogeological conditions that, modern scientific methods not withstanding, makes accurate prediction of responses exceedingly difficult. As if the situation was not difficult enough, our long coastline intersects many of the aquifers and further complicates their use by introducing the risk of sea-water intrusion.

The individual components of the circulation of water above, on and beneath the land surface have long been studied, though their essential interrelationship is a matter of relatively recent acceptance. Once development of a ground water supply is initiated in any area, the hydrological cycle is necessarily modified, and if such development is to continue then further artificial modification is inevitable. Enough information has been gathered on a national and international basis to allow some anticipation of the consequences of such changes which are as much concerned with quality as with quantity.

4. GROUND WATER SUPPLIES

Although the preceding comments have applied to Britain as a whole, the substance of the present section is restricted to England and Wales by virtue of the lack of readily available data from Scotland and Northern Ireland in a form suitable for comparative purposes. Given the nature of the geology, topography and climate over most of Scotland and Northern Ireland, one might expect a pattern of ground water development and utilization more in accord with that in Wales where less than ten per cent of the total supply is derived from ground water.

4.1. ABSTRACTION

The overall amount of ground water abstracted in Britain relative to the total water requirements is very much smaller than that of many countries in Europe. For example, total licensed ground water abstraction in England and Wales in 1967 and again in 1969 made up only 11 per cent of all licensed abstractions, though Ineson (1970) and Downing (1971) suggest that if one excludes the large quantities of water taken by the Central Electricity Generating Board for cooling purposes, then ground water licenses account for about 25 per cent of the total.

Reliance on values of licensed abstraction may be misleading to the extent that although they represent the maximum allowable abstraction, it is nonetheless a common occurrence for the quantities actually abstracted to be less than half the licensed amounts. Accordingly, a breakdown has been undertaken of the most recently available data, namely 1974, under the categories of both licensed quantities and actual abstraction, as well as including and excluding the CEGB demands. The results are presented in Table 2 which shows only slight increases in the percentage of total licensed ground water abstraction, with the anticipated higher percentage for actual ground water abstraction. If the criteria of the mean total percentage be adopted as an arbitrary boundary then the regional water authority areas can be classified into two divisions with respect to ground water abstraction, and there will be no surprise regarding the composition of the divisions. The table emphasizes just how much regional variation there is from the national mean, and confirms what would have been expected given the geological constraints mentioned previously.

One should not read too much into the results, which suffer from the usual inadequacies of simple percentage expressions. However, Figure 1 goes part of the way to presenting a more balanced version by considering actual quantities of ground water abstraction on a regional basis including and excluding CEGB requirements. In no way does it confirm the order of ranking based on percentage of abstraction , though Thames, Severn-Trent, Southern and Anglia remain in the group of larger ground water abstractors, with North-West displacing Wessex. No account has been taken of numbers of abstractors, size of authority region or degree of re-use, any of which could modify the results. Even so, it may be salutory for ground water hydrologists to note that the overall water requirements of the country as a whole and most of the regional authorities are largely met from surface water sources and will remain so for as far as one can see ahead into the future. More importantly, however, given the increasing modification of the hydrological cycle, the division into separate categories of surface-water and ground water abstractions will have increasingly less hydrological significance. Annual returns of ground water abstraction in England and Wales since implementation of the Water Act of 1945 are given in Table 3.

Up to 1963 there was a steady increase in abstraction at a rate of about 2 per cent per annum, though the reliability of the data may be judged from its rounding off to the nearest one million cubic metres. With the repeal in 1963 of Section 6 of the Water Act, 1945, the returns for 1964 were made on a purely voluntary basis and turned out to be far from complete with a resultant gap in the long term record. From 1965 onwards, returns of licensed ground water abstraction show an annual total that has remained more or less at or about 4000 million cubic metres. Actual abstraction over the same period is inevitably less, but that too has remained relatively steady just below 2500 million cubic metres in 1974.

5. USE

The regional use to which ground water was put in 1974 is summarized in Table 4 under the major categories of utilization. Public water supplies dominate in all regions except Wales where industry takes first place, while the South West is notable for agriculture and industrial use making up a more significant proportion of the total ground water abstraction than elsewhere.

The categories have changed over the previous twenty-five years so that a strict historical comparison is not possible though a breakdown by percentages has been attempted on a national basis in Table 5 for three individual years, namely 1948, 1967 and 1974. The use of ground water for public water supplies (including more than 10 per cent provision to other categories) has always dominated. This is possibly better illustrated in Figure 2 where, over the past twenty-four years, Public Supply abstraction may be seen to have increased markedly while Industry and Agriculture appear to have remained relatively unchanged in their requirements.

6. ADVANTAGES AND DISADVANTAGES

Having demonstrated the increased demand for and utilization of ground water, it might be opportune to consider the particular criteria that make it such an acceptable alternative to surface-water sources even in a country where so-called 'droughts' are the exception rather than the rule. Those of us who advocate greater utilization of ground water resources in Britain would do well to understand their limitations. Considered under the major headings of availability, quality and economics, there are both advantages and disadvantages to the use of ground water. The success or failure of any long-term development project depends on one outweighing the other, and particularly important is the recognition that any form of development upsets the dynamic equilibrium of the continuum. It follows that it is essential to know the prevailing hydrogeological conditions well enough to be able to predict the areal and temporal changes in quantity and quality likely to be brought about by any particular pattern of development.

Item	Advantages	Disadvantages
availability	vast resource large yields 'safe yield'	areally variable limitations of aquifer decline in yields limitations of replenishment
quality	constant potable biologically pure	areally variable liable to pollution
economics	low costs	many sources needed

7. UTILIZATION

7.1 PAST

The traditional development of ground water resources in Britain was centred in those areas having most favourable hydrogeological conditions, with competition by public water undertakings, industry and agriculture for the best sites with regard to quality, yield and centres of demand. Inevitably, there was an emphasis on potable waters with a concentration of source resulting in excessive declines of water levels. Ground water was considered as an individual component of the hydrological cycle with little or no regard for the consequences of its large scale abstraction on the related components, and even less for its disposal after use. Such practice exacerbated the natural constraints, so that falling water levels and a perceptible worsening of water quality became diagnostic features of unco-ordinated development.

7.2. PRESENT

Legislation introduced by the Water Resources Act, 1963, and revised and updated by the Water Act, 1973 allowed the creation of central and regional institutions operating within a co-ordinated framework to attempt management of the whole hydrological cycle. In particular these two acts were responsible for the formation and dissolution, respectively, of the Water Resources Board, which wielded much influence and contributed significantly to the growing importance of ground water. This was the decade of regulating reservoirs, conjunctive use, as well as consideration of artificial recharge and the use of ground water storage for deliberate but limited overdevelopment. Nevertheless, it appeared that only because of opposition to and repeated rejection of surface reservoir sites did ground water come to general favour with engineers. Be that as it may, during this period investigations into the potential of regional ground water development either for river regulation or direct abstraction increased from the Lambourn pilot scheme of the then Thames Conservancy to the list given in Table 6.

With the rapid increase in knowledge of regional variations in hydrogeological conditions within our aquifer systems, it became clear that large scale contamination of Chalk and Bunter aquifers by saline waters had already occurred along coasts and estuaries, as well as from migrating water in inland areas. Growing evidence of numerous small-scale local pollution due to industrial, agricultural and domestic sources of effluent and waste of many kinds demonstrated the risk to which ground water is susceptible in the absence of stringent control.

7.3 FUTURE

The potable fresh ground waters in British aquifers have finite limits and, therefore, an ultimate maximum yield to whatever regional combination of integrated use is utilized. One may anticipate further in the future a threefold development of increased use of subsurface storage by:

1) conventional ground water reservoirs containing potable waters with the formulation of operating rules to minimize problems of quality control;

2) non-conventional ground water reservoirs with brackish and less saline water used directly for irrigation or cooling, or blended with potable water to produce an acceptable mixture;

3) non-conventional ground water reservoirs with saline and highly mineralized waters for the temporary storage of large masses of less dense fresh water or alternatively for the disposal of toxic waste slurries.

8. CONCLUSIONS

1) Hydrogeological conditions in Britain are complex as a result of many factors including geological units of varying thickness, lithology, degree of fracturing, boundary conditions, partial cover of clay glacial drift, contained waters of different quality, and the relatively small size of both the aquifer systems and the country as a whole.

2) Ground waters include fresh, brackish, saline and contaminated waters; the non-potable waters are as much part of the water cycle as potable waters, and just as much in need of management.

3) Given the non-uniform distribution of demand and the pattern of past and present development, it seems clear that aquifer systems are under increasing stress.

4) Ground water is an integral but interrelated part of the hydrological cycle so that any form of development will affect related components to some degree.

5) Sophisticated management needs scientific techniques in order to identify and predict the consequences of continuing modification of the hydrological cycle, but the variable ground conditions will limit the precision of such predictions.

6) With the scale of development envisaged in Britain, ground water pollution is inevitable. Large-scale contamination has already occurred, but small-scale pollution from industrial, agriculture and domestic sources is likely to pose the most difficult problems in the future.

REFERENCES

DOWNING, R.A.	1971. Ground water management in England and Wales. Quart. J. Eng. Geol., 4(4), 328-334.
INESON, J.	1970. Development of ground water resources in England and Wales. J. Instn. Wat. Engrs., 24, 155-177.

TABLE 1 : British aquifers and some of their characteristics.

Rank	Aquifers	Age	Gross Lithology *	Dominant flow pattern **	Max. thickness (metres)	Typical yield (l/sec)
Major	Chalk	Cret.	lst, soft	I/F	500	150
	Coal Measures	Carb.	sst,mst	F	2000	-
	Bunter	Tri.	sst.	I/F	600	100
Intermediate	Lr. Greensand	Cret.	sst. soft	I	250	50
	Magnesian Lst.	Perm.	lst, hard	F	250	50
	Inf. Oolite	Jur.	lst,cl,sst.	F	200	50
	Keuper	Tri.	sst.	I/F	300	100
	Superf. Deposits	Rec.	s+gr.	I	10	-
	Carb. Lst.	Carb.	lst,hard	F	1000	150
Minor	Millstone Grit.	Carb.	sst.+sh	F	900	5
	Ur. Greensand	Cret.	sst.	I	50	25
	Wealden	Cret.	sands	I	250	10
	Gt. Oolite	Jur.	lst+cl.	F	50	50
	Lr.Lond.Tert.	Tert.	s+silts	I	50	25
	Crag	Plio-pl.	sands	I	50	10
	Lias	Jur.	sst.	I/F	50	25

Devonian, ORS, Culm Measures and Lr. Palaozoic strata also provide small yields from boreholes and springs.

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* lst limestone; sst. sandstone; mst mudstone; cl clay; sh shale; s sands; gr. gravels.

** I interstitial flow; F fissure/fracture flow

TABLE 2 : Regional annual abstraction of ground water expressed as a percentage of all water (surface and ground-water) abstraction for 1974.

Regional Water Authority	Licensed abstraction *%	Licensed abstraction **%	Actual abstraction *%	Actual abstraction **%
Southern	70	43	73	52
Anglian	47	37	54	43
Thames	46	39	47	42
Wessex	38	38	41	41
Severn-Trent	27	11	37	18
South West	21	12	19	14
North West	14	10	18	15
Yorkshire	13	6	16	6
Northumbrian	7	7	12	12
Welsh	6	2	8	4
Total: %	26	14	31	19
Total: x10^6 m^3	4080	4095	2686	2689

* percentage of total abstraction excluding CEGB

** percentage of total abstraction including CEGB.

TABLE 3 : Annual returns of ground-water abstraction in England and Wales, 1948-74.

Ground-Water Abstraction (X10^6 m^3/ann)

Year ending 31 October	Actual*	ending 31 October	Actual*	Year ending	Licensed**	Actual**
1948	1687	1956	2066	Sep.1964	-	-
1949	1726	1957	2094	Sep.'65	4012	-
1950	1836	1958	2241	Sep.'66	4092	-
1951	1851	1959	2314	Sep.'67	4112	-
1952	1885	1960	2358	Sep.'68	4076	-
1953	1924	1961	2456	Sep.'69	4438	2391
1954	1967	1962	2416	Dec.'70	3984	2407
1955	2040	1963	2478	Dec.'71	3986	2451
				Dec.'72	3990	2434
				Dec.'73	4014	-
				Dec.'74	4095	2689

* returns made under Water Act 1945 (after WRB)

** returns made under Water Resources Act 1963

TABLE 4 : Regional ground-water use, 1974 (x10^6 cubic metres).

Regional Water Authority	Public Water Supplies	Industry		Agriculture	
		CEGB	Other	Irrig.	Other
Thames	546	1	81	2	1
Severn-Trent	463	1	90	1	4
Southern	309	-	73	1	2
Anglian	265	-	72	5	5
North-West	224	-	104	-	1
Wessex	117	1	8	-	3
Yorkshire	79	-	33	-	-
Welsh	37	-	66	-	3
Northumbrian	35	-	12	-	-
South-West	22	-	8	-	6
TOTAL	2097	3	547	10	25
TOTAL (%)	78	<1	20	<1	1

TABLE 5 : Percentage ground-water use in England and Wales.

Category	1948		1967*	1974	Category
Stat.Wat. Undertak. & Misc.	70	61	60	78	Public Water Supplies
Industry	29	26	20	<21	Industry
Agriculture	1	1	<2	<2	Agriculture
Mine Drainage	-	12	18	-	-
TOTAL	100	100	100	100	TOTAL

* From Ineson (1970).

TABLE 6 : Regional ground water investigations. (After H.J.Richards).

Regional Water Authority	Aquifer	Type of use *	Yield (10^3 m^3/d)
Northumbrian	Magnesian Limestone	R	50
	Fell Sandstone	R	100
Yorkshire	Triassic	R	270
	Jurassic	R	50
	Chalk	R	140
Severn- Trent	Triassic (Salop)	R	225
	Triassic (Notts)	C	50
Anglian	Chalk (Lincs.)	C	50
	Chalk (Gt. Ouse)	R	450
	Chalk (Suffolk)	R	150
	Chalk (Essex)	D	35
	Crag	D	50
	Lincs. Limestone	C	90
	Lr. Greensand	D	50
Thames	Chalk (Thames)	R	455
	Chalk (Lee)	R	10
	Jurassic	R	50
Southern	Chalk (Kent)	C	100
	Chalk (Sussex)	D	150
	Chalk (Hants)	R	270
	Lr. Greensand	C	160
Wessex	Chalk	C	100
	Jurassic	C	25
	Triassic	R	100
South West	Triassic (Devon)	R	50
	Permian (Devon)	R	150
Welsh	Triassic (Clwyd)	R	30
	Triassic (Ches.)	D	30
North West	Triassic (Fylde)	C	150
	Triassic (Mawdesley)	D	25
	Triassic (Cumbs)	C	35
	Permo-Triassic	R	230

* R River regulation; D Direct supply; C Combined use.

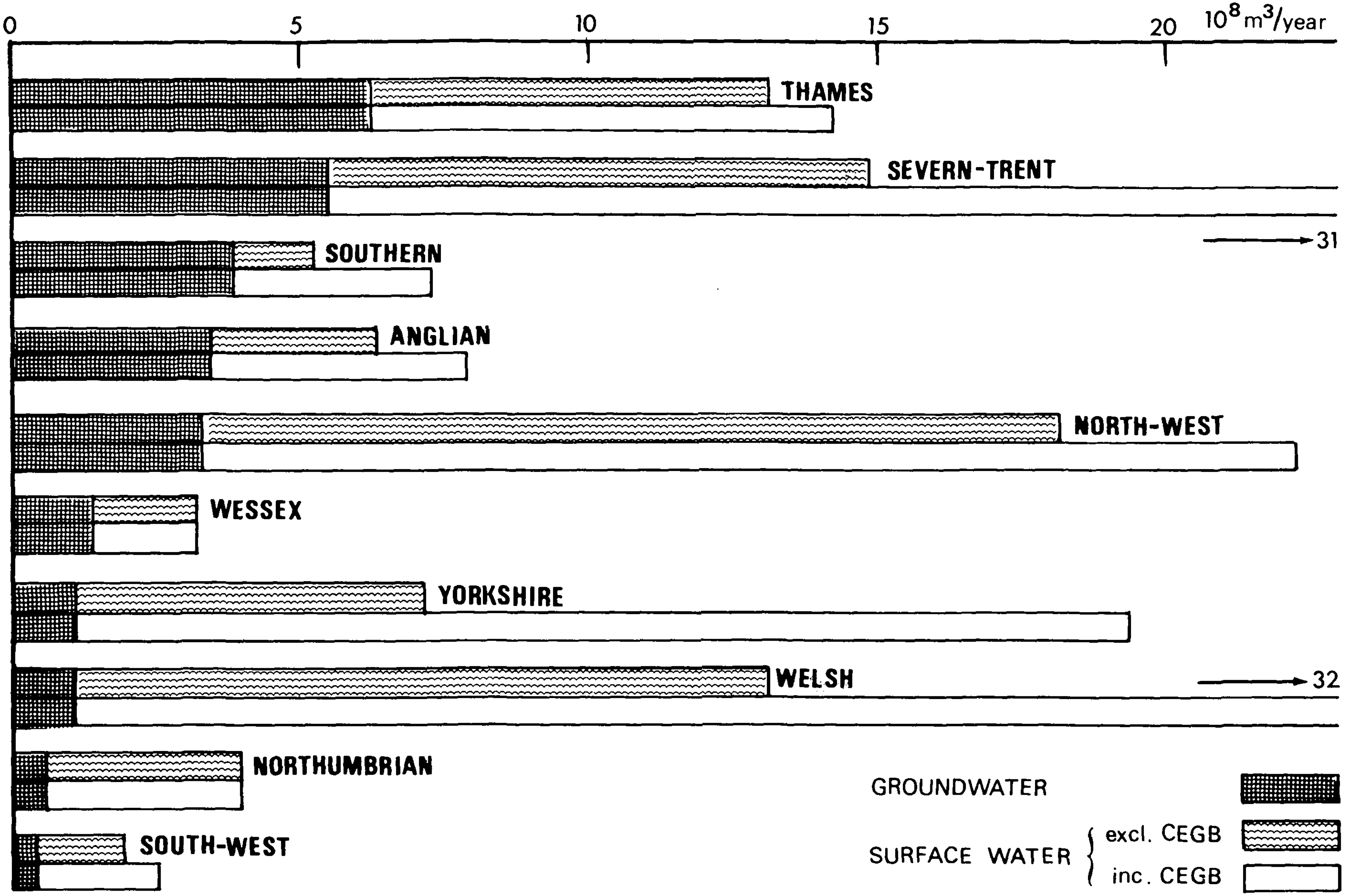

Figure 1. Regional abstraction of groundwater in 1974.

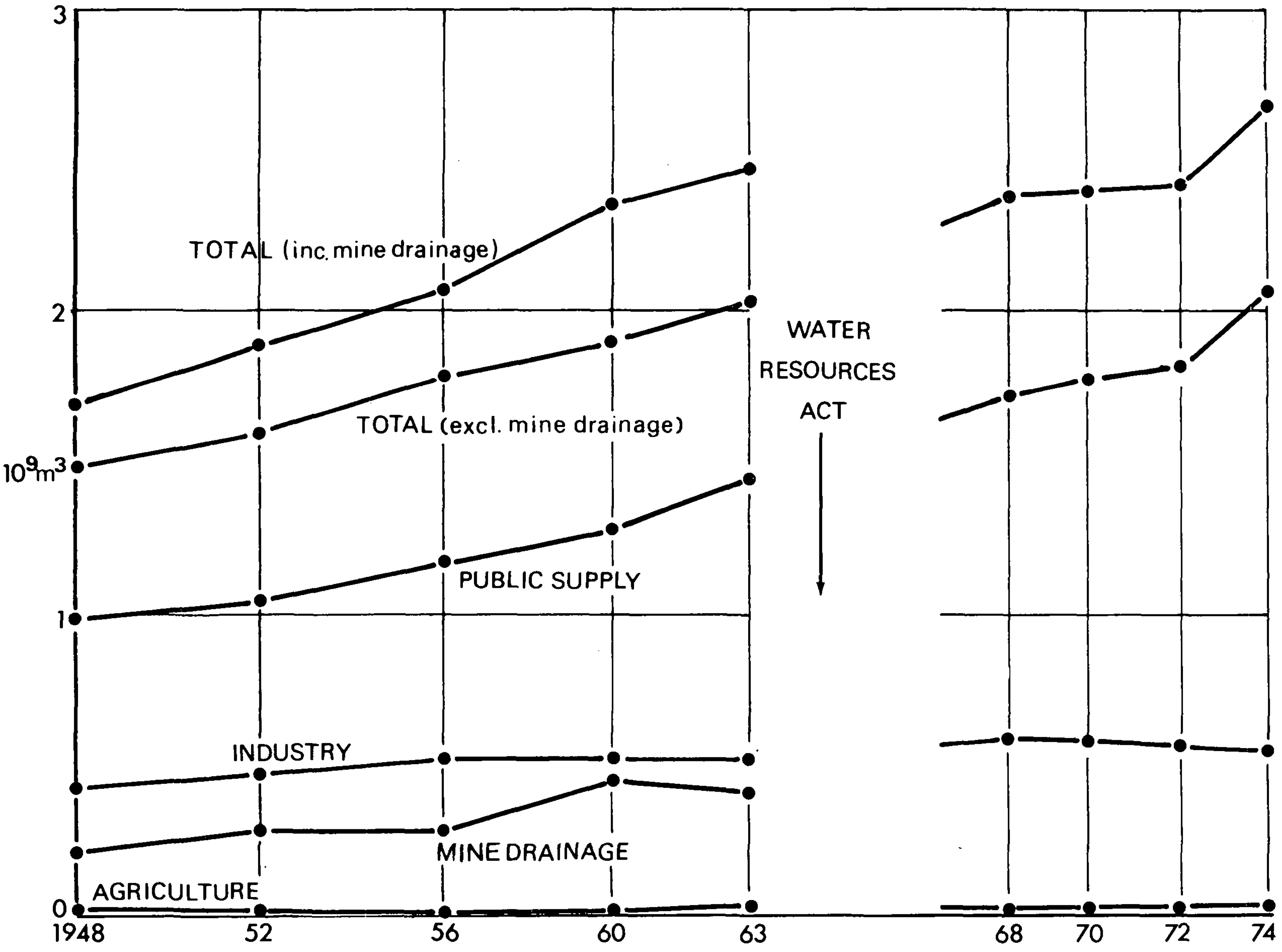

Figure 2. Groundwater use 1948-74.

PAPER 2

GROUNDWATER POLLUTION PROBLEMS IN THE UNITED STATES

Jack W. Keeley

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1. INTRODUCTION

It is apparent that groundwater pollution problems in the United States are similar to those in the United Kingdom, and that the dependence of both countries on this source of water provides the impetus for its protection.

Of the total fresh water used in the United States in 1970, about 21 per cent was taken from groundwater. This includes supplying 20 of the largest 100 cities and 95 per cent of rural America. One-half of the total population relies on groundwater for their domestic water supply.

We are aware of the protracted effect of contamination on groundwater as compared with its surface counterpart, and that restoration of underground water quality is difficult at best and always expensive. Indeed, in almost all cases the cost of restoring the integrity of groundwater quality exceeds its intrinsic value. It follows that our scientific, legal, social and economic goals must be based on the protection of groundwater quality rather than its restoration.

This concept necessarily requires that the possible sources of contamination be prioritized according to their severity and that scientific and legal means for control be made available. Finally, a groundwater resource must be optimized, according to existing economic and social constraints, by controlling the amount of water withdrawn and the quantity and quality of waste returned.

2. SOURCES OF GROUNDWATER POLLUTION

Five reports have been completed in which groundwater availability, use and background quality are described for various geographical areas of the United States (1) (2) (3) (4) (5). In addition, the significant pollution problems are discussed and placed in priority for each area and suggestions are offered as to how these problems might be addressed. The five geographical areas studied are shown on Figure 1 and the prioritized pollution problems for each are presented in Table 1.

Table 1. Priority sources of groundwater pollution

	South-West	South Central	North-East	North-West	South-East
1.	Natural leaching	Natural pollution	Septic tanks & cesspools	Septic systems	Septic systems
2.	Irrigation return flow	Oil field brines	Buried pipelines and storage tanks	Sewage treatment plant discharge	Urban and industrial landfills
3.	Sea water encroachment	Well construction	Highway de-icing salts	Irrigation return flow	Surface impoundments
4.	Solid wastes	Overpumping	Landfills	Dry land farming	Drainage wells and abandoned water wells
5.	Disposal of oil field brines	Irrigation return flow	Surface impoundments	Abandoned oil wells and test wells	Fertilizers and pesticides
6.	Animal wastes	Land application of wastes	Spills and surface discharges	Brine injection	Leaks and spills
7.	Accidental spills - hazardous materials	Solid wastes	Mining activity	Disposal wells	Brine injection wells
8.	Water from fault zones & volcanic origin	Evapotranspiration from native vegetation	Petroleum exploration and development	Surface impoundments	Feedlots
9.	Evapotranspiration from native vegetation	Animal wastes	Salt water intrusion	Mine drainage and mine tailings	Irrigation return flow
10.	Injection wells for waste disposal	Waste lagoons	River infiltration	Urban and industrial landfills	Abandoned oil and gas wells

Three additional studies are planned which will cover the Mid Western States, the North Central States, Hawaii, and Alaska. The South Western report was completed in 1971, followed by the South Central in 1973. Reports covering the North Eastern and North Western States were completed in 1974 and that for the South East was completed this year.

Some problems indigenous to one area may not exist in others, but several sources of groundwater contamination are dominant at a high or moderate degree of severity in each area investigated. Among these, septic tanks and cesspools, petroleum exploration and development, landfills, irrigation return flows, and surface waste impoundments appear to be the most troublesome problems. A more complete summary of these studies is presented by Miller and Scalf (6).

The application of municipal and industrial sludges to the land has not been a major problem in the past, but is expected to be so in the future due primarily to Federal legislation seeking to eliminate stream discharges by 1985. Similarly, coal mining activities are increasing in the United States, due to the energy shortage, and are expected to present greater groundwater pollution problems in the future.

The four pollutants most commonly reported in these five regional investigations are chlorides, nitrates, heavy metals, and hydrocarbons. This brings into focus our need to more actively include organic and biological parameters in future studies.

Blair gave an excellent description of the possible sources of groundwater contamination during the 1972 Reading Conference. It will suffice here to limit discussions to those problems indigenous to the United States, or to those requiring amplification due to their importance.

2. 1. INDIVIDUAL SEWAGE DISPOSAL SYSTEMS

Over 17 million families in the United States are served by septic tanks or other means of subsurface seepage (7). This accounts for something over 30 per cent of the population, as compared to 6 per cent for the populations of England and Wales.

Assuming that 190 litres per capita are discharged to these systems daily, it can be estimated that nearly 13 billion litres of waste are introduced directly into the subsurface environment each day. Even this does not account for other large contributions by commercial and industrial sources.

Traditionally, septic tank studies have been concerned primarily with chlorides, nitrates, and members of the coliform group as indicators of pollution. Considering the magnitude of this problem and the diversity of chemicals being introduced into the home each year, we will have to use more sophisticated indicator parameters in future studies.

2.2. PETROLEUM

The exploration and development of oil has played a long and important role in the United States. The industry has changed tremendously since its early days, when little attention was paid to the efficiency of recovery or to the consequences of environmental degradation.

The major water pollution problem stems from the brines recovered with crude oil at an average ratio of about ten to one, depending on the age of the well. In the early days these brines were discharged to streams or pits or anywhere else, and allowed to run where they might. Today most brines are reinjected for disposal or to repressure an oil horizon in secondary recovery projects.

The number of active and abandoned oil and gas wells, salt water disposal wells and holes drilled for exploration run into the hundreds of thousands. These holes can allow salt water and fresh groundwater to interchange when the casing is missing or has corroded. Many of these old and often forgotten holes continuously discharge brines to the surface. Although the use of unlined brine disposal pits has essentially been stopped, they will continue to leach salts for many years to come.

We do not have adequate means, and in many instances knowledge, to locate and adequately plug the thousands of wells which were abandoned in the years before regulations came into being. The problem is so extensive and complex, and our knowledge to cope with it is so meagre, that this will continue to be a major source of contamination.

2.3. WATER WELL CONSTRUCTION

A major problem found in almost all parts of the country is concerned with the integrity of water wells. Many were constructed without proper consideration of sanitary conditions, while others failed in this respect after many years of service.

Wells in which the casing has failed or was inadequate when constructed, allow for the interchange of waters between fresh and salty aquifers or the contamination of groundwater from surface sources. These problems have been noted particularly along the coasts where salt water intrusion has occurred, and in areas where salt water underlying fresh water was given an avenue for interchange.

There is an obvious need to develop technology to locate and plug those wells which were abandoned before records were kept. There is also a need to develop an economical way to restore the integrity of those wells still in service, particularly in cases where the owners cannot afford to construct a new facility.

2.4. HIGHWAY DE-ICING SALTS

The use of salts to control highway ice is confined to the Northern States and is apparently of more concern in the North East than the North West. As an example, Massachusetts used more than 11 000 kilograms per single-lane kilometre during a winter season (6) while the North Western States used a tenth of this value.

Highway salts enter groundwater either by infiltration of the salt-laden runoff or from precipitation on salt piles at central storage areas. Equipment modification and driver education have been successful in reducing the amount of salt distributed during a single winter storm, and efforts are being made to cover or otherwise improve salt storage facilities.

2.5. GENERAL

There are a number of other problems which cannot yet be fully evaluated in terms of their pollution potential due to a lack of detailed information and, indeed, the ability to make the evaluations necessary. Among these are included the disposal of solid municipal and industrial waste, applying wastes to the land for treatment, and high density animal feeding operations.

The basic problem in dealing with these sources of contamination, and some of those already mentioned, is the technical ability to sample and analyse for those parameters not ordinarily considered in groundwater investigations. There are thousands of organic chemicals associated with municipal and industrial wastes both in the liquid and solid phase. Characterizing the total aerobic and anaerobic microbiological population is beyond the economic and manpower capabilities of most regulatory bodies. Searching for antibiotics and hormones in the soils beneath animal feedlots presents difficult sampling and analytical problems. When we realize that the subsurface transport processes of these parameters and their degradation products must be understood before adequate waste management schemes can be undertaken, our problems are exponentially complicated.

It is important to note that the problems, as prioritized in the five area reports, have not been selected on the basis of hard statistical information. Such information simply does not exist. Problems associated with the exploration and development of oil and gas have been well documented primarily because of their existence over long periods of time and the relative ease of making chloride determinations. Industrial lagoons and landfills, on the other hand, have enjoyed relative anonymity due to their inaccessibility and the complexity of the waste involved. Many other potential sources of groundwater contamination were found to be sparsely covered in the literature or the files of regulatory agencies. For these reasons, priorities were mainly established on the basis of the experience of those authorities who have worked in the areas studied.

3. FEDERAL LEGISLATION

Until very recent years, the nation's groundwater resources have not been appreciated in terms of Federal legislation aimed at their protection. This is due in large measure to misconceptions by those untrained in the subject. The general public still believes that groundwater runs in underground streams and is located by the behaviour of a forked stick. As late as the turn of the century, the courts held that the causes which govern and direct the movement of underground water were secret, mysterious, and occult. In spite of the remarkably accurate observations of da Vinci in the 15th century and John Ray and Descartes in the 17th century, these misconceptions still exist to a great extent today.

The River and Harbor Act of 1899 was aimed at preventing waste discharges which resulted in obstructions to navigation. It is still in effect and serves as the basis for permits for waste discharges administered by the Corps of Engineers and EPA. This legislation was used recently against a landfill operator because of leachate being discharged to navigable waters.

The Water Pollution Control Act of 1948 was amended over the years and evolved into Public Law 92-500 in 1972. The Law addresses the nation's groundwater in several sections either directly or by implication. One section of the Law, in which groundwater is specifically mentioned, deals with the preparation of comprehensive programmes for preventing, reducing, or eliminating pollution of navigable waters and groundwater and improving the sanitary condition of surface and underground waters. Groundwater is also mentioned in the section entitled 'Research, Investigations, Training and Information' which provides, among other things, the legislation under which the Environmental Protection Agency carries out its work in groundwater research. Also included in this section are technical assistance to other organizations, water quality surveillance and waste treatment studies. Another section, in which groundwater is not specifically mentioned, provides a potentially-effective tool for quality protection in calling for State or area-wide planning in pollution control, giving consideration to non-point sources of pollution. Groundwater is also mentioned in another section calling for information on the presence of pollution and processes, procedures and methods by which it can be controlled.

The National Environmental Policy Act implemented in 1970 did not create a regulatory vehicle, but did require that Federal agencies consider the environmental consequences of their actions. Under the Act, Environmental Impact Statements must be prepared for projects which might have a significant adverse effect on surface or groundwater quality or quantity.

The Safe Drinking Water Act became law on 16 December 1974. It provides for safe drinking water for all Americans served by public water systems, and in doing so adds a large dimension to the protection of groundwater. In addition to establishing minimum drinking water standards, regardless of the source, it addresses the protection of underground water quality and provides for research, technical assistance, and personnel training. One section of the law allows EPA to determine that an aquifer is a sole or principal source of drinking water. If such a determination is made, no project requiring Federal assistance may be entered into which may contaminate the aquifer through a recharge zone and result in a significant hazard to public health.

The Water Pollution Control Act is aimed primarily at pollution control of navigable waters, with its eventual goal being the elimination of waste discharges to these waters. Ironically, this philosophy may result in increased stresses of groundwater resources because those wastes previously discharged to streams will go instead to the land or be injected underground.

The Safe Drinking Water Act is weak in some respects because of certain problems in definition and interpretation.

A major problem with legislation at all levels of government is the ability of enforcement. The people and monetary resources required to carry out the laws are generally inadequate.

4. TECHNICAL PROBLEMS

Once groundwater problems have been identified, it becomes necessary to select those parameters best suited to describe the effects of those problems and to develop methods for sampling and analysing for those parameters.

This sounds naive, but one need only consider the problems involved in collecting a subsurface sample for anaerobic bacteria analysis,or in measuring the oxidation-reduction potential at a considerable depth in order to realize the complexities which might be encountered. These are very important considerations because we must understand the subsurface environment as a receptor of pollution.

We have only to read our technical journals to find that many people still measure BOD in groundwater. BOD measures the depletion rate of oxygen in a small bottle. It is a test in which the rate of reaction and ultimate oxygen demand are dependent upon contact between the oxidizable matter contained in water and microbiological systems. If a sample is taken from an aquifer, which has a tremendous surface-to-volume ratio, and placed in a BOD bottle, the intent of the test is nullified.

Escherichia coli is successfully used in surface water investigations to indicate the presence of pathogenic organisms. In size, E. coli is in the order of one or two microns, as compared to a polio virus which is about 0. 01 microns. In the subsurface matrix filterability would negate any correlation between the movement and fate of these two parameters. Considerable work needs to be done to define reliable biological indicators for the presence of pathogenic micro-organisms in groundwaters and to develop effective biochemical tests, such as ATP (adenosine triphosphate) or specific enzyme analyses, for total biological activity and hence the potential for biodegradative attenuation of pollutants in subsurface regions.

There are hundreds of thousands of possible organic contaminants. Obviously, we cannot consider each in a manner necessary to describe its fate and manner of transport in the subsurface environment. Organic analyses are difficult and expensive. Instead, indicators must be discovered which will to some degree account for the behaviour of large classes of organic compounds. We are ultimately concerned with the chromatographic movement of potential organic contaminants and their products of degradation.

The use of stable isotope ratios shows promise for being a valuable tool in determining the source of contamination in groundwater and shows promise in telling us something about the chemical and biological alterations that take place during the movement of contaminants through the ecosystem. Investigations in West Texas (8) using the N^{15}/N^{14} ratio indicated that extremely high nitrate concentrations in groundwater were of natural origin rather than from septic systems, fertilizers or animal pens. The work also showed that denitrification was taking place in water wells and that the isotope ratio concept might provide information on the biokinetics involved. Considerable work is yet to be done, not only with nitrogen but with the isotopes of sulphur and oxygen, among others.

We all know that modelling pollution transport phenomena in the subsurface is in its infancy, particularly with respect to the unsaturated zone and especially in terms of organic and biological contaminants. Before these models can be adequately developed, we must define those coefficients which describe the movement and fate of these parameters and their degradation products, where required. Models of this nature are prerequisite tools for enlightened water resources management. We are all aware that groundwater is only one part of the hydrologic system, and tools of this nature would enable us to include groundwater and surface water in a complete basin management programme which addresses waste disposal, irrigation, surface and groundwater withdrawal, and the other facets of land use.

5. ECONOMICS

Establishing the economic consequences of groundwater pollution proves to be one of the most perplexing problems with which we are forced to deal.

The benefit of restoring polluted surface waters can be roughly established by equating it to the cost of treating the source of pollution or obtaining an alternate source of water, giving due credit to aesthetics and recreation. The decision to restore surface water is always made realizing that the quality will soon be restored after the sources of pollution are removed. Obviously, the benefit exceeds the cost because polluted streams have been restored all over the world.

This philosophy does not hold with groundwater because it will remain polluted decades or even centuries after the source of pollution is removed. There are no benefits to be derived from aesthetics or recreation except in the rarest of circumstances. On occasion, the threat of litigation of damages provides that necessary incentive to at least attempt the restoration of a polluted groundwater resource.

In one of our Southern States, an alluvial aquifer was polluted by oil field brines which had seeped from an 'evaporation pit'. High capacity wells tapped this aquifer to irrigate extensive rice fields. Due to the low tolerance of rice to salt, the problem was soon discovered, but not until a considerable portion of the aquifer was contaminated. After intensive investigations, it was concluded that under natural gradients it would take approximately 250 years for the aquifer to cleanse itself and attempts to artificially restore the aquifer could not be justified.

If the leachate from a landfill threatens a city's well field, the alternatives include collecting the leachate for treatment or obtaining another source of water. Considering the protracted period over which the leachate would require treatment, the most viable alternative would almost always be the latter.

There is little doubt that our goal should be to protect rather than restore the quality of groundwater. It is necessary, however, that some means be developed by which the intrinsic value of groundwater can be determined so that this goal can be placed in its proper perspective. This value must include the consequences of allowing this valuable resource to be unavailable to us for several generations.

Controlling groundwater pollution necessarily requires rules and regulations and the resources for their enforcement. Some States have excellent personnel and programmes directed towards protecting groundwater while others are sadly deficient. The cost to regulatory agencies at all levels of government will be reflected by the personnel, equipment and programme requirements for satisfactory levels of performance. These costs will increase additionally as the level of sophistication increases to meet the complex problems of the future.

Adequate regulations will also impose a financial burden on the public community in terms of increased costs for waste treatment facilities and, in some cases, improved well construction. Industry will also be expected to treat properly those wastes which are now reaching groundwater or develop an alternate means of disposal. Both municipal and industrial concerns will probably require additional monitoring facilities.

6. CONCLUSIONS

Our unquestionable goal must be the protection rather than the restoration of groundwater quality. Although this goal will impose an economic impact on both the public and private sector, it will be meagre compared to the alternative of quality restoration. Allowing this resource to be destroyed and unavailable for future generations is conceptually unacceptable.

Legislation aimed at protecting groundwater has improved dramatically in recent years, but additional rules and regulations will be needed as technology is improved. The various levels of government must gain an appreciation for groundwater so that adequate resources can be dedicated to its protection.

Technology applicable to surface water investigations is often unsuitable in dealing with underground problems. Indicator parameters are required particularly for organic and biological contaminants, along with appropriate sampling and analytical methods.

The problems which threaten groundwater quality can only be prioritized empirically due to the crippling lack of information on the number of various sources of contamination, the contaminants with which we should be concerned, and the manner by which these move, adsorb, and are degraded in the subsurface environment.

Models which describe the movement and fate of pollutants in the unsaturated and saturated zones are required to establish pollution source control criteria. This will allow groundwater to assume its proper place in the hydrologic system so that proper and complete water resources management can provide for water supply and waste disposal needs for generations to come.

Although groundwater pollution problems may vary in importance in and among countries, our problems and our goals are very much the same. The exchange of ideas is essential and conferences such as this can assist each of us in protecting the world's most abundant supply of fresh water.

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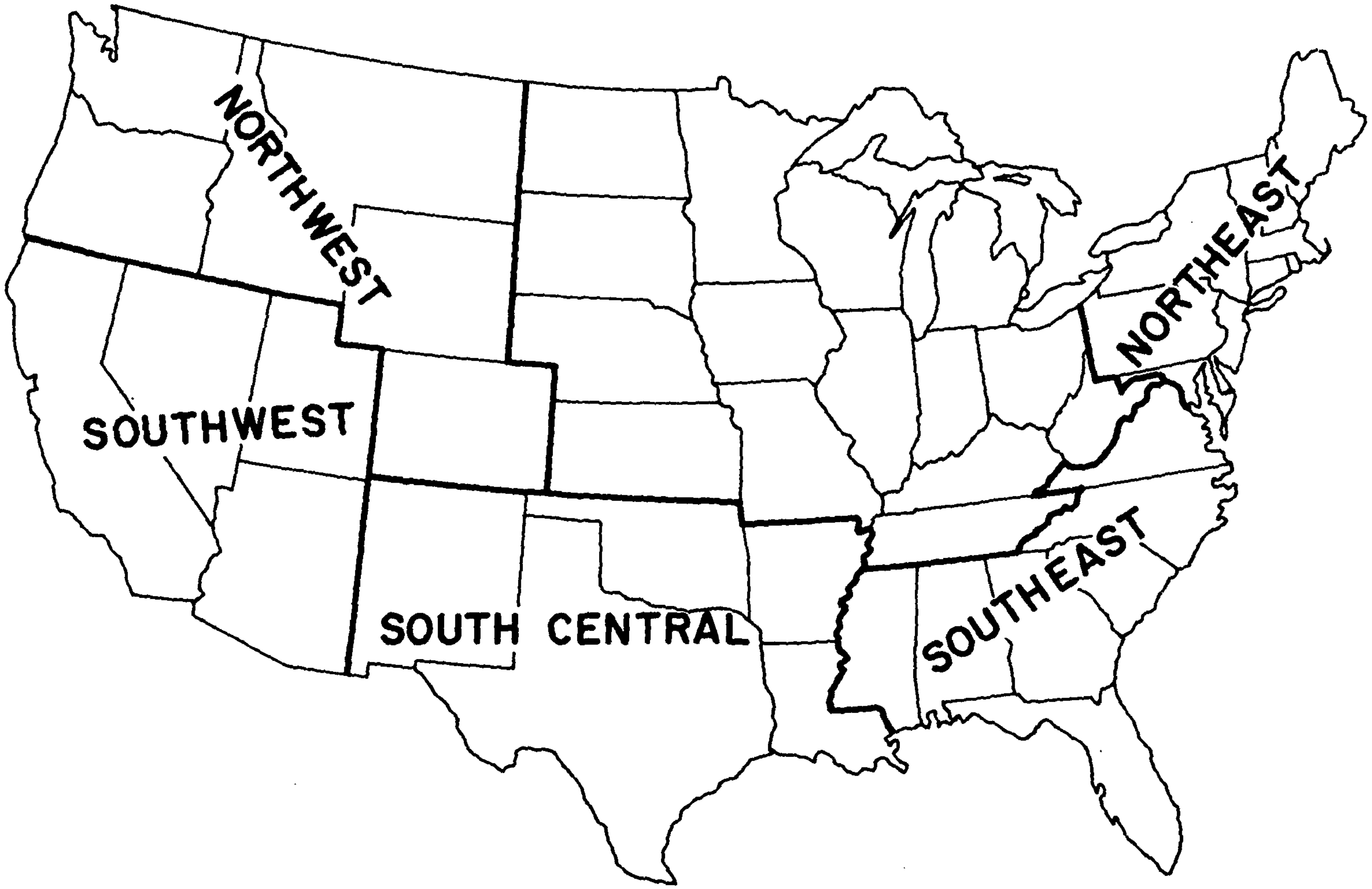

Figure 1. LOCATIONS OF COMPLETED GROUND-WATER INVESTIGATIONS IN THE UNITED STATES

PAPER 3

UTILIZATION OF GROUNDWATER

Prof. Ir. L. Huisman

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1. THE HYDROLOGIC CYCLE

Water is indispensable for the existence of plants and animals, including man. In this respect it is very fortunate that so much water is available on earth. The total amounts to 1370 M km^3, corresponding to a layer with a thickness of 2700 m when spread out over the whole earth surface (510 M km^2). According to Table 1, however, 99.4% of this water cannot be used for the purposes mentioned above, either because its salt content is too high or because it occurs in the solid state.

Table 1. Water on earth

Type	Volume (10^{15} m^3)	Percentage
Seas and oceans	1330	97.25
Glaciers and polar ice	29	2.12
Underground water	8.4	0.61
Lakes and rivers	0.2	0.01
Atmosphere	0.013	0.00
Biosphere	0.0006	0.00
Total	1368	100

For the sustenance of life on earth, only groundwater and the surface water in lakes and rivers is available. Their total volume amounts to 8.6 M km^3, which, spread out over the whole land surface of the earth (136 M km^2), corresponds to a layer with a depth of only 63 m. Moreover, when it is considered that half of this amount occurs at a depth of more than 800 m below ground surface, where its salt content is often too high and in nearly all cases recovery is too expensive, the available fresh water on earth becomes a precious commodity indeed.

Fresh water, however, is not a mineral such as coal and oil, where on one hand consumption means destruction and on the other hand new supplies are not formed in our times. On the contrary, when using water, its quality may deteriorate (toilet flushing for example) or it may be converted into another state (transpiration losses in agriculture), but it always remains as water. The most important difference, however, is that fresh water is constantly being reformed. This is due to the fact that all the water on earth, whether as water vapour in the atmosphere, as surface water in streams, lakes, seas and oceans, or as groundwater in the interstices of the subsoil, is not at rest but is in a continuous circulatory movement. There is a never-ending transformation from one state to another, known as the hydrologic cycle (Figure 1). Water from the atmosphere falls to the ground as rain, hail, sleet or snow and gathers above ground as well as at depth. Not all this downward moving atmospheric water adds to surface or groundwater supplies since there is a continual return to the atmosphere. Part of this water does not even reach ground surface at all but is intercepted by the vegetation and evaporates from there. The water on the ground, in pools and marshes, is exposed to evaporation, as well as the water which flows in rivers and lakes. Water in the pores of the subsoil is also subjected to these losses while another part is consumed by vegetation. That water which remains either flows over or directly beneath the ground surface to open water-courses, or moves further downward through the aerated upper strata until it reaches the groundwater table and recharges the groundwater supply. This groundwater is not stagnant, but flows through the soil in the direction of the downward slope of the groundwater table. Sooner or later it appears again at the surface, visible in the form of springs and invisible as groundwater flow to rivers and lakes. The smaller streams combine to form larger rivers which carry the water to the sea. Here, evaporation returns it to the atsmosphere and the cycle begins once more.

The volume of the hydrologic cycle, that is the amount of water flowing yearly from land to sea and vice versa, may be calculated by drawing up a water balance for the combined land and sea areas of the world. As an average over a long period, the resulting flows are represented in Figure 2. Over the land surface of the earth, the residual rainfall has a capacity of 30 000 km^3/year, which for a total fresh water volume of 8.6 M km^3 corresponds with an average retention time of nearly 300 years. Taking into account that only part of this flow follows the underground route, the average retention time of groundwater is much higher and will easily surpass a span of five centuries.

According to Figure 1, groundwater originates from two sources:

(a) a downward percolation of residual rainfall over large areas;
(b) a local infiltration of surface water when the groundwater table is situated at a greater depth;

to which nowadays may be added:

(c) a man-made increase in groundwater supply by induced and artificial recharge.

These ways of groundwater recharge have a tremendous influence on groundwater quality, as will be elucidated in the next section.

2. GROUNDWATER COMPOSITION

For the greater part, groundwater originates from rainfall, but this rainwater is not a clean water. Already the transformation of water vapour to raindrops occurs around dust particles as condensation nuclei, while during the fall through the air atmospheric gases are taken into solution and other substances are washed down either in a dissolved or a suspended state. Near the coast, the salt content will be greatly enlarged. Over continental areas and in particular over deserts, terrestrial compounds will predominate, while near industrialized regions a further increase in suspended particles, such as soot and fly-ash, and in dissolved gases, such as CO_2 and SO_2, may be expected.

The saturation concentration of gases in contact with atmospheric air varies strongly with temperature as shown in Table 2.

Table 2. Dissolved gases in equilibrium with atmospheric air

Temp. in °C	0	10	20	30
N_2 in mg/l	22.8	17.9	14.7	12.6
O_2	14.6	11.3	9.1	7.5
CO_2	1.0	0.7	0.5	0.4

The concentrations of nitrogen and carbon dioxide in rainwater conform with these values, but the oxygen concentration is 5 to 10% smaller. The ion content of rainwater varies from one place to the other (Table 3) and is generally larger as the amount of rainfall is smaller.

Table 3. Dissolved ionic concentrations in rainwater expressed in mg/l

	Coastal areas	Continental areas	Industrialized regions
Na^+	15	4	6- 15
K^+	2	0	
Ca^{++}	2	4	
Mg^{++}	2	1	
NH_4^+	2	0	
Cl^-	25	6	20- 50
SO_4^{--}	15	10	30-500
HCO_3^-	1	0	
NO_3^-	2	1	

The pH normally lies between 5.6 and 6.4 but may drop to values as low as 3 when the industrial production of CO_2 and SO_2 is high, and may rise above

9 in calcareous areas. The content of micropollutants in rainwater is certainly not negligible. Average values in µg/l are: total organic carbon 2000; iron and manganese 250; zinc 80; lead 30; copper 20; heavy metals 10; pesticides 0.1.

When rainwater meets the ground surface, a tremendous increase in its pollution load will occur, with inorganic and organic soil particles, debris from vegetable and animal life, remains of natural and artificial fertilizers, pesticides and micro-organisms; these are carried along by the water in suspension or in solution. During the flow through the upper aerated soil layers, a great improvement in water quality will take place. Suspended particles are almost completely removed by filtration, organic substances are degraded and mineral components are taken up by the plant roots. Despite contact with the atmosphere, the oxygen content of the soil water falls and the carbon dioxide content increases by a factor between 10 and 100.

After passing the top of the capillary fringe, the downward percolating soil water becomes groundwater and has lost all possibilities of gas exchange with the atmosphere. In the upper 0.5 to 2 m, a further improvement in water quality will take place. Filtration will remove all remaining suspended and colloidal dissolved particles, while bio-oxidation converts organic matter, including ammonia, into simple mineral substances and precipitates various iron and manganese compounds, for example:

$$C_5H_7O_2N + 7O_2 \rightarrow 3H_2O + 5CO_2 + NO_3^- + H^+$$

$$NH_4^+ + 2O_2 \rightarrow H_2O + NO_3^- + 2H^+$$

$$4Fe^{++} + O_2 + (2n + 4)H_2O \rightarrow 2Fe_2O_3.nH_2O \downarrow + 8H^+$$

$$2Mn^{++} + O_2 + 2H_2O \rightarrow 2MnO_2 \downarrow + 4H^+$$

while the hydrogen ions react with bicarbonate when present

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2$$

Conforming to these reactions, the oxygen content of the water will drop and the carbon dioxide content will rise according to the equilibrium reaction.

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

After the entry phase described above, the water will flow more or less horizontally through the aquifer over extended distances involving long periods of time. Intimate contact between the groundwater and the aquifer material will now occur, increasing as the grain size becomes smaller and the retention times are larger. By this contact, many substances are dissolved, in particular those which abound in the lithosphere such as $CaCO_3$, $MgCO_3$, $CaSO_4$, NaCl and KCl. Some go into solution directly, others need hydrolysis

$$CaCO_3 + H^+ \rightarrow Ca^{++} + HCO_3^-$$

or the chemical attack by carbon dioxide

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{++} + 2HCO_3^-$$

increasing both the hardness and the alkalinity. Further changes in water quality depend, for a large part, on the presence or absence of oxygen. In aquifers of clean sand and gravel, the water will remain aerobic and the quality changes are only minor and always favourable. By adsorption and oxidation, the organic matter content will show an additional reduction, lowering the chemical oxygen demand as well as the taste and odour of the water. By the absence of suitable organic food, intestinal bacteria and viruses will die away. By adsorption and ion exchange, especially when clay colloids are present as a thin coating around the sand grains, heavy metals, pesticides and radio-nucleides are retained. In many cases this groundwater may be distributed as drinking water without any treatment.

Larger and often very unpleasant changes in water quality will occur when the subsoil contains greater amounts of degradable organic matter thereby lowering the dissolved oxygen content of the water. When this content has dropped to 0.5 mg/l, nitrates present in the water will start to act as oxygen donors. With organic carbon as a reducing agent

$$2C + NO_3^- + 3H_2O \rightarrow NH_4^+ + 2HCO_3^-$$

and under anaerobic conditions

$$5C + 4NO_3^- + 2H_2O \rightarrow 2N_2 + CO_2 + 4HCO_3^-$$

Judged by itself, the reduction in nitrate content is an advantage, but the production of ammonia is decidedly unpleasant. The carbon dioxide formed, now or previously, will attack iron and manganese compounds present in the aquifer, for example

$$FeCO_3 + CO_2 + H_2O \rightarrow Fe^{++} + 2HCO_3^-$$

But the absence of oxygen prevents redeposition as ferric oxide-hydrates. Ferrous and manganous ions consequently stay in solution and the groundwater recovered will need treatment to make it suitable for public and many industrial supplies. The increase in bicarbonate content may move the equilibrium reaction

$$Ca^{++} + 2HCO_3^- \rightleftarrows CaCO_3 + CO_2 + H_2O$$

to the right, precipitating calcium carbonate and removing phosphates and fluorides in calcium complexes such as apatite. This reduces the hardness, but it may also lead to a blocking of the formation, in particular around well screens. Under strict anaerobic conditions, sulphates may also be reduced

$$2C + SO_4^{--} + 2H_2O \rightarrow H_2S + 2HCO_3^-$$

The hydrogen sulphide formed imparts a very unpleasant odour to the water. When iron is present, ferrous sulphide may result

$$Fe^{++} + H_2S \longrightarrow FeS + 2H^+$$

giving the aquifer grains a black colour. Theoretically at least, carbonates may also act as a source of oxygen, producing methanes, but this will only occur when retention times in the subsoil are extremely long. After all the available oxygen has been used, organic matter may still be degraded anaerobically, but this is a very slow process.

As described in Section 1, groundwater will also be formed by natural or artificial infiltration of surface waters from rivers and lakes, with the most important difference being that the salt content is commonly a factor of 10 higher than that of rainwater (200 to 700 mg/l) raising the mineral content of the groundwater recovered. In cases where the content of biodegradable matter is high and the oxygen content correspondingly low, anaerobic conditions will certainly arise during the underground travel. Additional and often troublesome compounds such as iron and manganese will now be picked up from the aquifer while nitrates may be reduced to ammonia, necessitating treatment of the groundwater recovered before it can be used for public and industrial supplies.

Summing up, it may be said that in physical and bacteriological respects, groundwater has an excellent quality. Due to the long retention time in the subsoil, the temperature will be constant and pathogenic bacteria and viruses will be absent, making the water safe hygienically. The chemical composition will also show little variation and when the water remains aerobic, its quality will generally be high. In cases where the underground formations contain adequate amounts of calcium and magnesium compounds, the water will be non-agressive and can be used without any treatment. The hardness may be a disadvantage, but it prevents the occurrence of unpleasant substances such as heavy metals, fluorides, phosphates, etc. Without the presence of calcium and magnesium salts, the water needs stabilization by removal of excess carbon dioxide, mechanically by aeration and chemically by the addition of lime or sodium hydroxide. Anaerobic groundwater generally has too high a content of iron and manganese and although harmless to human health, the bitter taste and the brown/black stains that would result in laundry require their removal. Treatment by aeration and filtration is certainly a complication, but compared with surface water purification it is simple and inexpensive and may be done without expert supervision; the latter consideration being very important for small supplies.

3. GROUNDWATER RECOVERY

From times immemorial, groundwater has been used for domestic and small scale agricultural supplies in those places where surface water from rivers or lakes was unavailable. Before the middle of the 19th century, the advantage of groundwater in terms of hygienic safety was unknown and it was not until the cholera epidemic of 1892 in Hamburg, Germany, before this benefit was fully recognized. With 20 000 people affected, of which 8000 died, the public water supply industry was forced to redefine its terms of reference. From this moment began two schools of thought, where on one hand the maritime nations acknowledged the need for purification of surface water under all circumstances, while the continental countries on the other, rejected surface water completely. Only groundwater was thought fit as a source for public supply and, until a few years ago, the German law required that 'with respect to its origin, drinking water must be appetizing'. The authorities concerned interpreted this demand by rejecting all plans for river or lake based public water supplies, allowing provision for groundwater only. Taking into account the enormous advances in technical possibilities and in particular in reliability of surface water treatment processes during the last decades, this position is no longer tenable and today even Germany uses river and lake supplies.

At the present time, groundwater is still used on a large scale and for a variety of reasons, the most important being:

(a) for individual supplies where treatment is impossible;

(b) for small towns and small scale rural supplies, where the possibilities of local abstraction do away with the need for transportation over great distances. Where treatment is required, it is simple and cheap, while the constant physical and chemical composition and the absence of bacteriological pollution do away with the need of continual expert supervision;

(c) for industrial supplies where private, on the spot, abstraction of groundwater is cheaper than taking water from a public supply grid;

(d) for cooling purposes where the constant temperature of groundwater is very attractive.

For large cities, groundwater abstraction has little appeal. Taking into account the low yield of an aquifer, enormous areas must be set aside for this purpose, while extensive recovery works are necessary thereby increasing the cost of groundwater abstraction. However, a tendency to change from surface to groundwater supplies may be noted. Apart from the well known advantages of constant quality and natural reliability, two other reasons have lately come to the fore:

(a) each year laboratories all over the world synthesize about 20 000 new chemicals, of which about 400 are ultimately produced on a commercial scale. Sooner or later these chemicals and their degradation products will reach the river and contaminate the drinking water. The long term effect of these chemicals on human health is largely unknown, giving a preference for groundwater which, by virtue of its age, cannot contain them;

(b) rivers often act as busy shipping lanes and run through highly industrialized areas. Under such circumstances a catastrophic pollution of the river is not impossible,

> making the drinking water derived from it unfit for human consumption and for many industrial applications. Storage reservoirs with a volume of at least two months' consumption are now required, but these increase cost; this also makes groundwater abstraction more attractive.

Today, public water supplies in continental Europe are still largely based on groundwater abstraction, the percentage varying from 99% in countries like Denmark and Austria to 65% in the Netherlands. For the future, a further growth in drinking water consumption may be expected; this is due to an increase in the population causing an increase in the domestic per capita consumption and also, perhaps, by increasing industrial demands. As stated before, the possibilities of groundwater recovery are, however, rather restricted. To elucidate this point Figure 3 shows a groundwater catchment area situated between two rivers and without surface run-off. The illustration to the left assumes that the area involved is the property of the water supply company and that there are no restrictions whatsoever on the lowering of the groundwater table. The maximum yield now equals the amount of residual rainfall. With a value of 220 mm/year (world average), this means an allowable abstraction of 220 000 m^3/year km^2, adequate for 1500 people with a per capita consumption of 400 l/day. In most cases, however, other interests have to be taken into account, for instance agriculture and preservation of nature, severely limiting the permissible recovery of groundwater. Assuming a high figure of 30% of the recharge by rainfall (Figure 3 to the right), one square kilometre of catchment area can only supply water to 450 people, meaning that 20% of the total land surface area in a country such as France and 90% in a country such as the Netherlands, must be available for groundwater abstraction. This is simply impossible, and in future surface water supplies must be used on an ever increasing scale. Some advantages of groundwater, such as hygienic reliability, constant quality and the possibility of storage, are still obtainable by the process known as artificial recharge and indeed this treatment method has made considerable advances over the whole of Europe.

4. GROUNDWATER POLLUTION

Groundwater pollution may be classified in many ways, but in the first instance a distinction should be made between pollution caused by the abstraction itself and pollution caused by the action of other parties.

Pollution due to abstraction itself is mostly caused by over-extraction. Figure 4 shows a few examples which are self-explanatory. The brackish water upconing of Figure 5 on the other hand can never be prevented, while the lateral diffusion of Figure 6 is difficult to predict. A pollution which still haunts continental water engineers occurred in Breslau, Germany, in 1906. Here groundwater was abstracted from fluviatile deposits, containing among other things insoluble ferrous sulphide and equally insoluble manganous oxides. Abstraction had lowered the groundwater table and when at the end of a long dry spell a further lowering of the groundwater table occurred, atmospheric oxygen reached the deposits mentioned above. Ferrous sulphide was oxidized to soluble ferrous sulphate and sulphuric acid

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4$$

The sulphuric acid transformed manganous oxides to soluble manganous sulphate

$$MnO + H_2SO_4 \longrightarrow MnSO_4 + H_2O$$

while the presence of large amounts of ferrous sulphide and organic matter limited further oxidation and hydrolysis to insoluble ferric oxide and manganese oxide hydrates according to the (simplified) reactions

$$2FeSO_4 + \tfrac{1}{2}O_2 + (n+2)H_2O \longrightarrow Fe_2O_3.nH_2O\downarrow + 2H_2SO_4$$

$$MnSO_4 + \tfrac{1}{2}O_2 + (n+2)H_2O \longrightarrow MnO_2.nH_2O\downarrow + 2H_2SO_4$$

$$H_2SO_4 + 2HCO_3^- \longrightarrow 2H_2O + 2CO_2 + SO_4^{--}$$

In the subsequent wet period, the dissolved ferrous and manganous sulphates were flushed out, raising the iron content to 400 mg/l and the manganese content to 200 mg/l in the aquifer.

Pollution caused by the action of third parties may be classified according to the extent of time and place. With both parameters being either small or large, four cases may be distinguished:

(a) a diffuse pollution of long duration, with the most important pollutants being the fertilizers and pesticides used in agriculture;
(b) an incidental diffuse pollution, for example radioactive fall-out caused by accidents in a nuclear energy plant;
(c) a continuous point pollution with many possibilities such as leaching water from municipal and industrial solid waste dumps, leaking domestic oil tanks next to industrial waste disposal with injection wells,and domestic waste disposal with cesspools;
(d) an incidental point pollution, for example, caused by salt used for de-icing of roads, by oil and other chemicals from a burst pipeline, by traffic accidents, etc.

The importance of the pollution not only depends on its magnitude, but in particular on its subsequent fate during underground travel. In this respect another classification may be more important:

(a) by pathogenic organisms. Although this pollution occurs in massive amounts, by manure for example, it is completely removed by self-purification accompanying underground travel;
(b) by mineral substances. Very objectionable as they mostly stay in solution and are carried along by the flowing groundwater;
(c) by soluble organic compounds. Very unpleasant, in particular because of secondary effects. After sufficient dilution has taken place, however, they are mostly degraded and converted into mineral substances;

(d) by insoluble organic compounds such as oil, which are retained by capillary forces in the immediate vicinity of the point of infiltration and are slowly degraded by oxidation;

(e) by taste and odour producing substances, mostly originating from the degradation products mentioned under (c) and (d);

(f) by poisons. Inorganics such as heavy metals, organics such as pesticides and radio-active materials. Potentially they are extremely dangerous, but in practice the chromatographic effects of adsorption and the spreading due to dispersion causes such a dilution that only in the immediate vicinity of the place of administration can toxic levels be reached.

With regard to the enormous diversity in groundwater pollution, it is impossible to consider all aspects. According to the outline given above, pollution by minerals, rather than the innocuous or poisonous substances, is most important and some of its causes are considered below.

For agriculture, fertilizers are indispensable. In the past farm yard manure was mostly used for this purpose, but the amounts available were rather limited. By the development of artificial fertilizers, much higher applications became possible and today economy has become the deciding factor. With the rising food prices and the growing cost of labour the amounts of fertilizers used has steadily increased. Nowadays nitrogen applications of a few hundred kg N/ha a year and phosphorus applications of a few tens of kg P/ha a year are quite normal. These substances are partly used for plant growth and partly flushed down to the groundwater table, polluting the groundwater supply. When in the root zone or below, near anaerobic conditions prevail, nitrates are reduced to ammonia (Section 2) which, by its positive charge, is firmly bound to the negatively charged soil particles. In cases where the aquifer contains large amounts of organic matter, fully anaerobic conditions will develop, further reducing the nitrates to N_2 and other gaseous compounds such as N_2O and NO. For grassland on clayey soils the nitrate content of the groundwater will be small, corresponding to less than 5% of the amount applied, while for arable land on sandy soils this percentage may be as high as 50%. Assuming, for the latter case, a nitrogen application of 200 kg N/ha a year and a residual rainfall of 300 mm/year, the nitrogen content of the groundwater will rise to

$$c = \frac{(200)10^3}{(0.3)10^4} \frac{1}{2} = 33 \text{ mg N/l} = 148 \text{ mg } NO_3/l$$

This is well above the allowable limit for drinking water (50 to 100 mg NO_3/l) and will lead to serious eutrophication problems after reaching surface water.

With phosphorus, the situation is quite different. The amount applied as P is a factor of 5 to 10 times smaller and, yet even more important, the geochemical mobility of the various compounds is extremely reduced by ion-exchange with clay-minerals and binding to metal ions, forming insoluble deposits. As a result, a noticeable movement of phosphorus down into the soil seldom surpasses a depth of 0.5 m, limiting total phosphate contents in groundwater to values of 0.1 to 0.5 mg/l only. These values are of no consequence for drinking water, but they again promote the eutrophication of surface water. Biocides in groundwater are again of little importance; some are slightly soluble in water, others are degraded rapidly; all are adsorbed by clay and organic matter particles present in the sub-soil.

Although occurring only locally, the leaching of so-called sanitary landfills may seriously pollute groundwater supplies over large areas. For municipal wastes, the approximate mineral composition of the leachate (residual rainfall about 500 mm/year) is given in Table 4, while the pH varies from 7.2 to 8.2.

Table 4. Dissolved salts in the leachate from municipal refuse dumps expressed in mg/l

Na^+	1500	Cl^-	1500
K^+	500	SO_4^{--}	100
Ca^{++}	500	HCO_3^-	4000
Mg^{++}	100	NO_3^-	2
NH_4^+	200	PO_4^{---}	1
Fe^{++}	20		
Mn^{++}	1		

By the presence of large amounts of organic matter (BOD_5^{20} 100-200 mg/l) further acidification and reduction will occur and additional minerals will be dissolved from the aquifer. Apart from the magnitude of the salt content, the composition differs little from those found in natural waters, meaning that by dilution major difficulties can be avoided. The water described in Table 4 has a total salt content of 8500 mg/l. Reducing this to 500 mg/l by mixing with water having a salt content of 200 mg/l, requires a mixing ratio n determined by

$$8500 + n.200 = (n + 1)500 \text{ or } n = 27$$

this is certainly not an impossible proposition.

In practice, industrial waste deposits constitute the most serious meance to groundwater quality. In principle any toxic substance may be present: heavy metals such as arsenic, chromium and mercury; organics such as cyanide and pesticides; radioactive compounds. Most of these substances are very stable and when they are soluble and have an adequate geochemical mobility, groundwater sources over large areas may be affected. When after the Second World War the chemical industry grew rapidly, many cases of groundwater pollution occurred in western Europe, making various private supplies and even some public supplies unusable. An even greater danger to groundwater quality originates from liquid waste disposal using (shallow) wells, injecting the fluid into water bearing formations which are not completely sealed from overlying aquifers and again many examples of irreparable damage could be quoted.

By itself, waste heat can hardly be called a contaminant. It raises, however, the temperature of the groundwater, accelerating the solution of soil materials, increasing their solubility and in this way augmenting the mineral content of the groundwater concerned.

5. PROTECTION OF GROUNDWATER QUALITY

Pollution of water may be defined as a modification of its physical, chemical or micro-biological properties, making it less fit for any subsequent use. Underground, pollution travels very slowly from the point of application to the point where the groundwater is recovered or discharged. Once pollution has reached the aquifers it will remain there for extremely long periods. In contrast with rivers, such a pollution cannot be flushed away, therefore protection of groundwater quality can only be obtained by preventitive measures.

In our modern society, many causes of groundwater pollution can be distinguished:

(a) by the normal activities of man. For example, cess-pools and leaking sewers, sewage treatment plants and solid waste deposits, hospitals and graveyards. To these are added detergents, leaking oil from domestic fuel tanks and waste oil from cars;

(b) by agriculture using natural and artificial fertilizers, oil and pesticides and in particular leading to the production of enormous amounts of manure and offal for which no beneficial use can be found;

(c) by industry, manufacturing and storing a wide variety of compounds, some of which may cause problems (for example ammonia and phenols), some contain heavy metals, unnatural organics, poisons or may even be radioactive. A secondary source is air pollution, which eventually is washed out by the rain and flushed down to the groundwater body. In some areas the mining industry contributes heavily, for example, opencast mining of coal bringing ferrous sulphide into contact with atmospheric oxygen, lowering the pH considerably and drilling for oil with the accompanying dangers of groundwater pollution by drilling mud, salt water and oil itself;

(d) by traffic, with a continuous pollution by lead from petrol, oil from leaking cars and salt from de-icing of roads (500 M mg each winter in the Netherlands) and an incidental pollution by road and railway accidents, plane crashes, etc. The pollution caused by leaking or bursting pipelines is, on average, negligible, but locally it may be of great importance.

According to the last paragraph of Section 3, a major portion of the land surface in western Europe serves as a catchment area for groundwater supplies. To ban from such large areas all the causes of pollution, as mentioned earlier in this Section, is simply impossible. A more sophisticated approach is necessary, allowing less pollution as the distance to the aquifer decreases and vice versa. In many European countries this has led to the setting up of protection zones, commonly arranged as described below:

I. the well field itself in which no activity by third parties is allowed. Depending on local geo-hydrologic conditions it reaches out to a distance of 20 to 50 m from the source area and should be fenced in order to prevent tresspassing;

II. the inner protection zone in which no possibility of pollution whatsoever can be accepted. To protect the recovered groundwater against bacteriological contamination originating from outside this zone, its width should be at least 50 to 100 m and as large as is necessary to obtain a travel time of 2 to 3 months, again depending on local geo-hydrologic conditions;

III. the outer protection zone in which all physical and chemical pollutions should be prevented which are not removed by self-purification during underground travel towards the aquifer. If possible this zone should comprise the full catchment area. When this cannot be obtained, Zone III should be subdivided as follows:

IIIA. the inner band of the outer protection zone with a retention time of four years in which all non-degradable pollution should be avoided;

IIIB. the middle band of the outer protection zone with a retention time of six years, in which only those non-degradable pollutions can be accepted of which the influence on groundwater quality can be treated;

IIIC. the outer band of the outer protection zone with a retention time of 10 to 20 years, the same requirements of Zone IIIB.

The philosophy behind the subdivision of Zone III (Figure 7) is that non-degradable pollutions originating from outside Zone IIIA need four years (plus two to three months) to reach the collectors, which is sufficient time to design and install additional treatment facilities. When Zone IIIC is not present, irreparable damage needs 10 years to manifest itself, in which period a new catchment area can be found and taken into use. When Zone IIIC is present, the existing catchment area may continue to operate for another 20 to 30 years, allowing normal depreciation so that additional expenses are avoided. It should be noted in the meanwhile that Figure 7 supposes the groundwater before abstraction to be at rest. Usually this is not the case, considerably changing the configuration of the various protection zones. An example of this is shown in Figure 8.

The greatest difficulty with protection of groundwater against pollution is that remedial measures can only be taken against known sources. Unknown sources, including accidents, remain an ever present threat to groundwater quality, or in other words:

> 'the real danger of groundwater pollution is not pollution itself but the ignorance of pollution problems'.

6. RESEARCH NEEDS

In our complicated society with its ever increasing number of man-made chemicals, we simply do not know the dangers of groundwater pollution. Are those chemicals toxic in the long term? What about the raw materials of which they are made and their degradation products after use? Many instances are known about chemicals in normal use for long periods which, subsequently, are suspected to be carcinogenic, teratogenetic or mutagenic, as for example sweeteners and colouring agents in some recent cases. Remedial measures are certainly possible, but they are only taken after recognition of the problem. When mercury was discovered as being the causative agent for the Minamata illness in Japan, the mercury consumption of the salt industry in the Netherlands was reduced to 10% of its original value! The European Economic Community are attempting to establish grey and black lists for dangerous chemicals but good results can only be obtained after industry has revealed its respective trade secrets.

During underground flow, many changes in water quality occur, some favourable, others disadvantageous (Section 2). With our present knowledge of geochemistry, however, reliable predictions can only be made for the most simple cases under near ideal circumstances. In particular this came to the fore when artificial recharge was introduced to supplement groundwater sources. For better forecasts, much research is still needed.

In problems of groundwater protection, as with those of artificial recharge, the retention time plays an important role, not only the average value but also its variability. Up till now, the main interest of hydrologists centres around the lowering of the groundwater table accompanying abstraction. For this problem, the overall value of the coefficient of transmissibility as determined by pumping tests for example, is adequate. According to Figure 9, however,

$$k_a H = k_1 H_1 + k_2 H_2 + k_3 H_3 + k_4 H_4$$

The average retention time is easy to determine

$$T_a = \frac{\mu H L}{q_o} \quad \text{with } q_o = k_a H \; S,$$

μ as specific yield and S as slope of the piezometric surface. This gives a retention time for the various layers

$$T_i = \frac{k_a}{k_i} \; T_a$$

which may show an enormous variation. For the simplified case of Figure 10 and $q_1 + q_2$ constant

$n =$	1	2	5	10
$\frac{T_2}{T_a} =$	1	0.55	0.28	0.19
$\frac{q_2}{q_1 + q_2} =$	0.1	0.18	0.36	0.53

Crude methods to determine the variation of the coefficient of permeability from one layer to another are available, but better ones are needed.

7. LITERATURE

Excellent literature surveys can be found in:

Die Beschaffenheit des Grundwassers
Prof. Dr. Georg Matthess
Gebrüder Borntraeger, Berlin-Stuttgart,
1973

Groundwater Pollution
Jean J. Fried
Elsevier Scientific Publishing Company
Amsterdam-Oxford-New York,
1975

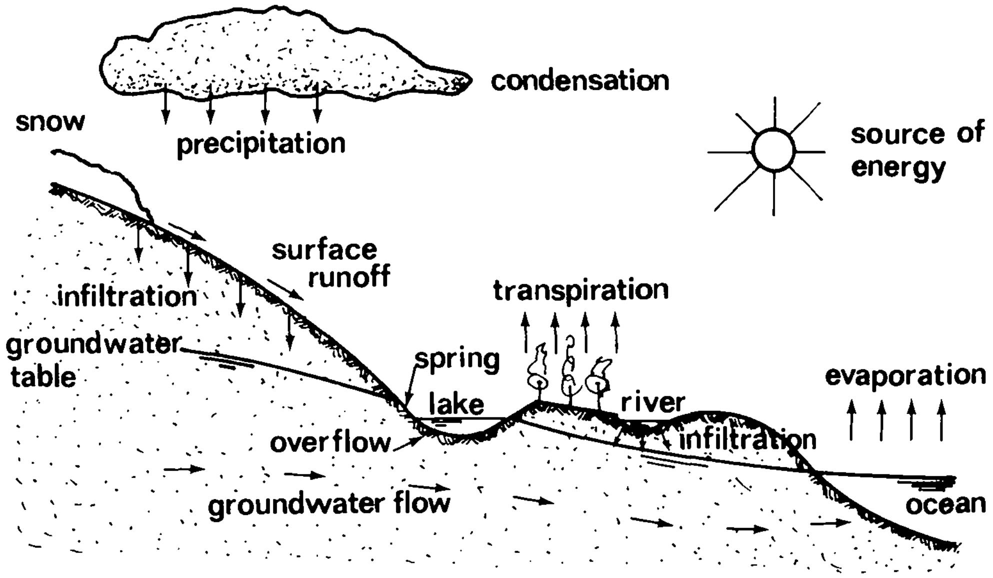

Figure 1. Hydrologic cycle

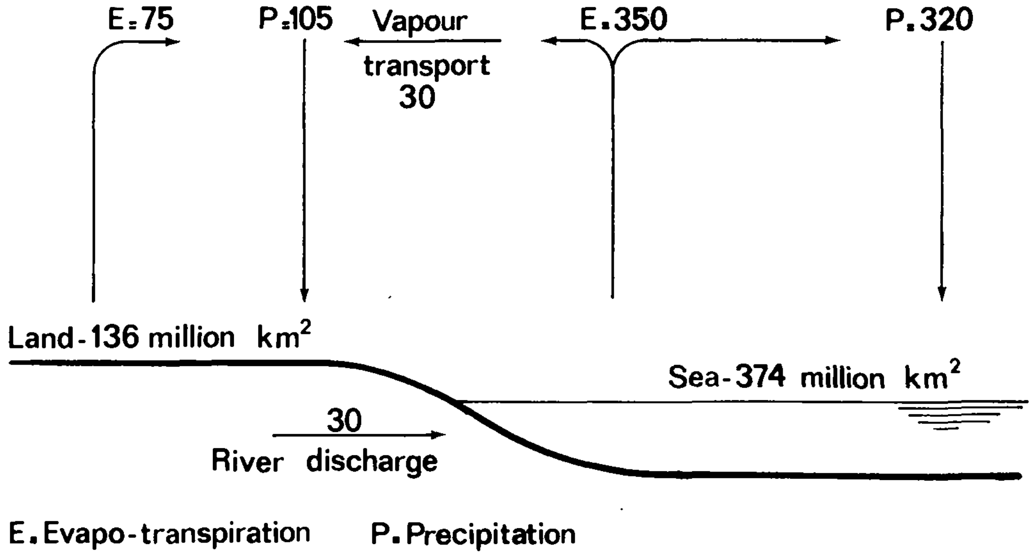

Figure 2. Global water movements in 1 000 km^3/year

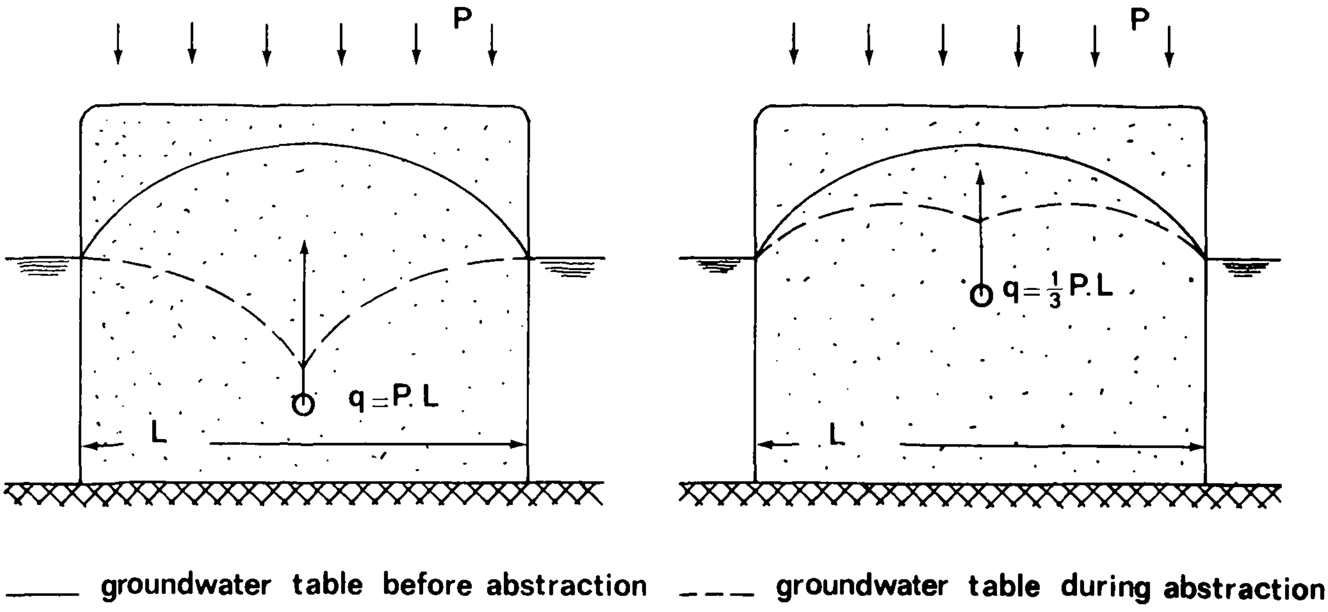

Figure 3. Groundwater recovery

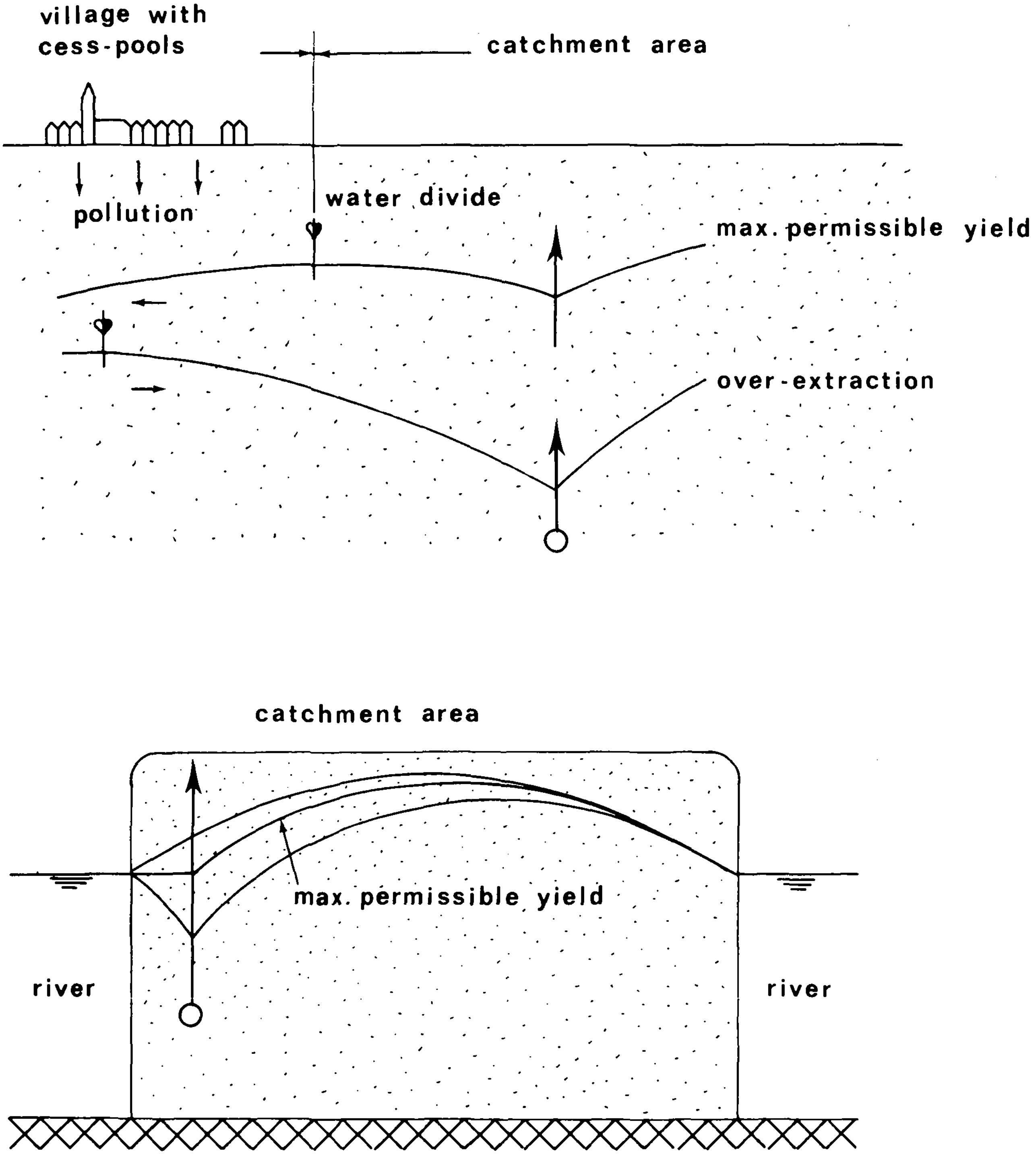

Figure 4. Groundwater pollution by over-abstraction

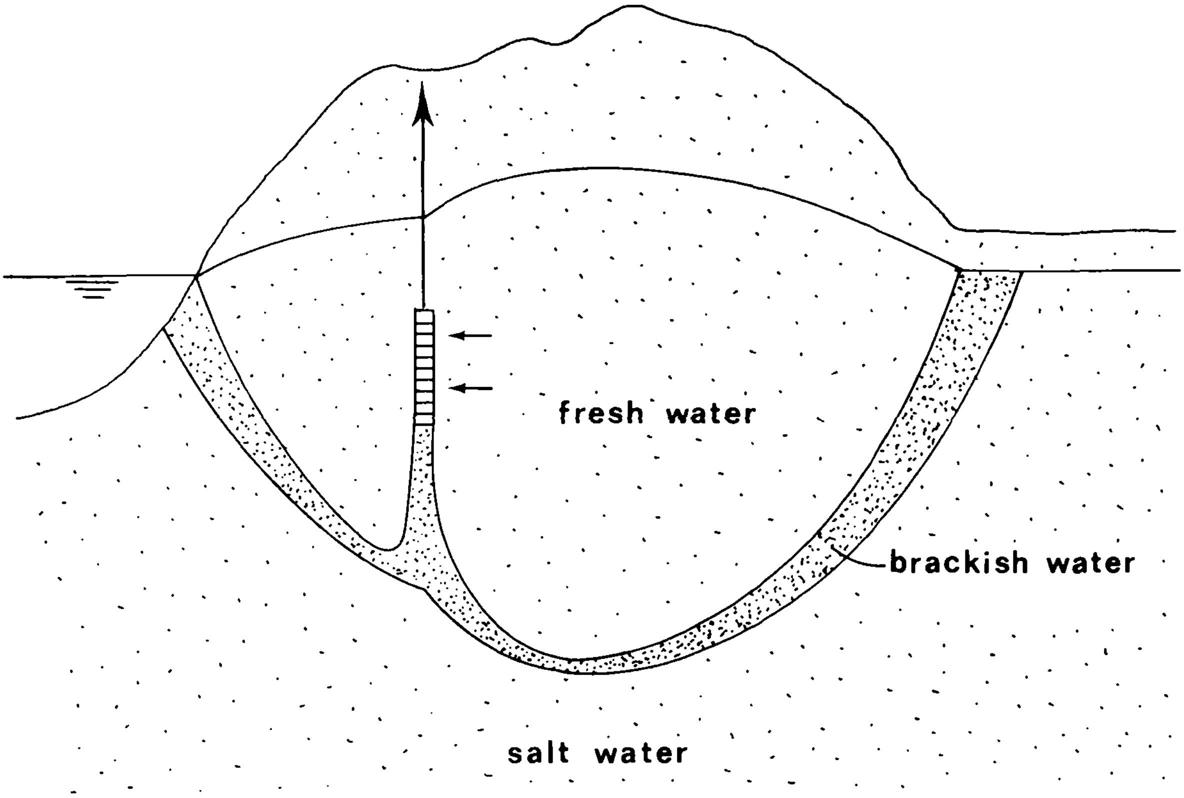

Figure 5. Upconing of brackish water

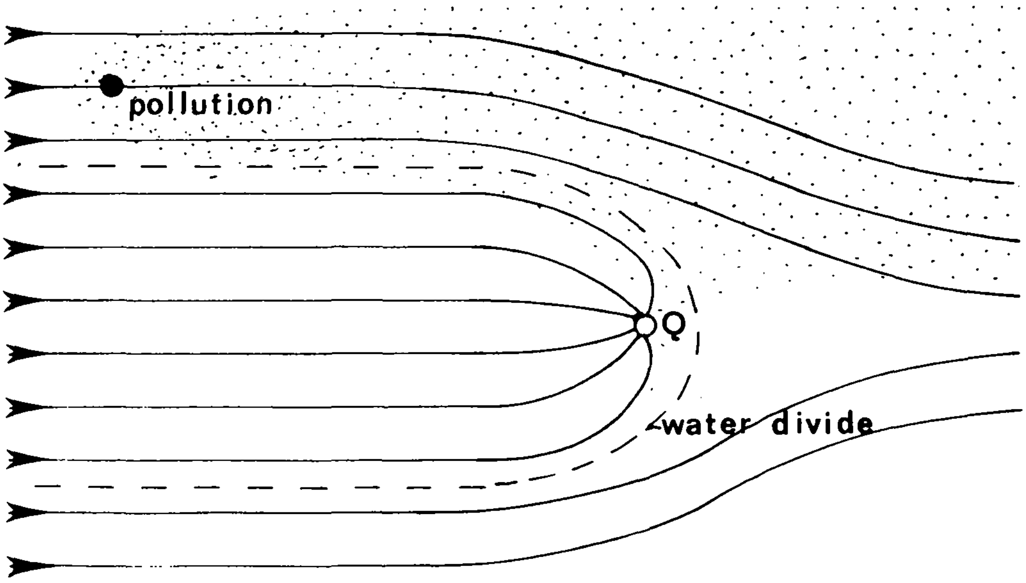

Figure 6. Pollution by dispersion

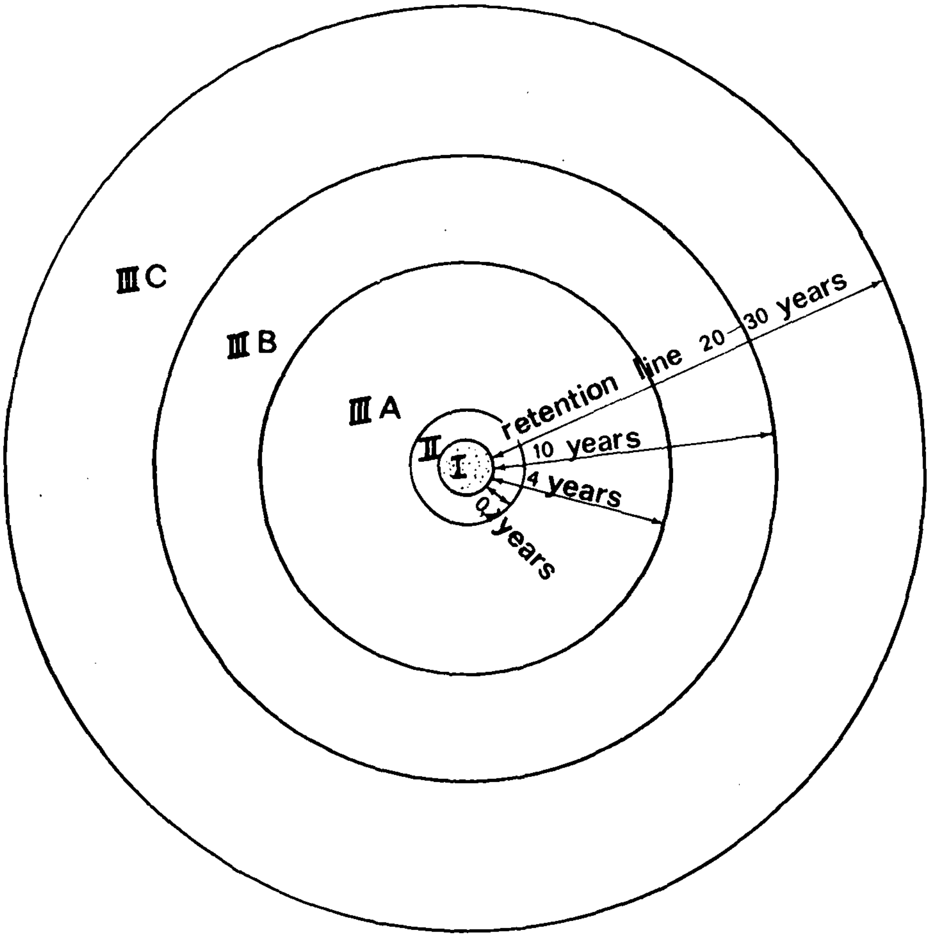

Figure 7. Subdivision of protection zones (no preceding groundwater flow)

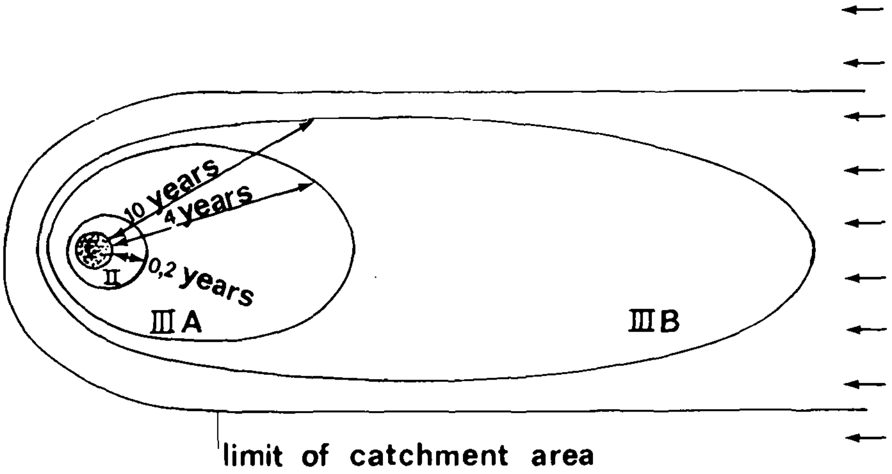

Figure 8. Protection zones with preceding one-dimensional groundwater flow

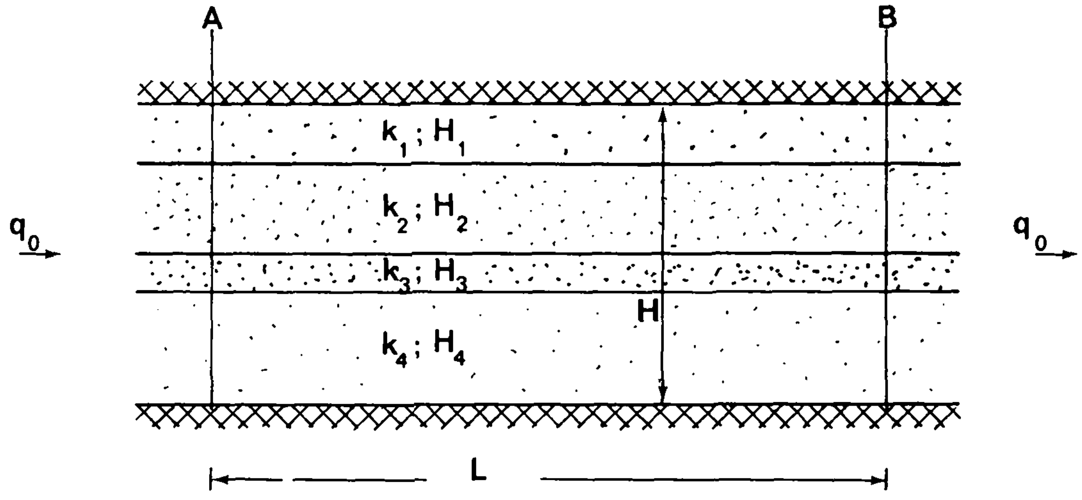

Figure 9. Artesian aquifer composed of various layers with different values for the thickness and the coefficient of transmissibility

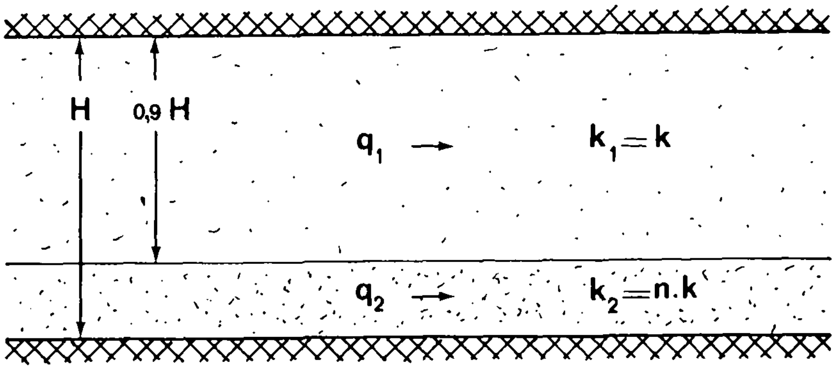

Figure 10. Artesian aquifer composed of two layers

DISCUSSION - SESSION 1

Mr R.A. DOWNING, in opening the discussion, said that the three papers presented in Session 1 had adequately set the scene for the following sessions. It was clear that although there were differences in the approach to groundwater development in Britain, Europe and the USA, the increasing importance of maintaining groundwater quality was common to all.

The last 10 or 12 years have seen a change in attitude to groundwater development in England. The realization that aquifers not only provide water supply, but also maintain adequate river flows for, amongst other purposes, diluting effluents, has led to schemes for regulating rivers by using groundwater storage. Consequently, the cost of producing groundwater has increased - a price that has to be paid for preserving the environment. Similarly, the need to maintain the groundwater environment - that is its quality - involves a cost and again this price is necessary and will have to be paid. Preserving groundwater quality is now one of the major tasks of hydrogeologists.

Mr Jones had commented in Paper 1 that aquifer systems in Britain are under increasing stress. The comment could be misinterpreted and it should be emphasized that fresh water in the main aquifers far exceeds the storage necessary to balance uneven distributions of rainfall. Rainfall and pumping capacity are the factors limiting the development of groundwater rather than storage limitations and pollution constraints. This is being emphasized during the current drought.

Looked at generally, groundwater pollution in England is due to:

1) Use of nitrogeneous fertilizers. This is a diffuse source and a serious problem. Nitrate levels in groundwater in aquifers at outcrop in the drier eastern parts of England could ultimately exceed the recommended WHO limits.

2) Local problems due to landfills
sewage effluents
industrial wastes including oil seepages
agricultural wastes

3) Saline water intrusion - even this is a local problem that has arisen because of the absence of effective management control in the past. It can be corrected at a price.

The legal basis for the control of groundwater pollution in Britain is set out in the Control of Pollution Act of 1974. The problems arise as Mr Keeley pointed out, in effectively implementing the law and the cost of monitoring the systems. Enforcement of the law in so far as it relates to groundwater pollution has always been a problem and will remain so because groundwater pollution is a slow, insidious process, and when it is discovered the finger may be pointed too late. In such situations problems have to be anticipated and avoiding action taken as far as this is possible. Pollution should be controlled by siting potential sources of pollution in appropriate areas after considering the geology and groundwater flow paths. For example, sites should be near outlets to aquifer systems or in aquifers of limited extent no longer in use, or likely to be used in the future for water supply. Advantage should be taken of the purification processes that occur in aquifers. Accidental pollution on aquifer outcrops can be a serious problem. The immediate action necessary to limit the effect of such incidents has been considered in the UK by the Oil and Water Industries Working Group and the wider issues, with regard to groundwater pollution generally, are now being considered with a view to establishing guidelines for preventative action. Protection zones around wells, such as those described in Professor Huisman's paper, exist in England but the width of the zones are invariably greater reflecting the importance of fissure flow in the principal aquifers.

Mr Downing said he did not need to remind the Conference that groundwater is a valuable resource. It is cheap to develop but in developed countries the true value of groundwater as a good quality water resource should probably be emphasized by charging an appropriate price for its use. If Professor Huisman's worry materializes about the petrochemical industry's influence on water quality and health, then groundwater will be even more valuable. In this context he thought that Mr Keeley had made a most important point in stressing that priority must be given to the protection of groundwater quality because the cost of restoring the quality once it has been polluted was in many cases prohibitive - even if possible.

Professor J. BEAR said that rather than discuss the advantages and disadvantages of groundwater, we should draw conclusions on the known merits of groundwater with respect to quality, quantity, storage etc. and make decisions on its correct use. We should encourage the use of groundwater. In the ideal situation this should be the conjunctive use of both groundwater and surface water.

He was rather surprised to learn from Mr Jones's paper that groundwater utilization in Britain is so small relative to what he believes to be its merits. In Israel, the reverse situation operates; about 80% of all abstracted water is groundwater with 20% surface water. Artificial recharge techniques are also extensively used.

The complex hydrogeological conditions in Britain have been emphasized by Mr Jones. Although on a large, country-wide scale the groundwater system may appear complex, this is not the case as in practice we are usually dealing with individual basins within this complex arrangement. When we look at individual aquifers on a regional scale, the complex picture is simplified. On a local scale a three-dimensional approach may be necessary to represent the complexities, but on a regional basis aquifers may be regarded as thin layers of large areal extent and the groundwater flow is two-dimensional.

Quantity and quality control are both part of management. Sometimes groundwater quality is intentionally reduced, for example by artificial recharge. Such changes can be made by proper management once the hydrogeological and chemical processes within the aquifer are understood.

In Professor Huisman's paper, idealized converging of radial flow to the pumping area with or without lateral flow is shown in the figures. The real situation in many cases is that wells are spread over a large area and a general flow-net approach should be used to predict changes in concentration that will take place. Flow nets, however, may be difficult to use because transient state conditions may prevail.

Mr G. P. JONES, in reply, said that problems become more, not less, complex as smaller basins are considered. The hydrogeological complexity that exists on a local scale, for example fissuring in aquifers, cannot be demonstrated on a regional scale. He felt the Israeli concept that groundwater should be 'pushed' regardless of the consequences should not be accepted. Until the hydrogeological characteristics of UK aquifers are fully understood the development of groundwater should not proceed.

The complex nature and variability in the subsurface conditions cannot be overemphasized if we are to prevent too ready an acceptance of the uniformity of the continuum within which the water cycle operates. Although data may be obtained from pumping tests which indicates that an aquifer is behaving as an isotropic medium, it is known from geological experience that the aquifer is not isotropic. Even more of a problem will arise when groundwater quality is looked at,since there are more variables to deal with.

Mr Jones went on to say that the work reported in every paper in the Conference was going to be affected by these complexities and none more so than the work on predictive models. He was not too happy about predictive models for quantitative work, particularly in view of the complexities that he had described. Ideal aquifers can be modelled, and indeed the resultant decision models are valuable, but the prototype used cannot be an exact copy of the ground, and conditions dealing with quality are even more difficult. Most pollution problems in Britain now and in the future, are and will be local rather than regional in scale, and modelling of such situations with prediction in mind will be fraught with difficulty.

Ir R.J. WILDSCHUT said that in Holland the geohydrological situation is much simpler than that described by Mr Jones and reliable two- or three-dimensional models can be used in such situations.

Dr M.J. O'SHEA said he was very reassured by the emphasis Mr Keeley placed on the fact that the protection of groundwater quality is fundamental. Some people in the UK, although not many hydrogeologists, take the view that certain major and minor aquifers can be written off. Pollution by landfill sites or liquid waste disposal sites can be allowed to occur, mainly because these aquifers are not at present being used as sources of potable groundwater.

Mr D.D. YOUNG said that Mr Jones had made the comment that the importance of groundwater quality lay in relation to its use. While he felt this was a fair generalization for many groundwaters, he was sure that it was not of universal application to shallow ones, where he thought an important interest very often lay in the protection of surface streams which were groundwater supported and may, in fact, simply be considered as an exposure of the water table. In this situation it may very often be environmental rather than use-aspects which are of concern.

Referring to the paper by Mr Keeley, Mr Young said he thought the comment on the validity, or rather lack of validity, of E. Coli was particularly well made, but he wondered how important it was in the situation where a supply was chemically disinfected before passing into use.

Referring to Professor Huisman's paper, he wondered in how many cases it is possible to draw the kind of circles and elipses that are shown in Figures 7 and 8. He believed that in many cases, perhaps in the majority of cases, it may be difficult to estimate the right order of magnitude for travel time from a given point in the aquifer to the well. He wondered how practical this approach was, particularly for the outer zones. He said that the reference in the paper to the United Kingdom attitude to grey and black lists was not, strictly speaking, correct. The objection raised by the UK was not to the existence and use of these lists, but simply the wish to make sure that they were established on a sound scientific basis.

In reply Mr J.W. KEELEY said that one of the uses of coliforms is as a tool to trace the movement of other biological pollutants, but it simply does not work for that purpose in groundwater. He agreed that if the water is chlorinated or otherwise treated it is not a problem, but in the United States there are a great many rural areas which take water from the ground and give it no treatment at all.

Ir R.J. WILDSCHUT, replying to Mr Young, said that in order to estimate travel times the transmissivity coefficient of the most permeable layer within an aquifer should be used, rather than the total transmissivity of the aquifer. However, at present it is difficult to obtain a reliable measurement of this.

Dr L.F. KONIKOW asked Mr Wildschut whether the concept of Protection Zones described in Professor Huisman's paper was just a proposal, or whether these had been implemented. He thought that defining protection zones on travel time would be very difficult to do, both on a legal and on a practical basis. He asked whether travel time was defined in terms of the mean velocity of the water or in terms of the arrival of the first detectable quantities of the contaminant, which would be sooner than indicated by the mean travel time. There would be different arrival times for different contaminants, depending on adsorption, ion-exchange and other chemical reactions. It would, therefore, be necessary to calculate different times of arrival for different chemical species from a particular source to a particular sink. Additionally, groundwater flow is frequently a transient phenomenon in that the velocity field itself is not constant over time and the velocities would be a function of hydraulic gradients, which would vary with pumping rates, regional recharge and so on. He thought that basically the idea was a good one, but was not sure how it could be implemented. There would also be problems in applying protection zones to deeper aquifers. What would be the effect of contamination at the surface on deeper aquifers ? Perhaps the concept of protection zones should be applied strictly to shallow aquifers, or else other modifications would be required.

Ir R.J. WILDSCHUT said he agreed with Dr Konikow's view. At present the concept of Protection Zones was just a proposal in Holland. The maximum velocity should be used to predict the first arrival of a contaminant, but its use depends on the kind of pollution. For safety the maximum velocity should be used. He thought that chemical reactions should be taken into account but only after initial legislation on protection zones has been introduced. In the case of deeper aquifers with, for example, an upper clay layer, the travel times should be based on the least permeable zone of the clay layer.

Session 2

CONCENTRATION AND MOVEMENT OF POLLUTANTS

Chairman:

B. J. Hardcastle, BSc, ACGI, DIC, FICE,
FIWES, MIMechE,
Divisional Manager,
Thames Water Authority.

Presented Papers:

Support Papers:

PAPER 4

FLOW MECHANISMS GOVERNING THE MOVEMENT OF A POLLUTANT IN A GROUNDWATER SYSTEM

N. R. Brereton and W. B. Wilkinson

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1. INTRODUCTION

In order to maintain a satisfactory water quality in his abstraction wells and groundwater spring flows, the Water Engineer will ask the following questions in relation to known sources of contamination.

Will the contamination enter the well or spring?

If so, in what concentration?

Will these be at an acceptable level for delivery to supply?

How long will the contamination take to reach the well or spring?

How long will the contamination persist?

What preventive measures may be taken?

If the contamination by-passes a particular well or spring system what area of the aquifer will it pollute and will this prevent the future development of new groundwater sources?

Should the contamination of a well or spring supply unexpectedly occur, the Engineer will ask the same questions and these will be posed in relation to a range of potential sources of pollution within the groundwater catchment in an attempt to identify the particular source or sources that are causing the problem.

Information on some or possibly all of the following is necessary in order to answer these questions:

(a) geology and hydrogeological boundaries of the aquifer and adjacent strata,

(b) hydraulic and physical properties of the aquifer which govern the movement of the pollutant,

(c) groundwater levels and flow patterns,

(d) rate of infiltration to the aquifer,

(e) meterological conditions over the groundwater catchment,

(f) nature of the pollutant at its source and the chemical and biological changes which will occur as it moves through the aquifer,

(g) surface water hydrology and the degree of hydraulic interconnection between the surface and the groundwater systems,

(h) past, present and future groundwater abstraction regimes and

(i) the range of analytical and modelling techniques that are available, their advantages and limitations, and the most appropriate to use in a given situation.

Having collected the data and undertaken an analysis a decision may be made on its results that could involve considerable expenditure. It must therefore be recognised that the processes governing the flow of a contaminant in a groundwater system are extremely complex and that simplifying assumptions are necessary in each area of (a) to (h) above before the final analysis (i) can be made. The present paper is concerned particularly with the flow mechanisms that govern the movement of a pollutant in a groundwater system ((a) to (d) above) and with the difficulty of collecting the basic data to describe these mechanisms and their representation in quantitative analysis and in models of the system.

2. PHYSICAL PROCESSES AND MODELLING PROCEDURES

This section describes the principle physical processes governing the transport of contaminants into and through an aquifer. It also outlines the procedures generally followed in order to predict the changes in concentration of a pollutant in an aquifer under a given groundwater flow regime. The steps in this procedure are summarised in Figure 1. Each step is numbered and these numbers are used in the following text when describing an analysis or activity which is shown in the figure.

2.1. SOURCE OF POLLUTION

The source of pollution may be located on the land surface and hence be external ② to the aquifer system,or it may be located either partly or wholly within the aquifer system. External sources cover leachate from landfill sites, agricultural wastes, spills etc. Internal ③ sources include salt water intrusion from the sea or from other mineralized water within the aquifer and direct injection of contaminants below the water table e.g. from deep waste disposal wells. An important difference between external and internal contaminants is that the former may be in solid form and requires to be leached, in addition to which, it will have to pass through the soil layer and the unsaturated zone of the aquifer. Internal contaminants will, however, generally be in liquid form and in hydraulic continuity with the main aquifer. Although it is convenient for the present purpose to consider this simple division of pollution sources into external and internal, there are clearly situations intermediate between the two, for example, naturally occurring minerals in the unsaturated zone of the aquifer may be leached by water infiltrating from the surface or by a fluctuating water table due to an imposed groundwater abstractional or recharge regime.

The concentration of a contaminant leaching from a surface pollution source and entering the soil or unsaturated zone of the aquifer depends upon the quantity of surface pollutant, chemical changes that may occur within the material with time, whether the material is in solid, liquid or sludge form, its solubility and the availability of infiltrating water ④. This concentration ⑤ is often difficult to predict as, for example, in the case of the quality of a leachate resulting from a landfill or the rate of release of nitrate from agricultural land.

2.2. ZONE OF AERATION

As water moves through the soil zone and the unsaturated aquifer ⑦, biological and chemical processes may cause major modifications to the nature and concentration of the contaminants. Harmful chemicals and organisms may be held or degraded in the zone of aeration and thus be removed from the infiltrating water. These are the very processes that lead to groundwater in general being of such high quality. An understanding of the chemical and biological changes that can occur both within the pollutant source and in the zone of aeration are essential to the solution of many groundwater contamination problems. A great deal of research is currently directed towards this area (Department of the Environment, 1975). It is, however, beyond the scope of this paper to deal further with these aspects and the subsequent descriptions of the flow processes assume that, contaminants behave in a conservative manner in all parts of the aquifer system ⑦ & ⑩, i.e. they are chemically and biologically inert.

Flow through the zone of aeration is essentially vertically downwards with only very limited lateral spreading. If the contaminant is fully miscible with the infiltrating water it is transported downwards by the water but the rate of movement of the solute and the water do not necessarily correspond (Bresler, 1973, Wilson and Gelhar, 1974). The solute may travel at a slower rate than the transported water.

In some aquifers it may take several years for a contaminant to progress from the surface through the zone of aeration to the water table. In others the movement may be extremely rapid. In a given situation it is difficult to predict the rate of travel of a pollutant down through the zone of aeration and normally conservative values are adopted. These problems will be discussed in more detail in the following section.

2.3. SATURATED ZONE

On reaching the water table ⑪ the pollutant is carried along by the predominantly horizontal groundwater flow. Vertical flow components may, however, be present in some parts of an aquifer e.g. near to wells and other boundaries.

The pollution problem may generally be placed in one of three categories according to whether the pollutant is:

(a) completely miscible with the groundwater and has a concentration such that the density and viscosity of the groundwater remain essentially unchanged - usually referred to as the tracer case ⑮ (Fried and Combarnous, 1971),

(b) miscible but with the density and viscosity sufficiently dependent upon the concentration to influence the groundwater flow patterns ⑯,

(c) an immiscible fluid ⑰, such as an oil with a lower density than groundwater which may float on top of the groundwater.

In the tracer case ((a) above) the direction and rate of flow at any point in the aquifer is dependent on the distribution of hydraulic conductivity within the aquifer ⑧, the storage capacity, the natural or artificial groundwater recharge pattern ④&⑧, the groundwater discharges ①&⑧, and the geological boundaries to the aquifer systems ⑧. Numerous regional groundwater flow models, based on the continuity equation and Darcy's law (usually referred to as flow models), have been analysed over the last decade in order to guide groundwater resource development and management (Kitching et al, 1975). The majority have been two dimensional plan models. They have generally been based on the assumptions that, as regional groundwater flow gradients are small, vertical groundwater flow components may be neglected and that the hydraulic conductivity variations over a vertical plane of the aquifer may be averaged and this multiplied by the saturated thickness of the aquifer gives a transmissivity, T, that may be applied over that particular area of the model.

The actual velocity distribution is generally not of importance in resources development studies if water quality presents no problems. It may, however, be determined from such models by dividing the apparent velocity (Darcy velocity) by the aquifer porosity. Having obtained the actual velocity distribution it may now be possible to determine from the model the rate of advance of a pollution front with a sharp interface (Sauty, 1972). However, if the liquids are miscible, dispersion blurs the sharp interface (Figure 3e). The term dispersion is used to describe a range of physical phenomena that leads to this blurring and the development of a transition zone.

Dispersion results from (a) mechanical mixing due to flow velocity differences at both the microscopic and macroscopic level in initially adjacent water streams and (b) molecular diffusion due to chemical concentration gradients. The dispersive properties of an aquifer, expressed as the coefficient of dispersion, D, (which is a combined term including both mechanical dispersion and molecular diffusion) depends on its porosity pore size distribution, tortuosity, degree of stratification and on the flow direction. Many laboratory measurements of D have been made, generally on homogeneous media (Bear, 1972), and five flow regimes have been recognized. At low velocities molecular diffusion predominates but as the velocity is increased mechanical dispersion becomes more important until it is dominant. The final stage is reached when at very high velocities turbulent flow develops and Darcy's law no longer holds. The fourth regime of mechanical dispersion appears to apply to many groundwater flow systems and in this case an approximately linear relationship between the dispersion coefficient D and the flow velocity u exist such that,

$$D = \alpha u$$

where α is a constant of dispersivity with dimensions of length and represents the effect of the structure of the pores on mechanical dispersion. Laboratory and field studies have shown that dispersion occurs not only in the longitudinal direction of flow but also in a direction transverse to it. The dispersion coefficients, $D_L = \alpha_L u$ and $D_T = \alpha_T u$ are found to have differing values. Laboratory tests on homogeneous sands give D_L from 5 to 20 times larger than D_T. However some field contamination studies have given D_L and D_T in close agreement (Robertson and Barraclough, 1973).

Molecular diffusion may be important in predicting the behaviour of pollutants in the groundwater system particularly in the unsaturated zone. This is discussed further in sections 3 and 5.

If the pollutant is miscible with water its concentration in the aquifer is governed by the FLOW EQUATION as described above and the CONVECTIVE DISPERSION EQUATION. For the tracer case ⑮ these two partial differential equations may be solved separately. The former giving the velocity distribution in the aquifer system. The velocities are then used in the latter equation to determine the distribution and concentration of the contaminant. The dispersivity values must be determined from field tracer tests or from the analysis of data collected from an existing pollution situation.

The suggestion has been made that in certain pollution problems of the tracer type, it may be possible to neglect the width of the transition zone because its relative width decreases with the square root of the distance travelled from the pollution source. In this case convective effects are more important than dispersive. The position of the pollution front can then be determined using only the convection equation and treating the problem as one of an immiscible contaminant (Sauty, 1972). Analysis is then greatly simplified.

When the flow pattern is dependent on the concentration of the pollutant, it is necessary to solve the flow and the convective dispersion equations simultaneously ⑯ Saline intrusion phenomena fall into this category. Such solutions are complex, time consuming and frequently costly. If, however, it can be assumed that the transition zone is narrow the problem degrades to type (c) above and can be treated as one of two immiscible fluids with differing densities ⑰

A model, as represented by the partial differential equations and the associated boundary conditions, is set up so as to reproduce all of the essential characteristics of the pollution situation under consideration. As we have seen above, it may be possible to simplify the model by discounting factors which are considered to be relatively unimportant and by doing this to reduce the cost of obtaining a solution and of data collection. In practice, however, it is often necessary in groundwater quality models to neglect certain, possibly important factors, because (a) complex physio-chemical relationships between components cannot simply be described, (b) a method of solution to a particular model is not available, (c) costs of obtaining a solution are prohibitive, (d) the quality of the field data is such that a sophisticated model is not warranted, and (e) the cost of obtaining the necessary field data is prohibitive.

Analytical solutions (13) (Anon, 1969) may be obtained but only for relatively simple boundary conditions. Model solutions to a number of idealized pollution situations (14) for a range of aquifer and fluid properties have been made (Pickens and Lennox, 1976; Oakes, 1976) and these are complementary to the analytical solutions. Both may be most valuable in obtaining a 'first feel' for the problem or for use in the situation where data and/or computer finance is somewhat limited. For more complex situations, purpose made physical, analogue, or numerical models have all been used (14). With the recent development in computer techniques and numerical methods the numerical models are able to represent complex physical situations and are now generally favoured.

A less rigorous approach may be to base decisions on a knowledge of the nature of the pollutant and a qualitative assessment of the hydrogeology (12) (e.g. Gray et al, 1974). A more quantitative scheme based on a weighted points system has been proposed by Le Grand (1965).

Whichever method of assessment or analysis is used the sensitivity of the solutions to the chosen aquifer and fluid properties must be checked (19) (Gates and Kisiel, 1974; Gillham and Farvolden, 1974; Pickens and Lennox, 1976). Such analyses highlight those parameters that are particularly important to the solution and may thus indicate those areas in which additional data is required.

2.4. THE CHOICE OF APPROACH

Following, or in anticipation of, a groundwater pollution problem the Engineer or Hydrogeologist may look to groundwater quality models to help in deciding on the course of action he should follow (20). He will ask 'do I need a model, of what type, how long will it take to obtain useful results, what is the cost of collecting additional data and making the model, and what degree of reliability can be placed on the results?'

Clearly in the case of a regional groundwater pollution where a large number of wells are involved, the cost of groundwater quality modelling is small in relation to the cost of any protective measures or rehabilitation. In this case advanced modelling techniques, together with extensive data collection, is generally fully justified. At the other end of the scale, the pollution of a single, low yielding well may not warrant a modelling study and unless the pollution is symptomatic of a much larger problem, or there is a particular research interest, a qualitative hydrogeological appraisal will suffice. Between these two extremes is an area of uncertainty and it is important that the hydrogeologist and the modeller should be able to explain the advantages and limitations of the range of analysis that are available to represent the flow of a pollutant within an aquifer system. In particular a detailed understanding of the flow mechanisms in the aquifer and the limitations of representing these quantitatively in a particular analytical or modelling process, is essential if the appropriate method of analysis is to be chosen and the reliability of the results understood and used in a sensible way ⑳.

3. FLOW IN THE UNSATURATED ZONE

The rate of downward movement of infiltrating water is controlled by the hydraulic conductivity of the zone of aeration and the hydraulic gradient distribution between the ground surface and the water table, both of which are dependent upon the distribution of moisture content within the profile. The pores and fissures of the soil and rock are occupied by moisture and by gases. At low moisture contents, possibly resulting from periods of low infiltration, high surface tension forces develop which may prevent any downward flow. As infiltration rates increase, so does moisture content leading to reduced surface tension forces and to increased flow rates. The surface tension forces that control the rate of flow of water are also dependent on pore and/or fissure size. The smaller the pore size, the greater the surface tension and the higher the moisture content required for downward flow. The flow process in the zone of aeration is complex and to predict the time of travel of the infiltrating water and an associated pollutant from ground level to the water table is by no means simple.

The water table may show a rise in level in response to surface infiltration but it does not follow that this represents that particular infiltration reaching the water table. It may simply be due to a pressure wave generated at the surface which moves through the unsaturated zone causing groundwater levels to rise. Correlations between the surface input and rise in water table may be invaluable in calibrating groundwater flow models but may not help at all in determining the location of the original input and its associated contaminants, which may still be held within the unsaturated zone.

The movement of the solute is even further complicated by dispersion which leads to a spreading of the solute front due to local velocity variations and molecular diffusion effects. The relative rates of movement of the contaminant in the water will also be modified by the presence of 'dead end pores' (Coats and Smith, 1964). These are pores or fissures which are not part of the main flow paths, but which are hydraulically connected to them. Contaminants may diffuse into these static water areas and be left behind the infiltrating water. The process is similar in some respects to a chromatographic column where the solute and solvent move at differing rates. This process may be important in controlling the movement of pollutants in the unsaturated zones of the Chalk and Permo-Triassic sandstone aquifers in the United Kingdom.

The unsaturated Chalk contains irregular vertical and horizontal jointing patterns giving a block size with maximum dimensions ranging from 1 to 2 cm to more than a meter. The matrix of the Chalk has a very low permeability (about 5×10^{-3} m/d) but a high porosity of about 0.3 to 0.4. The fissure porosity may be as low as 0.01. It has been proposed on the basis of tritium profiles that infiltrating water moves principally through the Chalk matrix and that the rate is controlled by the low permeability of the blocks.

It would appear much more likely, however, that the observed jointing and fissuring has a major influence on the infiltration rate. Foster, 1975a, and Young et al, 1976 suggested that solutes carried by water infiltrating through joints and fissures are able to diffuse into the static interstitial water within the blocks. Providing that the downward flow rate is sufficiently slow allowing sufficient time for equilibrium to be established, the solute will divide between the static water and the fissure water in the ratio of their respective volumes.

Furthermore, the relative velocity of the infiltrating water and the contaminant pulse is given by the ratio of the total porosity to the fissure porosity. If this mechanism operates in the Chalk the infiltrating water will move downwards at a rate some 20 times faster than the contaminant. The contaminant pulses from the surface will maintain their shape but some vertical dispersion will occur. The shape of the pulse will also be modified if the rate of infiltration is sufficiently rapid or the mobility of the contaminant is low so that full equilibrium between the static and fissure water is not established.

In a sense it is unimportant to know the rate at which the water infiltrates, as it is the rate of movement of the contaminant front that matters. Drilling and profiling of the unsaturated zone of an aquifer in order to identify the position of a pulsed contaminant input from the surface would seem to be a more direct and reliable approach to the problem of determining the movement of a pollutant through the zone of aeration than the use of complex physical models. Recent profiling investigations have examined a range of contaminants including chloride and nitrate (Stiff and Young, 1976). Thermonuclear tritium in rainfall has also been used as a tracer (Smith et al, 1970; Sukhija and Shah, 1976), and while tritium determinations are expensive there is the advantage that the surface input to the aquifer is usually well known. Two typical tritium profiles through the unsaturated Chalk and Bunter Sandstone are given in Figure 2 and by comparing the peaks in these with the peak input of tritium in rainfall in 1963 it can be concluded that the downward rate of migration of tritium at these sites is 0.8 m/yr and 1.8 m/yr respectively. It appears that these rates also apply to other mobile contaminants (Young et al, 1976).

4. UNCONSOLIDATED AQUIFERS

The results of carefully controlled pumping tests in homogeneous sand or gravel aquifers may generally be used to determine the hydraulic conductivity, transmissivity and storage coefficients of the aquifer. Problems may occasionally arise in the interpretation of these data in highly permeable aquifers due to the development of high velocities leading to non laminar flow and Darcy law deviations (Huyakorn, 1973). If the aquifer is unconfined during the test it may be possible to equate its effective porosity with the storage coefficient but if it remains confined its porosity may have to be determined in the laboratory by direct measurements on recompacted aquifer samples or indirectly from a knowledge of its grading characteristic. Dispersivity values of the aquifer may be measured in the field by the use of tracer tests. It may be noted that the dispersivity values determined from breakthrough curves of conservative solutes flowing through homogeneous porous media are usually of the order of 0.1 to 1 centimetres. In contrast,the values of dispersivity determined from field measurements may exceed laboratory values by several orders of magnitude. The number of reliable field measurements of dispersivity are very small and a great deal more work is required in this area.

For a particular groundwater contamination problem and given the hydraulic, storage and dispersivity properties of a homogeneous aquifer, it is possible to choose the method of analysis or model most appropriate to the scale and boundary conditions of the problem that will lead to a reliable prediction of the actual velocity distribution and of the concentration of contaminants within the aquifer and the arrival times of pollutants in wells and springs.

Unconsolidated aquifers are however, rarely homogeneous and isotropic. The sedimentary processes cause layering at a microscopic and macroscopic scale, cross bedding and grading and possibly a multiplicity of interconnected sedimentary facies within each layer and between layers. The presence of plate-like clay particles and layers of silt or clay and horizontal stratification in general gives rise to a higher lateral than vertical permeability.

Simplification is necessary if such complex natural systems are to be analysed. If we assume that their heterogeneity is principally due to horizontal stratification then the movement of a pollutant in a two layer system may be examined (Figure 3a). The two layers, with differing permeabilities are confined between upper and lower permeable boundaries and are subject to a steady horizontal flow. A tracer of constant concentration is introduced at the left hand vertical boundary. The tracer would travel more quickly in the permeable layer and in the absence of dispersion effects a concentration arrival time graph at the right hand vertical boundary of the type shown in Figure 3b would be obtained. Extending this to the case of a multi-layered aquifer where there is a wide distribution of permeability values (Figure 3c) a time concentration curve of the type shown in Figure 3d would result. This type of anisotropy is believed to be the major cause for the development of transition zones in the field and accounts for the measured field dispersivity values being much greater than those measures in the laboratory: Mercado (1967) analysed this system and concluded that the width of the transition zone is directly proportional to the distance travelled by the contaminant (see also Oakes, 1976). Mercado neglected hydrodynamic dispersion occurring within the individual layers.

Lateral dispersion within a layer will, however, blur the sharp interface and transverse dispersion will cause the transfer of the tracer between layers (Figure 3e) to give an arrival time graph of the type shown in Figure 3f (Curve 1). This case was analysed theoretically by Fried and Combarnous, 1971, who concluded that the dispersion behaviours of such a layered system approached an equivalent homogeneous system (Curve 2 Figure 3f) which can be represented by an equivalent dispersion term. In this case the width of the transition zone is proportional to the square root of the distance travelled by the contaminant.

In view of these different approaches it is clearly important in attempting to predict the movement of pollutants, particularly those of a hazardous nature, where minor concentrations may be critical, to have a detailed knowledge of the stratigraphy of the aquifer as it relates to the scale of the problem. If the layering is lenticular in nature the hydraulic and dispersivity values for the aquifer to be applied at a local scale may be different from those to be used in a regional study. Figure 4 shows diagrammatically a sand aquifer with lenticular layers of gravel. Wells are located at W1 to W3. A typical problem may be to determine the rate of movement of a pollutant from a river towards the wells. Pumping tests at W1 and W3 probably give differing values of transmissivity due to the heterogeneous nature of the aquifer but the storage coefficients would probably be of the same order. The pumping test transmissivity values may be applied to local problems, e.g. determining the velocities between the river and W1 or W2. Due to the lenticular nature of the aquifer however, they would not represent the regional transmissivities which probably would have smaller values. The groundwater pattern together with a knowledge of the aquifer boundaries and inputs may enable regional transmissivity patterns to be established (Emsellem and de Marsily, 1971; Nutbrown, 1975).

A similar problem, in relation to the scale, exists in determining the dispersivity values. Tracer tests between Wells W1 and W2 may, due to the stratification, yield a high dispersivity value which is time dependent (Mercado, 1967; Oakes and Edworthy, 1976). Tests between wells at a wider spacing may be precluded due to the scale of the problem and the time involved in obtaining results. The lenticular and somewhat random nature of the layering would, however, suggest that on a regional scale the spreading of the pollution front could be described by the dispersion equation as though the system were a homogeneous isotropic aquifer. It would be inappropriate to use the dispersivity values from the local tracer tests in the analysis of the regional problems. Regional dispersivity values may be determined by analysis of pollution plumes within the particular aquifer if such situations exist. It may be, however, that the problem is on such a scale that it can be simplified to one of the movement of a simple front, as described in section 2. This assumption clearly cannot be made unless the hydrogeology and flow mechanisms within the aquifer are clearly understood. It is evident that many more field measurements need to be made before more detailed guidance can be given.

5. FISSURED AQUIFERS

Groundwater flow in igneous and metamorphic aquifers is predominantly through fissures and fractures. This is also frequently the case with consolidated sedimentary rock aquifers (Lovelock, 1972; Reeves et al, 1975). The scale of fissuring may range from fine cracks to ducts transporting large quantities of water. The Chalk, a fine grained, soft limestone crossed by multiple horizontal and vertical joints and fissures is a good example of such an aquifer. The joints and fissures have been opened up by solution near to and below the water table and preferential flow paths have developed. The rock matrix is composed of fossil debris such that the pore diameters are generally less than 1 μm. Laboratory permeability measurements on core samples give values of the order of 5×10^{-3} m/d, while field permeability values determined from pumping tests may be four or five orders of magnitude greater. Atkinson and Smith (1974) have shown by the use of tracers that, at one location, springs emanating from the Chalk are directly linked to swallow holes some 5.8 km away. Groundwater flow velocities of 2.2 km/day were measured. At such velocities Darcy's law is invalid. The porosity of the Chalk varies between about 0.3 and 0.4 but pumping tests give an effective porosity (storage coefficient) of only 0.01 to 0.02. This represents the storage capacity of the fissures since water does not drain from the relatively impermeable rock matrix. However, the porosity of the Chalk blocks may be important in controlling the movement of pollutants, as described later.

The bulk hydraulic properties of fissured aquifers are usually determined from standard pumping tests and generally these implicitly assume isotropic homogeneous behaviour. But pumping test analysis and theoretical consideration of groundwater flow specifically to take account of fissuring are now being made (Wilson and Witherspoon, 1974; Barenblatt et al, 1960; Gringarten and Witherspoon, 1972). Properly conducted pumping tests including a number of observation wells are relatively expensive and in a given area are usually rather limited in number. Data from abstraction wells with a single observation well, or frequently no observation well at all, is much more common. The value of the latter on their own are somewhat limited but combined with geophysical borehole logging may lead to an understanding of the aquifer flow mechanisms. A number of pumping tests conducted at different locations within a fissured aquifer will undoubtedly give a wide range of bulk aquifer properties but regional patterns of high and low transmissivity, possibly related to geological structure or topography, have been observed (Ineson, 1957; Water Resources Board, 1972).

Clearly the difficulties described in the previous section of choosing the appropriate parameters in relation to the scale of the problem also apply in fissured aquifer systems. Figure 5a shows diagrammatically the location in plan of the principal fissures in an aquifer. Supply wells are located at A and B and a source of pollution, for example a landfill site, at X. The parameters determined from local pumping tests may be applicable to determining the pollution threat to well A and those from regional flow analysis in the case of B. A proper appreciation of the hydrogeology in relation to the scale of the problem is thus essential.

Davis (1969) has reported a decrease in permeability and porosity with depth in igneous and metamorphic aquifers and this is also observed in indurated sedimentary rocks such as the Chalk. Monkhouse and Fleet (1975) have shown, on the basis of geophysical borehole logging that the movement of saline water in a Chalk coastal aquifer is controlled by fissuring and that while the total thickness of the aquifer is 250 m there is little or no effective groundwater flow below about 100 m. Evidence for this decrease of the hydraulic properties of the Chalk with depth has also been proposed on the basis of pumping test results (Water Resources Board, 1972; Foster, 1975b).

Flow velocities must be known accurately before one can hope to model groundwater quality. At a local level in a fissured aquifer this presents a problem in deciding which of a range of transmissivities should be used. Tracer tests between wells may help in deciding this but in their absence a high transmissivity should be adopted which would lead to a conservative solution. At a regional scale, many groundwater models of fissured aquifers have been built and calibrated against historic groundwater level fluctuations. If the calibration is good the regional values of transmissivity and storage coefficients should give reliable values of flow velocity across the region.

Further difficulties are introduced if fissuring causes an anisotropic permeability of the type shown in Figure 5b. Such anisotropy is common in carbonate rocks but it is difficult to quantify either by pumping tests or flow models. The latter are calibrated against groundwater level contours and isotropic flow, i.e. flow lines crossing the contours at right angles, is usually assumed. The importance of anisotropy may be illustrated by the simple example shown in Figure 6.

A group of wells are shown located between a recharge and a discharge boundary and a landfill site is located up gradient of the wells. The isotropic and anisotropic cases are considered. For the former case the flow net shows that the leachate from the landfill is carried to the wells (Figure 6a). However, if the aquifer is anisotropic the stream lines are modified and the leachate is swept past the wells (Figure 6b). It may be noted that in this second case the groundwater levels and stream lines do not intersect at right angles. High anisotropy ratios of this type may be present in many fissured aquifers where the fissures have been developed by solution. Quantitative data is, however, rather lacking.

It is likely from the random nature of fissuring that the spread of a pollutant may be described by the dispersion equation and on this basis Bredehoeft and Pinder (1973) were able to model a fractured system. In view of the heterogenity of fissured aquifers there are clearly problems not only in conducting tests to measure dispersivity values but also in determining the ratio of α_L / α_T. The dispersivity ratio may have a marked effect on the shape and spread of a pollution plume (Pickens and Lennox, 1976; Oakes, 1976).

An important aspect of flow through a fine grained aquifer such as the Chalk is the diffusion of pollutants between the relatively static pore water contained within the Chalk blocks and the network of fractures between the blocks. The pollution concentration gradient would encourage diffusion into the interstitial pores thereby creating a relatively immobile reserve of contaminant which could diffuse back into the fissure flow system should the concentration gradient be subsequently reversed. Evidence for this effect has been demonstrated during the analysis of Chalk core interstitial water samples taken during saline intrusion and mine drainage aquifer contamination studies (Headworth and Wilkinson, 1976).

The flow in many sandstone aquifers is both intergranular and through fissures. This is certainly the case for most of the Permo-Triassic sandstones in the United Kingdom (Lovelock, 1972; Reeves et al, 1975). Fissuring in this formation may be at shallow angles related to bedding plane features or it may be high angled and of tectonic origin. The strong bedding also leads to larger horizontal than vertical permeabilities. Except possibly in the case of strong tectonic faulting, it is unlikely that fissure systems in sandstone will be as extensive as those that develop in carbonate aquifers. Their behaviour with respect to the spread of contaminants probably resembles those of the unconsolidated layered sands.

6. CONCLUDING REMARKS

1. A detailed understanding of the flow mechanisms in an aquifer is essential if the relevant data is to be collected and the most appropriate method of analysis adopted in order to answer the questions posed in the introduction in relation to groundwater quality predictions.

2. Most aquifers are heterogeneous in nature from a microscopic to a regional level due to layering and/or fissuring. The aquifer properties such as transmissivity and dispersivity to be used in prediction analysis may thus be dependent on the scale of the problem. Properties determined at a local level from, for example, pumping or tracer tests, may not be applicable on a larger, possibly regional, scale. There is a need to analyse small and large groundwater pollution incidents and to make many more field dispersion measurements so as to attempt to relate these parameters to the scale of the problem. Some authors have suggested that a statistical approach may be adopted (Bibby and Sunada, 1971; Freeze, 1975).

3. Anisotropic effects are difficult to quantify and are frequently neglected but may have a profound effect on the concentration of a pollutant in the aquifer and on the shape of the pollution plume.

4. The diffusion of pollutants from fissures into the relatively immobile interstitial water of fine grained rocks may retard the rate of movement of the pollutant both in the zone of aeration and the saturated aquifer.

5. Flow in the zone of aeration is complex and the rate of movement of a

pollutant is best estimated by a direct approach using tritium or other tracers. The relative rates of movement of mobile ions requires further investigation.

6. A wide range of groundwater modelling techniques have now been developed to the point where they have outstripped the quality of the data. Models and the associated data requirements are costly and purpose built models are only justified in practice where a major source is at risk. In other situations analytical or idealised solutions used in combination with hydrogeological judgement may be all that is warranted.

7. An appreciation of flow mechanisms will give an indication of the likely range of values of the parameters to be used in an analysis. The sensitivity of solutions should be checked against this range and the results presented in a form that will be easily understood by those responsible for taking action. An attempt should be made to state the degree of reliability of each solution.

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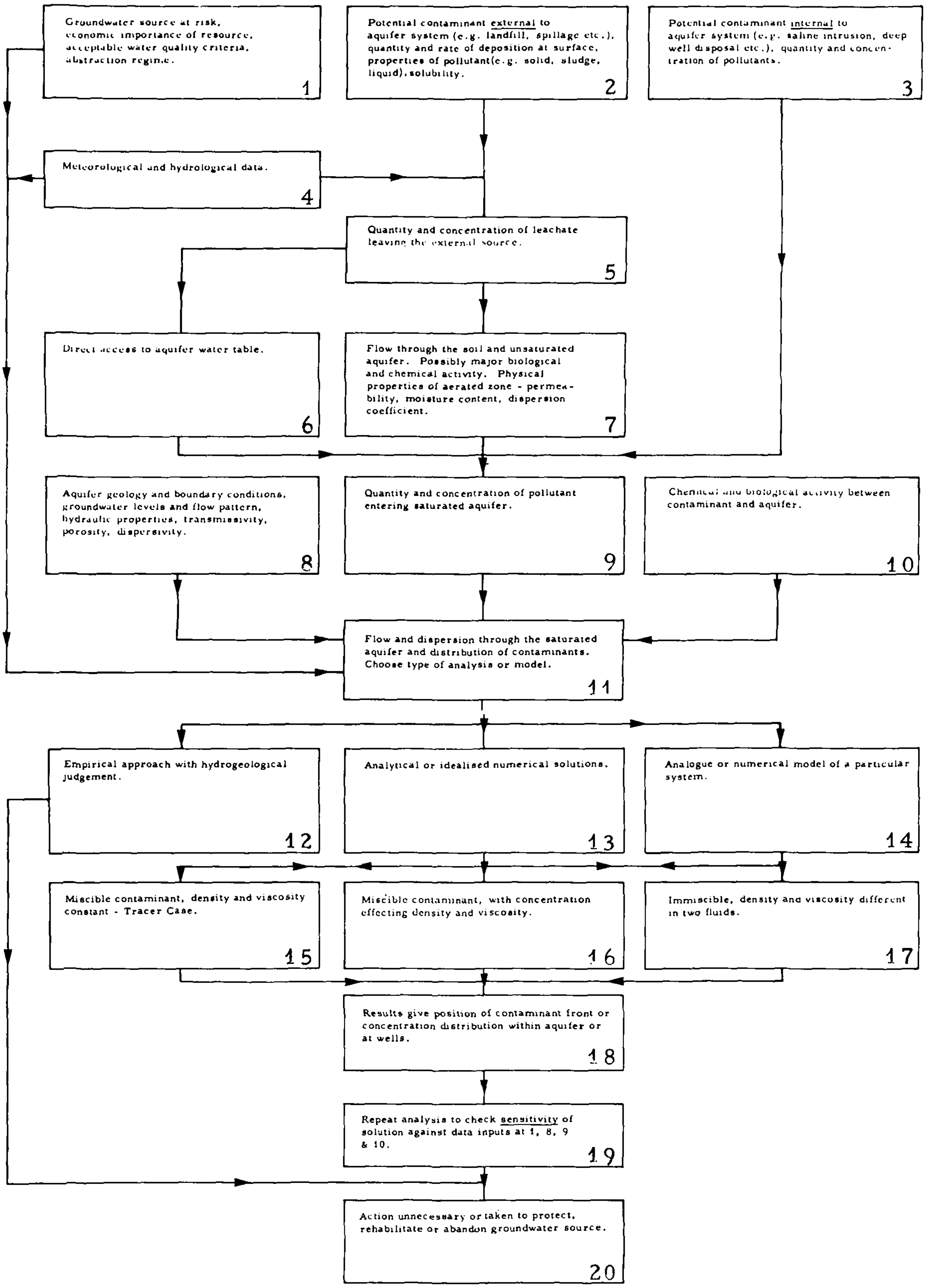

Figure 1. Steps in predicting the behaviour of a pollutant in an aquifer.

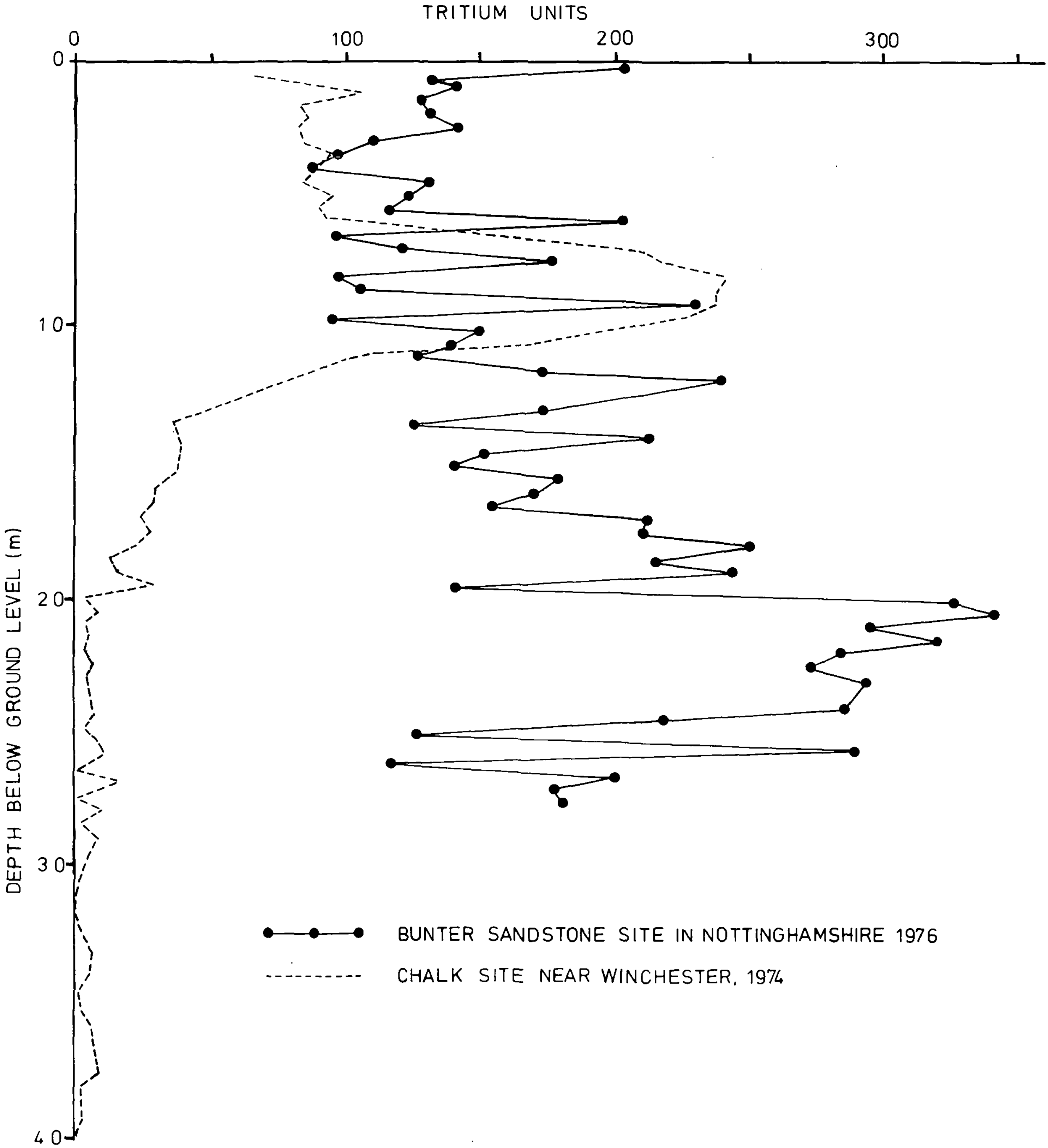

Figure 2. Measured tritium profiles in the Chalk and Bunter Sandstone.

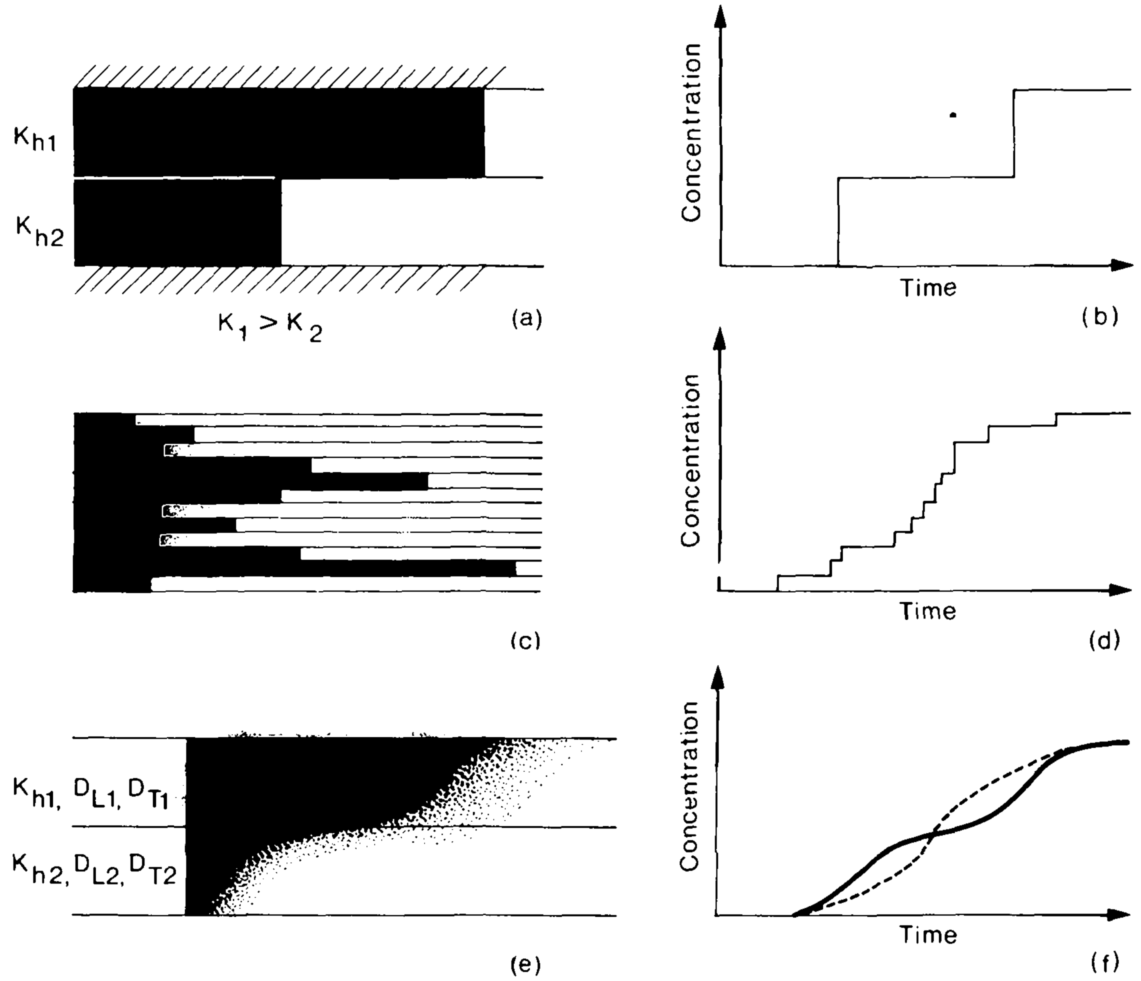

Figure 3. Movement of a pollutant in a layered aquifer.

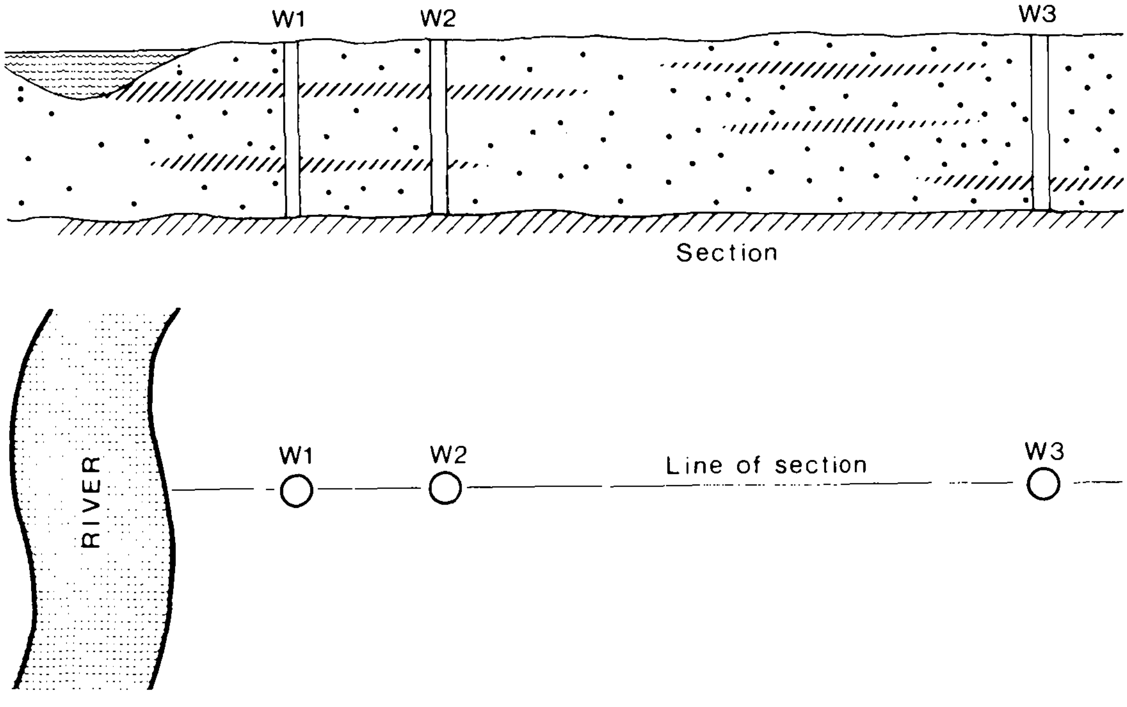

Figure 4. Sand aquifer with lenticular layers of gravel.

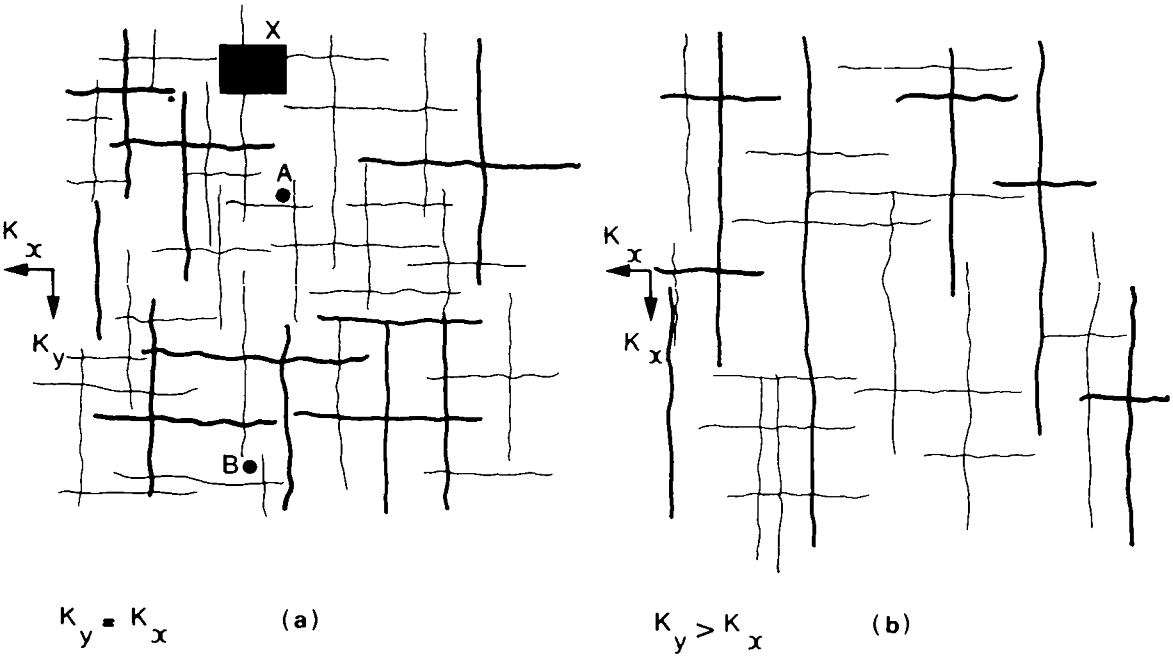

Figure 5. Fissured aquifer (a) isotropic (b) anisotropic.

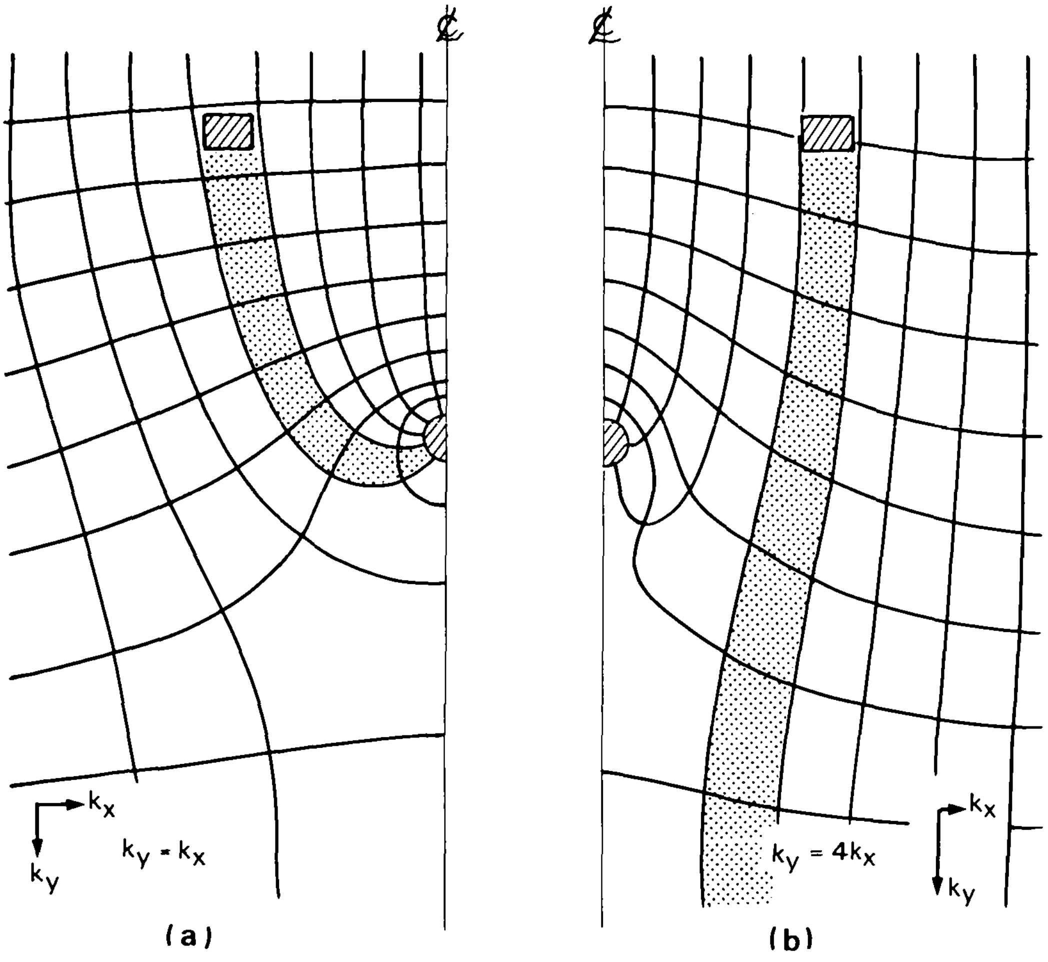

Figure 6. Flow pattern around a pumping well in (a) an isotropic (b) an anisotropic aquifer.

PAPER 5

CURRENT DEVELOPMENTS IN ASSESSING THE ROLE OF SUBSURFACE BIOLOGICAL ACTIVITY IN GROUNDWATER POLLUTION

James F. McNabb

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1. INTRODUCTION

Groundwater in the United States and many other countries is being increasingly threatened by a vast array of pollutants from such diverse sources as sanitary landfills, soil treatment systems, septic tanks, and subsurface disposal wells. Although groundwaters are less easily polluted than surface waters, there is a growing realization that pollutants persist for much longer periods in groundwaters than surface waters. It is, therefore, necessary that any potentially harmful activity be thoroughly evaluated for its impact on groundwater quality so as to protect our groundwater resource before irreparable harm occurs.

Basically, pollutants enter groundwater by either of two principal pathways: percolation through the unsaturated portion of the earth's crust above a water table, or by direct entry into groundwater without passage through the upper soil layers. In either case, pollutants are subject to possible physical filtration, sorption, abiotic chemical alteration, or alteration resulting from the metabolic activities of micro-organisms. Of these possibilities, alteration by biological activity has received the least attention, although biological processes are often the most significant occurring within an ecological system (1).

This subordination of the role of micro-organisms in determining the fate of pollutants in groundwater is due to several reasons. One factor is a belief by many that life does not exist in subsurface regions below the upper soil zones due to the physical remoteness and supposed unfavourable environmental conditions of such regions. This assumption is partly due to early investigations by soil microbiologists on the spatial distribution of microbes within the soil profile. By the methods they used, early microbiologists found such a rapid decrease in microbial numbers with depth, that many apparently concluded the regions below the first soil layers were sterile for all practical purposes (2) (3) (4). It is not unusual today to read in a current microbiology text that the biosphere, that portion of the earth containing living organisms, extends only a few metres into the surface of the earth (5).

However, the most decisive reasons for ignoring subsurface ecosystems are the immense technical problems and great expense involved in subsurface investigations. Not only do such studies involve the same problems which confront surface ecologists, but they are further complicated by the inaccessibility of the subsurface. In the past, microbial ecologists have had insufficient justification and, therefore, financial support to devote much effort or expense to the study of regions below the upper soil layers. The only exceptions have been petroleum microbiologists, who have had a continued interest in the microbiology of subsurface regions since the 1920s. Unfortunately, most of their efforts have dealt primarily with oil or gas bearing regions and not those portions of the earth's crust containing potentially useful groundwater (6) (7) (8).

Today, because of a growing concern for the safety of our groundwater resource, investigations are being instigated to determine the extent and nature of microbial activity in subsurface regions before and after the introduction of pollutants. This paper comprises a brief discussion of known information concerning subsurface biological activity as it relates to groundwater pollution, current research being conducted or supported by the Ground Water Research Branch of the United States Environmental Protection Agency to expand that information base, and the need for additional research studies. Because information concerning biological activity in the upper soil layers is widely available (4) (9) (10) (11) (12), this paper will devote primary attention to those regions of the earth's crust lying below the soil zone.

2. THE SUBSURFACE AS AN ECOLOGICAL SYSTEM

An ecological system or ecosystem is any given unit of the biosphere that contains both living (biotic) and non-living (abiotic) components which interact upon each other. The non-living components normally constitute the habitat in which the living components carry on their activities, although living elements may be part of the habitat in certain cases. Ideally, an ecosystem should have some sort of boundary to delineate it from other systems and be fairly uniform and homogeneous so that a small sample of the system is representative of the whole.

Microbial habitats vary widely in size. If the composition and the environmental conditions of a given unit are relatively uniform over a large area, as in the ocean, then the habitat may be large and contain other habitats within it. In many cases, however, microbial ecosystems are very small, lack definite boundaries, and have little uniformity. This is especially true with soil ecosystems.

The upper continental crust of the earth is composed of crystalline basement rock interspersed with and overlain by unconsolidated rock materials such as sand, clay, silt and gravel, and consolidated rocks such as shale, sandstone, limestone, dolomite, gypsum, and lava in deposits of varying sizes, shapes, and depths. These rock materials, together with organic deposits and the liquids and gases filling the voids or interstices within them, comprise the habitats in which subsurface micro-organisms exist and function. Of course, it is actually within the aqueous phase filling the interstitial spaces and forming films around rock particles that active metabolizing microbes must live. This is because required nutrients must evidently be in solution to be utilized.

The crust of the earth is not homogeneous in nature, but varies widely from point to point in composition and environmental conditions and, hence contains a multitude of small, discrete microhabitats in which a great many intricate and differing ecological interactions may occur. In reality then, subsurface regions of the earth's crust are highly compartmentalized, collectively consisting of a vast number of microhabitats which may be no larger than a soil particle and the water film surrounding it (12). Each microhabitat may be an independent entity, linked only to other microhabitats by shared water bridges. The environmental conditions such as pH or oxidation-reduction potential in one microhabitat may be entirely different from the adjacent microhabitat. Due to differing conditions, neighbouring microhabitats may have different microbial populations which act upon pollutants in different ways. Therefore, the total effect of microbial activity upon a groundwater pollutant in the earth's crust is a culmination of the interactions between that pollutant and possibly many differing microbial populations.

In a recent review, several conclusions are made concerning subsurface biological activity in relation to groundwater pollution (13). First and foremost is the conclusion that previous investigations, by petroleum microbiologists and others, clearly show beyond a reasonable doubt that many subsurface regions lying below the soil zone are not hostile to microbial life and, in fact, contain a varied and apparently metabolically active microflora. In most subsurface regions, particularly those of sedimentary origin, environmental conditions such as temperature, hydrostatic pressure, pH, or spatial limitations do not appear so severe as to prohibit some type of microbial activity until depths are attained where temperatures exceed microbial tolerance levels. These depths are apparently in excess of 2000 metres in most regions.

The environmental factors which previous investigations indicate may be the most important in determining the extent and nature of microbial activity in subsurface habitats, include the oxidation-reduction conditions prevailing within a habitat, the availability of nutrients, and the nature or structural composition of the rock materials which constitute the solid phase of the habitat (13). However, it must be realized that the importance of these and other factors cannot easily be evaluated separately. Most chemical, physical, and biological ecological factors are interrelated and their expression is the sum of numerous interactions between each other so that an alteration in one factor affects the other factors and, eventually, the entire condition of the environment (12) (14).

A microbial habitat must provide to resident micro-organisms in a soluble, utilizable form, all the nutrients which they require for synthesis of cell materials and for generation of energy to carry on their biosynthetic processes. For generation of cell constituents a suitable carbon source, either carbon dioxide or organic carbon compounds, must be available along with smaller quantities of nitrogen, phosphorus, and sulphur, and low levels of various other elements. Potential sources of carbon for microbial utilization are relatively plentiful in many subsurface environments, since the upper continental crust of the earth is variously estimated to contain in the neighbourhood of 10^{19} to 10^{20} kg of carbon (15) (16). Most of this carbon is present as inorganic compounds, principally carbonates, but an appreciable portion occurs as organic matter, much of which was incorporated into sedimentary deposits at the time of their formation and has not been completely mineralized over geological ages. Large quantities of organic compounds are found concentrated in petroleum deposits, but vastly greater amounts are dispersed throughout sedimentary rocks in a finely disseminated state (17) (18).

A review of available data indicates that essentially all subsurface waters probably contain significant quantities of dissolved organic matter (13), resulting both from leaching of organics from sedimentary rocks and transport of fresh organic matter from the surface. Humic substances, naphthenic acids, fatty acids, and phenols are known to comprise part of the dissolved organic matter in groundwaters near petroleum deposits, but the specific composition of the naturally occurring organic matter of groundwaters generally remains largely unknown.

The growth of heterotrophic bacteria may often proceed when very low levels of organic matter are available (12). It would appear likely, therefore, that the organic substances present in most subsurface environments of sedimentary origin are sufficient in quantity to support microbial activity, both as sources of carbon for synthesis of protoplasm and as electron donors for generation of energy. However, microbial activity in the subsurface may be limited by the type, rather than the quantity, of subsurface organic matter. For example, much of this material may consist of substances resembling soil humus components which yield to microbial degradative processes only very slowly, even under the most favourable conditions. Also, some compounds may not be utilized by microbes in the absence of oxygen per se, and some may even be microbial inhibitors (19).

Carbon dioxide is potentially available as a carbon source for chemolithotrophic (autotrophic) micro-organisms in many subsurface regions. Inorganic electron donors which might be oxidized by such microbes for generation of energy are also encountered with some frequency in subsurface environments. For example, molecular hydrogen is often present in subsurface gases (20), and elemental sulphur and hydrogen sulphide are not uncommon in the earth's crust.

Nitrogen, phosphorus, and sulphur are probably present in essentially all sedimentary formations as constituents of organic and/or mineral matter, albeit the concentration of one or more of these elements, most likely nitrogen and phosphorus, may be extremely low in specific locations. However, the levels of these elements required to maintain a minimum level of microbial activity in such environments would appear very low. It seems unlikely that nitrogen, phosphorus, and sulphur concentrations would often be so low in subsurface environments as to completely preclude all microbial activity, although the probability appears high that limited availability of one or more of these elements in a readily utilized form will restrict the level of microbial activity which can possibly occur in many subsurface regions.

Inhibition of microbial activity in subsurface environments solely because of unavailability of mineral elements would also be unlikely, since all subsurface waters are mineralized to some extent due to leaching of the rocks with which they come in contact,and the concentrations of inorganic ions required for microbial growth are usually extremely low. In this connection, Kartsev states that mineral compounds necessary for growth of hydrocarbon-utilizing microbes have been found in a wide variety of subsurface formations, although clay interbeds deficient in the minerals required for development of these bacteria have been observed in rare cases (21).

Generation of energy by non-photosynthetic micro-organisms is supplied by oxidation-reduction reactions in which electrons are transferred from an electron donor to an electron acceptor. Required electron donor materials may be either oxidizable organic compounds or, for some organisms, oxidizable inorganic substances such as molecular hydrogen, reduced sulphur compounds, ammonia, nitrite, or ferrous iron. Required electron acceptor sources may be molecular oxygen, the electron acceptor required by obligate aerobes, or may be some other substance such as nitrate, sulphate, carbon dioxide, or reducible organic compounds. Some microbes are facultative in nature - usually preferring oxygen as an electron acceptor when it is available and using other compounds when oxygen is absent. Metabolic activity in soils apparently changes from aerobic to anaerobic when the concentration of oxygen declines below 3×10^{-6} M (22).

Determinations of both molecular oxygen concentrations and oxidation-reduction potentials in subsurface environments are subject to formidable methodological problems because of the difficult accessibility of these regions. Consequently, definitive data concerning subsurface oxidation-reduction conditions are scarce. However, those data which have been reported, coupled with general observations concerning the probable availability and consumption (reduction) of molecular oxygen and other reducible substances in subsurface regions, provide a limited insight regarding probable oxidation-reduction conditions in subsurface zones.

In the zone of aeration gas in the rock interstices is, for the most part, potentially subject to constant interchange with atmospheric gases. It has been widely assumed, therefore, that high oxygen tensions generally prevail within the zone of aeration. However, the situation is probably not so simple as this assumption implies.

Regions of oxygen deficiency are known to occur with some frequency even in supposedly well-aerated surface soils, although oxygen replenishment by gas interchange should be most effective near the surface. These oxygen-deficient regions probably occur because oxygen is not replenished by gas interchange as quickly as oxygen is utilized by soil micro-organisms.

The rate of gas exchange between the overlying atmosphere, the soil atmosphere, and the liquid phase of the soil environment is governed by a variety of environmental factors, including temperature, pH, atmospheric pressure, concentration gradients, and adsorption coefficients. Because most factors are limiting in nature, the rate of oxygen exchange between the soil and the overlying atmosphere is relatively slow. After entering the soil atmosphere oxygen to be utilized is probably in a dissolved state, since it must pass through the water film that surrounds any actively-metabolizing micro-organism. Therefore, since oxygen is relatively insoluble in water, it seems probable that micro-habitats in which there is a high level of microbial activity would rapidly become anaerobic.

Microbial activity and, hence, oxygen consumption is almost certainly significantly less in the intermediate and capillary subzones of the zone of aeration than in the soil subzone in most situations. However, the rate of gas interchange with the atmosphere is also likely to be low in these deeper regions of the zone of aeration. It is, therefore, logical to suspect that regions of oxygen deficiency may be at least as likely to occur in the deeper subzones of the zone of aeration as in the more shallow soil water subzone.

Since the deeper regions of the zone of saturation are far removed from the zone of aeration and the rates of groundwater movement within these regions, and the rates at which they are recharged with waters containing oxygen and other reducible substances normally range from very low to essentially zero, it appears unlikely that appreciable oxygen and other easily reduced substances could be present in them. This supposition is supported by data obtained in the USSR during studies related to the genesis of, and exploration for, petroleum (23) (24).

On the other hand, considerable variations in rates of reductive processes and replenishment of oxidized substances appear possible in the upper regions of the zone of saturation. It seems likely that oxidation-reduction conditions in these regions may vary over a significant range of possibilities, although somewhat reducing conditions would appear to be generally favoured.

Limited observations of redox potentials in subsurface samples indicate that the total exclusion of microbial activity in subsurface environments by unfavourable oxidation-reduction conditions seems unlikely, although the possibility exists that some deep regions of the zone of saturation might become so reduced as to preclude microbial growth (25) (26). Also, since different species of microorganisms are usually able to grow well only within a relatively narrow range of redox values, the oxidation-reduction conditions that prevail within a particular subsurface region will limit the species of microbes which may successfully inhabit that region, and will often control the metabolic pathways and products of these microbes. For example, sulphate-reducing bacteria require an environmental E_h of -200 mv or less for initiation of growth, and reduction of nitrate by facultative microbes in soil has been found not to proceed unless the redox potential is less than +338 mv at pH 5.1 (27) (28).

Although molecular oxygen is, with some exceptions, undoubtedly absent from the deeper regions of the zone of saturation and is likely available in variable and often limited quantities in upper regions, other substances which serve as terminal electron acceptors for anaerobic organisms, or which may be utilized as alternate electron acceptors by facultative organisms, are widely distributed in subsurface regions. Sulphate, the required terminal electron acceptor of the obligately anaerobic sulphate-reducing bacteria, is probably present to some extent in most subsurface waters, often in relatively high quantity. Carbon dioxide, as previously noted, is present in many subsurface environments and may be utilized as terminal electron acceptor by several species of methane bacteria. Nitrate, the alternate electron acceptor for many facultative microbes, occurs often in subsurface waters, particularly at relatively shallow depths. Simple organic compounds, which may serve a number of microbes as electron acceptors via fermentative metabolic pathways, are also likely present in many subsurface environments, although such substances probably become progressively more scarce with increasing depth (29).

In total, the availability of electron acceptors is probably sufficient in many subsurface regions to support at least a minimum level of microbial activity. However, the rates at which electron acceptors can be replenished in various subsurface environments appear likely to limit the levels of microbial proliferation which may be sustained therein. Insufficient availability of suitable electron acceptors to sustain significant microbial activity may well be a principal factor in the survival for geological ages of organic matter, particularly petroleum deposits, in the earth's crust.

The physiological characteristics of the organisms reported isolated from subsurface samples tend to support available evidence concerning possible subsurface environmental conditions (13). The sulphate reducer, Desulfovibrio desulfuricans, appears to be uniquely adapted to thrive in subsurface environments, and seems to be almost ubiquitous in such regions (27) (30). Other microbes found in subsurface samples, such as Pseudomonas, Mycobacterium, and Actinomyces species, are easily isolated from surface soil and appear to be physiologically suited to many subsurface habitats.

The observations presented in the above section concern mostly subsurface environmental factors in natural environments unaffected by human activities. Unquestionably, such activities could profoundly alter the environmental conditions in many subsurface regions. For example, low levels of readily utilizable carbon sources, electron acceptors, and possibly phosphorus and nitrogen, appear most likely to limit microbial activity in many subsurface environments. Disposal or groundwater recharge activities which result in the entry of liquid or solid wastes containing microbial nutrients into regions below the soil zone, would be likely to considerably alter this situation in the surrounding subsurface environment.

Microbial populations, and hence microbe-pollutant interactions, in subsurface regions receiving pollutants are likely to be profoundly affected by the nature and quantity of pollutants introduced and their effect on the native subsurface environment. For example, microbial species which are very minor members of the native ecological community may become dominant in the environment created by entry of pollutants. Also, microbes contained in the waste introduced into a subsurface region may proliferate there and become the dominant species in the ecosystem.

Surface microbe-pollutant interactions are likely to be mainly beneficial, producing such desirable results as elimination of organic pollutants from subsurface waters by mineralization or removal of nitrate by denitrification. Such interactions could be detrimental, resulting in production of undesirable metabolic products which enter and pollute groundwater or reduce aquifer permeability through clogging of interstitial spaces.

3. CURRENT DEVELOPMENTS

Previous investigations of subsurface microbial activity have been concerned primarily with delineation of the types and numbers of native microbes in essentially undisturbed subsurface environments, mostly in formations deep within the zone of saturation. These investigations provide a limited indication of possible microbe-pollutant interactions which might be expected to occur in some subsurface environments. However, they provide practically no information concerning:

(i) the extent and nature of native microbial activity in the zone of aeration below the soil zone and in the upper regions of the zone of saturation; and

(ii) microbial activity in subsurface environments altered by the introduction of pollutants.

In order to provide such information, the development of new technology is required. Initially, sampling methods must be developed by which subsurface environments may be examined. Secondly, better analytical methodology must be developed so that in situ characteristics of subsurface ecosystems may be determined.

The problems involved in sampling subsurface environments and the resultant expense, have always been the main deterrent to subsurface investigations. Obviously, terrestrial environments far below the earth's surface cannot be directly examined. Instead, biological activity in subsurface environments must be characterized by examining natural spring waters, or by drilling wells and examining the resultant cores and well waters. Spring waters give an indication of the chemical nature of the producing aquifer, but are not necessarily biologically or chemically representative of deep stratal waters (6) (31). In essence, they provide information concerning the biological situation in the vicinity of the outcrop where the spring occurs, but are unlikely to accurately reflect microbial activity deeper within the aquifer formation.

Well waters are considered to provide more representative information concerning subsurface ecosystems than spring waters, but they are likely to reflect contamination resulting from drilling operations. They may not be quantitatively indicative of the microbial population in an aquifer, since the movement of water from the surrounding aquifer rocks into a well during pumping is likely to be much more rapid than the movement of microbes. Samples obtained aseptically from undisturbed cores undoubtedly provide the most representative information concerning subsurface microbial activity, but the acquisition of such samples is fraught with difficulties. Also, since subsurface strata are not homogeneous, cores or water samples from a single site or depth may not be representative of the entire formation.

However, the difficulties in attempting to obtain representative, uncontaminated, and undisturbed cores are not insurmountable if reasonable precautions are taken. Coring equipment is currently available which can be used in many investigations, especially when coring in formations which do not require the use of drilling fluids or muds. Drilling fluids are a definite source of bacterial and chemical contamination in coring operations (6) (32).

Three types of coring devices - a Denison core barrel, a piston sampler, and a dry-tube sampler - have been tried in subsurface studies being conducted by the Ground Water Research Branch of the US Environmental Protection Agency. The dry-tube coring device has proved to be the most effective of the three in these studies which involve coring in alluvial formations with a shallow water table. The core barrel used is a simple steel tube approximately 46 cm in length and having an inside diamter of 7.3 cm. The tube is fitted with a 'shoe' and pushed into the formation by a rotary drilling rig. After raising the coring device, the core barrel is immediately placed into a clamp and a hydraulic jack is used to extrude the core. As the core is extruded, the first 6 to 10 cm are aseptically removed and the centre of the core is subsampled with a sterile, stainless steel core barrel approximately 1.5 cm in diameter. The subsample is aseptically handled and immediately placed in appropriate sterile containers. The remainder of the core material is utilized for chemical and physical analyses. By subsampling the interior of the original core, contamination from the core barrel and problems with smearing can be prevented.

After coring, it has been found that boreholes which have been cored without the use of drilling fluids can be cased and completed to serve as water sampling wells.

Even if sampling obstacles can be overcome, the problems involved in estimating the numbers of organisms in a sample, identifying them, and determining the extent of activity they are capable of performing in the in situ environment, are immense. Basically, there are two approaches taken by microbial ecologists in characterizing microbial ecosystems. The first approach is qualitative in nature, and involves attempting to determine what types of organisms are present and what their physiological capabilities are in the laboratory.

It can be useful to have some knowledge of the types of organisms present in an environment. Such knowledge can be used to identify the functional types present and to monitor fluctuations in environmental conditions. The main obstacle to such studies is the impossibility of devising an isolation technique by which all the organisms present in a sample can be isolated, nor is it possible by such methods to determine how active the isolated organisms are in the native habitat. Therefore, the organisms reported isolated from subsurface environments in previous investigations were not necessarily the only or the dominant organisms present. In fact, the cultural methods used were almost always selective for either sulphate reducers, hydrocarbon-utilizers, or aerobic heterotrophs (13).

One isolation technique being developed by the Ground Water Research Branch to examine subsurface cores is an adaptation of techniques used by medical and veterinary microbiologists to grow obligate anaerobes. Since a great majority of subsurface habitats are anaerobic, and probably have been for centuries, it seems logical to assume that any organisms inhabiting those regions are anaerobic in nature. It has been found in medical laboratories that by taking samples from anaerobic regions and processing them without exposure to oxidizing conditions, it is possible to isolate organisms which were previously unknown (33). Our limited studies with core samples using strict anaerobic techniques indicate that subsurface populations are comprised of large and diverse anaerobic microflora.

The second approach to microbial ecology is the measurement of the total biological activity in the in situ environment without determining the specific types of micro-organisms present. This may be considered the 'quantitative' approach to microbial ecology. The technical problems involved in such determinations have been discussed in detail by a number of microbial ecologists, who all emphasize that at present it is impossible to accurately enumerate the microbial population of any ecosystem, soil or otherwise, and measure the extent of that population's activity directly within the natural habitat, although intensive efforts to develop methodology to do so are being made by the world's microbial ecologists (10) (12) (16) (34) (35) (36) (37).

The Ground Water Research Branch of the US EPA is currently evaluating a number of proposed methods of measuring the level of biological activity in soils and subsurface formations for their potential usefulness. These methods include analyses for specific compounds such as adenosine triphosphate (ATP), organic phosphate esters, nucleic acids, and proteins and also include assays for activity of specific types of enzymes such as phosphatases, nucleases, transaminases, dehydrogenases, and hydrolases.

Since it is normally found only inside living cells and is an essential component in metabolic processes, ATP is one of the most promising indexes of total biomass within an ecosystem. However, the sensitivities of presently-available analytical procedures for ATP in soils are inadequate for meaningful analysis of samples from regions of relatively low activity, apparently because of poor recoveries achieved in extraction of ATP from soil matrices and the presence in the soil extracts of high levels of substances which interfere with the Luciferan-Luciferase method for ATP measurement. Efforts are currently being directed toward alleviation of these problems in order to achieve the sensitivity potentially inherent in the ATP method.

Another potential method of studying subsurface ecosystems is the construction of physical model systems by placing subsurface materials, uncontaminated by sampling, into sterile columns or containers and simulating subsurface conditions of temperature, gaseous composition, etc. By using such systems, it is possible to follow the fate of various compounds and wastes placed in them.

Such an approach was used by the Ground Water Research Branch of the US EPA to investigate the fate and effect of nitrilotriacetic acid (NTA) in anaerobic groundwater environments (38). Simulated aquifers were built using four-litre aspirator bottles containing three litres of natural sand obtained from a shallow aquifer underlying a river floodplain. Aquifers were charged with ^{14}C-NTA (uniformly labelled) and maintained under a nitrogen atmosphere. These studies indicated that NTA entering an essentially anaerobic groundwater environment would undergo anaerobic degradation to yield primarily methane and carbon dioxide.

The Ground Water Research Branch of the United States Environmental Protection Agency is currently responsible within the US EPA for developing sampling and analytical methodology for groundwater pollution studies. The sampling and analytical techniques discussed in this section are being developed and tested in conjunction with various studies involving such groundwater pollution sources as septic tanks and soil treatment systems. Obviously, many of the problems associated with studying micro-organisms in their environments are largely technical and as our technology improves, our knowledge will expand.

4. CONCLUSIONS

Available information clearly shows that microbial activity is both possible and probable in most subsurface regions below the soil zone. The significance of such activity to groundwater pollution resides in the interactions of pollutants and micro-organisms in subsurface regions, and the ultimate effect of such interactions on the quality and availability of groundwater.

However, current knowledge concerning microbial populations and microbe-pollutant interactions in subsurface regions receiving pollutants is extremely limited and further investigations are needed. Such investigations are dependent on the continued development of sampling and analytical methodology.

The ultimate objective of such investigations will be the development of information which can be used to predict the fate and effect of pollutants in groundwater, define the capacity of subsurface regions as pollutant receptors, and eventually result in the ability to plan and control any activities affecting groundwater.

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PAPER 6

GROUNDWATER GEOCHEMISTRY - CONTROLS AND PROCESSES

W. M. Edmunds

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1. INTRODUCTION

An effective study of processes in groundwaters requires an interdisciplinary approach by chemists and geologists, occasionally with a little help from the biologist. The chemists' traditional approach is to simplify the natural system, to isolate particular reactions within it and to examine these from an experimental and/or theoretical standpoint. The geologist usually recognizes the complexity of the system, identifies solute distributions within it and, from certain trends, tries to identify natural processes both in space and in time. Fortunately the interface between the disciplines has been bridged over the past 20 years or so by geochemists who have applied chemical techniques, notably chemical thermodynamics, to natural geological processes such that a foundation has been laid on which complex processes in subsurface waters in particular can be studied (Garrels and Christ 1965, Kitano 1975).

In addition to geochemistry, it is important that groundwater quality is also considered in relation to the hydrogeology, so that the dynamics of groundwater movement and storage can be set in context. In the present paper the main processes controlling the development of groundwater mineralization will be outlined and illustrated by field situations, from UK and elsewhere, which can usually be interpreted by geochemical methods.

In applying chemical principles to natural reactions, we are immediately faced with multicomponent rather than simple reactant solutions, and impure, disordered, reactant solid phases or reaction products (minerals). Natural reactions take place over the complete range of ionic strength from distilled water to natural brine, and if all types of subsurface waters are considered, over a wide range of physical conditions - from temperate zone dilute, shallow groundwaters to hot formation brines. Nearly all water in the earth's crust is mobile - on a time scale ranging from km/day in karstic formation to less than mm/10^6 year in interstitial waters of deep basins - in response to hydraulic, thermal or chemical gradients.

It should be evident, therefore, that the chemistry of any natural water can be interpreted most satisfactorily in terms of the geochemistry of the host rock and its mineral assemblage, and that the processes involved can best be described in terms of interaction between water and rock. It is also important to recognize the significance of the biological and organic component of groundwaters. Traces of organic carbon are found in most groundwaters (Leenheer et al. 1974); bacteria are common, not only in shallow groundwaters but may be present and active in deep groundwaters of sedimentary basins (Kuznetzov et al. 1963) where they catalyse some of the most important geochemical reactions. Decomposition of organic matter in rocks is generally exothermic and provides major energy reservoirs for driving other geochemical reactions.

The main processes influencing groundwater composition can be subdivided into physical, geochemical and biochemical. Physical processes are briefly considered here, with most attention being paid to geochemical processes. The relative importance of biochemical processes is indicated in the concluding section, but is not considered in detail: the reader is referred to Kuznetzov et al. (1963) and Golwer et al. (1976).

2. PHYSICAL PROCESSES

Physical processes, especially mixing, dispersion and filtration, may be important on their own or coupled with geochemical or biochemical processes in modifying the chemical composition of groundwater. In assessing the significance of physical and some geochemical processes, it is important firstly to consider the relative importance of solute transport mechanisms, and secondly the particle size of the components of the groundwater in relation to the primary and secondary porosity of the aquifers.

It is now widely accepted that fissure flow is quantitatively more important than intergranular flow in the majority of aquifers. Fissure storage, however, is commonly a small fraction of the total storage in sedimentary aquifers and the rates of solute transport in the intergranular pore space will be much slower than in fissures. Thus a compositional disequilibrium may exist between water in rapid transit via fissures, and that moving at much lower intergranular velocities and/or by diffusion, as represented schematically in Figure 1. This situation probably occurs quite widely in groundwater systems and is of fundamental importance to the interpretation of groundwater quality. Until equilibrium within the system is established, continuous modification to the groundwater chemistry would be predicted and the rates of intergranular flow and diffusional transport, together with the relative geometry of the system, will be limiting on many geochemical processes by regulating the availability of reactants.

The heterogeneity may be detectable as a difference in elemental composition between fissure water and intergranular water as described, for example, from the Chalk of Berkshire (Edmunds et al. 1973) and which probably accounts for similar compositional anomalies in the groundwaters from other terrains such as the glacial tills of parts of Canada (Grisak et al. 1976). On the other hand, dissimilarities in elemental composition may not exist and the differences could be only in the age of water in the two components. This may be detectable, for example, as a difference in the levels of tritium between fissure drainage and intergranular storage, as in the Chalk (Smith 1969, Foster 1974).

The intergranular reservoir can therefore have a long-term effect on the groundwater quality. The composition of water abstracted from a newly developed aquifer will undergo a gradual change from the steady state formation water composition to a new composition, representing dynamic equilibrium between induced recharge and the intergranular storage.

The physical size of the solutes and suspended matter relative to the rock framework can have an important bearing on several processes - notably filtration but also coprecipitation, adsorption/desorption and related surface reactions. The principal size fractions of mobile particles relative to the pore diameters of principal aquifers is represented in Figure 2, where the common sampling reference limit of 0.45 μ used to separate suspended and dissolved fractions is also shown. It is apparent that much clay grade material including amorphous ferric and other hydroxides will be effectively removed on intergranular movement, although there is still scope for transportation via major fissures. It is also noted that bacteria would be excluded from the interstitial pore space of the fine grained carbonate matrix of aquifers such as the Chalk and Jurassic Limestones.

3. GEOCHEMICAL PROCESSES

Significant advances in recent years in the theoretical treatment of natural waters (Garrels and Christ 1965, Stumm and Morgan 1970) together with rapid improvement in the precision and speed of analytical techniques, have provided a basis for the study of geochemical processes. It is important that investigation of processes be undertaken with initial emphasis on field relationships; experimental and/or theoretical studies can only be meaningful if they relate to real situations in natural systems.

Geochemical processes in groundwaters can be subdivided into eight themes, discussed below.

3.1. GEOCHEMICAL ABUNDANCE

Hydrogeochemical concentrations of the elements may not always be directly related to their abundance in the lithosphere due to the influence of solubility controls. Thus aluminium, being one of the most abundant elements in the earth's crust, can only be considered a trace constituent of most natural waters in view of the low solubility of parent minerals. On the other hand cesium and rubidium may occur in significant concentrations in some groundwaters, despite their low crustal abundance, due to their occurrence in highly soluble minerals. For the majority of elements, however, it is initially desirable to take account of their relative geochemical abundance, since this will exert a fundamental control on availability. Although mean geochemical abundances for a given rock type (Wedepohl 1969) can provide a broad guide, for detailed interpretation of the hydrogeochemistry it is desirable to know the compositional variability of the aquifer rock and minerals.

The solute levels of most major elements are frequently controlled by equilibrium reactions involving parent minerals. On the other hand levels of minor and trace elements, which may occur as impurities in these rock-forming minerals, may be limited by the solubility of less common minerals.

The increase in strontium in the Lincolnshire Limestone groundwater (Edmunds 1973) provides a good example of this process. Calcium levels are buffered near outcrop by carbonate equilibria but strontium (Figure 5), well below solubility limits imposed by strontianite, continues to increase regularly down-gradient from 0.3 to 1.8 mg/l until checked by other competing processes.

3.2. SOLUTION - PRECIPITATION REACTIONS

Water-rock interactions are dominated by solution and precipitation processes. All minerals are soluble to a greater or lesser extent and the solubility will vary depending on the subsurface physical and chemical conditions. Unlike most inorganic compounds, however, the solubilities of several significant minerals (e.g. calcite, gypsum) are inversely proportional to temperature; pressure effects relative to those of temperature are relatively insignificant.

For many minerals of geological importance, thermochemical data is not yet sufficiently reliable to permit accurate equilibrium calculations. Data for pure inorganic counterparts, although extensive, has often been proved inadequate when reassessed for geochemical calculations; for the application to natural systems it is important that the consistency between data sets is first established.

Our understanding of carbonate hydrogeochemistry has evolved progressively as a result of a number of studies of limestone terrains, using an equilibrium approach (Back 1963, Holland 1964, Langmuir 1971). It is interesting to note, for example, that the dissociation constant for calcite has recently been substantially revised by experimental work (Jacobson and Langmuir 1974), following a careful field investigation of groundwaters in Pennsylvania (Langmuir 1971) and for carbonate minerals there now exists a reasonably consistent set of thermochemical data. It can be concluded that most carbonate groundwaters, with the significant exception of the English Chalk, are controlled effectively by mineral equilibria involving pure or substituted calcites or dolomites.

Supersaturation and undersaturation are nevertheless recorded from various carbonate areas. It is likely that departure from chemical equilibrium is most frequently related to kinetic factors, but may also be due to the microcrystalline nature of the controlling mineral. Very high levels of carbonate saturation in interstitial waters in the English Chalk (Bath and Edmunds in preparation) are considered to be due to the fine grain size (~ 0.5 μ) of the rock matrix and the resultant higher free energy of the solid phase. Solution of gypsum by groundwater at a more rapid rate than the carbonate will nucleate/precipitate, has also been proposed (Mercado and Billings 1975) to explain supersaturation. Sluggish nucleation rates may also explain some of the observed cases of supersaturation, the nucleation rate of calcite varying for a number of reasons including the ratio of Ca^{2+} to other ions such as Mg^{2+} (Möller and Rajagopalan 1975). Clearly each case of supersaturation has a unique explanation which must be explained in terms of the local geochemical conditions in the aquifer.

Rates of attainment of carbonate equilibrium have been studied in several localities. Although saturation may be reached relatively quickly in days rather than years in percolating groundwaters (Holland et al. 1964), several carbonate aquifers contain tracts of groundwater typically undersaturated with respect to carbonate minerals. Spring discharge in karstic areas such as the Lower Palaeozoic Limestones of the Appalachians (Langmuir 1971), and the Carboniferous Limestone of Derbyshire (Edmunds 1971) frequently exhibit carbonate undersaturation, and a distinction may be made between diffuse flow where saturation generally obtains, and conduit flow springs where undersaturation is commonly observed (Shuster and White 1972). Extensive hydrogeological and geochemical studies of the artesian Floridan aquifer (Back 1963, Back and Hanshaw 1971) have demonstrated the extent of undersaturation with respect to calcite and dolomite. The three-dimensional extent of dolomite undersaturation is considerably greater than that for calcite. In conjunction with radiocarbon determinations, it has been demonstrated that equilibrium with calcite is reached in 4000 years and with dolomite in 15 000 years, and that further migration of the waters down-dip produces a degree of supersaturation (Back and Hanshaw op. cit.).

In the Lincolshire Limestone of Eastern England there is excellent correlation between observed values and predicted calcite equilibria (Figure 3a). In the upgradient section of the confined aquifer (see map Figure 4) calcite saturation indices (SI values) demonstrate equilibrium well within limits of error, both experimental and those resulting from thermodynamic data; all groundwaters, however, still remain undersaturated with respect to dolomite. Further down gradient the calcite saturation control is diminished as other processes, including ion exchange, become more important.

In the Triassic Sandstones of the West Midlands, the degree of carbonate saturation can be broadly interpreted in relation to vertical changes in sandstone lithology (Figure 3b). Most groundwaters from the Keuper Sandstone and Lower Mottled Sandstone, both of which have relatively abundant carbonate cement, show calcite supersaturation and a few are saturated with respect to dolomite. In contrast waters from the underlying Bunter sandstone, which is typically low in carbonate, are characteristically undersaturated with respect to both calcite and dolomite (Edmunds and Morgan-Jones 1976).

3.3. IONIC STRENGTH AND COMPLEX FORMATION

The total mineralization of a groundwater, represented by the ionic strength, has a direct effect on equilibrium concentrations of ionic species. The activity coefficients, which relate the thermodynamic activities to the observed concentrations, decrease as the ionic strength increases (Figure 6). Thus the ion activity product at equilibrium requires greater ionic concentrations. Furthermore the formation of ion pairs and complexes also reduces the activity of specific ion species and, therefore, tends to raise the equilibrium concentrations of solubility-controlled ions. From Figure 6 it can be seen that activity coefficients of multivalent ions are most susceptible to ionic strength changes and a similar dependence on charge exists for complex ion stability.

To illustrate the extent of ion pairing in natural waters, the degree of complexation in sea water (Garrels and Thompson 1962) is compared in Table 1 with that in various UK groundwaters, calculated using a Fortran computer program (Bath 1975). It is seen that free Ca, Mg, SO_4 and carbonate concentrations are reduced to a variable extent even in relatively dilute groundwaters, but that monovalent ions are generally unassociated to levels as high as sea water. The most important ion pairs in natural waters are Ca CO_3^{o} and Ca SO_4^{o} which are generally present in significant amounts and Mg·SO_4^{o}, $MgHCO_3^{+}$ and $CaHCO_3^{+}$ in trace or negligible quantities (Jacobson and Langmuir 1974) and the combined effect of these is illustrated in Table 1.

Table 1. Percentage free ions in selected UK groundwaters relative to sea water (Garrels and Thompson 1962). Ionic concentrations in mg/l.

	Sea water*		Bunter Sandstone Copley, Salop		Lincolnshire Limestone Billingborough		Lincolnshire Limestone Crowland	
	Ionic	% Free Ion	Ionic	% Free Ion	Ionic	% Free Ion	Ionic	% Free Ion
Ca	401	91	71	96.4	134	90.7	10	89.7
Mg	1312	87	19	94.7	6.3	90.4	16.4	91.2
Na	11030	99	115	100	14	100	1150	100
K	391	99	5.6	100	2.4	100	7.4	100
Cl	19852	100	200	100	22	100	1480	100
HCO_3	146	69	232	98.2	279	98.6	719	96.7
SO_4	2688	54	46	89.0	124.7	79.3	87	92.8
CO_3	16.2	9	0.57	51.9	0.42	39.2	10	91.8
pH	8.15		7.45		7.12		8.36	
Ionic strength	0.7		0.013		0.011		0.055	
Total mineralization	35836		689		582		3477	

In dilute groundwater at pH 7 and 25°C the equilibrium calcium value will be around 80 mg/l in the absence of sulphate. However, the addition of 500 mg/l sulphate ion to this solution will permit the equilibrium calcium concentration roughly to double due to the formation of the $CaSO_4^o$ ion pair (Langmuir 1972).

The stability of many minor and trace elements in solution is increased considerably by the formation of complex ions, particularly at higher ionic strengths, and aqueous concentrations may often be considerably higher than predicted from solubility products of pure compounds. This is notable in the case of the transition metal sulphides, for example where the formation of bisulphide and chloride complex ions may account for the high geochemical mobility of elements such as lead (Nriagu and Anderson 1971).

The geochemical behaviour of uranium provides a good illustration of the control over solubility by complex ion formation (Garrels and Christ 1965). In the absence of carbonate, the solubility of uranium as the uranyl species (UO_2^{2+}) is probably controlled by the hydroxide $UO_2(OH)_2H_2O$ and mobility of uranium would be insignificant above pH 6. In the presence of carbonate species, and therefore in most groundwaters, uranium forms two soluble complex ions - $\left[UO_2(CO_3)_2(H_2O)\right]^{2-}$ and $\left[UO_2(CO_3)_3\right]^{4-}$, which effectively remove the stability control of the hydroxide and ensure uranium mobility in neutral and slightly alkaline oxidizing conditions.

3.4. ACID-BASE REACTIONS

Most natural waters are effectively buffered in the pH range 6.0 to 8.5 by the carbon dioxide - carbonate system. Outside this range the pH of waters will be controlled most commonly by oxidation-reduction reactions. Biochemical oxidation will lead to a decrease in pH whilst denitrification and sulphate reduction, for example, will contribute to a raising of pH levels - this is illustrated in the deeper groundwaters of the Lincolnshire Limestone (Figure 4).

The solubilities of almost all minerals, and hence aqueous ionic concentrations, are dependent on pH as well as the various other factors discussed here. This is because intermediate complexes involving H^+ or OH^- are a common feature of solution equilibria. This is illustrated for the case of iron in Figure 7. On the Eh -pH diagram the Fe^{2+} - $Fe(OH)_3$

stability field has been contoured over the range 10^{-3} to 10^{-7}M (56 to 0.006 mg/l) and the effect of pH is to consistently increase the equilibrium Fe^{2+} concentration by three orders of magnitude over one pH unit. It should be clear therefore that very small pH changes can drastically affect the predicted (and actual) aqueous levels of ions in solution so that the accurate, in situ measurement of pH in natural systems is of basic importance.

3.5. OXIDATION - REDUCTION REACTIONS

Oxidation - reduction reactions involve only those elements or species which can take part in electron transfer and in natural waters, therefore, have the greatest relevance to the hydrogeochemistry or iron and related transition metals and to subsurface biochemical reactions involving the C, N, O and S cycles. Redox reactions involving iron and some transition metals are relatively rapid and reversible, and individual reactions can be described theoretically using equilibrium methods (Hem and Cropper 1959, Garrels and Christ 1965); those reactions involving biochemical steps are characteristically slow (Stumm and Morgan, 1970). In natural waters it is usual for several redox reactions to contribute to the oxidation condition, and the contribution of individual redox couples may be difficult to identify. Nevertheless a consideration of the redox equilibria is probably the best way in which to assess the likely participants, to follow the direction in which natural reactions may proceed and to test whether the observed field conditions are controlled by single or multiple redox reactions.

The equilibrium constants (K) for several redox reactions which may be important in groundwater systems are reproduced in order of decreasing oxidizing intensity at pH = 7 as indicated by $p\epsilon^{o}$ (W) values in Table 2. It can be seen for example that NO_3 is a more powerful oxidizing agent than SO_4 and, in general terms, those reactions higher up the list should have the greatest impact in a competitive situation with several redox reactions involved in reduction processes.

In view of the complexity and/or impossibility of direct measurement of the amounts of individual oxidized or reduced species in a natural water, it is

Table 2. Equilibrium constants (K) for some possible redox reactions in groundwaters (based on Stumm and Morgan 1970). The relative electron activity values ($p\epsilon^{o}(W)$) permit grading of the reactions in order of their oxidizing intensity at pH = 7.

$$p\epsilon^{o} \equiv \log K, \qquad p\epsilon^{o}(W) = p\epsilon^{o} + \frac{n_H}{2} \log K_W$$

where n_H is the number of moles of protons exchanged per mole of electrons and K_W is the equilibrium constant for the dissociation of water (10^{-14}).

REACTION OXIDIZED = REDUCED	log K	p ^{o}(W)
$\frac{1}{4} O_2(g) + H^+(W) + e^- = \frac{1}{2} H_2O$	+ 20.75	+ 13.75
$1/5\ NO_3^- + 6/5\ H^+(W) + e^- = 1/10\ N_2(g) + 3/5\ H_2O$	+ 21.05	+ 12.65
$\frac{1}{2} MnO_2(s) + HCO_3^-(10^{-3}) + 3/2\ H^+(W) + e = \frac{1}{2} MnCO_3(s) + 3/8\ H_2O$	-	+ 8.5
$\frac{1}{2} NO_3^- + H^+(W) + e = \frac{1}{2} NO_2^- + \frac{1}{2} H_2O$	+ 14.15	+ 7.15
$1/8\ NO_3^- + 5/4\ H^+(W) + e = 1/8\ NH_4^+ + 3/8\ H_2O$	+ 14.90	+ 6.15
$1/6\ NO_2 + 4/3\ H^+(W) + e = 1/6\ NH_4^+ + 1/3\ H_2O$	+ 15.14	+ 5.82
$\frac{1}{2} O_2 + H^+ + e = \frac{1}{2} H_2O_2$	+ 11.54	+ 4.54
$\frac{1}{2} CH_3OH + H^+(W) + e = \frac{1}{2} CH_4(g) + \frac{1}{2} H_2O$	+ 9.88	+ 2.88
$\frac{1}{4} CH_2O + H^+(W) + e = \frac{1}{4} CH_4(g) + \frac{1}{4} H_2O$	+ 6.94	- 0.06
$FeOOH(s) + HCO_3^-\ (10^{-3}) + 2\ H^+(W) + e = FeCO_3(s) + 2\ H_2O$	-	- 1.67
$Fe\ (OH)_3(s) + 3\ H^+ + e = Fe^{2+} + 3\ H_2O$	+ 18.8	- 2.2
$\frac{1}{2} CH_2O + H^+(W) + e = \frac{1}{2} CH_3OH$	+ 3.99	- 3.01
$1/8\ SO_4^{2-} + 5/4\ H^+(W) + e = 1/8\ H_2S(g) + \frac{1}{2} H_2O$	+ 5.75	- 3.50
$1/8\ SO_4^{2-} + 9/8\ H^+(W) + e = 1/8\ HS^- + \frac{1}{2} H_2O$	+ 4.13	- 3.75
$\frac{1}{2} S(s) + H^+(W) + e = \frac{1}{2} H_2S(g)$	+ 2.89	- 4.11
$1/8\ CO_2(g) + H^+(W) + e = 1/8\ CH_4(g) + \frac{1}{4} H_2O$	+ 2.87	- 4.13
$1/6\ N_2(g) + 4/3\ H^+(W) + e = 1/3\ NH_4^+$	+ 4.68	- 4.68
$H^+(W) + e = \frac{1}{2} H_2(g)$	0.00	- 7.00
$\frac{1}{2} HCOO^- + 3/2\ H^+(W) + e = \frac{1}{2} CH_2O + \frac{1}{2} H_2O$	+ 2.82	- 7.68
$\frac{1}{4} CO_2(g) + H^+(W) + e = \frac{1}{4} CH_2O + \frac{1}{4} H_2O$	- 1.20	- 8.20
$\frac{1}{2} CO_2(g) + \frac{1}{2} H^+(W) + e = \frac{1}{2} HCOO^-$	- 4.83	- 8.73

convenient to use Eh (the oxidation - reduction potential) as a working parameter in field investigations. The Eh can be used qualitatively for example to map the zones of oxidation and reduction in natural waters and, under favourable circumstances, semi-quantitatively to interpret the redox reactions involved (Barnes and Back 1964). Eh measurement will be most effective in moderately reducing environments and should indicate those reactions which are reversible on the platinum electrode surface. The measurement itself may be unreliable in some reducing groundwaters where sulphide may react irreversibly with the platinum itself, poisoning the electrode. In oxidizing environments the electrode may function as a PtO electrode and rather than respond to Eh, may act more like a pH electrode (Whitfield 1969, 1974). Various other problems associated with in situ Eh measurement are described by Barnes (1963) and Whitfield (1969). For groundwater systems, the only meaningful results for in situ conditions will be obtained from artesian overflow or from turbine pumped depth samples for which anaerobic measurement conditions can be maintained.

In moderately oxidizing groundwaters the redox potential is controlled primarily by the dissolved oxygen content of the water, probably by way of the oxygen-peroxide couple (Sato 1960). Disappearance of oxygen and onset of reducing conditions indicated by low Eh values will depend particularly on aquifer lithology and bacterial activity. In the Triassic Sandstones of the West Midlands (Edmunds and Morgan-Jones 1976) oxidizing conditions extend generally for 80 to 100 m below surface and reflect the virtual absence of reducing lithologies. The levels of dissolved iron are maintained below 0. 5 mg/l under oxidizing conditions by the stability of amorphous ferric hydroxides. Within the zone of oxidation, fluctuations in the levels of dissolved iron may be controlled by slow ageing and recrystallization of the $Fe(OH)_3$ to goethite (Langmuir 1969, Langmuir and Whittemore 1971).

In the Lincolnshire Limestone of Eastern England, the change in oxidation-reduction potentials can be followed as the water moves down-dip in the confined aquifer (Edmunds 1973). There is a gradual decline in the amount of dissolved oxygen (Figure 4) over a distance of 10 km, to the level of analytical detection (0. 2 mg/l). Throughout this zone the Eh is effectively buffered (poised) but undergoes a sudden drop of some 300 mv over a short distance, indicating an apparent sharp geochemical boundary between oxidizing and reducing zones in the aquifer. There is an intermediate zone for some three km down gradient of this boundary where reducing conditions occur, but through which there is little or no detectable sulphide or appreciable lowering of dissolved sulphate concentrations. From mineral equilibrium calculations (Pearson F. J. written communication) it is likely that in this intermediate zone the dissolved Fe^{3+}/Fe^{2+} levels are still controlled by the peroxide - dissolved oxygen couple; the in situ Eh values are comparable with those calculated using the oxygen detection limit values. It is therefore possible that the measured Eh boundary does not locate the true limit to oxygen-controlled reactions in the aquifer.

In the down gradient reducing section of the aquifer, the Eh becomes progressively more negative; the decrease in sulphate and the appearance of reduced sulphur species and fine grained black precipitate at the well head, plus an increase in HCO_3^-, suggests that the reactions:

$$SO_4^{2-} + 2CH_2O + H^+ = HS^- + 2CO_{2(g)} + 2H_2O \qquad \ldots\ldots\ldots \quad 1$$

$$Fe^{2+} + HS^- = \underset{\text{(pyrite, mackinawite)}}{FeS} + H^+ \qquad \ldots\ldots\ldots \quad 2$$

must be taking place. Mineral saturation calculations, however, again suggest that reduced sulphur levels are far too high for sulphate-sulphide equilibrium. It is possible therefore that additional redox reactions are involved, or that there are kinetic factors which allow a build up of an excess of dissolved sulphide.

The redox processes in the groundwater can be closely correlated with the limestone diagenesis. At outcrop the limestone is typically uniform light brown with occasional grey lenses, but from core samples taken down gradient a sequence of alterations confirm the evolution of the light brown oxidized limestone from a reduced grey limestone by interaction with groundwater (Figure 4d). The development of oxidation zones parallel to fissures demonstrates that the interaction is physically controlled by zones of rapid groundwater flow in conjunction with diffusion with the adjacent wall-rock. The finely disseminated iron sulphide in the grey limestone is unstable under the high Eh of the recharging groundwater and oxidizes to ferric hydroxide. In the reducing zone of the aquifer, the finely disseminated pyrite is mobilized initially as Fe^{2+} according to reaction 3 but is reprecipitated as FeS (pyrite or mackinawite, Berner, 1963) dependent on production of further reduced sulphur:

$$FeS_2 + 8H_2O = 2SO_4^{2-} + Fe^{2+} + 16H^+ + 14e \qquad \ldots\ldots\ldots\ 3$$

The observed concentrations of iron in the groundwater fit reasonably well with the theoretical concentrations and with the boundaries of the predicted stability fields (Figure 7) suggesting that the levels of iron in solution behave overall as expected from equilibrium considerations. The higher dissolved iron concentrations ($Fe^{2+} > 0.5$ mg/l) are found in those groundwaters lowest in pH and Eh.

3.6. ION EXCHANGE AND SURFACE REACTIONS

Many rock-forming minerals are capable of exchanging cations or in some cases anions at their surfaces. From the work by soil scientists in particular, it is well documented that many clay minerals can have large cation exchange capacities (Table 3) but it is less well known that certain other minerals can also have significant exchange capacities.

Table 3. Cation exchange capacities of various minerals and colloids. Data from Carroll (1959) and Rosler and Lange (1972).

Mineral	Cation exchange capacity (meq/100 gm) at pH7
Kaolinite	3 - 15
Montmorillonite	50 - 150
Nontronite	75 - 80
Illite	10 - 70
Vermiculite	100 - 150
Chlorite	10 - 40
Glauconite	11 - 20
Humic Acids	100 - 500
Organic matter	up to 300

For a mineral to have ion exchange properties, it is necessary for there to be a charge imbalance in the crystal structure or at its surface. Thus other silicates with repetitive negatively charged frameworks may have certain deficiencies due to their cation substitution. Minerals, such as carbonates, forming in natural environments are initially impure and have poorly ordered crystal structures, which may give rise to charge imbalances. Colloidal minerals, such as iron hydroxides, may also show similar properties.

In most natural waters an affinity series is observed where an ion with a larger hydrated radius will tend to become displaced from the mineral lattice/surface by an ion with smaller hydrated radius:

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$$

Ion exchange processes involving Group I and Group II elements can again be illustrated using the Lincolnshire Limestone. Locally the limestone may by in hydraulic continuity with basal argillaceous facies of the overlying Upper Estuarine Series (Anon 1969) but otherwise the clay mineral content of the limestone is low and ion exchange sites are likely to include the fine grain size interstitial organic matter and iron minerals of the aquifer.

The principal cation exchange reaction ($Ca^{2+} \rightleftharpoons 2Na^{+}$) can be followed as the groundwater moves down gradient (Figure 5). The exchange only becomes significant to the east of the Eh boundary, which suggests that the organic matter and ferrous iron are more effective ion exchange media than is the ferric hydroxide of the oxidized limestone further up gradient. The equivalence point in the exchange reaction occurs at the approximate point where mixing with formation water (using Cl^{-} as index) is detectable. With the removal of Ca^{2+} from the system, the calcite solubility control is no longer effective, being replaced by $NaHCO_3$, and the oxidation of further organic matter to produce CO_2 is shown by the increase in HCO_3^{-} (Figure 4).

Potassium, which one might predict to participate in the ion exchange, decreases only slightly in concentration and then increases with the admixing of saline water. Lithium remains inert throughout the process except for an increase as mixing with saline water occurs. Rubidium and cesium, although present in trace quantities, show a slight but significant increase down gradient. Although ion exchange theory might predict their removal, the control on behaviour would appear to be the low geochemical abundance; whilst swamped by Na^{+} in the base exchange reactions therefore, their increase can be best explained in terms of the increased time of water-rock contact.

Strontium and, to a less marked extent, magnesium are apparently controlled by solution phenomena for some 20 km east of outcrop, but their sharp decrease after this point is attributed to exchange reactions. The field relationships would indicate that ion exchange only takes over as the main control on both elements once the Ca^{2+}/Mg^{2+} or Ca^{2+}/Sr^{2+} decreases below a critical level; in the case of Mg^{2+} this would be near 1:1 and with Sr^{2+} below 20:1 which is consistent with the affinity series. For all these elements therefore the absolute concentrations must be taken into account when considering their participation in ion exchange processes.

3.7. MEMBRANE FILTRATION

A large amount of experimental and field evidence (White 1965, Kharaka and Berry 1973) indicates that clays and similar geological materials can act as semipermeable membranes which will restrict or retard the flow of charged solutes. When the fluid is subjected to flow in response to hydraulic, chemical, thermal or electrical gradient, the effluent solution will be lower in concentration in comparison to the residual, hyperfiltrate. The type of geological material involved will be important in controlling the amount or type of individual solute that will be retarded or transmitted. From experimental data using bentonite and shale (Kharaka and Berry op. cit.) the relative retardation sequence was found to be:

$$Li^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+$$

$$Mg^{2+} < Ca^{2+} < Sr^{2+} > Ba^{2+}$$

and in general the monovalent ions were retarded more than the divalent. Although there is an increasing amount of field evidence which suggests that membrane filtration is a significant process in some deep sedimentary formations and in modifying the composition of saline waters (Kharaka and Berry 1974), other studies (Collins 1974, Edmunds 1975) would indicate that alternative processes might be more important.

Although favourable geological situations, for example shales with permeable sandstones above and below, occur frequently in producing aquifers, it is unlikely that large enough head differences (>1000 psi) exist within those aquifers that are important from a water resources viewpoint, to permit any significant membrane effect.

4. CONCLUDING DISCUSSION

Although individual processes have been considered in turn, it is important to realise that each process is dependent to a greater or lesser extent on some other process, and that the change in concentration in one ion is likely to influence the concentration of others. Thus the removal of Ca^{2+} from solution in the Lincolnshire Limestone by ion exchange reduces the CaF_2 solubility control on F^- concentration, and fluoride levels are allowed to rise in the down gradient aquifer. Similarly, the oxidation of organic matter is probably a partial control on the increase of some minor elements such as iodide and fluoride (Edmunds 1973).

It should be apparent from the preceding discussion that elemental concentrations in the majority of groundwaters are not true equilibrium concentrations considered in terms of one reaction or process. The extent of the departure from a simple equilibrium model however, may provide an important indication of the validity of a particular control or whether multiple processes may be operating. The examples quoted for carbonate supersaturation or undersaturation provide a good illustration and can be extended in relation to other minerals.

With the current spate of activity in the area of groundwater pollution, it may be overlooked that natural processes will control the major and trace element concentrations in the large majority of waters. This geochemical background will differ from one lithology to another and will be affected by subsurface processes as described earlier, but over wide areas characteristic values can frequently be identified. Typical concentrations are illustrated for Sr^{2+} and Zn^{2+} for the Triassic Sandstones of the West Midlands, the Carboniferous Limestone of Derbyshire and the Lincolnshire Limestone (Figure 8). Cumulative frequency curves for Sr^{2+} show a normal distribution but background levels (as defined by the median value) are higher in the two carbonate aquifers. Zinc, on the other hand, tends towards lower values in the carbonate aquifers. For both elements, extreme values, an order of magnitude above or below the median, are found which, in some cases, can be explained by contamination but generally are the result of natural processes.

A tentative allocation of processes controlling the occurrences of major and some trace elements in groundwaters is given in Table 4. These results are based where possible on field data from UK studies, some of which are mentioned above, but otherwise are supported by theoretical considerations and data from Langmuir (1972). This classification probably holds for a wide range of aquifer rock types, the principal variation being that of intensity. For example, the carbonate cement of arenaceous lithologies is likely to have an important influence on the types of process taking place, but elements such as Sr^{2+}, under parallel conditions, are likely to attain higher aqueous levels in carbonate as compared with sandstone aquifers (Figure 8).

The understanding of natural processes has an obvious relevance to several aspects of groundwater management. The recognition of natural baseline values and their controls mentioned above, is essential in pollution control studies whilst the explanation of local and regional variation in elemental abundance is important in relation to potability. It is possible to utilize geochemical zonation of an aquifer in order to exploit the various types of quality. It is possible, as in the Lincolnshire Limestone, to take advantage of natural ion exchange reactions in one sector of an aquifer to provide soft groundwater for specialized use. Similarly the naturally occuring reducing zones of an aquifer provide a source of virtually nitrate-free groundwater, and this feature could be more widely utilized in several UK aquifers where high nitrate in near outcrop waters presents supply problems.

Table 4. Processes controlling the occurrences of some constituents of groundwater. (Minor controls are indicated by brackets.)

	PHYSICAL		GEOCHEMICAL								
	Dispersion	Filtration	Geochemical Abundance	Complex Formation	Ionic strength	Acid-Base	Oxidation-Reduction	Solution-Precipitation	Adsorption-Desorption	Membrane Filtration	BIOCHEMICAL
Ca^{2+}	x			(x)	x			(x)	x	(x)	
Mg^{2+}	x			(x)	x			(x)	x	(x)	
Na^+	x								x	(x)	
K^+	x								x	x	
Sr^{2+}	x		(x)		x			(x)	x	x	
Ba^{2+}	x		(x)		x			(x)	x	x	
Li^+	x		x						(x)	(x)	
Rb^+	x		x						x	x	
Cs^+	x		x						x	x	
NH_4^+	x			(x)		x	x		x	x	x
As	x		x	x	x	x	x	x	x		
Fe	x	x		x	x	x	x	x	x		
Mn	x	x	(x)	x	(x)	x	x	x	x		
Cu	x	(x)	x	x	(x)	x	x	x	x		
Zn	x	(x)	x	x	(x)	x	x	x	x		
Pb	x	(x)	x	x	(x)	x	x	x	x		
Ni	x	(x)	x	x	(x)	x	x	x	x		
Co	x	(x)	x	x	(x)	x	x	x	x		
Cd	x	(x)	x	x	(x)	x	x	x	x		
HCO_3^-	x			(x)		x		x		(x)	(x)
SO_4^{2-}	x			(x)	(x)	(x)	x	(x)	(x)	x	(x)
CL^-	x			(x)						x	
NO_3^-	x					(x)	x				x
HPO_4^-	x		(x)	x	x	x		x	x		x
F^-	x		(x)	x				x	x		
H_3BO_3	x		(x)	(x)	(x)					x	
Br^-	x		(x)							x	
I^-	x		x							x	
SiO_2	x	(x)		x		x		x			

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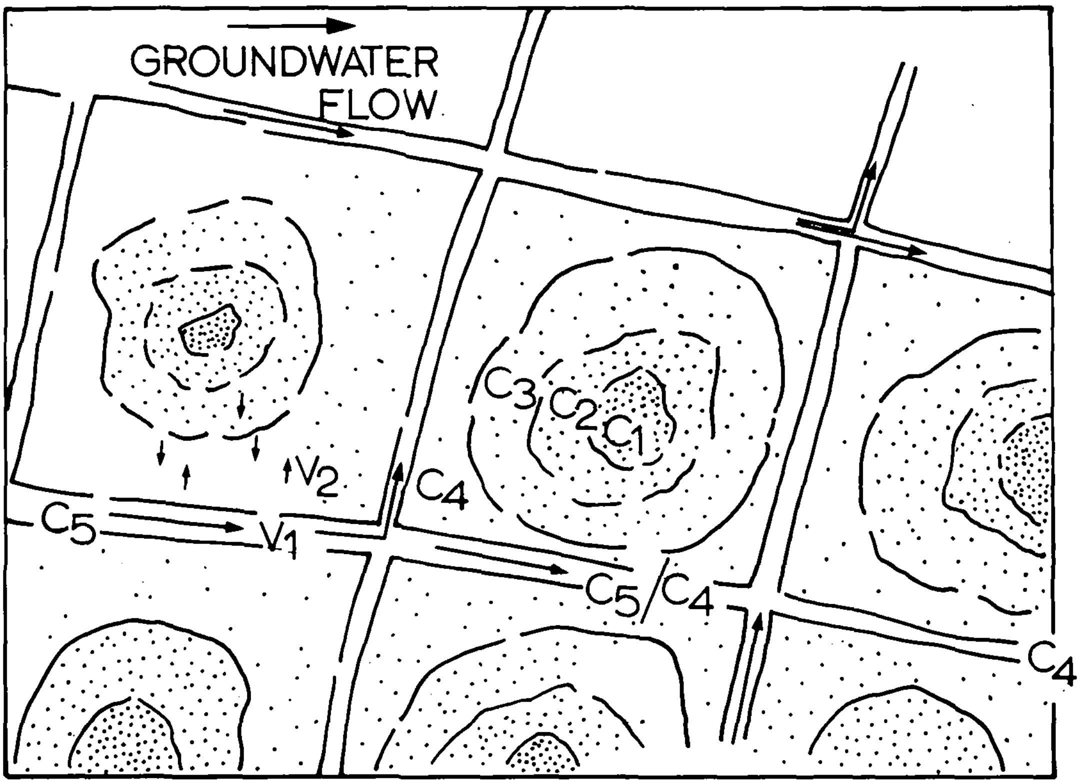


$$V_1 >> V_2$$

$$C_1 > C_2 > C_3 > C_4 \geq C_5$$

Figure 1. Schematic representation of concentration disequilibrium in an aquifer with mixed fissure and intergranular flow (or diffusion) processes; fresh water (C_5) displaces more mineralized water (C_1).

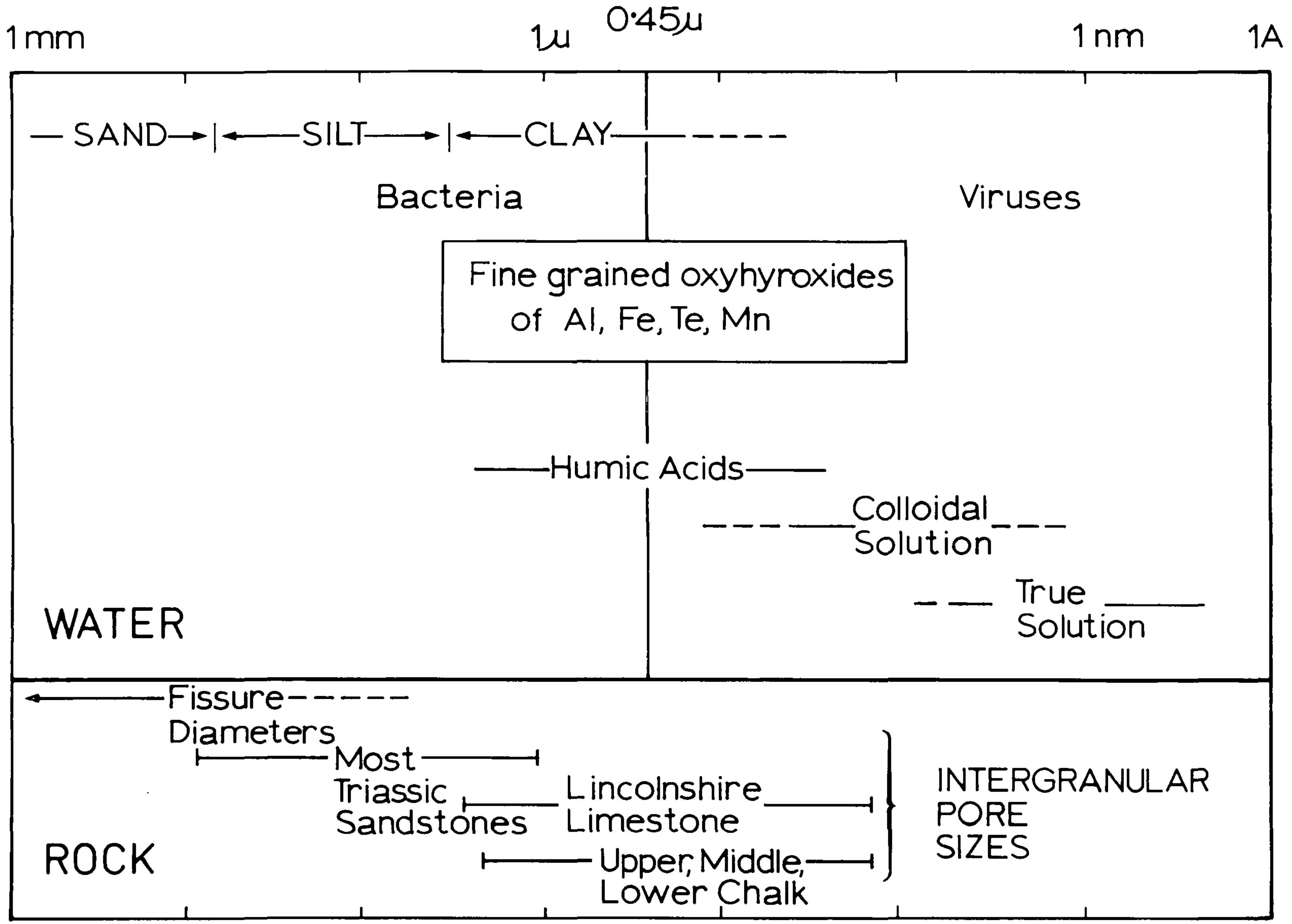


Figure 2. Sizes of solute and suspended particles in natural waters in the range 10^{-3} to 10^{-10} mm compared with mean intergranular pore and fissure diameters for UK aquifers. Data from Bird (1974) and other unpublished IGS sources.

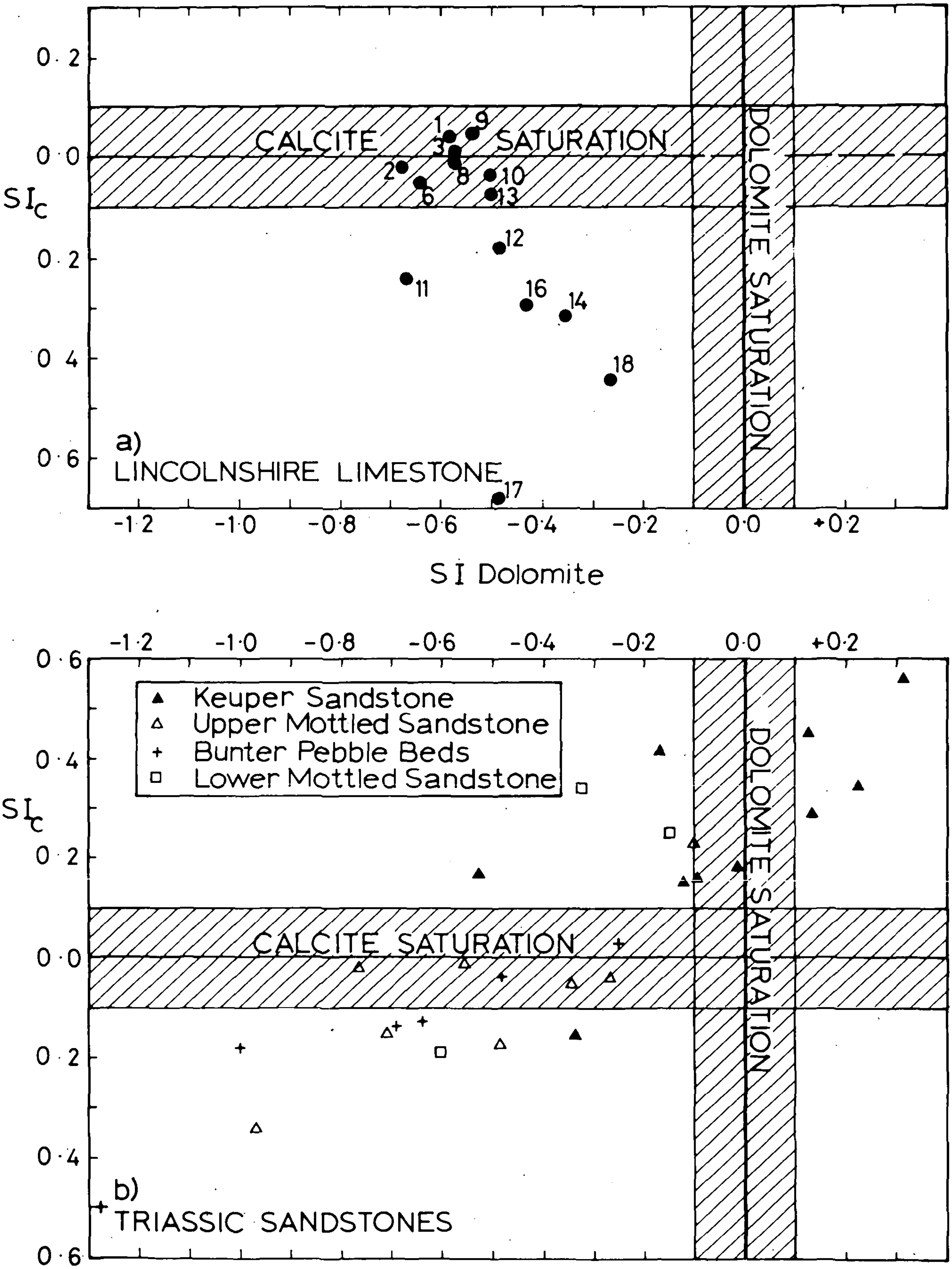


Figure 3. Saturation with respect to calcite and dolomite in (a) the Lincolnshire Limestone and (b) the Triassic Sandstones of the West Midlands - main aquifer units distinguished by symbol. SI_c and SI_d values computed using an IGS Fortran computer program (Bath 1975) using data from Jacobson and Langmuir (1974).

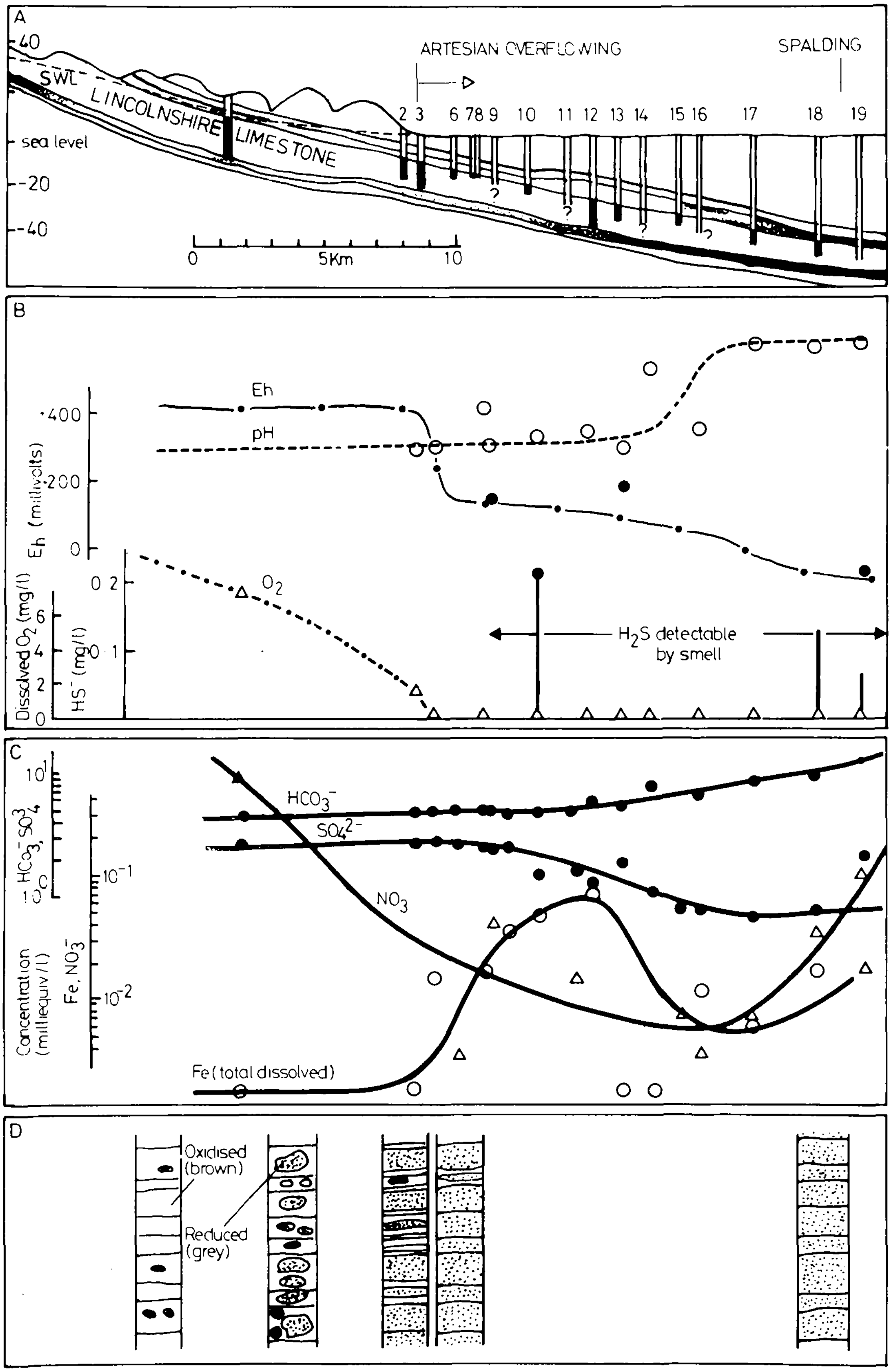


Figure 4. Oxidation-reduction in the Lincolnshire Limestone groundwaters and rock matrix. (a) Geological section through the limestone, NW-SE through Spalding, showing principal boreholes sampled (see Edmunds 1973 for further details) (b) Down gradient variation in Eh, pH, dissolved O_2 and H5. (c) Down gradient variation in main species affected by redox reactions. (d) Schematic representation of oxidized and reduced lithologies in the limestone from borehole evidence.

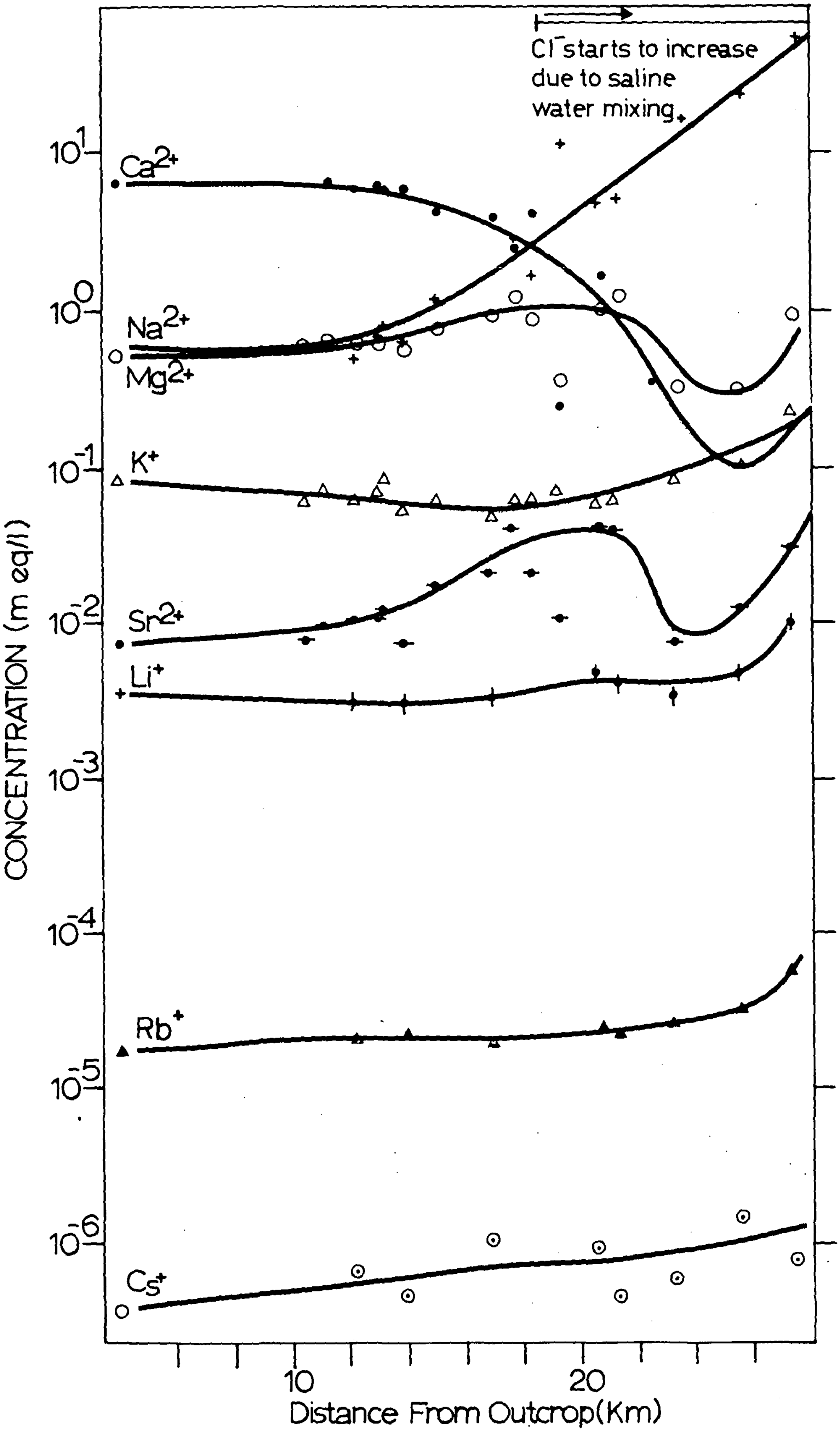


Figure 5. Down gradient variation of Group I and Group II cations in the Lincolnshire Limestone.

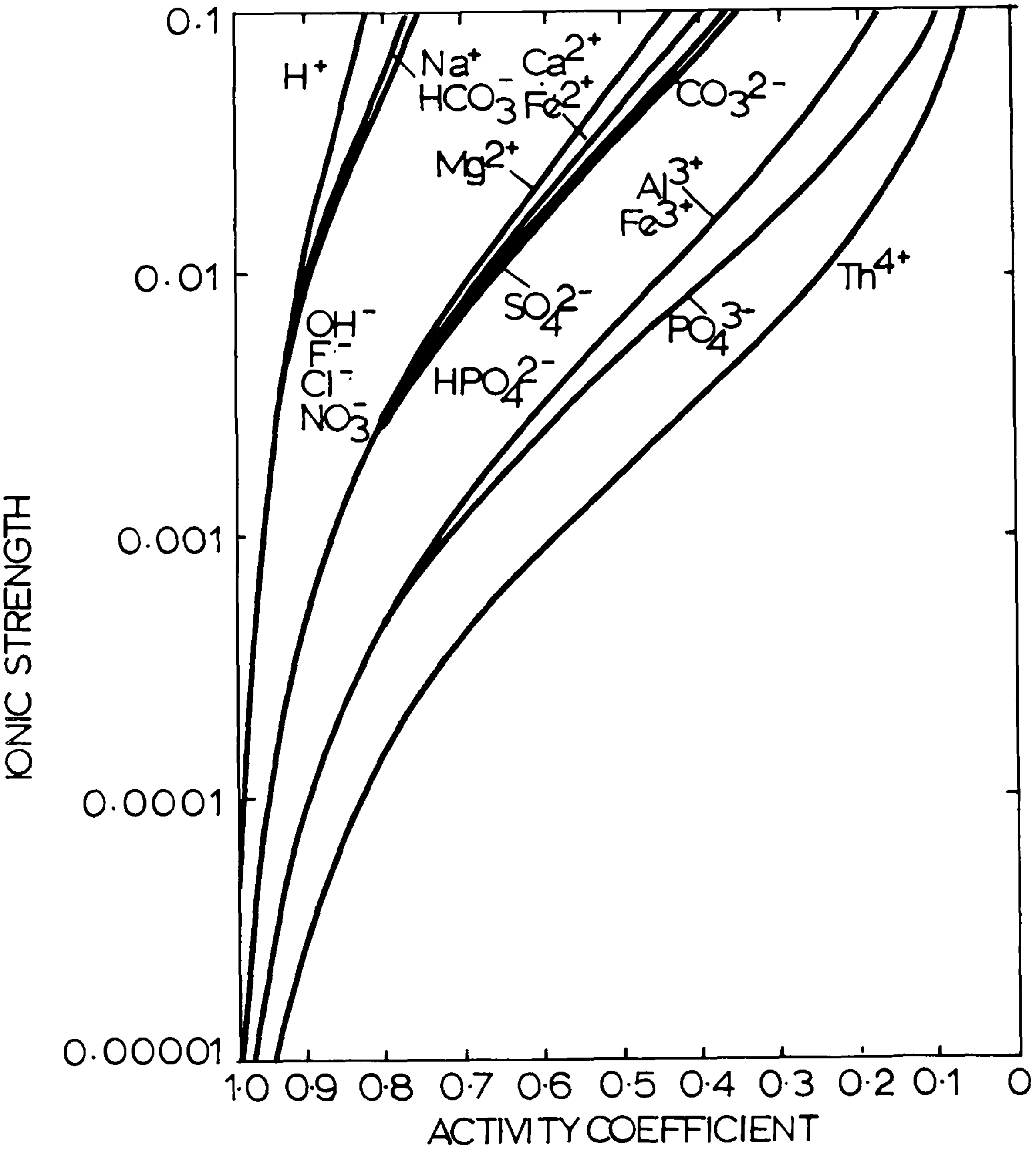


Figure 6. Relationship between activity coefficients for single dissolved ions to ionic strength of solution (After Hem 1970).

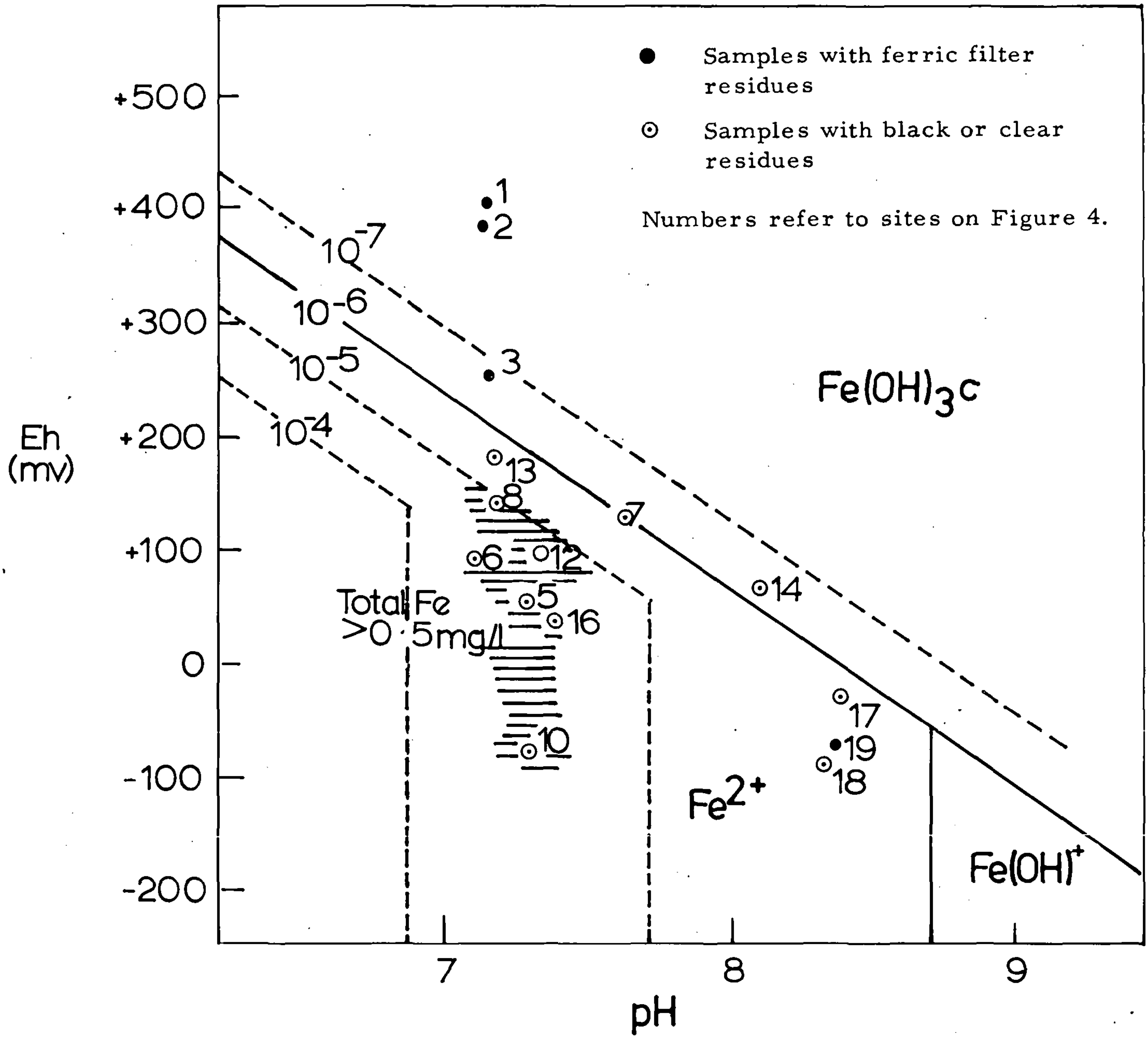
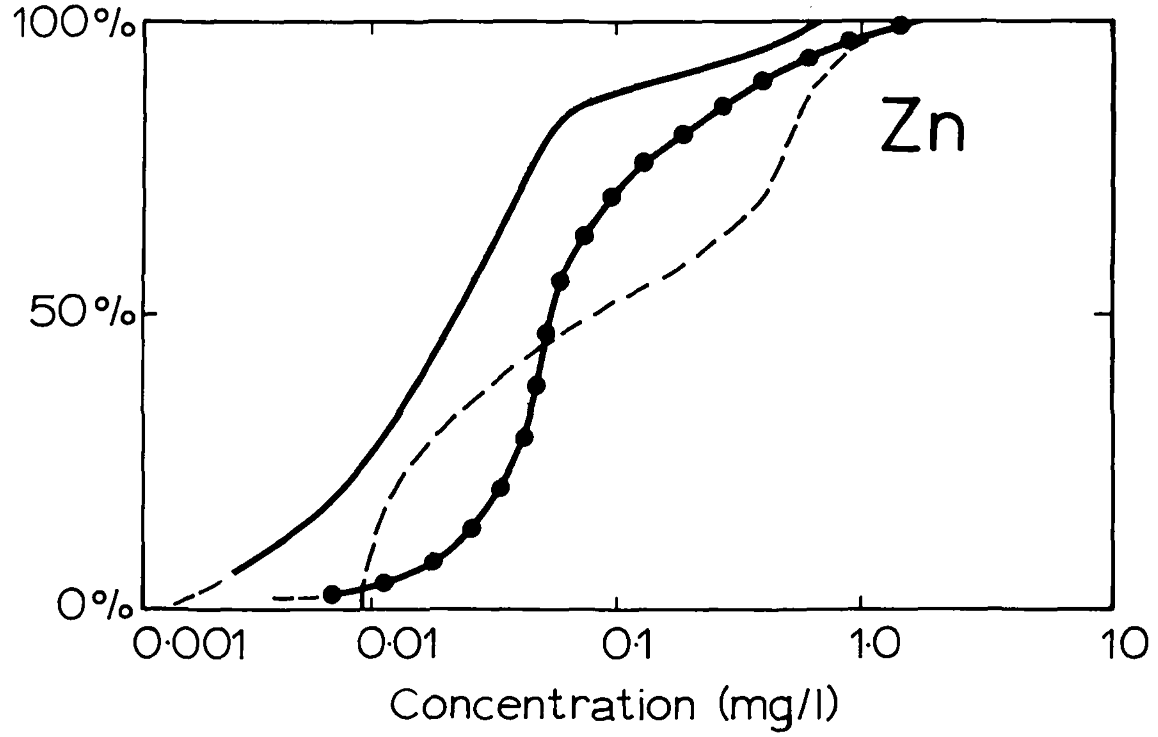


Figure 7. Eh - pH diagram showing theoretical aqueous ferrous-ferric equilibria (10^{-4} to 10^{-7} M total iron activity), compared with observed total dissolved iron concentrations in the Lincolnshire Limestone groundwaters.



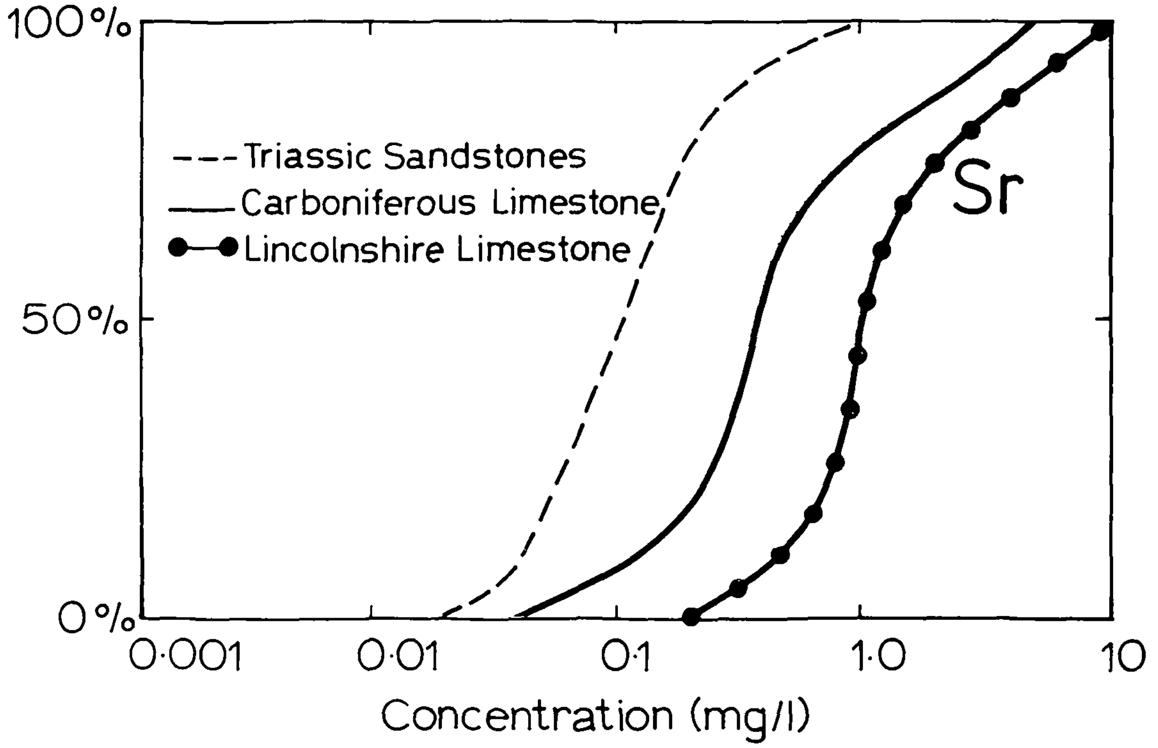


Figure 8. Cumulative frequency curves for Zn and Sr in the Triassic Sandstones, Carboniferous Limestone and Lincolnshire Limestone. Data from Edmunds (1971) and Edmunds and Morgan-Jones (1976).

PAPER 7

REVIEW OF EQUATIONS GOVERNING THE MOVEMENT AND ACCUMULATION OF A POLLUTANT IN AN AQUIFER

Prof. Jacob Bear

1. ABSTRACT

The paper briefly reviews some principles related to hydrodynamic dispersion in porous media, the objective being to present the basic ideas and nomenclature related to the movement of pollutants in aquifers.

The main mechanisms affecting the transport of a solute (= pollutant) in a porous medium, namely, convection, mechanical dispersion, molecular diffusion, solid-solute interactions and various chemical reactions and decay phenomena, which may be regarded as source-sink phenomena for the solute, are described.

Following some comments on the passage from the microscopic to the macroscopic scales of describing phenomena in porous media and the definition of an average of a property over a representative elementary volume, the microscopic balance equation for a solute in multiphase flow through porous media is presented and averaged to yield the generalized equation of hydrodynamic dispersion. This balance equation includes the effects of convection, dispersion, molecular diffusion, transfer across the boundary of the considered phase and source-sink phenomena representing chemical reactions and decay of the considered solute. The movement and accumulation of pollutants is governed by this equation. The general equation is reduced to simpler forms for some particular cases of practical interest. Of special interest is the case of unsaturated flow in the presence of adsorption.

The generalized boundary conditions for the balance equation are discussed. With this information, the mathematical statement of the problem of pollution transport and accumulation is presented.

The various dispersion and diffusion coefficients appearing in the balance equations are discussed. The relationship of the coefficient of hydrodynamic dispersion to certain porous medium geometrical properties, to the solvent's velocity and to molecular diffusion, is presented in detail.

Finally, some comments are made on methods for solving the balance (or hydrodynamic dispersion) equation in order to derive the distribution of pollution concentration in aquifers.

2. INTRODUCTION

We are dealing with mass transport in porous media, where the considered 'mass' is that of some solute moving with the solvent in the interstices of a porous medium.

Hydrodynamic dispersion in a porous medium is a term often used to describe the actual difference between the spreading of a solute in flow through a porous medium and that which would have occurred had all the fluid (= solvent) particles been moving at the average velocity.

As the solute is transported, its mass concentration $C=C(x,y,z,t)$ - measured, for example, as mass of solute per unit mass of solution - varies from point to point and with time in the flow domain. In order to handle pollution, we should be able to determine the solute's concentration C in a given domain under specified boundary conditions imposed on the domain's boundaries. A description of this kind can be obtained by solving the partial differential equations which govern the solvent and solute mass balances, subject to the appropriate boundary and initial conditions.

The objective of the following paragraphs is to present these equations and to comment on the various parameters appearing in them. It is by no means a literature survey. The material presented is well documented in the literature and, therefore, only a very small number of references is cited.

Mass transport phenomena occur in many problems of groundwater flow. Several examples may be cited:

(a) The continuous variation of the concentration of total dissolved solids, or of some specific constituent, as flow takes place in the aquifer.

(b) Groundwater pollution from some localized source, such as a faulty sewage installation, or waste dump.

(c) Groundwater pollution from a distributed source, such as fertilizers and pesticides applied to the area overlying the aquifer.

(d) Sea water intrusion into a coastal aquifer.

(e) Encroachment of saline, or brackish water, into an aquifer as a result of changes in the hydrologic regime.

(f) Seepage of polluted surface flow through pervious river beds or lakes.

(g) The movement of pollutants from the ground surface to the underlying water table, under unsaturated flow conditions (e.g., landfills).

Hydrodynamic dispersion is a macroscopic phenomenon, i.e., at the porous medium continuum scale of reference. However, in order to understand it, and describe it at the macroscopic scale, one has first to understand what happens at the microscopic scale, i.e., at points in the fluid present inside a pore. At each point within the solute occupying the pore space, or part of it, the solvent is transported with the solute at the latter's <u>local velocity</u>. This velocity varies in magnitude and direction from point to point inside a pore.

In saturated flow, we assume zero velocity at the solid wall and a maximum velocity at some interior point of the pore.

The presence of an intricate network of passages causes streamlines to fluctuate with respect to the mean direction of flow. When combined with the variation in solvent velocity, this produces spreading, or dispersion, of any group of initially close solute particles. This part of the total dispersion, caused only by velocity variations and the presence of the complex network of pores, is often called mechanical dispersion. It is primarily due to the geometry of the pore space. We have spreading in the direction of the flow, resulting from the difference between the average velocity in that direction and components of the local velocities in the same direction, but we also have spreading perpendicular to the direction of flow. The former is called longitudinal dispersion while the latter is called lateral (or transverse) dispersion. Obviously no mechanical dispersion takes place when the fluid is at rest or in the absence of the channel system which produces velocity variations.

We should keep in mind that since concentration varies from point to point, molecular diffusion is always present, adding its influence to the spreading produced by mechanical dispersion.

At each (microscopic) point inside a pore, we have a local solute concentration and, as the solute's concentration varies from point to point, a local solute concentration gradient. According to Fick's law of diffusion, a concentration gradient produces a flux of the solute by molecular diffusion. One should note that molecular diffusion may also take place if the solute as a whole is at rest.

Finally, chemical reactions and decay (e. g. , radioactive) phenomena in the solute, as well as various interactions between the solute and the solid surface of the porous matrix, may take place, affecting the solute's concentrations at points within the pore space. Surface phenomena may take the form of adsorption of solute particles on the solid surface, deposition, solution, ion exchange, etc.

In general, variations in solute concentration produce changes in the solvent's density and viscosity. These, in turn affect the flow regime (i.e., velocity distribution) that depends on these properties. At relatively low concentrations - often referred to as the 'ideal tracer approximation' - the variations in solvent properties are very small and may be neglected.

3. THE BALANCE EQUATION

Thus, at the microscopic level (i.e., in the solute continuum) solute is transported by two mechanisms: convection and molecular diffusion. At the same time chemical reactions and fluid-solid interactions may take place in the fluid continuum which completely, or partially, fill the pore space. However, in order to enable the solution of problems of practical interest, such that results in the real world can be measured and compared with such solutions, a passage to the description of the transport problem at the macroscopic level is needed.

At the macroscopic level of description, at every (mathematical) point of the domain occupied by the porous medium, we define a small volume around it, with the considered point as its centroid, and average the considered property (e.g., pressure, velocity, solute concentration) over this small volume. The resulting average value is assigned as the macroscopic value at the considered point. In this way, we disregard the question within which phase (fluid, solid, or any phase, in the case of a multi-phase flow) this (mathematical) point happens to fall. We refer to the small volume over which the averaging is performed as the <u>Representative Elementary Volume</u> (REV) of the considered porous medium. The size of the REV should be such that at that volume $(\mathcal{U}_0)$ any incremental change of the latter does not affect the resulting average.

Accordingly, let us consider a tensorial field $G(\underset{\sim}{x},t)$, e.g., solute concentration or velocity, in a porous medium composed of several phases (denoted by $\alpha = 1,2,3,\ldots$). For example, in unsaturated flow we have a solid phase, a fluid phase and a gaseous phase. The average value $\bar{G}_{\alpha}(\underset{\sim}{x}_0,t)$ of G at time t, within the domain $(U_{\alpha 0}) \subset (U_0)$ centred at $\underset{\sim}{x}_0$, is defined by:

$$\bar{G}(x_0,t) = \frac{1}{U_{\alpha 0}} \int_{(U_{\alpha 0})} G(\underset{\sim}{x}_0; \underset{\sim}{x}, t)\, dU(\underset{\sim}{x}) \qquad \ldots\ldots\ 1$$

Thus, the domain of averaging is the volume $U_{\alpha 0}$ occupied by the α-phase within U_0.

The quantity:

$$\overset{0}{\underset{\alpha}{G}}(\underset{\sim}{x}_0; \underset{\sim}{x}, t) \equiv G(\underset{\sim}{x}\cdot;\underset{\sim}{x}, t) - \bar{G}(\underset{\sim}{x}_0, t) \qquad \ldots\ldots\ 2$$

is the deviation of G at a point x inside $U_{\alpha 0}$, centred at $\underset{\sim}{x}_0$, from its average over $(U_{\alpha 0})$. It follows that $\overline{\overset{0}{\underset{\alpha}{G}}} = 0$ and $\overline{(\overset{0}{\underset{\alpha}{G}})} = \overset{0}{\underset{\alpha}{G}}$.

The space $\underset{\sim}{x}$ is the microscopic space, while the space $\underset{\sim}{x}_0$ is the macroscopic one.

Defining the volumetric fraction θ_α of the phase α at a point $\underset{\sim}{x}_0$ at time t by:

$$\theta_\alpha(\underset{\sim}{x}_0,t) = U_{\alpha 0}(\underset{\sim}{x}_0,t)/U_0;\ \sum_{(\alpha)} \theta_\alpha = n = \text{porosity}, \qquad \ldots\ldots\ 3$$

we obtain from Equation 1;

$$\theta_\alpha \bar{G}_\alpha(\underset{\sim}{x}_0,t) = \frac{1}{U_0} \int_{(U_0)} G(\underset{\sim}{x}_0; \underset{\sim}{x}, t)\, dU_\alpha \qquad \ldots\ldots\ 4$$

where $\theta \bar{G}_\alpha$ is the macroscopic value of G in the α-phase at point $\underset{\sim}{x}_0$ at time t. For example, for $\underset{\sim}{G} \equiv \underset{\sim}{V}$, $\theta_\alpha \bar{\underset{\sim}{V}}_\alpha \equiv \underset{\sim}{q}_\alpha(\underset{\sim}{x}_0,t)$ is the specific discharge of the α-phase (or the macroscopic velocity of the α-phase).

With this background, we now turn to develop the macroscopic balance equation for a solute in multi-phase flow through porous media (Bachmat and Bear, 1972).

Let e_α denote the specific value (i. e., per unit mass) of an extensive property E in the α-phase, and let ρ_α denote the mean density (= mass per unit volume) of the α-phase:

$$e_\alpha = dE/dm_\alpha \; ; \; \rho_\alpha e_\alpha = dE/dU_\alpha \qquad \ldots\ldots \; 5$$

The microscopic differential balance of E within the α-phase is given by (Truesdell and Toupin, 1960):

$$\partial(\rho_\alpha e_\alpha)/\partial t = -\mathrm{div}[\rho_\alpha e_\alpha \underset{\sim}{V}_\alpha + \underset{\sim}{J}(e_\alpha)] + \rho_\alpha \Gamma(e_\alpha) \qquad \ldots\ldots \; 6$$

where $\underset{\sim}{J}(e_\alpha) = \rho_\alpha e_\alpha[\underset{\sim}{V}(E) - \underset{\sim}{V}_\alpha]$ is the difference between the total flux of E and its part convected by the α-phase, $\underset{\sim}{V}_\alpha$ is the velocity of the α-phase and $\Gamma(e_\alpha)$ is the rate of production of E per unit mass of α.

In order to arrive at a macroscopic balance of E, we have to average Equation 6, using the definition of average as given by Equation 1. In addition, we need the following averaging rules (e. g., Bachmat, 1972, and Slattery, 1967).

(a) Average of a Product:

$$\overline{G_1G_2} = \bar{G}_1\bar{G}_2 + \overline{\overset{o}{G}_1\overset{o}{G}_2} \; ; \; \overset{o}{(G_1G_2)} = \overset{o}{G}_1\bar{G}_2 + \bar{G}_1\overset{o}{G}_2 + \overset{o}{G}_1\overset{o}{G}_2 - \overline{\overset{o}{G}_1\overset{o}{G}_2} \qquad \ldots\ldots \; 7$$

(b) Average of a time derivative:

$$\overline{\left(\frac{\partial G}{\partial t}\right)}_\alpha = \frac{1}{\theta_\alpha}\left[\frac{\partial}{\partial t}(\theta_\alpha \bar{G}_\alpha) - \widetilde{Gu_n}_\alpha \sigma'_\alpha\right] \; ; \; \tilde{G} \equiv \tilde{G}_\alpha = \frac{1}{U_{0\alpha}\sigma'} \int_{(U_{0\alpha}\sigma')} G(\underset{\sim}{x},t)\, dS \qquad \ldots\ldots \; 8$$

where u_n denotes the speed of displacement, along the outward normal, of a point on the interface between the phase α and the other phases within U_0 and σ'_α is the specific surface (i. e., per unit volume of U_0) of the total area of the interface surface between the phase α in (U_0) and the other phases, possibly comprising a part of the surface area bounding (U_0). When the configuration of the α-phase is nondeformable, $u_n = 0$

(c) Average of spatial derivative:

$$\overline{(\partial G/\partial x_i)}_\alpha = \frac{1}{\theta_{\alpha_1}}\left[\frac{\partial}{\partial x_{i_0}}(\theta_{\alpha_1}\overline{G}_{\alpha_1})^{(1)} + Gn_i\,\sigma'_{\alpha_1}\right] \quad \ldots\ldots\ 9$$

where x_{i_0} is the co-ordinate x_i in the macroscopic space, and n_i is the i-th component of a unit vector pointing outward normal to the interface of the α-phase in U_0. In Equation 9, the subscript 1 indicates that we take only the multiple connected part of the α-domain. Henceforth, only such domains will be considered and this subscript will be omitted.

With these rules, we now average Equation 6, obtaining the <u>general macroscopic balance equation</u> of an extensive property of a phase in a porous medium (Bachmat and Bear, 1972).

$$\frac{\partial}{\partial t}(\theta_\alpha\overline{\rho_\alpha e_\alpha}) = -\mathrm{div}\left[\overline{\rho_\alpha e_\alpha}\,\underset{\sim}{q}_{\tilde{\alpha}} + \theta_\alpha\overline{(\overset{\circ}{\rho_\alpha e_\alpha})\overset{\circ}{\underset{\sim}{V}}_{\tilde{\alpha}}} + \theta_\alpha\overline{\underset{\sim}{J}(e_\alpha)}\right] - \left[\widetilde{J_n(e_\alpha)} + \widetilde{\rho_\alpha e_\alpha(V_\alpha - u_{\alpha n})}\right]\sigma'_\alpha + \theta_\alpha\overline{\rho_\alpha\Gamma(e_\alpha)} \ldots .10$$

It is of interest to note, by comparing the microscopic balance (Equation 6) with the macroscopic one (Equation 10), that the latter contains two additional terms introduced as a result of the averaging process:

$\theta\overline{(\rho_\alpha e_\alpha)\underset{\sim}{V}}$ which is the macroscopic dispersive flux of E in excess of average convection by the α-phase, and

$[\widetilde{J_n(e_\alpha)} + \widetilde{\rho_\alpha e_\alpha(v_{\alpha n} - u_{\alpha n})}]\,\sigma'_\alpha$ which describes the transfer of E across the interface between the α-plane and all other phases.

Let us now apply Equation 10 to some special cases:

(a) Volume balance for the volume of a phase. In this case, $E = \underset{\alpha}{U} =$ volume of α-phase; $\underset{\alpha}{e} = 1/\underset{\alpha}{\rho} =$ specific volume of α-phase; $\underset{\sim}{J}(1/\underset{\alpha}{\rho}) = \underset{\tilde{\alpha}}{V} - \underset{\tilde{\alpha}}{V} = 0$. Equation 10 reduces to:

$$\frac{\partial \underset{\alpha}{\theta}}{\partial t} = -\operatorname{div} \underset{\tilde{\alpha}}{q} - \widetilde{(\underset{\alpha n}{V} - \underset{\alpha n}{u})}\ \underset{\alpha}{\sigma}' + \underset{\alpha}{\theta}\overline{(\operatorname{div} \underset{\tilde{\alpha}}{V})} \qquad \ldots\ldots 11$$

where $\underset{\tilde{\alpha}}{q} = \underset{\alpha}{\theta}\overline{\underset{\tilde{\alpha}}{V}}$ is the specific discharge of the α-phase.

In incompressible flow div $\underset{\tilde{\alpha}}{V} = 0$. If there exists no transfer of volume across the surface bounding, the α-phase (i. e., the bounding surface is a material surface of α), the middle term on the R. H. S. of Equation 11 also vanishes and Equation 11 reduces to:

$$\partial \underset{\alpha}{\theta}/\partial t = -\operatorname{div} \underset{\tilde{\alpha}}{q} \qquad \ldots\ldots 12$$

This equation is usually used to describe unsaturated flow of water in porous media. In saturated flow through a non-deformable porous medium, $\underset{\alpha}{\theta} = n$ and $\partial \underset{\alpha}{\theta}/\partial t = \partial n/\partial t = 0$.

(b) Mass balance of a phase. In this case, $E = \underset{\alpha}{m}$; $\underset{\alpha}{e} = 1$; $\Gamma(\underset{\alpha}{1}) = 0$ and $\underset{\sim}{J}(\underset{\alpha}{1}) = \underset{\alpha}{\rho}[\underset{\sim}{V}(\underset{\alpha}{m}) \cdot \underset{\tilde{\alpha}}{V}]$ is the diffusive flux of the mass of the α-phase which can be expressed by Fick's law of diffusion. Equation 10 becomes:

$$\frac{\partial(\underset{\alpha}{\theta}\underset{\alpha}{\bar{\rho}})}{\partial t} = \operatorname{div}[\underset{\alpha}{\bar{\rho}}\underset{\tilde{\alpha}}{q} + \overline{\underset{\alpha}{\theta}\underset{\alpha}{\mathring{\rho}}\underset{\tilde{\alpha}}{\mathring{V}}} + \theta\overline{\underset{\sim}{J}(\underset{\alpha}{1})}] - [\widetilde{J_n(\underset{\alpha}{1})} + \widetilde{\underset{\alpha}{\rho}(_{\alpha n} - u_{\alpha n})}]\underset{\alpha}{\sigma}' \qquad \ldots\ldots 13$$

For saturated flow of a single phase, $\underset{\alpha}{\theta} = n$, $\underset{\alpha}{\bar{\rho}} \equiv \bar{\rho}$, neglecting the effect of grad $\bar{\rho}$ and assuming $\bar{\rho}\bar{\underset{\sim}{V}} >> \overline{\mathring{\rho}\mathring{V}}$ Equation 13 is usually reduced, to:

$$\partial(n\bar{\rho})/\partial t = \operatorname{div} \bar{\rho}\underset{\sim}{q} \qquad \ldots\ldots 14$$

(c) Mass balance for a solute γ in the α-phase. In this case, the solution is the α -phase, $\underset{\alpha\gamma}{\rho} = d\underset{\alpha\gamma}{m}/d\underset{\alpha}{U}$, $\underset{\alpha}{e} = \underset{\alpha\gamma}{\rho}/\underset{\alpha}{\rho}$ and Equation 10 reduces to:

$$\frac{\partial(\theta_{\alpha}\bar{\rho}_{\alpha\gamma})}{\partial t} = -\operatorname{div}[\underset{\textcircled{1}}{\bar{\rho}_{\alpha\gamma}\, q_{\tilde{\alpha}}} + \underset{\textcircled{2}}{\theta_{\alpha}\overline{\overset{\circ}{\rho}_{\alpha\gamma}\overset{\circ}{V}_{\tilde{\alpha}}}} + \underset{\textcircled{3}}{\theta_{\alpha}\overline{J(\rho_{\alpha\gamma}/\rho_{\alpha})}}] - [\underset{\textcircled{4}}{\widetilde{J_n(\rho_{\alpha\gamma}/\rho_{\alpha})} + \widetilde{\rho_{\alpha\gamma}(V_{\alpha n}-u_{\alpha n})}}]_{\sigma'_{\alpha}} + \underset{\textcircled{5}}{\theta_{\alpha}\overline{\rho_{\alpha}\Gamma(\rho_{\alpha\gamma}/\rho_{\alpha})}}$$

which is the generalized equation of hydrodynamic dispersion for a solute in the multiphase system. In this equation, we identify the convective flux of the α-phase ①, the dispersive flux of γ, ② which is an extra flux resulting from the variations in velocity at the microscopic level, the diffusive flux of γ, ③ transfer across phase boundaries, e.g., due to adsorption, desorption, precipitation, ion exchange, etc., ④ and production (or decay) of the considered solute ⑤.

Let us rewrite Equation 14 in a more common nomenclature

(1) Denote $\overline{\rho_{\alpha\gamma}/\rho_{\alpha}} = C$ and assume that $\rho_{\alpha} = \text{const.}$

(2) Assume that the dispersive flux of γ, $\overline{\overset{\circ}{\rho}_{\alpha\gamma}\overset{\circ}{V}_{\tilde{\alpha}}}$, can be expressed by a Fickian type relationship:

$$\overline{\overset{\circ}{\rho}_{\alpha\gamma}\overset{\circ}{V}_{\tilde{\alpha}}} = -\underline{\underline{D}}\,\text{grad}\,\bar{\rho}_{\alpha\gamma},$$

where $\underline{\underline{D}}$, a second rank tensor, is the coefficient of mechanical dispersion.

(3) The diffusive flux can also be expressed by Fick's law of diffusion:

$$\overline{J(\rho_{\alpha\gamma}/\rho_{\alpha})} = -\underline{\underline{D}}_d^{*}\,\text{grad}\,\bar{\rho}_{\alpha\gamma},$$

where $\underline{\underline{D}}_d^{*}$, a second rank tensor, is the coefficient of molecular diffusion in a porous medium.

(4) We shall assume $\theta_{\alpha}\overline{\rho_{\alpha}\Gamma(\rho_{\alpha\gamma}/\rho_{\alpha})} = \theta_{\alpha}\,\bar{\rho}\bar{\Gamma}_{\alpha\alpha\gamma}$. Often the production function is such

that $\bar{\Gamma} = C\bar{\Gamma}(C)$. For example, if the production is due to radioactive decay of γ only, $\Gamma(C) = -\lambda C$, where λ is the decay constant of the solute (i.e., the reciprocal of the solute's mean half life).

(5) Equation 15 can also be written for the solid phase. Denoting the transfer across the interface term by f_s and assuming $V_s = 0$, no diffusion in the solid phase, and $\theta_s \rho_s \overline{\Gamma(\rho_{s\gamma}/\rho_s)} = \theta_s \bar{\rho}_s \bar{\Gamma}_s$, we obtain:

$$\frac{\partial(\theta_s \bar{\rho}_{s\gamma})}{\partial t} = -f_s + \theta_s \bar{\rho}_s \bar{\Gamma}_s \qquad \ldots\ldots 16$$

Thus, denoting term (Equation 4) in Equation 14 by f_α, we have $f_\alpha = -f_s$. In this way f_α denotes the transfer (= mass of γ per unit volume of system per unit time) due to the interaction of the α-phase and the surface of the solid matrix (e.g., adsorption).

Often f_s is related to the concentrations of both the α-phase and the solid phase, $f_s = f_s(\rho_{\alpha\gamma}/\rho, \rho_{\alpha\gamma}/\rho_s) = f(C,F)$. Many expressions exist for $f(C,F)$, called isotherms or adsorption equations. For example:

$$f(C,F) = -k(C - mF) \quad m, k = \text{constants} \qquad \ldots\ldots 17$$

is often used.

If F also undergoes radioactive decay, $\bar{\Gamma}_{s\gamma} = -\lambda F$.

Obviously, in the above case, the transfer from the α-phase to the solid phase takes place only across part of σ'_α (the one opposite the solid).

Introducing all these assumptions into Equation 15, we obtain:

$$\frac{\partial(\theta_\alpha \bar{\rho}_\alpha C)}{\partial t} = -\operatorname{div}[\bar{\rho}_\alpha C \tilde{q}_\alpha - \theta_\alpha \underline{\underline{D}} \operatorname{grad}(\bar{\rho}_\alpha C) + \theta_\alpha \underline{\underline{D}}_d^* \operatorname{grad}(\bar{\rho}_\alpha C)]$$

$$- \frac{\partial(\theta_s \bar{\rho}_s F)}{\partial t} + \theta_s \bar{\rho}_s \bar{\Gamma}_s + \theta_\alpha \bar{\rho}_\alpha \bar{\Gamma}_{\alpha\gamma} \qquad \ldots\ldots 19$$

where $\theta_s = 1-n$ is the volumetric fraction of the solid. In addition, we also have:

$$\frac{\partial(\theta_s \bar{\rho}_s F)}{\partial t} = -f(C,F) + \theta_s \bar{\rho}_s \bar{\Gamma}_{s\gamma} \qquad \ldots\ldots 20$$

For the special case: $\bar{\rho}_{\alpha}$ = const, $\bar{\rho}_s$ = const, θ_s = const, $\bar{\Gamma}_{\alpha\gamma} = -\lambda C$, $\bar{\Gamma}_{s\gamma} = -\lambda F$, and $f(C,F)$ expressed by Equation 17, we obtain:

$$\bar{\rho}_{\alpha} \frac{\partial(\theta_{\alpha} C)}{\partial t} + \bar{\rho}_s \theta_s \frac{\partial F}{\partial t} = -\mathrm{div}[\bar{\rho}_{\alpha} C \underset{\tilde{\alpha}}{q} - \bar{\rho}_{\alpha}\theta_{\alpha}\underline{\underline{D}}' \,\mathrm{grad}\, C] - \bar{\rho}_s \theta_s \lambda F - \bar{\rho}_{\alpha}\theta_{\alpha}\lambda C \qquad \ldots\ldots 21$$

and:

$$\frac{\partial F}{\partial t} = k'(C-mF) - \lambda F \;;\; k' = k/\theta_s \bar{\rho}_s \qquad \ldots\ldots 22$$

where $\underline{\underline{D}}' = \underline{\underline{D}} + \underline{\underline{D}}^{*}_{d}$ = coefficient of hydrodynamic dispersion.

Thus, the pair of Equations 19 and 20, or for the special case considered here, Equations 21 and 22 describe the transport of a solute in the presence of some interactions of the solute with the solid surface.

In addition to Equations 19 and 20, we need an expression for $\underset{\tilde{\alpha}}{q}$:

$$\underset{\tilde{\alpha}}{q} = -\frac{\underline{\underline{k}}(\theta_{\alpha})}{\mu_{\alpha}} (\mathrm{grad}\, \bar{p}_{\alpha} + g\bar{\rho}_{\alpha} \underset{\sim}{1z}), \qquad \ldots\ldots 23$$

and the relationships $\underline{\underline{k}} = \underline{\underline{k}}(\theta_{\alpha})$ = relative permeability, $\bar{p}_{\alpha} = \bar{p}_{\alpha}(\theta_{\alpha})$ = pressure in the α-phase, $\bar{\rho}_{\alpha} = \bar{\rho}_{\alpha}(C)$ and $\mu_{\alpha} = \mu_{\alpha}(C)$ = viscosity of the α-phase, in case ρ_{α} and $\bar{\mu}_{\alpha}$ are affected by C.

For an incompressible fluid, div $\underset{\tilde{\alpha}}{V} = 0$ and in the absence of volume transfer across the α-phase boundary (i.e., the bounding surface of α is a material surface), $V_{\alpha n} - u_{\alpha n} = 0$, we obtain from Equation 11:

$$(\partial\theta_\alpha/\partial t) = -\operatorname{div} q_{\tilde{\alpha}} \qquad \ldots\ldots 24$$

Thus, the distributions $C(\underset{\sim}{x},t)$, $F(\underset{\sim}{x},t)$, $q_{\tilde{\alpha}}(\underset{\sim}{x},t)$, and $\theta_\alpha(\underset{\sim}{x},t)$ can be derived by solving Equations 21, 22, 23 and 24 simultaneously. If the fluid and possibly the solid matrix are compressible, Equation 24 is replaced by another one obtained from Equation 10 by letting $e_\alpha = 1$ (i.e., $'E = m_\alpha$).

In the absence of adsorption, $k=0$, and Equations 21 and 22 become independent. Equation 21 reduces to

$$\frac{\partial(\theta_\alpha C)}{\partial t} = -\operatorname{div}(Cq_\alpha - \theta_\alpha \underline{\underline{D}}' \operatorname{grad} C) - \theta_\alpha \lambda C \qquad \ldots\ldots 25$$

In the absence of radioactive decay, $\lambda=0$.

By combining Equations 25 and 24, we obtain:

$$\theta_\alpha \frac{\partial C}{\partial t} = \operatorname{div}(\theta_\alpha \underline{\underline{D}}' \operatorname{grad} C) - q_{\tilde{\alpha}} \operatorname{grad} C - \theta_\alpha \lambda C \qquad \ldots\ldots 26$$

Again, in all these cases, we also need an equation from which the distribution of $q_{\tilde{\alpha}}$ can be derived.

In saturated groundwater flow through aquifers, we sometimes assume that porosity (n) is a constant so that θ is replaced by n. In regional studies we also often assume that the flow is essentially horizontal and that $C = C(x,y,t)$.

A phenomenon often encountered in hydrodynamic dispersion is the presence of dead-end pores. These are pores, or more generally, stagnant (or practically so) static fluid bodies, e.g., in unsaturated flow into and out of which the solute is moving by molecular diffusion only. Thus, this behaviour of this portion of the pore space is equivalent to that of sources or sinks for the solute. This phenomenon may be represented by a model similar to that used above for describing adsorption. With θ_d and $\rho_{d\gamma}$ denoting the fractional volume of the fluid filled dead-end pores and the mass of γ per unit volume of fluid in these pores, respectively, we have

$$\partial(\theta_{\alpha d}\bar{\rho}_{\gamma d})/\partial t = -f_{\gamma d} \qquad \ldots\ldots 27$$

where $-f_{\gamma d}$ represents the net flow of γ by molecular diffusion from the moving fluid having the fractional volume $\theta_{\alpha m}=\theta_\alpha-\theta_{\alpha d}$ into the (practically) stagnant water in the dead-end pores (per unit time and unit volume of system). An expression for $f_{\gamma d}$ could take the form $f_{\gamma d} = \beta\bar{\rho}_\alpha D^*_d(C_d-C)$, where C and $C_d = \bar{\rho}_{\gamma d}/\bar{\rho}_\alpha$ *represent the concentrations of* γ *in the moving and stagnant fluids, respect*ively, and β is some coefficient representing the geometry of the region through which the transfer takes place. Equation 19, in the absence of sources and sinks, will then become:

$$\partial(\theta_{\alpha m}\bar{\rho}_\alpha C)/\partial t = -\,\mathrm{div}(\theta_{\alpha m}\bar{\rho}_\alpha C\underset{\sim}{V}_\alpha - \theta_{\alpha m}\underset{=}{D}'\;\mathrm{grad}\;(\bar{\rho}_\alpha C) - f_{\alpha\gamma}\;; \qquad \ldots\ldots 28$$

where $f_{\alpha\gamma} = -f_{\gamma d}$.

4. BOUNDARY CONDITIONS

The solution of Equations 26, 21 or 19, the last two simultaneously with an appropriate equation for F, requires the specification of conditions which C has to satisfy on the boundary of the given flow domain.

Bachmat and Bear (1972) developed the general boundary conditions for the above (mass balance) equations. Essentially, we require that the total flux of E across the (macroscopic) boundary be continuous. Obviously, this is true if the boundary itself does not behave as a sink or a source-surface for E.

For the mass of a solute γ in the α-phase, the boundary condition becomes:

$$[\bar{\rho}_{\alpha\gamma}(q_{\alpha n}-\theta_\alpha\bar{u}_n) + \theta_\alpha\rho_{\alpha\gamma}\overline{\overset{\circ\circ}{V}_{\alpha k}n_k} + \theta_\alpha\overline{J_n(\rho_{\alpha\gamma}/\rho_\alpha)}]_{1,2} = 0 \qquad \ldots\ldots 29$$

where $\underset{\sim}{n}$ is a unit vector in the direction of the outward normal and $\bar{u}_n$ is the macroscopic velocity of displacement of the boundary and the symbol $[A]_{1,2}$. denotes the jump in A across the boundary, from side 1 to side 2. The L. H. S. of Equation 29 will be different from zero if somehow γ accumulates on the surface of the (macroscopic) boundary. What Equation 29 states is that the total transfer of γ by convection, dispersion, and diffusion is unchanged as the boundary is crossed. For the set of assumptions leading to Equation 26, Equation 29 may be written as:

$$[C(q_{\alpha n}-\theta_\alpha \bar{u}_n) - \theta_\alpha D'_{ik} \frac{\partial C}{\partial x_k} n_i]_{1,2} = 0; \quad \underline{D}' = \underline{D} + \underline{D}^*_d \qquad \text{......30}$$

For a stationary boundary, $\bar{u}_n \equiv 0$.

Consider the following cases of particular interest, where, for the sake of simplicity, the flow is assumed one-dimensional and $\bar{u}_n \equiv 0$.

(a) Both 1 and 2 domains are porous media of different character. The boundary condition (Equation 30) becomes:

$$\{Cq_\alpha - \theta_\alpha D'(\partial C/\partial x)\}_1 = \{Cq_\alpha - \theta_\alpha D'(\partial C/\partial x)\}_2 \qquad \text{......31}$$

(b) Region 2 is an α-phase liquid continuum which is assumed to be continuously mixed so that its concentration is maintained at a constant C_2. On the boundary, we have also to maintain $q_{\alpha 1} = q_{\alpha 2} \equiv q_\alpha$. The boundary condition (Equation 31) reduces to

$$\{q_\alpha(C-C_2) - \theta_\alpha D'\partial C/\partial x\}_1 = 0 \qquad \text{......32}$$

We could assume $C_2 \neq$ const. and molecular diffusion to take place in region 2.

(c) Assuming that in case (b) above, we have, after a sufficiently long time, $C=C_2$, i. e., the same concentration on both sides of the boundary, Equation 32 reduces to

$$\{\partial C/\partial x\}_1 = 0 \qquad \ldots\ldots 33$$

This boundary condition is also applicable to the case where the external domain 2 is a vacuum or a gas continuum.

It is important to note that if both regions are porous media of different properties, we may have $[\theta]_{1,2} \neq 0$. This is, for example, the case of unsaturated flow in a layered domain.

5. THE COEFFICIENT OF DISPERSION

The coefficient of mechanical dispersion $\underline{\underline{D}}$ (dim. L^2/T) appearing in Equation 19 was introduced by the assumption that the dispersive flux is linearly related to the concentration gradient:

$$\overline{\overset{\circ}{C}\overset{\circ}{V}}_{\tilde{\alpha}} = -\underline{\underline{D}}\ \text{grad}\ C \qquad \ldots\ldots 34$$

Various models have been employed in order to reach an expression relating the flux resulting from mechanical dispersion to averaged variables (e.g., velocity or concentration) and measurable (or at least determinable) macroscopic parameters of the porous matrix. These are well reviewed in the literature and need not be described here (see, for example, reviews by Fried and Combarnous, 1971; Bear, 1972). Two approaches have commonly been employed. In the first one, the porous medium is replaced by a greatly simplified fictitious model in which the mixing, or spreading, of the solute can be analysed by exact mathematical methods. A single capillary tube, a bundle of capillaries, or other ordered assemblies of tubes or mixing cells, have been employed by various investigators. However, as the model becomes simpler, fewer factors effecting dispersion, and especially transverse dispersion, can be taken into account.

The second approach is to construct a statistical (conceptual) model of the microscopic motion of the marked solute (or tracer) particles and to average these motions in order to obtain a macroscopic description of the dispersive flux.

In either approach, one must start from the spreading that takes place in an elementary tube or step (see, for example, de Josselin de Jong, 1958, Saffman, 1959 and 1960, and Wilson and Gelhar, 1974).

Sometimes the two approaches are combined by taking a regular geometry of the channels, but introducing some statistics, for example, to the distribution of channel diameters.

Bear and Bachmat (1967), who employed a model composed of a network of interconnected capillary tubes, derived Equation 34 with the following expression for the relationship between D , porous matrix geometry, flow velocity and molecular diffusion:

$$D_{ij} = a_{ijkm} \frac{\bar{V}_k \bar{V}_m}{\bar{V}} f\,(Pe,\delta) \qquad \ldots\ldots 35$$

where $V = |\underset{\sim}{\bar{V}}|$, Pe = Peclet number $= L\bar{V}/D_d$, L being some characteristic length of the pores, D_d = coefficient of molecular diffusion of the solute in the considered liquid phase, δ = ratio of length characterizing the individual channel of a porous medium to its hydraulic radius, and $f(Pe,\delta)$ is a function which introduces the effect of transfer by molecular diffusion between adjacent streamlines at the microscopic level. This effect is coupled with mechanical dispersion. It is distinct from the flux due to molecular diffusion in the porous medium expressed by $\underset{\sim}{\bar{J}} = \underline{\underline{D}}^*_d \operatorname{grad} \bar{\rho}_{\alpha\gamma}$.

The coefficient a_{ijkm}, a fourth rank tensor (dim L), called the <u>dispersivity of the porous medium</u>, is a property related to the geometrical configuration of the considered phase. It is, therefore, a function of the saturation. Bear and Bachmat (1967) in dealing with <u>saturated flow</u> through porous media, suggested

$$\bar{a}_{ijkm} = [\overline{(\overset{\circ}{BT}{}^{*}_{ir})(\overset{\circ}{BT}{}^{*}_{js})} \;/\; (\overline{BT^{*}_{rk}}\;\overline{BT^{*}_{sm}})]\,L \qquad \ldots\ldots 36$$

where BT^*_{ij} is an oriented conductance (dim L^2) of a flow channel in the considered porous medium model and T^*_{ij} (a second rank tensor) has the meaning of tortuosity (Bear, 1972, p. 614). For an isotropic porous medium $\bar{T}_{km} = \bar{T}^*\delta_{km}$, $1/3 \leqslant \bar{T}^* \leqslant 2/3$. They also showed that the permeability of the saturated medium is expressed by:

$$k_{ij} = n\,\overline{BT^*_{ij}} \approx n\,B\overline{T^*_{ij}}; \quad n = \text{porosity} \qquad \ldots\ldots 37$$

In a similar way,

$$D^*_d = \underline{\underline{\bar{T}}}^* D_d \qquad \ldots\ldots 38$$

where $\underline{\underline{\bar{T}}}^*$ is the tortuosity of the porous medium.

Thus, while the permeability is proportional to the square of a length characterizing the cross-section (area and shape) of the openings of a porous medium, the dispersivity is proportional to the relative variance of this length and to a characteristic length of the channels.

In dealing with unsaturated flow, let us assume a simple model such that at any saturation, part of the pore space is completely saturated, while the remaining part is completely empty. As the water content is reduced, the larger pores empty first. The size of the largest pore diameter through which flow takes place can be found from the retention curve. With the capillary pressure (p_c) related to the water content θ by $p_c(S) = 2\sigma^*/r$, where σ^* is the surface tension and r is the radius of the considered pore, it is possible to calculate for every θ, the largest radius through which flow still takes place. We can, therefore, use the pore-size distribution curve to calculate the average radius of the saturated portion of the void-space for every θ. This should be used as a characteristic length in calculating the Peclet number.

Similarly, as the tortuosity and conductance may highly be affected by θ, the dispersivity is also a function of θ.

In Equation 35, we recognize the influence of the geometry of the void space through a_{ijkm}, the velocity and the Peclet number, which may be regarded as expressing the ratio between transport by convection and transport by molecular diffusions. For saturated flow, Bear and Bachmat (1967) suggested

$$f(Pe,\delta) = Pe/(2+Pe+4\delta^2) \qquad \ldots\ldots 39$$

For an isotropic porous medium, the medium's dispersivity a_{ijkm} is related to two constant a_I = longitudinal dispersivity of the medium and a_{II} = transversal dispersivity of the medium. With these parameters, the components of the medium's dispersivity may be expressed by

$$a_{ijkm} = a_{II}\delta_{ij}\delta_{km} + \frac{a_I-a_{II}}{2}(\delta_{ik}\delta_{jm} + \delta_{im}\delta_{jk}) \qquad \ldots\ldots 40$$

where δ_{ik} is the Kronecker delta.

By combining Equation 40 with Equation 35, assuming $f(Pe,\delta) \equiv 1$, we obtain

$$D_{ij} = a_{II}\bar{V}\delta_{ij} + (a_I-a_{II})\bar{V}_i\bar{V}_j/\bar{V} \qquad \ldots\ldots 41$$

If we choose a cartesian co-ordinate system at a point, such that one of its axes, say x_1, coincides with the direction of the average uniform velocity $\bar{V}$, then Equation 41 reduces to:

$$D_{11} = a_I\bar{V},\ D_{22} = a_{II}\bar{V},\ D_{33} = a_{II}\bar{V},\ D_{ij} = 0 \text{ for } i \neq j \qquad \ldots\ldots 42$$

The axes of the co-ordinate system in which D_{ij} is expressed by Equation 42 are called the principal axes of the dispersion. D_{11}, D_{22}, and D_{33} are the principal values of the coefficient of mechanical dispersion. In this case, D_{11} is called the coefficient of longitudinal dispersion while D_{22} and D_{33} are called coefficients of transversal dispersion.

Many experiments and some analytical studies seem to indicate that the coefficient of dispersion is not linearly related to the velocity, as seems to be indicated by Equation 35, unless f is regarded as introducing the non-linear effect of the velocity expressed here as a Peclet number.

Often, expressions of the form

$$D_{11} = a_I \bar{V} P_e^{m_1} \qquad D_{22} = a_{II} \bar{V} P_e^{m_2} \qquad \ldots\ldots 43$$

where m_1 and m_2 are constants, are found in the literature. Obviously, for unsaturated flow a_I, a_{II}, m_1 and m_2 will be functions of the water content.

Practically no work has been carried out on the dispersivity of anistropic media.

x x x

We have thus shown that presently we are in a position to state, at least in principle, any aquifer pollution problem mathematically in terms of an appropriate partial differential equation - the equation of hydrodynamic dispersion - and an appropriate set of boundary and initial conditions. In the case of an ideal tracer ($\bar{\rho}_\alpha$ = const, $\bar{\mu}_\alpha$ = const), the solution for the velocity or head distribution can be derived independently and then introduced as a known input into the dispersion equation. Otherwise, the two fields - $\bar{V}$ and $C_{\tilde{\alpha}}$ - have to be solved for simultaneously.

One should note that the passage from the basic Equation 10 to the more particular equations, involves assumption with respect to the various fluxes (e.g., the dispersive flux $\overline{\mathring{\rho}\mathring{\underset{\sim}{V}}}$), interphase transfer terms (e.g., $[J_n(C) + \rho_{\gamma\alpha}(V_{\alpha n} - u_{\alpha n})]\sigma'_\alpha$) and source terms. This kind of information has to come from research into the physics of the phenomena involved. The same is true with respect to the various transport coefficients, e.g., the coefficient of dispersion, and their relationships to matrix properties, to the velocity, to molecular diffusion and to other parameters.

Except for relatively simple cases (one-dimensional, or certain uniform flows in two dimensions) an analytic solution is not possible. This is certainly true for cases of practical interest, where the flow domain is inhomogenous, the flow is non-uniform and the geometry of domain boundaries and of sink and source areas (of pollution and of waters) may be rather complicated. In such cases, the forecast of pollution spreading and accumulation is obtained by a numerical solution of the dispersion equation, or the appropriate set of equations. To date, very accurate and efficient numerical solutions are available, using finite difference or finite element techniques (see, for example, a large number of articles in a recent International Conference on Finite Elements in Water Resources, Princeton University, July 1976).

Obviously, in order to solve the forecasting problem, information is required with respect to the various transport coefficients appearing in the balance equations. These have to be derived by solving what is usually referred to as the 'inverse problem'. To solve the problem, we use data with respect to solute concentration, water levels, pumping rates, etc., obtained by observations in the field of interest in the past. These data are inserted into the balance equations which thus turn into equations for the unknown parameters. Although, in principle, this sounds straight-forward, the actual implementation is most difficult and requires special techniques. Nevertheless, to date, a number of methods have been presented in the literature, often on the basis of some numerical representation of the partial differential balance equation, for deriving the transport coefficients from field data.

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SUPPORT PAPER A

SEQUENCES IN REDOX AND BASICITY VARIATIONS IN SULPHIDE-ENRICHED AQUIFERS

E.S. Hall.

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1. INTRODUCTION

The depositional environment of most subaqueous sediments is chemically reducing in comparison with the atmospheric condition, which is oxidizing. This division has been generated at the Earth's surface by sunlight, through the process of photosynthesis by which plants and all derivative organisms gain their existence. Reducing substances occur in ancient sediments depending upon the biological activity during their deposition and the extent to which further organic contamination or re-oxidation has subsequently occurred. Exploitation of groundwater causes changes which promote the recombination of the reduced and oxidized conditions by:

(i) increasing the depth of the zone of aeration by lowering of the water table and

(ii) enhancing recharge of aquifers using fully oxygenated water either naturally or more especially by artificial recharge techniques.

Compositional changes occurring in organic sediments during their formation and subsequent re-oxidation follow the general sequence:

(a) fresh biological matter
(b) partially decayed or transformed organic matter (peat, lignite, fossil fuels)
(c) sulphides, selenides, arsenides, etc, and associated heavy metals, notably iron and manganese
(d) divalent metal ions (carbonates and exchangeable silicates)
(e) insoluble higher oxides.

The composition of groundwater is governed in general terms by the extent to which the aquifer has already undergone oxidation during geological time and the re-oxidation which continues with exploitation of groundwater. The consideration is relevant to highly permeable formations and particularly to sands, which offer a large and generally uniform capacity for the accumulation of biological matter by filtration and accommodation of microbial activity during their deposition. These usually contain significant amounts of iron and manganese in various stages of oxidation. For example, the Tertiary sands of the London Basin which immediately overlie the Chalk contain abundant iron and manganese, largely occurring as the sulphides, and are part of an aquifer system in which the process of re-oxidation has only partially occurred because of the effective confinement afforded by the overlying London Clay (1).

Oxidation-reduction processes involved in the formation and destruction of organic and sulphur compounds are accompanied by acid/base changes involving transformations of carbon dioxide and sulphuric acid. In these, the original meaning of 'oxygen' as an 'acid-producer' is evident with the formation of carbon dioxide and sulphuric acid by oxidation. Changes which occur in reducing sediments, either during original diagenesis or from subsequent re-oxidation, in general have come about through the movement of groundwater bringing in reactants or biological nutrients and transporting away products of reaction. Depending therefore upon the nature of groundwater and its direction and rate of flow, a sequence of oxidation-reduction conditions in an aquifer and associated acid-base properties may be postulated in terms of the possible existence of certain compounds based upon their known thermodynamic properties.

The purpose of this paper is to consider what these sequences might be in order to provide a base for comparison with actual variations in aquifer and groundwater composition that occur with time and location. In this way, sensible predictions might be possible about groundwater quality change resulting from the exploitation of an aquifer.

2. FORMATION AND TRANSFORMATION OF SULPHIDE/CARBONATES

The formation and distribution of sulphur, iron, manganese and other heavy metals in aquifers concerns the comparative solubilities of sulphides, carbonates and hydrated oxides, as well as ion-exchange affinities of metal ions for clays and other minerals. Chemical equilibria affecting these species are known to be the basis for compositional changes occurring during the diagenesis of sediments (2) and attention need be given here to only a few of the processes involved.

2.1. FORMATION OF IRON SULPHIDE

The bacterial reduction of sulphate to sulphide may be associated with variable basicity changes according to the availability of iron which precipitates the sulphide as FeS or iron pyrite, FeS_2:

iron absent:

$$SO_4^{2-} + 2C + 2H_2O \longrightarrow H_2S + 2HCO_3^- \quad \ldots\ldots\ldots \quad 1$$

iron present:

$$SO_4^{2-} + 2C + Fe^{2+} \longrightarrow FeS + 4\,CO_2 \quad \ldots\ldots\ldots \quad 2$$

$$4SO_4^{2-} + 7C + 2Fe^{2+} + 2H_2O \longrightarrow 2FeS_2 + 4HCO_3^- + 3CO_2 \ldots \quad 3$$

For all cases it is assumed that the carbon energy source is organic matter deposited with the sediment and that sulphate enters the system subsequently. The organic matter would have included dispersed microbial matter as well as lignite residues giving pyrite of recognizable shape. The basicity represented by the bicarbonate in reaction 1 equilibrates between the various carbonic species resulting partly in the formation of calcite from calcium associated with sulphate contained in migrating water. Iron pyrite has much lower solubility of iron than FeS but it is the more slowly formed. Iron sulphide precipitates first in the form of FeS, without base production but transformation to FeS_2 ensues by partial oxidation and with base production:

$$2\,FeS + H_2O + [O] \longrightarrow FeS_2 + Fe^{2+} + 2OH^- \quad \ldots\ldots\ldots \quad 4$$

In an alkaline water, Reaction 4 would result in the precipitation of $FeCO_3$, but this would not normally be detected as contributing to basicity by acid/alkali titration because of oxidation and hydrolysis of Fe^{2+}:

$$2Fe\,CO_3 + 3H_2O + [O] \longrightarrow 2Fe(OH)_3 + 2CO_2 \quad \ldots\ldots\ldots \quad 5$$

For the same reason, Fe^{2+} in the absence of an equivalent amount of base would contribute negatively to basicity. Therefore the formation of a sulphide deposit in an alkaline water is always associated with carbonate precipitation although the basicity of the latter will vary with the proportions of iron and calcium depending upon their availability during diagenesis.

It is possible in principle for the generation of H_2S in Reaction 1 to be of such an intensity as to precipitate iron, manganese and other metals as the sulphides at such low concentrations as to preclude their precipitation as the carbonates. Figure 1 shows the calculated solubility of FeS for three concentrations of H_2S in comparison with the solubility of ferrous and manganous carbonates. The accompaniment of iron sulphide by ferrous and manganous carbonates requires that the generation of the reduced state is not unconstrained. An assumption that leads to calculated conditions similar to those found in practice is that the iron contributing to the formation of sulphide comes from haematite in the rock. The extent to which Fe^{2+} is precipitated as FeS by the reaction:

$$Fe^{2+} + H_2S \rightleftarrows FeS + 2H^+ \qquad \ldots\ldots\ 6$$

is then constrained by the consumption of H_2S also for haematite reduction,

$$4\,Fe_2O_3 + H_2S + 14H^+ \rightleftarrows 8\,Fe^{2+} + SO_4^{2-} + 8H_2O \qquad \ldots\ldots\ 7$$

Free energy values given by Latimer (3) lead to the following corresponding equilibrium relations:

$$\frac{\left[Fe^{2+}\right]\left[H_2S\right]}{\left[H^+\right]^2} = 10^{4.025} \qquad \ldots\ldots\ 8$$

and

$$\frac{\left[H_2S\right]\left[A^+\right]^{14}}{\left[Fe^{2+}\right]\left[SO_4^{2-}\right]} = 10^{-57.419} \qquad \ldots\ldots\ 9$$

from which it follows that the co-existence of FeS and haematite (assuming $\left[SO_4^{2-}\right] = 10^{-3}$) governs the Fe^{2+} concentration according to the relationship,

$$\left[Fe^{2+}\right] = 10^{7.16} \left[H^+\right]^{16/9} \qquad \ldots\ldots\ldots 10$$

Comparison of this relationship with that for the solubility of ferrous carbonate (Figure 2) shows that the latter could also co-exist at pH 7.2, and when the corresponding H_2S concentration would be about 1 mg/l. Higher pH values would favour the precipitation of iron only as FeS in the presence of calcite.

It is of interest to compare in Table 1 the conditions governing the solubility of iron and manganese with the solubilities of other metals in the form of their sulphides and carbonates. For the calculation of solubility the respective values for pH and bicarbonate concentration have been chosen as 7.2 and 4×10^{-3} for consistency with the presence also of calcite.

Table 1. Solubilities of sulphides in equilibrium with haematite and carbonates in equilibrium with calcite

Ion	Solubility (log molar)	
	sulphide	carbonate
Fe^{2+}	-5.09	-5.09
Mn^{2+}	-1.02	-5.27
Cd^{2+}	-15.32	-5.72
Co^{2+}	-9.45	-6.56
Cn^{2+}	-24.28	-4.04
Hg^{2+}	-41.29	-
Ni^{2+}	-8.84	-1.21
Pb^{2+}	-16.3	-7.38
Zn^{2+}	-10.93	-4.23

The solubility of manganese as the sulphide is too great to account for its presence as a discrete compound and therefore the lower limit of abundance of manganese in iron appears to be an impurity level in iron sulphide. It may be significant to the occurrence of metals in mixed sulphide/carbonate systems that iron and manganese are the only elements having similar or smaller solubility in the carbonate form. The ability of ferrous and manganese carbonates to precipitate at concentrations liberated from sulphides during oxidation-reduction transformation may be the reason why only these heavy metals are retained in significant amounts in sulphide/carbonate sediments.

2.2. WEATHERING OF SULPHIDE/CARBONATES

Oxidation of sulphides occurs naturally through the agency of bacteria of the genus Thiobacillus of which several species exist according to the pH under which they function (4). The products of oxidation are first hydrated ferric oxide and sulphuric acid, followed by the dissolving of the former when the oxygen supply fails. In addition to oxygen (in dissolved gaseous form or as nitrate), the organisms require also the usual suite of essential elements for the life-process. Since these will most commonly be available at the ground surface, the progress of colonization of an aquifer most probably occurs by gradual penetration from the surface. Taking the unweathered situation to be a uniform mixture of Fe, Mn sulphides and carbonates with calcite, a sequence of progressive weathering may be postulated on the basis of increasing oxidation and diminishing basicity being effected by a flow of water containing available oxygen. Solution of carbonates by liberated sulphuric acid occurs in the order calcium, iron and manganese. Fe^{2+} and Mn^{2+} liberated at one point are reprecipitated when carried into contact with further deposits of calcite, with calcium sulphate being carried away with moving water as the product of the first stage of weathering. By this process, iron and particularly manganese may be concentrated as secondary deposits of carbonates. Where calcite disappears before sulphide, the next products of weathering are Fe^{2+} and Mn^{2+} which may be retained by ion-exchange capacity of silicate minerals or evolved from the system. Where still further sulphide remains to be oxidized, the final stage of weathering is the displacement of Fe^{2+} and Mn^{2+} from silicates by H^+. Where calcite remains after the oxidation of sulphide a residuum of iron and manganese carbonates would remain to be slowly dissolved by naturally occurring carbon dioxide although this may not be of likely occurrence. These sequences are represented in Figure 3 as the development of a spectrum of chemical states ranging from H^+ ions remaining from oxidation through to unoxidized sulphide/carbonate with migrated calcium sulphate.

3. INTERPRETATION OF AQUIFER CONDITIONS

Whether the complete sequence of conditions represented in Figure 3 would be observable in a single aquifer would depend on the one hand upon its degree of confinement which preserves sulphide/carbonate, and on the other by the ingress of oxygenated water or air to produce oxidized zones. Two aquifers which the WRC has studied in relation to aquifer composition and water quality are the Folkestone Beds at Hardham, partly confined by the Gault Clay, and the Tertiary sands of the London Basin confined by London Clay (1). Core samples of Folkestone Beds have not been examined extensively, but the groundwater from parts of the aquifer has a record of unusually high iron and manganese content (5). Iron pyrite occurs at about 0.02 % in the south-west neck of the aquifer, while the water in the centre is soft, acidic with only traces of iron and manganese held in ion-exchange capacity with the sand. The sequence is consistent with a history of groundwater flow from the outcrop areas towards the main body of the Folkestone Beds in the south-west, with the weathering process now having nearly reached completion. However, this is not the prevailing regime now that water is abstracted from the aquifer for public supply.

In contrast, Table 2 gives a summary of some analyses of Tertiary sands in the Lee Valley of the London Basin. The analyses performed were:

(i) iron, manganese and sulphate determinations upon bromine/hydrochloric acid extracts
(ii) basicity reactive to 0.1N hydrochloric acid.

Also, semi-quantitative information was obtained using a thermobalance about the presence of gypsum and calcite in samples from their respective decompositions:

(a) at 130°, the dehydration of $CaSO_4 \cdot 2H_2O$ (limit of detection, 0.4%)
(b) at about 800°, $CaCO_3 \longrightarrow CaO + CO_2$ (limit of detection, 2%)

It is beyond the scope of the present paper to relate these results in detail to the particular geological system, but attention may be drawn to certain relationships in the data that bear upon the question of weathering that has occurred in the aquifer. Further details of the investigation are given in references (6) and (7). Figure 4 shows a direct correlation between the manganese content and the content of iron calculated to be in excess of that in combination with the sulphur content assumed to occur as FeS_2. This quantity was taken as a measure of iron in a higher state of oxidation than the sulphide, such as in $FeCO_3$ or Fe_2O_3, but a low or negative value would be caused by the appreciable presence of calcium sulphate. Figure 5 shows that high manganese content was nearly always associated with high basicity, but that no quantitative correlation existed between them.

Table 2. Summary of compositions of Tertiary Sands for three groups of iron and manganese levels, giving means and standard deviations

Composition groups	% Fe	% Mn	% S	Basicity (% $CaCO_3$)	Occurrence of calcite	Occurrence of gypsum
1 Fe $\leq$ 0.38% (66 samples)	0.20 ±0.09	0.00061 ±0.00037	0.19 ±0.10		1 sample	20 samples
2 Fe > 0.38% Mn < 0.002% (21 samples)	0.61 ±0.42	0.00105 ±0.00040	0.62 ±0.42	-0.38 ±0.52	1 sample	13 samples
3 Fe > 0.38% Mn > 0.002% (16 samples)	0.83 ±0.40	0.0081 ±0.0089	0.66 ±0.38	3.3 ±4.1	7 samples	6 samples

In comparison with the theoretical sequences represented in Figure 3, only one out of 103 samples examined contained appreciable calcite without there having occurred much oxidized iron and concentrating of manganese. All of the other samples containing appreciable calcite appeared to have undergone secondary precipitation of ferrous and manganese carbonates with enhancement of iron: Fe ratios (group 3). These were nevertheless in a minority and occurred commonly near to interfaces in geological sequences where the persistence of basicity may have been influenced by reduced permeability. The majority of samples contained little or no basicity, with some iron in excess of FeS_2 (group 1). Complete weathering of the sulphide appears not to have occurred anywhere except in the upper samples from a borehole near to a supply borehole where the groundwater level has been drawn down since early this century.

To the south of this location samples from a series of boreholes along the line of the river Lee contained appreciable amounts of gypsum. Most of these showed negative basicity, indicating the presence of ferrous sulphate, and low Mn:Fe ratios indicating the absence of secondary carbonate precipitation (group 2). One or two samples containing gypsum also contained calcite with somewhat elevated Mn:Fe ratios and generally very high iron concentrations (0.4 - 2.2%) indicating the absence of weathering. The presence of gypsum, with or without calcite, may have represented the downstream end of the weathering sequence, governed in former times by an artesian head existing in the river valley and now capable of yielding very large amounts of sulphate and iron which have accumulated in the Tertiary Sands and possibly also the overlying clays.

Sequences related to the vertical weathering of sulphide/carbonates are not generally to be expected nor are they generally observed in the Lee Valley cores because of the lower vertical permeability of bedded formations containing intervals of clay. However, the occurrence of a vertical sequence of redox and basicity conditions may be good evidence for groundwater movement occurring vertically on a local scale and the examination of data in this light is worthwhile for what information they might provide about recharge routes. More generally, the assignment of aquifer composition to stages of weathering of sulphide/carbonates on a regional basis would be an indicator of the cumulative pattern of groundwater flow and facilitate predictions of future groundwater quality.

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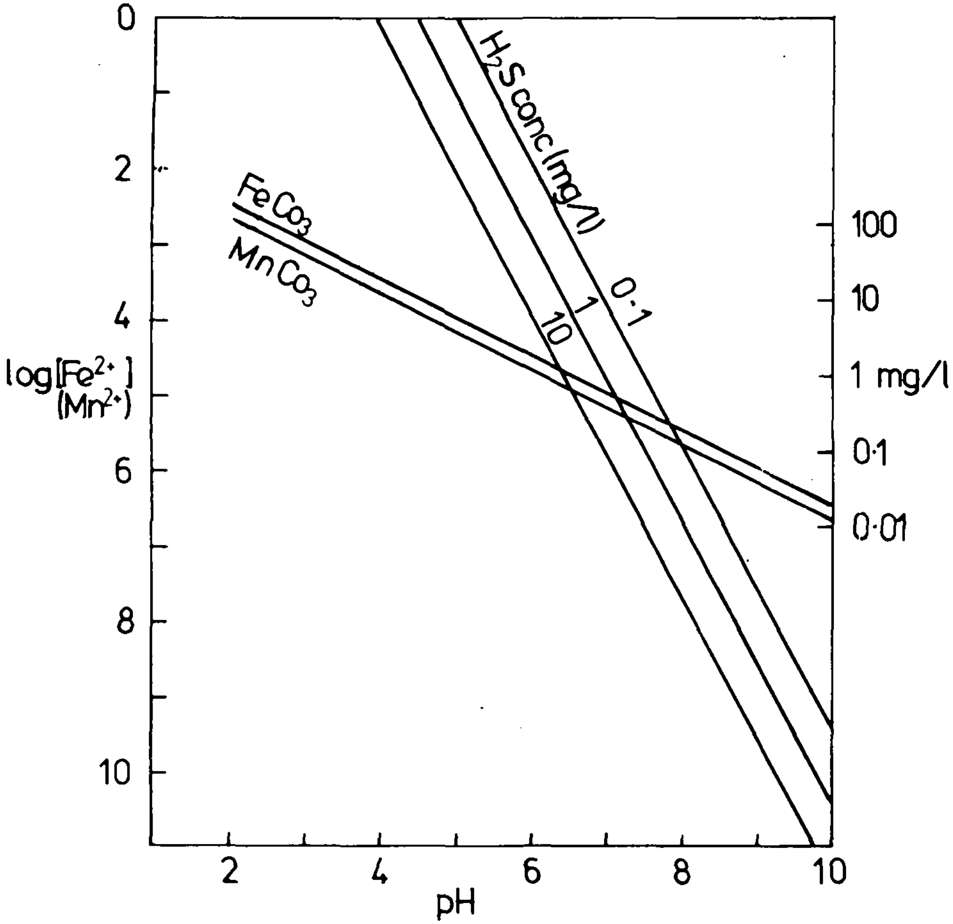

Figure 1. Solubility of iron sulphide, FeS for various H_2S concentrations compared with the solubilities of ferrous and manganous carbonates in equilibrium with calcite

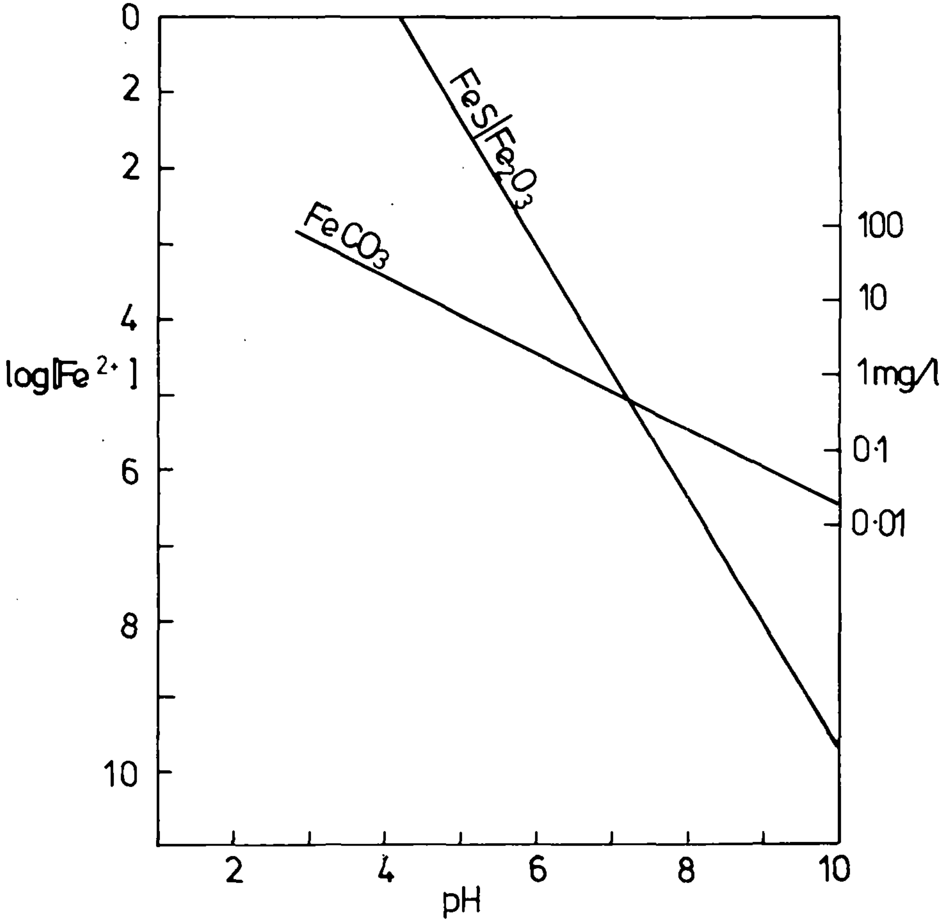

Figure 2. Solubility of FeS in equilibrium with haematite, Fe_2O_3, compared with the solubility of ferrous carbonate in equilibrium with calcite

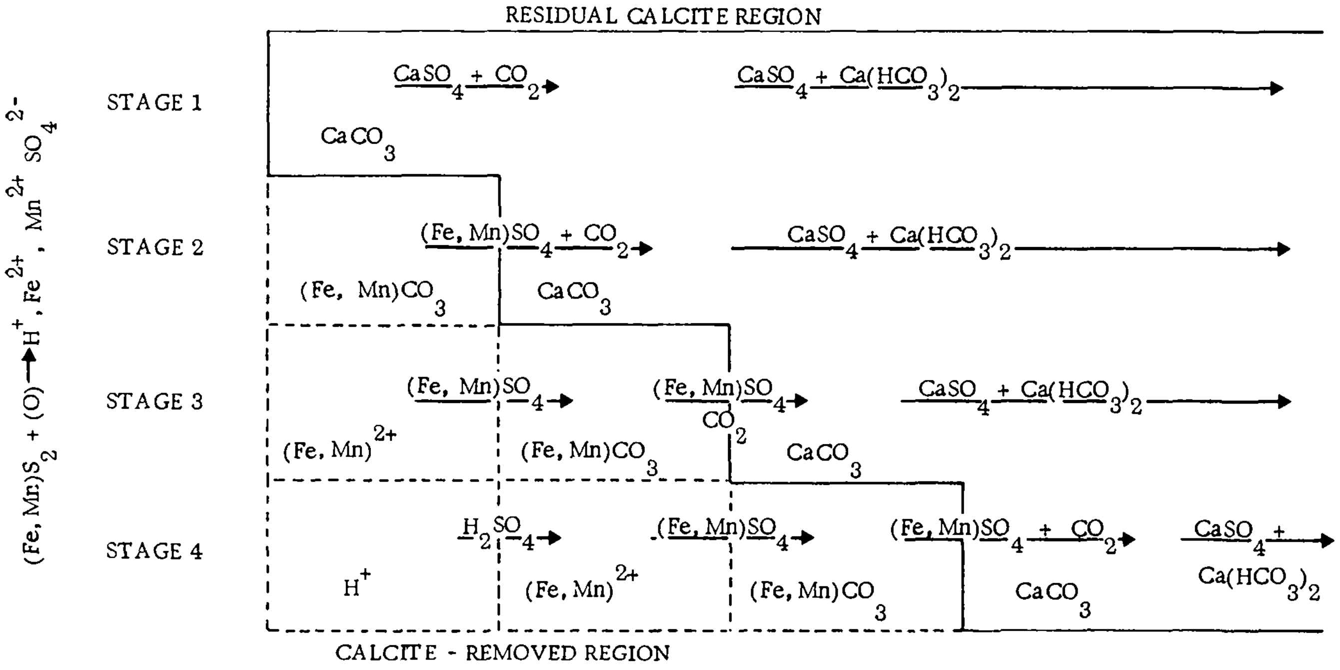

Figure 3. Four stages in the oxidative dissolution of iron/manganese sulphide and carbonates and the resultant sequence of iron, manganese and sulphate distributions

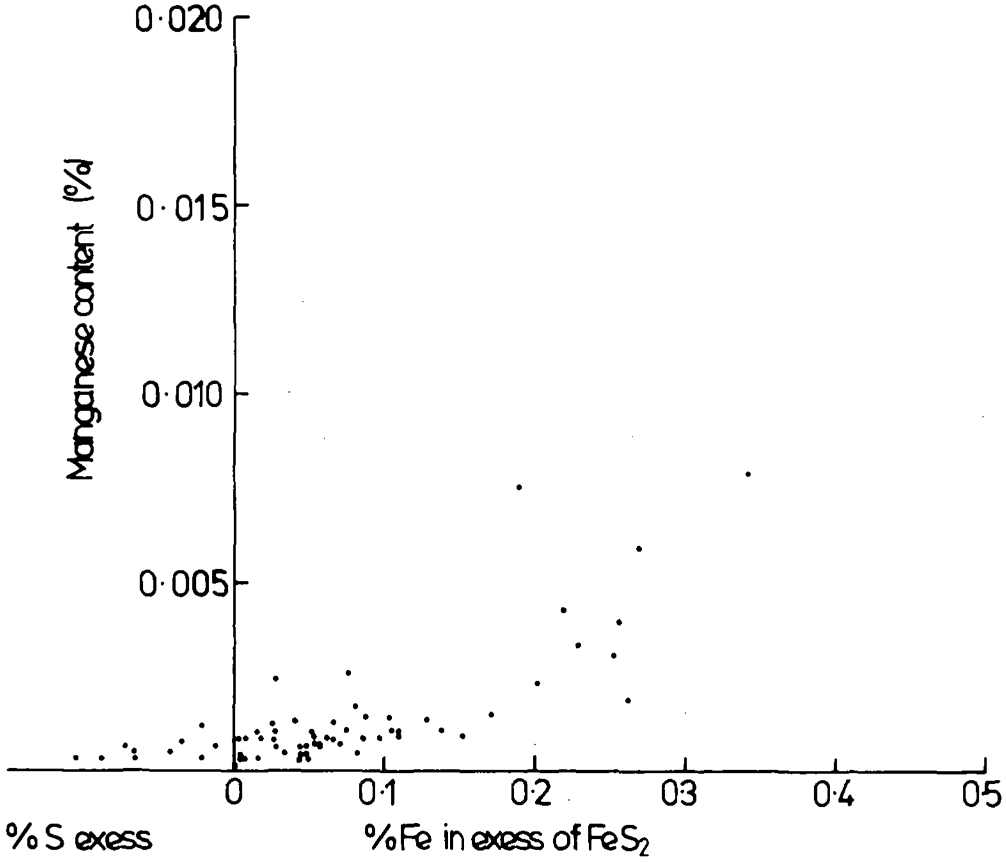

Figure 4. A correlation between the manganese content of sand and the content of iron calculated to be in excess of that for the formation of FeS_2 from the S present

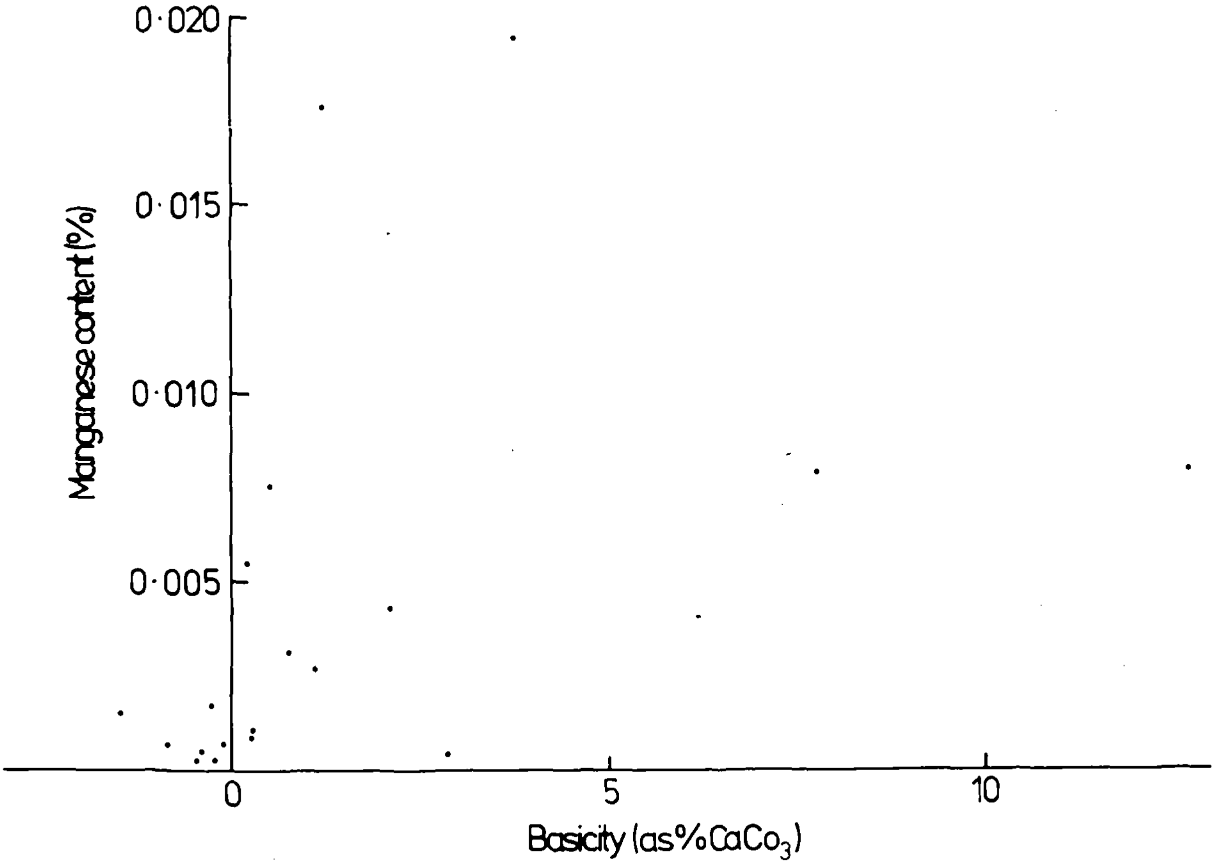

Figure 5. The association of high manganese contents of sand with the presence of calcite

DISCUSSION - SESSION 2

Mr E.S. HALL, referring to Mr McNabb's paper, said that in his own experience there was considerable reluctance to recognize the existence of biological processes in the aquifer. Biological processes are forgotten when descending into the 'purity' of the rock, and only thought to be important in the soil layers. The importance of biological processes was realized during former WRA experiments on the passage of river water through sand filters associated with artificial recharge. Progressively contaminated sand was eventually clogged, causing changes in the microbial regime associated mainly with a change in the redox potential. Notable symptoms of such a change were the onset of denitrification and the generation of ammonia. Other possible biological processes are the precipitation of iron and other metal sulphides.

It was necessary to analyse the solid phase of the aquifer for biological activity and related components in order to predict what may happen when groundwater migrates downwards through the unsaturated zone. The reason, he thought for earlier non-recognition of biological activity was that abstracted groundwater was usually biologically uncontaminated, even in grossly polluted situations. This was probably due to the presence of a nutritional advantage for bacteria, which caused the bacteria to remain stationary by attachment to rock grains in a flow of moving water carrying food and oxygen or other nutrients. Biological activity generally occurred following a change of circumstances that renewed nutrient and food sources or produced favourable conditions for secondary colonization. Three examples of a change in circumstances in the aquifer and a corresponding change in the biological regime were:

(a) Where organic pollution enters the ground.

This was exemplified by the natural seasonal variations in organic matter introduced to soil by plant growth and decay. Similar considerations apply when unnatural organic pollution provides a carbon source and variable conditions of biological activity at greater depths than the soil.

(b) Nitrogen fertilization of systems previously nitrogen deficient.

Nitrogen-deficient biological systems typically contain extra-cellular carbohydrates as a product of metabolism that cannot be used for cell growth. The WRC has found such carbohydrates in samples of chalk in quantities ranging from 60 mg to 1 g for 1 kg of dry chalk, and preliminary results suggested that the quantity varies inversely with nitrate fertilization of the site. Concentration was highly variable depending upon sample size, 10-g quantities apparently being necessary for representative sampling. The variability was thought to mark the micro-fissuring in the Chalk, by which path these substances originally gained access from the soil. It was possible that nitrate fertilization of the ground results in a slow but progressive spread of biological activity through the fissure system (this being the only habitable environment) with deposited carbohydrates providing the food source.

(c) The provision of nutrients for microbial growth.

The calcium carbonate of Chalk is a hostile environment for microbial growth because of the chemical limitations to concentrations of phosphorus, iron and other trace metals. However, recent biological activity is indicated by the presence of the unstable nitrite at occasional horizons to considerable depth in unsaturated zones of aquifers studied in the course of the recent nitrate investigations by the Centre. This indicates that microbial nutrients are made available in the aquifer, possibly during conditions of appreciable fissure flow.

Mr Hall concluded that his researches included a more positive identification of biological activity, not by enzyme analysis as described in Mr McNabb's paper, but by analysis of the organic C, H, N content of aquifers and whether this was degradable by microbial contamination. Such analysis required a concentration of the organic component of the rock matrix, which for Chalk simply involved the dissolving of the $CaCO_3$ in hydrochloric acid and leaving biological matter in the residue.

Mr J.F. McNABB said that he did not disagree with the statement by Mr Hall.

Mr R.E. JACKSON said he had detected a difference between the redox potential data of Mr McNabb and that of Dr Edmunds concerning sulphate and nitrate reduction. Mr McNabb's paper gave values of -200 mV for sulphate reduction and +338 mV at a pH 5.1 for nitrate reduction. The data of Dr Edmunds are higher than this.

Mr Jackson said he had data similar to that of Dr Edmunds and he was thus suspicious of Mr McNabb's results which could be misleading. He agreed with Mr Hall that such redox reactions were extremely complex and said that a host of other factors were involved such as the presence of dissolved organic carbon, and various trace inorganics such as enzymes.

Mr J.F. McNABB, in reply to Mr Jackson, said that the figures given in his paper were based on laboratory studies by various microbiologists. He commented that one possible explanation is that within the subsurface environment there is microbial activity in numerous separate 'micro-habitats' such as the thin film of water surrounding each grain. Within these micro-habitats conditions may vary widely. He was uncertain as to how the redox potentials or the sulphate and nitrate reduction reactions, that are occurring in these micro-habitats,could be measured.

Dr W.M. EDMUNDS commented that a discussion of the measurement of natural redox potentials could well fill a whole day. However, the Eh values that he had obtained in the reducing section of the Lincolnshire Limestone aquifer, quoted in his paper, range from +100 to -100 mV. Sulphate reduction is first observed at the positive end of this scale (see Figure 4). There are few, if any, comparable aquifer systems where bulk Eh values exceed -100 mV. Whilst Eh cannot be related directly to any one redox reaction (of which there are several in this aquifer), there is a clear inference that the controlling Eh for sulphate reduction under field conditions must be higher than the value quoted by Mr McNabb.

It would appear from the work of Baas Becking and Wood (1), however, that Desulfovibrio can commence the reduction of sulphate at pH 7.5 to 8.0 at an Eh of about +100 mV.

Mr J.F. McNABB agreed with Dr Edmunds and Mr Hall as to the complexity of the situation. Any suitable microbial habitat must have adequate nutrient. The nutrient may be the limiting factor and will depend upon the availability of a suitable electron-acceptor such as oxygen, sulphate or nitrate. If nitrate was added to such a system, then quite probably there would be microbial activity. Laboratory experiments have been conducted in the United States in an attempt to use microbial activity to remove petroleum from an aquifer. It was found that nitrogen, phosphates and oxygen were the limiting nutrients. In such a complex situation as described by Dr Edmunds and also by Mr Hall, the measurement of nutrients is a very difficult task.

Mr L.J. ANDERSEN said that he disagreed with the flow mechanism, described in the paper by Brereton and Wilkinson, whereby the solutes in the water infiltrating through joints and fissures were able to diffuse into the more static interstitial water in the pores, thus leading to different downward flow rates for the water and the solutes. Fissure flow, in a rock formation containing interstitial voids in blocks between the fissures, exists only under heavy infiltration conditions. The water in the fissure has a much lower tension than that in the much smaller interstitial pores surrounding the fissures. The higher tension in the pores will move the fissure water into the pores and, consequently, move the recharge around the fissure, if the hydraulic conductivity of the pore space is sufficient to transmit the recharge. He was of the opinion that a contradistinction exists between the unsaturated and saturated flow. Under saturated conditions the main flow will be in the fissures. This may be illustrated by high flow velocities measured with tracers (tritium) in fissured and carstificated limestone. Under unsaturated conditions the main part of the flow in double porous rocks takes place in the interstitial voids, namely where they are saturated or contain water above the field capacity. The tritium profiles in Figure 2 show peaks at 9 metres below the surface for Chalk and 22 metres below for Bunter Sandstone. The difference in the depths of the peaks may be due to the difference in soil moisture content of the two geologic formations. He therefore did not agree with Drs Brereton and Wilkinson in their statement that the infiltration rate is unimportant. The downward movement of the recharging water (together with its contaminants) is primarily governed by the infiltration rate and the soil moisture content of the formation, e.g. increasing flow velocity by higher infiltration rates or lower soil moisture contents, and vice versa. By using a simple displacement model a recharge amount of 300 mm per year and a soil moisture content of 30 to 35% of the Chalk should result in a downward rate of migration of 0.85 to 1 metre per year.

Mr R.A. DOWNING submitted the following written discussion on the paper by Brereton and Wilkinson.
An important aspect in any consideration of groundwater pollution is the rôle of storage in the micro-fissures and other small voids in a fissured aquifer with a high matrix porosity, such as the Chalk. It has been appreciated for many years that aquifer storage contributing to well yields is not just derived from the main fissures. That this is the case is confirmed by the fact that water pumped from the Chalk in highly developed areas, such as the Lee Valley in east London, has a mean age of several thousand years. This has a bearing on pollution problems as a much larger volume of storage is available in the saturated zone for diluting a pollutant, and the residence time is considerable allowing an opportunity for improvement in quality with time. It also casts some doubt on the feasibility of rehabilitating a polluted aquifer with such a 'double porosity' in a reasonable time period and at an acceptable cost. A further implication is that the length of time required for the recovery of a saline interface, after protracted landward movement due to the development of storage in a drought, may be considerable.

Drs BRERETON and WILKINSON, in their reply to Mr Andersen, said it was not their intention to suggest that the downward movement of water and solutes in the unsaturated zone of a fissured aquifer with 'double porosity' is entirely by fissure flow, or by 'piston displacement'. The two important factors which will control the balance between these are: the degree of saturation in the pores and fissures, and the ratio of pore to fissure volumes. In the case of the Chalk however, some recent measurements of matrix permeability (3) gave average values of 10^{-3} m/d, and lower values in the range 10^{-4} to 10^{-5} m/d are common. It is these lower values that control intergranular flow, and these cannot be reconciled with the apparent flow rate drived from the tritium results of approximately 3×10^{-3} m/d.

The pores in the Chalk matrix are so small that all the water they contain must be held by capillary forces, and cannot drain under gravity. This static water will be in contact with the mobile water in the fissures. Measurements have recently been made at the Water Research Centre of the possible rate of diffusion of ions between these two phases, and these, together with a description of the proposed flow mechanism have been given by Oakes (2).

With respect to Mr Downing's comments, the authors agreed that the diffusion of pollutants between the moving water in the fissures and the static water in the matrix occurs in the saturated zone of the Chalk, and possibly other 'double porosity' aquifers. The authors had referred to this process in their paper.

Mr J.S. SHINNER said that Drs Brereton and Wilkinson had listed seven questions in their paper that a water engineer might well ask if faced with potential pollution of a source. The questions were admirably set out and he suggested that the water engineer should be entitled to an answer before any work was carried out which might affect the sources. Unfortunately, he said, the authors then went on to describe all the difficulties and pitfalls that lie in the way of collecting the data, doing the analyses and producing what might be called satisfactory answers to the questions. He was surprised,therefore, that while the authors recognized that the results of any decision could result in considerable expense, and also that the system is complex, they should suggest that simplifying assumptions are necessary before the final analysis can be made. He took issue with this, and suggested that this was the stage at which a lot of money should be spent, if necessary, and a lot of effort put into the work to ensure that a really soundly based scheme was evolved before any action was taken which could effect the source. He went on to say that it should be borne in mind that polluting activities, particularly landfills, can have irreversible and very long term effects on sources. Effort and money at the investment stage are, therefore, well spent.

In reply to Mr Shinner, Drs BRERETON and WILKINSON agreed that effort and money are well spent at the conceptual stages of a resource development if long term problems are to be avoided. However, to assess all the complex processes which could affect the flow of a contaminant, the detailed hydrogeological investigation of every potential source would considerably increase the development time and total cost of the source. The cost and effort involved in data collection, in terms of strategic importance or cost of replacement, must be related to the value of the source that is at risk. A compromise may therefore be necessary between the collection of data and analysis that the hydrogeologist would ideally like to undertake, and that which is economically justifiable. Simplifying assumptions, based on the hydrogeologist's or water engineer's past experience, may have to be made.

Commenting on Mr Shinner's remarks, Professor J. BEAR said that in order to understand a pollution problem one could proceed intuitively and sink boreholes, collect data, and on this basis produce contours of salinity or whatever, and make a qualitative assessment of the situation. However, he favoured the approach of examining the available data and then constructing a conceptual model of the behaviour, or exitation-response mechanism, of the system under consideration. This model could then be used to solve the problem on hand, or predict the future response to man's activities (say, in the form of pollution concentration levels) of the aquifer system. New observations should then be made to verify the model and determine its parameters. This is a more quantitative approach in which the model acts as a guide to further field work. Field observations should not be made just on a regular network basis, because flow patterns and directions are important and groundwater quality observation points should be selected with this in mind. The model can be improved as more data are collected.

In general, he believed the use of models to be the only approach which would give some hope for the handling of the very complicated phenomena which take place in a very heterogeneous media with complex boundaries. A suitable model should be constructed and calibrated for each problem.

Mr D.L. BROWN addressed his remarks to Professor Bear and Dr Wilkinson. He said that over the past two years he had been working on the artificial recharge of fresh water into saline aquifers, and also investigating potential sub-surface waste disposal sites.

In looking for potential sub-surface waste disposal sites that were structurally or technically fissured, Mr Brown was strongly opposed to the use of carbonate aquifers. He also made reference to a site in Norfolk, Virginia, where the injection of fresh waters into saline aquifers at 300 m depth was being investigated. A current-meter had been installed in the well during recharge to determine which points of the aquifer were accepting water. It appeared that for about 30 m of aquifer, 80% of the water was entering at only a third of that length. Mr Brown, felt, therefore,that flow meter monitoring should be installed in any toxic waste disposal well. He believed in mega-geology and mega-hydrology. The investigation in Norfolk, Virginia, had indicated the considerable mixing that occurs on abstraction. The overall quality of the abstracted water was 200 mg/l TDS, although samples taken at the entry points in the well from the aquifer (as detected by the current meter) varied from 50 to 1200 mg/l TDS. His point was that the mixed water abstracted at a concentration of 200 mg/l TDS may be harmless yet a zone of water of higher, possibly toxic, concentration (1200 mg/l TDS) had moved through the aquifer.

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Session 3

DATA REQUIREMENTS AND COLLECTION TECHNIQUES

Chairman:

J. B. W. Day, BSc,
Chief Hydrogeologist,
Institute of Geological Sciences

Presented Papers:

Support Papers:

PAPER 8

GROUNDWATER QUALITY NETWORKS

H. J. Richards

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1. INTRODUCTION

There is considerable natural storage of water underground and we try to make the best use of this valuable resource. In order to achieve full use of aquifers economically, there needs to be an understanding of the physical principles governing their natural replenishment, the flow of groundwater and its natural discharge through springs and seepages into rivers and sea. There must also be an understanding of the variations in quality of groundwater and of the factors controlling these changes. Our aim is to provide an ample supply of water of suitable quality to meet the growing demands of the public, industry and agriculture. In England and Wales more than 35 per cent of water used for public supplies is derived from groundwater sources, and in many other countries the percentage is greater.

Wherever groundwater is an important resource, high priority should be given to the design, evaluation and operation of networks for measuring the relevant part of the hydrological cycle, and thus network design and implementation is an essential part of hydrology.

Fluctuations in groundwater levels reflect changes in storage within aquifers; both long-term changes due to seasonal and other causes, and short-term changes resulting from intermittent abstraction and so on. In general, groundwater levels respond slowly to external changes and so continuous records are not usually necessary, systematic individual measurements being adequate for most networks. If fluctuations are rapid, a continuous record of water level is necessary to help determine the causes of such changes. In the same way changes in groundwater quality, wherever they occur, are usually slow and can be monitored by systematic collection of samples of water from representative wells for subsequent analysis in the laboratory. Rapid worsening in groundwater quality would be due to localized pollution or to the arrival of poor quality groundwater whose movement had been unsuspected or unforseen and therefore not monitored. In view of our understanding of the principles of groundwater movement there should be little likelihood of unexpected regional changes in groundwater quality.

Increasing use of groundwater in recent years has led to greater concern with the response of aquifers to large scale abstraction and with the long-term prediction of resources and quality. This concern is also related to changes in groundwater quality which may result from urban, industrial or agricultural conditions. Groundwater quality networks exist at present only as a result of ad hoc growth related to particular local problems such as the inflow of saline water, or even to the interests of an individual scientist or engineer. Although 'network' may be a misnomer, when systematic collection of groundwater quality information is just beginning, it is essential to build upon the sparse framework. Newer techniques of data collection and analysis will help in setting up an agreed network of sites for the continued measurement of a number of groundwater variables. Such a network will normally be designed to measure changes in groundwater levels reflecting changes in storage, and changes in the concentrations of defined constituents as well as changes in physical properties such as temperature.

2. THE NEED FOR NETWORKS

The efficient management of water resources requires the collection of enough information to be able to assess resources, plan methods of development and operation, continue to monitor the effects of water use, and ensure that surface and ground storage potential are fully utilized without creating long-term environmental problems. Information about groundwater storage and quality is thus essential for planning and for monitoring effects of development.

There have been many instances of groundwater development resulting in the inflow of saline or mineralized waters into fresh water aquifers. Contamination by mine drainage waters, polluted rivers, certain kinds of agricultural practises or effluent and waste disposal, has sometimes led to deterioration in groundwater quality. Such contamination can be very expensive to remove and can persist for periods of many decades. Pollution of groundwater has usually been the result of ignorance of the principles governing groundwater occurrence, or of accidental contamination, or of the lack of control or planning. Any regional or national groundwater network ought to include, therefore, provision for measurement of the quality of groundwater to help in the evaluation of the natural situation and in monitoring movement of possible contaminants either within the aquifer or from the land surface.

Consideration of networks could be restricted to systematic regional collection of data, leaving special problems to be dealt with as research studies. However, one outcome of such research should be recommendations for a network particularly designed to monitor the effects of development or remedial measures on groundwater quality. There is some danger that data collection can almost become an end in itself, but if thought is given to the purpose for which the information is to be used then a routine evaluation of the programme can take account not only of new technology but also of any changes in the requirements for the particular hydrological information.

Groundwater networks are needed to provide information during:

(i) reconnaissance surveys of any relatively undeveloped aquifer - to make a preliminary appraisal of resources;
(ii) the detailed aquifer tests of each stage of development - which will help in future planning of development;
(iii) periods when development and its effects may need to be monitored - these effects would include the movement of an interface between fresh and salt water or the operation of artificial recharge schemes;
(iv) research into particular problems.

Most of the available information on groundwater quality has been obtained from analysis of samples of water pumped from public supply wells. Samples are usually obtained also from newly drilled wells after short periods of pumping. A more systematic collection of samples is now required, especially if the information is to provide some of the data used in the preparation of mathematical models of groundwater flow systems or combined surface and groundwater systems. Such data of the required frequency and accuracy has rarely been available, except from research sites.

Groundwater management is complex but specialists can help to deal with the effects of accidental contamination, and better still to help control the potential dangers from sites for effluent and refuse disposal, storage of petroleum and chemical products. Much effective control is already exercised but new sites need to be examined with care.

Local or accidental contamination cannot be catered for within a regional network, and any potential local problem must be dealt with as an addition to the basic network.

3. INFORMATION REQUIRED

Sophisticated methods of data analysis are continually being developed and the historical data from many areas is not of high quality. Any network should, therefore, include provision for inspection of stations, for preliminary checking of data and comparison with other relevant factors. In the case of groundwater quality this resolves itself into checks regarding the source of a water sample, its transport and methods of analysis, and a comparison of any changes in constituents with changes in abstraction patterns or possible sources of contamination. It may also involve careful supervision of specially drilled wells, or the rehabilitation of existing wells, to ensure the collection of representative samples. At some sites more than one aquifer might be sampled.

To ensure acceptable groundwater quality data, care must be taken to obtain representative samples for analysis. If the geology and hydrogeology of an area has been studied then it will be relatively straightforward to decide whether aquifers are separated or are in hydraulic continuity. Any particular local peculiarities will also be known and the need for additional wells, or analysis for specific constituents, understood. If samples are acceptable then quality control of the data rests with the chemists who will carry out the analyses. If the data can be processed soon after sample collection and analysis then carried out, any anomalies can be determined and, if necessary, additional samples obtained.

Most of the information in the UK relates to the major aquifers, the Chalk and the Permo-Triassic sandstones, and chemical data have been obtained from partial mineral analyses comprising determinations of the main constituents, or of properties due to these. Some more complete analyses include estimates of the principal ions found in natural waters, and these have helped to provide some knowledge of regional variations in the chemical nature of groundwaters.

Probably 75 per cent of wells drilled in this country are between 25 m and 70 m deep and so the problems of obtaining any necessary samples from defined depths are not great. In order to carry out a partial mineral analysis, some 500 cc of groundwater are required, but a full mineral analysis requires 2 litres and a biological analysis up to 1 litre.

Partial analyses are usually carried out for total dissolved solids and the major constituents:

Cations	Anions
Calcium	Sulphate
Magnesium	Chloride
Sodium	Nitrate
Potassium	Carbonate
	Bicarbonate

Minor constituents are included as necessary to help study existing or potential problems, usually as part of research into the hydrogeology of a defined aquifer. These fuller analyses might include:

pH
Iron
Manganese
Nitrogen
Phosphate
Aluminium
Fluoride
Trace elements
Silica

In some groundwater studies it may be necessary to determine the presence of iron, nitrate or sulphate bacteria, but little is known, at present, about their distribution or importance in groundwaters.

The historical groundwater quality data are very variable in reliability because of variations in methods of analysis and great care has to be exercised in their use to interpret regional quality variations throughout an aquifer. A modern network would aim to ensure that uniform or compatible methods were used for measuring and analysing water samples.

4. PROBLEMS

A particular difficulty is to obtain sufficient funds for an adequate data collection network. There are direct costs: drilling of suitable observation wells (or suitably modifying selected existing wells); staff; vehicles and data processing. Indirect costs result from switching pumps on, or indeed shutting them off, in order to obtain samples under suitable conditions. The aim should be, therefore, to reduce data collection to the minimum commensurate with obtaining the essential information.

The chemistry of groundwater as well as the hydraulics of groundwater flow is controlled by the geology of the aquifers and formations in continuity with them. Processes of infiltration, inter flow, absorption, adsorption, oxidation, leaching and ion-exchange are involved, and these can be determined only from research studies and not from regional observation networks. Such networks can help to confirm or modify research findings. General regional trends in chemical quality of groundwater can be assessed but locally modifications occur and these are related, under natural conditions, to geological factors. Local variations may be brought about by differences in the chemical composition of the aquifer itself, or by variations in its physical properties which determine the rate and direction of groundwater flow and, hence, the time the water is in contact with the aquifer. Within a single bore, groundwater entering at different levels may differ in chemical composition. Superimposed, also on such a natural situation, are some fairly widespread changes in nitrate content of groundwaters as a result of agricultural use of fertilizers. The introduction of such factors may warrant the need to monitor quality in order to predict likely changes in stream flow quality.

Groundwater in England and Wales is derived for the most part from sedimentary rocks and a frequent feature is a gradual change from a calcium bicarbonate type groundwater, found beneath the outcrop, to a soft, alkaline, sodium bicarbonate type down dip beneath cover of argillaceous strata where groundwater flows are more restricted. These changes are associated with changes in total ionic concentration and alkalinity, and decreases in hardness down dip. Such factors will have a strong influence on the choice of sites in a network but depend, of course, on the results of hydrogeological studies already completed.

It is only after study of a region that the need for any continuous or frequent monitoring of water quality will be evident, and will usually be restricted to the zones of movement of fresh and saline waters. Forecasts can then be made of quality changes in individual wells. The representativity of groundwater samples is often difficult to determine and pumped samples from the zones of mixed waters can be misleading. Data collection should provide for systematic measurement of vertical profiles of electrical resistivity in selected wells to monitor the movement of interfaces between fresh and saline waters.

A large number of groundwater level measurements provide information for mathematical models of aquifer systems, but too many quality samples would place a heavy load on a laboratory, and intensive surveys should be restricted to once, or at most twice, a year.

Sometimes there are difficulties in arranging for observation wells because of the differences between a surface water catchment and the boundaries of a groundwater unit. They do not necessarily coincide and a well to monitor groundwater level and quality could lie inside a neighbouring administrative boundary. Co-operation between authorities can ensure the minimum number of wells to provide information for both.

5. OBSERVATION SITES

Wells, springs and seepages can be sampled to provide analyses of groundwater, but wells are by far the most convenient to use. Infiltration gauges, or lysimeters, can be used to measure quantity and quality of recharge to aquifers, but research is still needed to develop suitable installations. As far as possible existing wells should be used in a network provided the wells receive representative groundwater inflow from the contributary aquifer and are of easy access. Quite frequently money needs to be spent to make existing wells suitable, but this is very much cheaper than drilling new wells. Gaps in the existing distribution should be filled by specially constructed observation wells (Briggs & Fielder 1966, Taylor 1969). The construction of observation wells is one of the main items of expenditure in a groundwater study, prior to the construction of abstraction wells. Observation wells need to be cased through unconsolidated deposits and secure at the top to prevent direct ingress of any pollutant.

If there are several aquifers or sub-aquifers at different depths beneath a site then it may be wise to seal off an observation well into each. On balance it is probably better to have a separate well for each level, but the methods of construction must be left to the responsible agency in consultation with the specialist contractors.

Full use should be made of pumping wells to provide groundwater quality information. Those used for public or major industrial supplies are analysed regularly and these analyses could form part of the data collection network, provided the network agency has agreed with the well owners on methods of sample collection and analysis. It is probably wise for the agency responsible for the network, or a particular investigation, to be responsible for the maintenance of the observation well network, so as to ensure uniformity of standards. This may not always be possible or necessary if responsible well owners are prepared to provide the occasional help needed to obtain samples and forward results to the network agency. In the UK the water authorities are the responsible authority and maintain their own observation well networks.

When wells are abandoned for any reason the agency should ensure that they are not going to cause any danger of contamination of the aquifer from the surface, or between aquifers. Funds should be available to have such wells filled or sealed if necessary. The reasons for abandonment of wells are usually:

(1) poor well yield or quality;
(2) depletion of groundwater storage because of excessive abstraction;
(3) the provision of a new, deeper well as replacement;
(4) well no longer needed for research or abstraction.

6. SAMPLING

If samples are required from an abstraction well, it is then straightforward to obtain a sample of pumped water, which will be representative of all groundwater flowing into the well. 'Flow' samples can also be obtained from springs. Wells which are not pumped have to be sampled by lowering a sampler into the well and filling it at the required depth. Care must be taken to ensure that the sample is properly representative of groundwater at the required depth, and a number of suitable depth samplers have been developed. The borehole needs to be plumb and straight to allow passage of sampling tools as well as other logging tools.

When water samples have been collected some analyses can be carried out on site, but these usually have a low accuracy and can only be used as a guide, as errors could mark the natural fluctuations in the quantities of some unstable constituents. Normally the sample bottle is washed out two or three times before filling and sealing to prevent the escape of dissolved gases. Analysis should be carried out in a laboratory as soon as possible, and before any danger of the precipitation of such constituents as calcium, magnesium and iron.

In special investigations it may be necessary to obtain samples of rock for analysis of pore waters, but such sampling and analysis cannot be considered part of a routine water quality data collection programme. In the same way any use of remote sensing techniques is not yet a routine part of a network, although in some areas such methods may become feasible for collection of information from recording instruments at the more inaccessible sites. This is hardly likely for measurement of groundwater quality, however, for aquifers usually need to be exploited near the centres to be supplied.

The electrical conductivity of groundwater increases with increase in salinity and therefore changes in the concentration of dissolved minerals can be determined by the measurement of electrical resistivity of water. This is usually achieved by the use of a simple, portable resistance bridge measuring the resistance of a water sample in situ. Electrical resistivity loggers can be used to obtain a vertical profile, or log, of a column of water in a borehole. Temperature can usually be measured at the same time.

7. NETWORK DENSITY

It is not wise to lay down specific rules for the density of groundwater quality networks. Presumably one should aim to collect enough information to ensure that no significant regional changes are taking place, or if they are, then to be able to determine the trends of changes with time. Groundwater level measurements would be made in wells into each defined groundwater unit, if a representative well can be found. Correlation techniques allow the choice of one or two wells as representative. Similarly, these or other wells can be used to monitor quality within each groundwater unit, adding wells down dip in each of the hydrochemical zones of the aquifer if necessary.

The major aquifer in England is the Chalk and the density of water level observation wells averages one for 50 km^2 for manually measured wells and one for 200 to 250 km^2 for continuously recorded levels. The density may be much greater where specific investigations are under way. Such densities ought not to be aimed at for groundwater quality, except for special studies. Usually samples from one pumped well in every 100 km^2 would be adequate, but such a proposal is only a general guide. The aim should be one sample well in each groundwater unit. Judgement, therefore, has to be exercised because initially attempts are being made to collect information for purposes which may not become apparent for some time. Initially the aim should be for a network of minimum density to provide the required information. Most networks will help to elucidate the hydrology of a catchment or groundwater unit and so the individual stations must relate to hydrological and hydrogeological factors and the occurrence of saline or mineralized groundwaters.

An optimum network density can be developed from basic networks, or more readily from those used for research purposes; it should allow the interpolation between stations of values which would be of acceptable accuracy. For economic reasons the density should be kept to a minimum, and the wells sometimes drilled for research purposes cannot all be kept within operational networks.

Base or primary stations should be kept permanently, but secondary stations, to fill gaps, would usually be operated for a few years to obtain good correlation with base stations, and then perhaps another site chosen. A third category would augment these for particular investigations, usually to determine a specific set of data for research purposes.

Therefore, from a minimum network,time and experience will allow the definition of an optimum network. Existing stations should always be used if a systematic network is being developed so that correlation with a new station can be established before abandoning the old. Like all hydrological records, those of groundwater quality ought to be started in advance of need.

Once a technician is in the field there is little to be gained by deleting a few sites from a network and so, in general, it is better to carry out as complete a collection of samples as possible once or twice a year rather than a few very frequently. The regular analyses completed by statutory undertakings will provide a more complete time series for selected sites. The biggest saving comes from cutting down on the number of visits to an area for data collection and the aim should be to collect at as few times as possible. Research will obviously be needed, ideally in each area, to determine the optimal network of wells to give the essential data with the minimum number of visits, i.e. to allow good operational control of resources at minimum cost. For most regional networks groundwater quality data needs to be collected every three or six months.

Analysis of the water quality data will aim in part to produce contours on maps showing the variations in any one constituent. Those responsible for networks need to check such contour maps produced from a full swing against those produced from few data. Statistical methods can then determine if fewer data would give accuracy within required limits at any point in the area. Again, this recommendation about optimum networks should result from any research study of an area.

Planning water resource development would be almost impossible without measured data in the relevant area. By the use of physical or mathematical models a basic network can be extended into other areas to guide preliminary data collection, but network planning is a continuing process which must take account of changing demands for information.

The aim of the water quality network, therefore, should be to have at least one well in each groundwater unit, supplemented as necessary to monitor changes in regional quality or particular problems such as inflow of saline or mineralized groundwater. Particular problems of pollution and research may have to be monitored by additional wells.

8. DATA STORAGE AND RETRIEVAL

Water quality data form a time-series in the same way as groundwater levels and so can be correlated in time and space, and quality at certain points can be estimated by regression analysis from observations made at other points in time and space. Changes in groundwater quality are very slow and hence correlation between wells over short distances is usually high. Correlation between successively more widely spaced wells can be examined to ensure that the least number of wells are chosen as data collection sites to enable the whole volume of aquifer to be monitored with respect to possible changes in quality. Presumably most of us would err on the side of over-design, i.e. would include a few additional wells if funds were available for these.

Statistical analysis allows the determination of trends and monthly or annual deviations from these trends; and from the trends, predictions can be made regarding the water quality in any new well under natural conditions. With the help of modelling techniques, changes in groundwater pressure heads can be determined and, therefore, likely groundwater flows and any consequent quality changes.

These data analyses can be most readily carried out if the information is in a compatible form from each responsible authority. Groundwater units often straddle the boundaries between catchment or other administrative boundaries and, therefore, uniformity of data storage and presentation is essential. The information collected should be stored suitably, be easy to recover in tabular or graphic form, and related to administrative or hydrological boundaries, aquifer, types of use, agencies concerned, and so on.

Information relative to a well site and groundwater quality should include:

Site (National Grid reference and well number)
Aquifer
Hydrometric area
Water authority
Well details (depth, method of construction)
Type of sample (pumped, depth sample)
Date
Where analysed (laboratory)
Analysis (anions, cations, physical properties).

The Water Data Unit have brought together the water authorities to achieve a WATER ARCHIVE. They aim to provide listings of original data, statistical analyses and summaries of data, and graphical plots of data. The national archive will presumably be with the WDU or some other central agency, but individual water authorities will wish to store their own data. Wherever data is stored it should be made available to those carrying out surveys and research.

9. SUMMARY

A groundwater data network, including systematic measurement of quality, is essential for planning, development and operation of water resource systems, and this must be integrated with other hydrometric networks. A basic quality monitoring network should be created in any area where groundwater is likely to be developed. The responsible agency can enlarge the network by filling in gaps as and when necessary, this being decided in consultation with any other agencies responsible for groundwater, or combined use, development. In addition, specially designed networks may be necessary to monitor the possible inflow of poorer quality water into fresh water aquifers, or to monitor particular pollution problems, or of course for research purposes. Specialized studies should help to define parts of an optimum quality network.

In some instances only changes in groundwater quality can be monitored but scientific information from data networks, and interpretation, will lead to better management of the groundwater resource and, where necessary, to improved legislation. Long-term data collection will also allow a more critical analysis of groundwater data, helping with detailed studies of processes of groundwater pollution to enable better prediction, and indeed forecasting, of groundwater movement and changes in quality.

Well designed networks should also provide good quality data for use in mathematical models of groundwater and combined surface water and groundwater systems; these models becoming an essential tool of planning and management.

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PAPER 9

TECHNIQUES FOR INVESTIGATING GROUNDWATER POLLUTION AT LANDFILL SITES

C. Barber, J. A. Naylor and P. J. Maris

1. INTRODUCTION

Because of its low cost and simplicity, landfill is a common method of disposal of a variety of wastes (1), but the effects of such disposals (particularly on groundwater) are not fully understood.

It was to improve the state of knowledge of the behaviour of industrial wastes in landfills that the Department of the Environment set up a programme of research, which included the investigation of a number of landfill sites in the UK which had been used for the disposal of a variety of wastes. The site investigation work has been undertaken partly by the Water Research Centre, and partly by a team composed of staff from AERE Harwell and the Institute of Geological Sciences. One of the objectives of the research was 'to provide as much information as possible about the influence of the major variables that determine the behaviour and fate of hazardous materials under landfill conditions(2).

This paper describes the techniques and methods of analysis used by the Water Research Centre in the site investigations. It is hoped that the techniques developed during this research will be applied not only to investigation of existing and potential sites, but also to other groundwater pollution problems.

2. TYPICAL SITE INVESTIGATION

Site investigations are usually carried out in four phases, comprising

(i) an initial desk study of the landfill site and the region in which the landfill is situated,

(ii) an exploratory drilling and sampling programme,

(iii) a detailed drilling and sampling programme,

and (iv) monitoring of groundwater quality observation boreholes drilled during the detailed drilling programme.

The desk study, involving the collection and appraisal of all available information on the hydrogeological location and tipping history of the landfill, is considered to be an important part of any site investigation. Basic information, such as subsurface geology, thickness of any unsaturated zone and the regional groundwater flow pattern, is obtained from geological and topographical maps and from records of existing wells and boreholes. Details of the nature of the tipped wastes and of the operation of the landfill are obtained from a variety of sources, including the site operators, local authorities and aerial photographic records.

The information collected in the desk study, however, is of a general rather than a specific nature and an exploratory site investigation is usually required to confirm the data collected in this study and to provide the information necessary for the planning of a detailed drilling and sampling programme.

The exploratory work, an example of which is described graphically in Figure 1, (a) and (b), usually involves the drilling of shallow boreholes in a grid pattern within the site (Figure 1 (a)) to determine the shape and size of the landfill, and to recover samples of fill for analysis so that hazardous substances in the wastes can be identified and located. A limited number of boreholes are also drilled outside the landfill to below the water table, to determine the local groundwater gradient. The local flow direction can differ markedly from that inferred from the regional groundwater flow pattern.

The main programme of site work involves deeper drilling and more detailed sampling than in the exploratory work, the locations of the boreholes being dependent on the results of the exploratory work (compare Figure 1 (b) and Figure 1 (c)). At sites overlying an unconfined aquifer where unsaturated strata are present, boreholes are drilled through areas of interest within the landfill into the unsaturated zone, to within 5-10 m of the water-table (as in Figure 2 (a)).

Where a landfill is situated on an impermeable base, such as clay, boreholes within the landfill are terminated at the impermeable layer. Only when groundwater in the bedrock aquifer is in direct contact with wastes in a landfill are boreholes drilled through the wastes into saturated strata. This precaution is taken to avoid or minimize direct pollution by leachate of the bedrock aquifer caused by drilling operations although it is preferable, where possible, to drill boreholes within a landfill into the saturated zone to provide a complete depth profile of pollution beneath a site.

In addition to the boreholes drilled within the landfill, a pattern of boreholes is drilled on the perimeter of, and at various distances from, the landfill to depths necessary to define any plume of contamination (Figure 1 (c)).

The emphasis during the main site investigation is placed both on the collection and chemical analysis of water samples, and also on the systematic collection and chemical and physical analyses of solid samples from known depths within the landfill and adjacent strata.

The chemical analysis permits the determination of the overall, three-dimensional distribution of any landfill-derived contaminants at the time of drilling. The range of chemical determinations is comprehensive (see Figure 3); it includes COD and substances commonly present in refuse leachate (e.g. total and dissolved organic carbon, chloride, sulphate, sodium, and potassium) as well as specific hazardous substances known to be present in the wastes. This wide range of chemical analysis is carried out to determine, as far as possible, the full extent of any aquifer contamination, because multiple waste-migration patterns in groundwater can result from variations in leachate composition within a landfill, and from variations in the rates and directions of movement of contaminants within an aquifer (3). It is also important that physical analysis of rock core and geophysical logging of boreholes are carried out to determine the major hydrogeological controls over movement of any contamination.

The information collected in the main site investigation allows the estimation of the extent of contamination at the time of drilling, but gives little indication of variations in groundwater quality with time. Following completion of site work, therefore, a water-quality monitoring programme commences in which water samples are regularly taken for analysis from boreholes outside the site to measure variations in water quality with time. Groundwater levels are also recorded on sampling, to relate any water-quality variations to aquifer conditions.

3. DETAILS OF METHODS OF INVESTIGATION

3.1. DRILLING METHODS AND BOREHOLE CONSTRUCTION

The choice of drilling technique for each phase of the site investigation is controlled largely by the nature of the material to be drilled and by the requirements of the sampling programme.

In the exploratory drilling, the necessary information concerning the presence and locations of hazardous substances and the hydrogeological situation at the site can be obtained by relatively rapid drilling techniques, such as continuous flight augering.

More precise drilling is required during the main investigation; here the recovery of 'undisturbed' core samples forms an essential part of the drilling programme, and both air-flush rotary coring and drive coring methods have been used by WRC in different geological conditions to satisfy sampling requirements. Throughout the site investigations no drilling fluids are used, except where strictly necessary, to avoid contamination of interstitial water in the core or formation water in the borehole.

Boreholes which are drilled to below the base of a landfill are taken initially to the base of the fill material, where permanent casing is inserted and grouted in, and a 2-m thick cement grout plug formed in the base of the boreholes to prevent the transfer of leachate from landfill to unsaturated zone.

The boreholes are then deepened by drilling through the grout plug into the unsaturated zone, if present, to collect samples. On completion, the boreholes are backfilled and sealed with impermeable material to minimize access of leachate from the landfill into the groundwater.

Boreholes drilled outside the landfill are, whenever possible, left as permanent observation boreholes for monitoring and sampling groundwater (Figure 2 (b)). Initially, these boreholes were left 'open' and samples of groundwater were recovered from different depths in standing water present in the borehole, although this has proved to be unsatisfactory at some sites because of large-scale mixing of standing water from different levels within the boreholes. In addition, some changes in chemical composition of the water might be brought about by contact with the atmosphere in the boreholes, although no evidence of this has yet been found in the WRC studies. Alternative methods of groundwater sample recovery are now being used and evaluated in the research programme, including sampling from piezometer tubes set at pre-determined depths (Figure 2 (c)) and from pressure samplers made to a WRC design which are sealed in boreholes (Figure 2 (d)). No results from these sampling programmes are yet available.

3.2. HYDROGEOLOGICAL ANALYSIS

The hydrogeological environment in the vicinity of the landfill is important in controlling the rate and direction of movement of contaminants from the landfill. Consequently, hydrogeological assessment of landfill sites, involving the visual examination and laboratory physical analysis rock cores carried out in conjunction with geophysical logging of boreholes, is considered to be a necessary part of any site investigation.

Recovered rock cores are inspected to distinguish changes in lithology and to identify zones of potentially high permeability within the rock - for example where there are localized fractures and fissures or where coarse-grained horizons occur in mainly fine-grained rock. Determinations of porosity, centrifuged specific yield, and intrinsic permeability in both horizontal and vertical directions are made on selected cores using standard laboratory core analysis methods. The laboratory determinations of hydraulic properties of the aquifer are used to estimate theoretical travel times of contaminants in the saturated zone, which can then be compared with observed travel times obtained in the main site work.

Geophysical borehole logging is carried out to confirm the geological succession observed in the recovered core, and to provide information both on the groundwater flow system and also on the possible presence of contaminants at different levels in the boreholes. Changes in lithology and the presence of permeable horizons and fracture zones can be identified from lithological logs (gamma, caliper and formation resistivity logs). Preferential movement along permeable horizons or fractures and movement within borehole standing water can be indicated using fluid logs such as temperature and differential temperature logs, fluid conductivity and heat-pulse flowmeter logs. The combined use of standard lithological and fluid logs allows the determination of major hydrogeological influences on the movement of contaminants in the vicinity of the landfill.

3.3. SAMPLING AND CHEMICAL ANALYSIS

The objects of sampling and chemical analysis both in the exploratory and in the detailed main drilling programmes are different: the former is for the identification of hazardous substances present in samples of fill, the latter for the determination of the overall distribution of contaminants and of identified hazardous substances in solid and liquid samples in and around the landfill.

The methods of sample recovery used in exploratory and main drilling programmes also differ. In the exploratory work, sample recovery is somewhat imprecise and only bulk samples of fill are taken from boreholes. The requirement in the main drilling programme is the recovery of undisturbed samples of fill or rock from specific depths; samples of core are therefore taken systematically, usually at metre intervals. This frequency of sampling, which is limited by the analytical load which can be handled, has been adequate in our investigations of groundwater in uniform massive sandstone and chalk, and in alternating clay/peat sequences.

Samples collected during the main site investigation are analysed as soon as possible after recovery. Where storage of samples is unavoidable, solid samples are kept at -18°C, and liquid samples and solid samples from which interstitial water is to be extracted are maintained at 4°C. Storage of solid samples at 18°C for several months produced no significant change in the concentrations of oil, 'phenol' or halogenated solvent in test samples. Interstitial water, however, showed some changes in composition with storage of test samples of chalk core at both 4°C and at room temperature. Changes which were noted were loss of low levels of TOC, and increase in the concentration of sulphate, each of which was most marked in samples stored at room temperature.

Contamination of solid samples and of interstitial water during drilling is almost inevitable under most field conditions. In our investigations, tracer tests with lithium nitrate solution have indicated some intrusion of water present in boreholes during drilling into the outer 1-2 cm of rotary drilled core, and some oil contamination of the outer part of core from drilling equipment has also been noted. The outer 2-3 cm of the 11-cm diameter cores is therefore discarded and analyses are carried out on the remaining inner body of the core.

The analyses carried out as part of the main site investigations are more detailed than those in the exploratory work, examples of the range of determinations being shown in Figure 3. Solid samples of fill and rock core are analysed for a variety of substances, depending on the nature of the wastes in the landfill, to determine the distribution of each analysed substance within the fill and in the adjacent strata. However, little indication of the concentration of these substances in the groundwater is given in this way, and therefore water samples are taken from known depths in each borehole, usually by centrifugal extraction (4) from systematically-sampled core, but also from borehole standing water, to determine the extent of groundwater contamination in the vicinity of a site.

The centrifugal extraction technique has proved particularly useful in the investigation of groundwater contamination in porous, consolidated rock such as chalk and sandstone, but is less than ideal with unconsolidated material such as coarse sand, and inappropriate with coarser gravels. The number of chemical determinations carried out on the samples of interstitial water is also restricted, by the generally small sample size, to parameters of major importance, e.g. hazardous substances such as heavy metals, and to parameters which are indicative of groundwater contamination. In the latter case we have found that TOC, ammoniacal nitrogen and chloride have been useful indicators of contamination from landfills containing large quantities of domestic refuse, although the composition of leachate from landfills can vary considerably.

The larger volumes of samples of borehole standing water recovered by a Casella sampler during drilling of the boreholes, although giving less precise information on water-quality variations with depth, allow a wider range of determinations to be carried out (Figure 3). Similarly, sampling and analysis of standing water from 'open' boreholes, as part of the groundwater monitoring programme, allow the determination of a relatively wide range of parameters. In addition, in-situ determinations of the dissolved-oxygen saturation and temperature are made during the monitoring programme, being useful indicators of landfill-derived organic contamination of groundwater.

4. RESULTS OF SITE INVESTIGATIONS

It is intended that the results of our investigations at nine landfill sites in the UK will be published on completion of the research programme in 1977, although a preliminary progress report has been published recently (2) and some conclusions from the work are being presented at this conference (5).

The type of information obtained in our site investigations, however, can be seen in the example shown in Figure 4, which details the results of an investigation of a waste-disposal site in a disused quarry in a dolerite dyke, intruded into Triassic sandstones. The main component of the leachate from this site is hexavalent chromium. The distribution of chromium in groundwater is clearly shown by its distribution in interstitial water in a vertical section along the plume of contamination in the sandstone. In addition, analysis of interstitial water for other constituents present in leachate allowed us to determine whether the decrease in concentration of contaminants in groundwater with increasing distance from the disposal site was due to preferential removal of contaminants or was simply caused by dilution. Hydrogeological analysis of the site suggested that flow in fissures associated with the emplacement of the dyke was responsible for large-scale vertical movement of chromium in groundwater. Intergranular flow was predominant in sandstone unaffected by intrusion of the dyke, and the greatest movement of chromium occurred along more permeable sandstone between 30-40 m below OD.

It is suggested that this sort of detailed information on aquifer properties and on the distribution of contaminants in groundwater, is necessary to elucidate the hydrogeological and geochemical processes which affect the movement of leachate, and modify the composition of contaminated groundwater within the aquifer. We consider that such information cannot be obtained only by determination of the gross permeabilities of drilled strata or by the analysis of water entering a borehole during or after drilling. It is also clear from other site investigations that analysis of liquid samples alone is insufficient to determine the environmental effects of a particular waste disposal. This is obviously true with oil wastes which can be mobile in unsaturated strata, but which are immiscible with water, and rarely recovered in samples of water. The distribution of these substances can only be adequately determined by analyses of solid samples of strata.

Finally, it should be noted that in our investigations it has been possible to determine the fate in a landfill and its surrounding strata of only those substances identified in the desk study and exploratory investigations. Identification of more than a limited number of hazardous substances in leachate or wastes is extremely complex and time-consuming, particularly for organic hazardous substances, and requires expensive analytical resources which are often not available to organizations involved in landfill research.

ACKNOWLEDGEMENT

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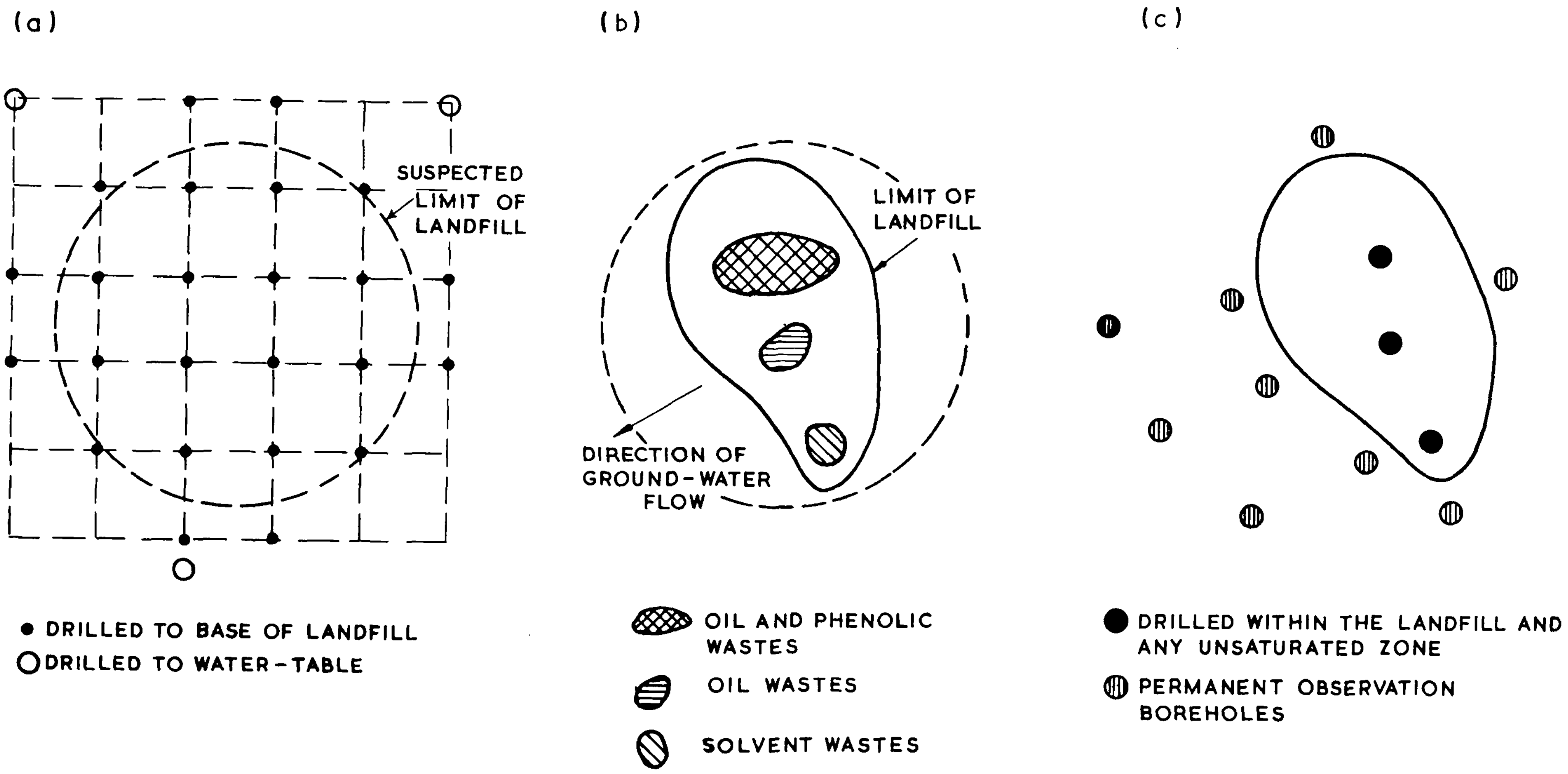

Figure 1. Drilling programme at a typical finished landfill site, following initial 'desk study': (a) pattern of exploratory auger holes; (b) determination of shape and size of landfill, direction of ground-water flow, and distribution of types of wastes; (c) boreholes drilled during main drilling programme.

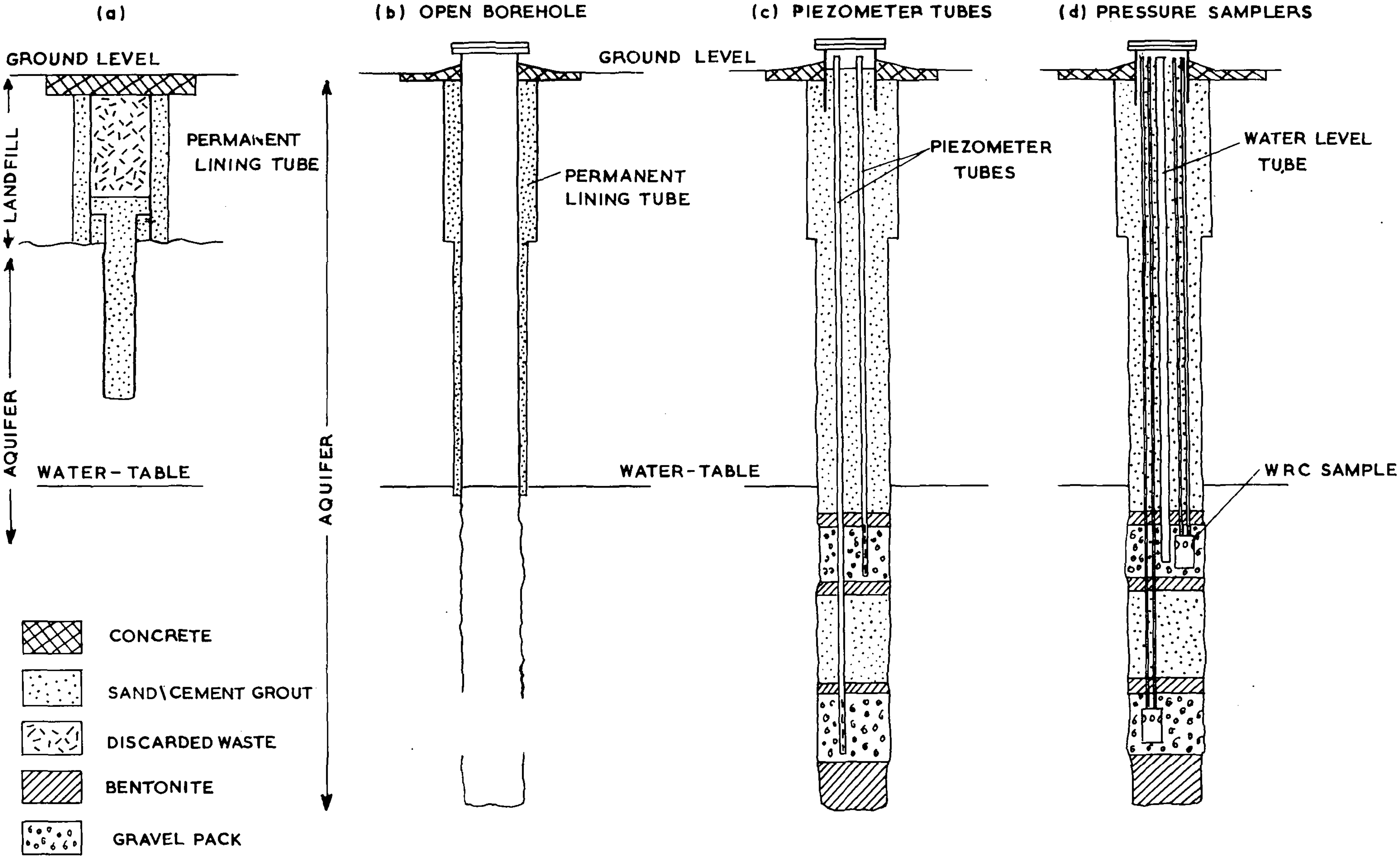

Figure 2. Construction of boreholes: (a) within the landfill; (b) - (d), permanent observation boreholes outside the landfill area.

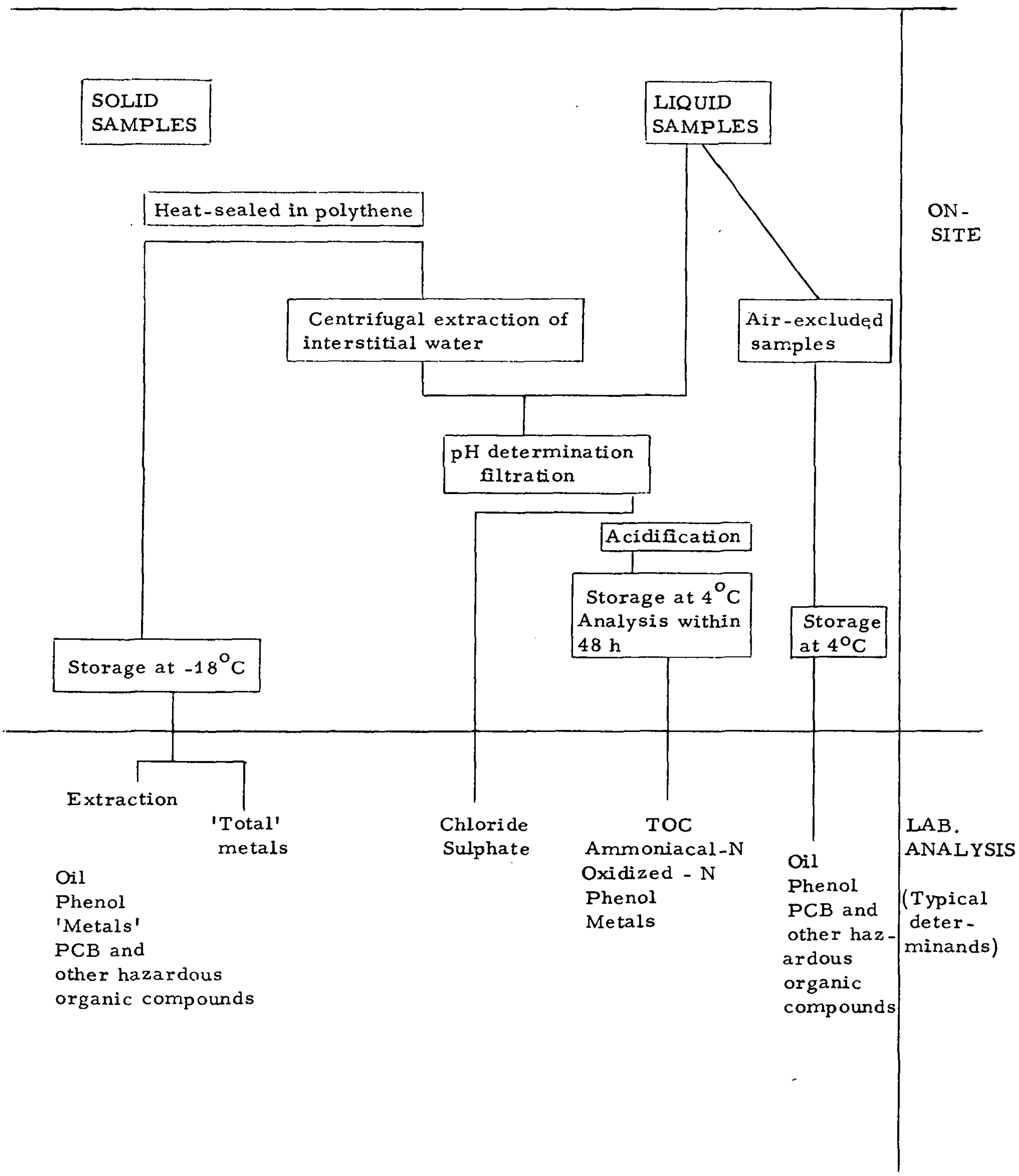

Figure 3. Flow chart summarizing the scheme of sampling and analysis of liquid and solid samples from landfill-site investigations.

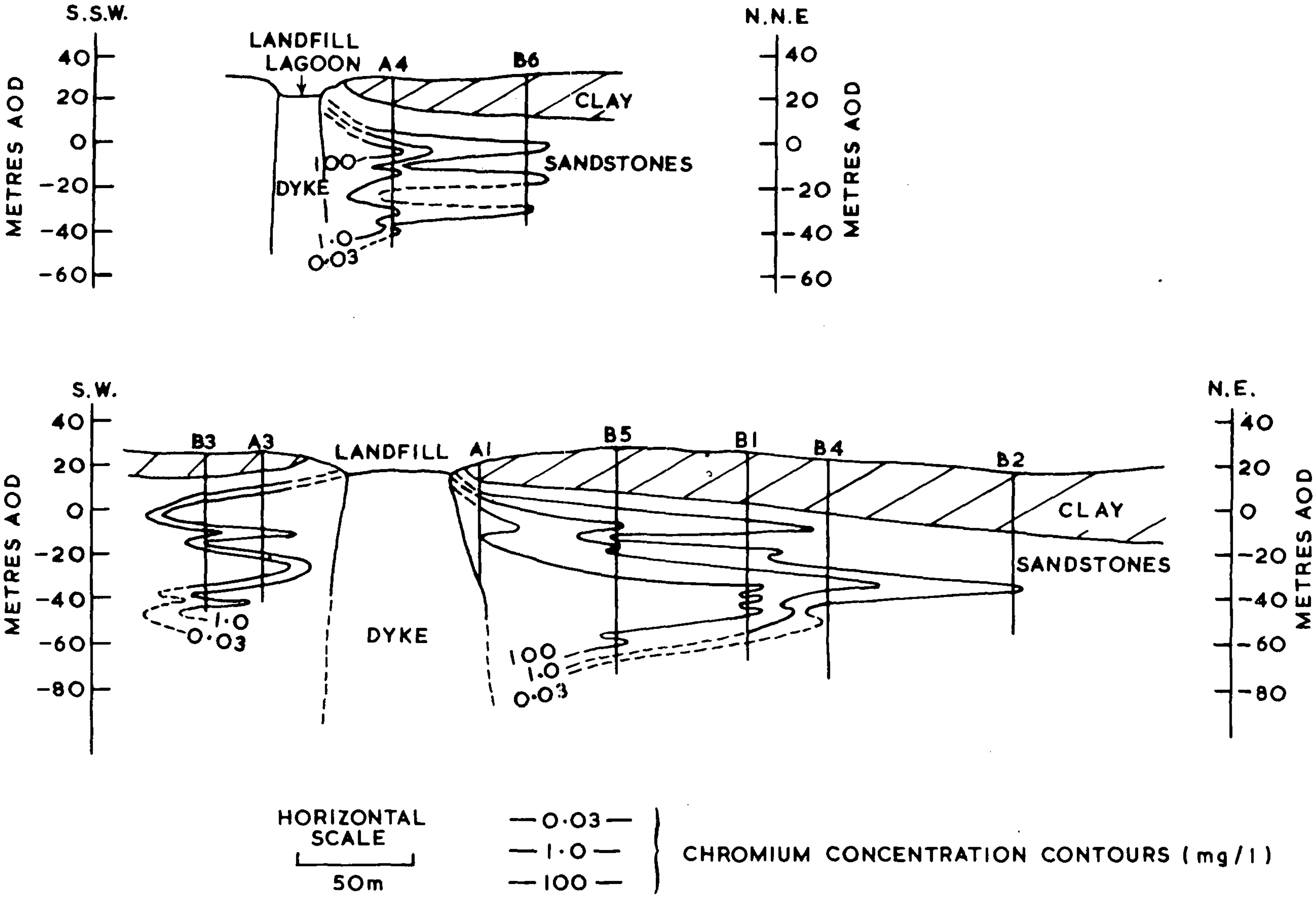

Figure 4. Distribution of chromium in sandstone interstitial water in two vertical sections across a landfill used for the disposal of hexavalent chromium.

PAPER 10

APPLICATION OF BOREHOLE GEOPHYSICS TO SELECTION OF POTENTIAL SITES FOR DEEP-WELL DISPOSAL OF LIQUID WASTES

Donald L. Brown

ABSTRACT

An important application of borehole geophysics in waste disposal studies is to determine the chemical quality of formation waters and to monitor changes in quality within a dynamic hydrologic system. An equally valuable application is the use of borehole geophysics as a tool in the process of identifying potential deep-well disposal sites.

Interpretive data obtained from geophysical logs of test holes provide information about the number and distribution of potential reservoirs and reservoir seals, porosity development, and the quality of formation waters. These data, synthesized into a regional or areally-extensive framework, are useful in outlining areas with both positive and negative potential for storing liquid wastes. The information, in quantitative form, is valuable for the evaluation and selection of optimal sites for subsurface storage of liquid wastes.

1. INTRODUCTION

Geophysical logs should be used by the hydrologist as both a predictive and quantitative tool, not just a means of correlating formations and selecting screen intervals. If the full value of calibrated geophysical logs is to be realized by the water industry, re-evaluation of our geologic techniques should be initiated. Many of the techniques used by the petroleum industry are directly applicable to solving problems faced by the hydrologist.

Borehole geophysics is predominantly used in the field of waste disposal as a detection device to record movement and passage routes of contaminants.

This is an important function of geophysical logs, but it is an application of the tool in a passive role. Why not use geophysical logs as the petroleum industry does; to explore, predict, and initiate directions of investigation ?

The purpose of this paper is twofold: to briefly review some of the geophysical tools presently being used to monitor waste disposal sites, and to describe some of the techniques that can be used to select potential deep-well injection sites on a regional basis.

Selecting potential disposal or waste storage sites in a region that has little subsurface control has long been a major problem to hydrologists. The environmental impact of long term storage of industrial and radioactive wastes are now being investigated by observing storage sites that were selected in the 1950's and early 1960's. Geophysical logs are one of the means used to monitor the possible movement of effluent from these older waste storage sites as well as to detect possible leakage of contaminants from newer sites. The application of porosity, gamma spectrometry, temperature and conductivity logs, current-meter surveys, and the acoustic borehole televiewer to the problems of waste storage monitoring is presented in the sections that follow. Further, a method for selecting potential waste disposal sites that is designed to quickly eliminate areas not meeting requirements and to define areas that will require further detailed investigation is presented. The technique would provide management with the information necessary to evaluate and select the best of all potential subsurface storage sites. Being able to reject large areas by this technique would enable the drilling budget to be concentrated on areas that would give the greatest return of information per dollar invested.

2. BOREHOLE GEOPHYSICAL LOGS FOR WASTE DISPOSAL MONITORING

The use of borehole geophysics as a down-hole monitoring system to detect the presence and movement vectors of contaminants is one of the more important uses of geophysical logs outside the petroleum industry. Keys and

Brown (1973) presented a review of the state of the art that indicated two categories of geophysical logs are useful in monitoring waste disposal sites; the first indicates movement or potential movement of fluid and the second identifies a specific component within a dynamic system.

In the first category, porosity and fracture logs indicate zones of potential fluid movement, while current-meter or spinner surveys establish direction and velocity of fluid movement within boreholes. Commercially available logs for determining effective porosity in various rock types include gamma-gamma density, neutron, and acoustic velocity logs. These logs indicate zones for potential fluid storage in lithologies where intergranular or intercrystalline porosity development is prevalent. In competent rocks such as tightly cemented sandstone, consolidated granite wash, and carbonates, the predominant porosity and permeability may be a result of fractures or solution openings. The location and orientation of fractures is important not only from the standpoint of reservoir potential, but also for determining the effectiveness of reservoir seals.

There are several commercial logs available that are designed to detect fractures, but probably the best borehole geophysical tool presently available is the acoustic borehole televiewer. The televiewer works on a principle similar to radar except it operates at a much lower frequency. A transducer, located in the tool, acts as both a transmitter and receiver of sound pulses. The distance the sound pulse travels as well as the character of the borehole wall affect the amplitude of the reflected sound. By rotating the transducer as the televiewer is pulled up the hole, a 360 degree scan of the borehole is achieved. The scans are triggered and thus oriented by a magnetometer in the probe. The display from the televiewer is presented on an oscilloscope that is monitored by a camera. The pictures show the well bore as though it were split open along the north axis and laid out flat. This allows a fracture to be measured for width, strike and dip.

The US Geological Survey is presently using a borehole televiewer in research projects ranging from study of induced fractures caused by hydraulic fracturing (Wolff and others, 1975; Bredehoeft and others, 1976) to monitoring radioactive waste disposal sites. Wolff (1975) pointed out that in the Piceance Oil Shale Basin of northwest Colorado, 'vertical fractures may be hydraulically induced at well-face injection pressure of about two thirds of the total overburden load. Further, the fractures will continue to propagate vertically as long as injection pressure exceeds the combined value of least principal horizontal stress and tensile strength ....' That statement emphasizes the importance of the televiewer as a monitoring tool to detect potential contamination pathways resulting from fractures induced during injection of waste fluids.

Some of the older radioactive waste storage sites in the United States were chosen, in part, because of a thick shale seal that was present at the disposal site. Prior to the development of the acoustic borehole televiewer, fracturing of a shale reservoir seal either by drilling or by injecting fluids could not be easily detected. W. S. Keys (oral commun., 1976), using gamma spectrometry logs, recently found radioactivity in strata below the disposal horizon at one of the older storage sites for radioactive waste in Tennessee. The borehole televiewer was used to confirm the presence of fractures in the shale. These fractures were probably the conduit for movement of radioactive effluent.

The borehole current-meter is an excellent tool for determining movement of fluid within a well. Current-meter traverses indicate where fluid is entering an aquifer, in the case of an injection well, or which zones are contributing fluid, in the case of a pumped or flowing well. One of the more obvious uses of this tool is to determine if injection zones within an aquifer clog or develop during injection.

Combining logs showing movement of fluid, with logs indicating qualitative changes, provide information on rate of movement and dispersion of injection fronts. Combinations of current-meter traverses and fluid conductivity logs were used to determine the movement of a freshwater injection front in a brackish water reservoir in a recent study at Norfolk, Va. (Brown and Silvey, 1973).

When the fluid movement within a well bore is too slow to register accurately on a current-meter, a temperature log is useful to indicate internal flow patterns. An intermittently pumped well in Virginia, that was screened in several intervals over a distance of about 1000 feet (300 m), suddenly began producing a high-chloride water (R. L. Wait, oral commun., 1976). The well was not pumped for several months, after which temperature and fluid conductivity logs were run in the non-pumping well. The logs showed that because of head differences in the aquifer, warm, salty water was moving up the well bore and was entering the upper formations.

In the second category of logs used in monitoring waste disposal sites, there are a large variety of geophysical logs, ranging from simple temperature logs to sophisticated gamma spectrometry logs, that will indicate changes in water quality at a monitoring station.

W. S. Keys (oral commun., 1976), using gamma spectrometry logs, had excellent results in detecting the spread of contamination near a radioactive waste storage site at Maxey Flats, Ky. Gamma spectrometry is a means of identifying both natural and artificial radioisotopes on the basis of characteristic radiation energy levels. As isotopes decay, they emit alpha or beta particles with a consequent loss of mass. Gamma radiation is also emitted by some radioisotopes. By monitoring gamma photons detected per time unit versus gamma energy, characteristic energy peaks are recorded that can be used to identify specific radioisotopes. At the Maxey Flats storage site, gamma spectrometry logs run in cased observation holes around the periphery of the storage area, detected the presence of cobalt 60, cesium 134, and cesium 137 isotopes (H. H. Zehner, oral commun., 1976). These particular isotopes, which do not occur in nature, were present in the stored radioactive waste and, therefore, provided documentation of movement of the contaminants away from the waste storage site. They had not been detected in water samples from the well, but were detected and identified behind the casing above the water table. One of the more important features of this log is that it can be operated in either a cased or open hole. This has special significance, in that cased wells could be used as monitor wells if the need arose.

3. AREAL EVALUATION TECHNIQUES FOR SELECTING POTENTIAL DISPOSAL SITES

The use of geophysical logs as monitoring tools is an established aspect of downhole geophysics. The use of geophysical logs to define the reservoir and to predict areas of potential reservoirs may prove to be an equally important application of downhole geophysics.

Brown and Reid (1976) devised a very effective regional method of quickly evaluating areas for suitability of deep-well waste storage. The method requires simple manipulation of geophysical logs and is especially adaptable to large areas with widely spaced data points.

The first step in an areal evaluation is to define the minimum criteria that an area must possess in order to be considered as a potential disposal site. Secondly, a series of maps is constructed from log interpretations that will progressively outline areas that have the geologic environment with the predefined criteria.

The following is a general set of criteria that were picked to illustrate the methodology of the technique. Individual characteristics can be adjusted to meet local needs in relation to the kind of waste to be injected.

(i) A formation water that has a total dissolved solids concentration high enough that the water will not be required for any further use.

(ii) A reservoir that has some minimum depth below the base of any fresh water present in the area.

(iii) A reservoir with sufficient porosity and permeability to permit the emplacement and storage of the waste fluid with reasonable injection pressures. Further, the reservoir should be a sand, rather than carbonate lithology to minimize loss of injection fluids through fractures and solution channels.

(iv) A reservoir with sufficient thickness of relatively impervious shale both above and below the reservoir so that the injected fluid will remain within the reservoir.

To begin this type of regional evaluation, it is necessary to correlate the geophysical logs into chronostratigraphic units so that a structural and stratigraphic evaluation of each unit can be made. In addition, a regional water quality map must be constructed for each unit. Combining structure and salinity maps will quickly delineate areas that will not require further investigation.

4. WATER QUALITY CALCULATIONS

A regional salinity map (Figure 1) is very important in an evaluation of this type. (The area and values depicted on Figures 1 - 6 in this paper are hypothetical and are used only as a means of illustrating the methodology.) Water quality data are invariably limited to areas of freshwater production or to scattered drill-stem tests in areas of poor water quality. Therefore, geophysical logs may have to be used to calculate water quality. Calculation of water quality using geophysical logs is not difficult; however, when working with fresh and brackish waters certain precautions are necessary that require some detailed explanation.

Techniques for calculation of water quality are available from many sources (Schlumberger, 1958; Alger, 1966; Brown, 1971) and it is not the purpose of this paper to discuss the theoretical aspects of resistivity and Spontaneous-Potential logs. What should be noted by the hydrologist is that geophysical logs and their subsequent interpretation were designed for salt-water-hydrocarbon environments. Therefore, techniques used by the petroleum geologist must be modified by the hydrologist when dealing with a fresh to brackish interstitial water.

There are two basic log interpretation techniques that may be used to calculate the approximate dissolved solid and sodium chloride content of interstitial fluids. They are: (a) the 'Resistivity Method' in which the mathematical relationship between the resistance of current introduced into the borehole and the porosity, interstitial water, and natural rock resistivity is resolved, and (b) the 'SP Method' in which a mathematical relationship between electrical potential and the chemical activity of the interstitial water and drilling mud is resolved.

5. RESISTIVITY METHOD

The basic formulas used in this method are (Schlumberger, 1958, p. 11):

$$F = \frac{0.62}{\phi^{2.15}} \qquad \text{..............} \quad 1$$

$$R_w = \frac{R_o}{F} \qquad \text{..............} \quad 2$$

where F = formation resistivity factor R_o = resistivity of rock 100 per cent saturated with water of resistivity R_w, R_w = resistivity of interstitial water in a porous rock, and ϕ = porosity.

Given the proper suite of geophysical logs, the Resistivity Method is probably more useful than the SP Method as it is less affected by lithologic variations such as shaliness and can also be used in massive carbonate sequences. In order to use the Resistivity Method with confidence, however, an accurate porosity value must be available and the formation should have minimum invasion of drilling fluids so that an accurate value for R_o can be determined.

As the interstitial waters become less saline, the effect of the bicarbonate radical on the apparent resistivity of the interstitial fluid is increased to the point that an error of nearly 200 per cent can be introduced in a sodium bicarbonate formation water with a salinity of only 2000 mg/l sodium chloride (Brown, 1971, Table 3). The per cent error will increase as the water becomes fresher and less concentrated because the bicarbonate radical, which is the dominant anion in many fresh waters, contributes only about 27 per cent as much conductivity as an equal weight of chloride ion (Alger, 1966, p. 5).

This means that a sodium bicarbonate solution will calculate to be apparently saltier using methods based on sodium chloride resistivities. The apparent resistivity derived from Equation 2 must be corrected at formation temperature by a factor of 1.75. The following example from a test hole drilled at Norfolk, Va. will illustrate the point.

The porosity for an unconsolidated sand, as determined from a gamma-gamma density log, is 38 per cent. Then, using the standard Schlumberger charts, the F value is read as 5.0 (1972, p. 14). The apparent resistivity, R_o, read from the deep curve of a dual induction laterolog is 8.0. By substituting into Equation 2

$$R_w = \frac{R_o}{F}$$

$$R_w = \frac{8}{5}$$

R_w = 1.6 ohm-metres (3300 mg/l NaCl) at formation temperature.

The actual resistivity, R_w, of a water sample collected from the sand is 2.75 ohm-metres at formation temperature. The effect of the bicarbonate is to imply that the water is apparently more saline than it actually is. By applying the correction factor of 1.75 for the bicarbonate anion the R_w calculates to be $1.6 \times 1.75 = 2.8$ ohm-metres (1800 mg/l NaCl) at formation temperature.

The correction becomes more critical as the water becomes fresher because of the logarithmic relationship between resistivity and NaCl concentration. Potential freshwater aquifers could be overlooked in a well because of apparent high salinities when in fact it is a sodium bicarbonate dominated freshwater.

6. SP METHOD

In many instances, limited geophysical log suites are run in wells so that the logs necessary for calculations using the Resistivity Method are not available.

An alternative technique of calculating water quality from geophysical logs is the SP or Spontaneous-Potential Method.

The technique of calculating water quality from SP curves has been previously described (Schlumberger, 1958; Alger, 1966; Brown, 1971). It is important to realize that the accuracy of the technique is grossly affected if the magnitude of the deflections of the SP curve are not accurate. The magnitude of the SP is suppressed by both shaliness and hydrocarbons in a sand and exaggerated by divalent cations in the interstitial fluids. In the first instance a formation water would appear fresher than it actually is and in the second instance it would appear much saltier.

If the hydrologist is using geophysical logs to calculate freshwater-brackish water interfaces, the divalent cation effect can introduce large errors as the water becomes fresher. For instance, in a test well at Norfolk, Va., the SP opposite a sand at 850 feet (259 m) gave a reading of -40 millivolts. Based on a water sample recovered from the unit, it should have given a reading of -23 millivolts. The reason for the exaggerated SP can be explained by the following formulas (Alger, 1966):

$$SSP = -K \log \frac{a(w)}{(a)mf} \qquad \ldots\ldots\ldots\ldots\ldots \quad 3$$

$$SSP = -K \log \frac{({}^{a}Na + \sqrt{{}^{a}Ca + {}^{a}Mg})\ W}{({}^{a}Na)mf} \qquad \ldots\ldots\ldots\ldots\ldots \quad 4$$

Where SSP = static spontaneous-potential

K = a constant related to absolute temperature

a(w) = electrochemical activity of interstitial water

a(mf) = electrochemical activity of mud filtrate

${}^{a}Na$ = electrochemical activity of sodium

${}^{a}Ca$ = electrochemical activity of calcium

${}^{a}Mg$ = electrochemical activity of magnesium

When the square root radical contains significant calcium and magnesium ions, the effect is great because the square root of a fraction is a larger fraction. The K value is also affected when the water has a relatively large divalent cation content.

When the R_w has been calculated as if it were a sodium chloride solution, the final R_w must be corrected by a factor of 1.75 in order to compensate for the divalent cation effect.

As in the case for the Resistivity Method, the effect of the correction for divalent cations is much more pronounced as the water becomes fresher. For instance, correcting an apparent R_w of 20 ohm-metres at 75°C by 1.75 will reclassify a water from brackish to fresh, whereas a correction of 1.75 applied to an apparent R_w of 2 ohm-metres at 75°C would not change the basic brackish water classification.

Any additional anions that are encountered in abnormal concentrations in dilute water, will also require a correction factor to be applied to the apparent resistivity. For instance, if sulphate (SO_4) is present as a major constituent in a sodium bicarbonate water, a correction of 1.5 must be made in addition to the correction of 1.75 for bicarbonate. To illustrate, a well drilled in Savannah, Ga. had a water sample collected from a clean sand interval at a depth of about 3000 feet (900 m). Geophysical logs indicate that the porosity is 38 per cent which gives an F value of 5 (Schlumberger, 1972, p.14). The apparent resistivity from the geophysical log is about 14 ohm-metres. Substituting in Equation 2

$$R_w = \frac{R_o}{F}$$

$$R_w = \frac{14}{5} = 2.8 \text{ ohm-metres at } 46.6^\circ\text{C } (116.5^\circ\text{F})$$

This has a calculated chloride value (Schlumberger, 1972, p.9) of about 715 mg/l. Chemical analysis of the water sample (H. Gill, written commun., 1976) showed that the major cations and anions consisted of:

$Ca = 6.5$ mg/l $\quad HCO_3 = 994$ mg/l

$Na = 560$ mg/l $\quad Cl = 230$ mg/l

$SO_4 = 120$ mg/l

By applying the HCO_3 correction of 1.75 the R_w calculates:

$$R_w = 2.8 \times 1.75 = 4.9 \text{ ohm-metres at } 46.6^{\circ}C.$$

which has a calculated chloride content of about 400 mg/l. Even with the bicarbonate correction, an error of about 60 per cent exists. However, if a sulphate correction factor is applied, in addition to the bicarbonate correction, the R_w calculates:

$$R_w = 4.9 \times 1.5 = 7.4 \text{ ohm-metres at } 46.6^{\circ}C.$$

This has a calculated chloride value of about 265 mg/l compared to the actual value of 230 mg/l.

An error of about 15 per cent still exists, but considering the accuracy of the instruments, the subjective nature of values from logs, and the rounding off of numbers, this amount of error may be expected. The effect of a 10 to 15 per cent error is more significant as the dissolved solid content of the formation water becomes less; therefore, in fresh or brackish water, care must be taken when determining values from logs and charts. The standard charts for converting water resistivity to water quality express the results in terms of milligrams per litre sodium chloride (Alger, 1966; Schlumberger, 1972). As the water becomes fresher than 1000 mg/l dissolved solids, it would probably be more accurate to determine the dissolved solid content and then by using local empirical data for individual formations in an area, convert the dissolved solids content to milligrams per litre sodium chloride.

7. STRUCTURAL-STRATIGRAPHIC EVALUATION OF POTENTIAL DISPOSAL SITES

Once the average water quality for each chronostratigraphic unit has been calculated from the geophysical logs, a regional water quality map can be constructed (Figure 2). The basic salinity map can indicate freshwater-saltwater interfaces, direction of intrusion, direction of recharge, and may even reflect structural trends if saltwater is leaking upward along fault planes.

These two basic maps, salinity and structure (Figures 1 and 3), used in conjunction with the predetermined requirements for waste storage can quickly eliminate large areas from further consideration as a potential deep-well waste storage site. If the minimum formation water quality that will be considered for a disposal-host is chosen as 3000 mg/l sodium chloride and the minimum depth of burial is chosen as 3000 feet (914 m) below sea level [1000 feet (304 m) below the deepest freshwater occurrence in the unit] then areas requiring further investigation can be defined by overlaying the two maps and outlining the areas that meet the basic requirements (Figure 4).

Once the high salinity and depth-of-burial requirements are met, it is necessary to determine if the other predefined requirements are present; that is, a sand reservoir and sufficient reservoir seal.

Again, the basic data can be derived by simple manipulation of the geophysical logs. At each well site, using electric, gamma, and sample logs the thickness and number of occurrences of sand, shale, and carbonate units within a chronostratigraphic unit should be recorded, along with depth and the various percentage values listed in Table 1.

By constructing 'sand lines' and 'shale lines' on the SP curve of the electric log, the thickness and number of occurrences of sand, shale, and carbonate beds within each unit may be determined.

Once the sand and shale lines are established, the presence or absence of a reservoir that meets requirements 3 and 4 [that is, 20 feet (6 m) thick, with 20 feet (6 m) of seal above and below] is easily established. The spatial distribution of areas containing reservoirs can be determined by placing the data in map form (Figures 5 and 6) which will further eliminate areas from consideration in a drilling programme.

It becomes apparent that the direction of this technique is to spiral inward towards a specific area, by eliminating areas that cannot meet predetermined geologic standards. The methodology is one of simple rejection. Brown and Reid (1976) did not stop there however; they further refined the method and by using the data in Table 1, devised a technique for prediction.

They constructed a series of six maps for each geologic unit under consideration for waste storage. The map series consist of:

(i) Average depth of the top of the unit's potential waste-reservoir sand.

(ii) Unit thickness and sand thickness map.

(iii) Thickness of potential waste-reservoir sand.

(iv) Average thickness, per foot of potential waste-reservoir sand, for the shale seals that immediately overlie the reservoir sand.

(v) Average thickness, per foot of reservoir sand, for the shale seals that immediately underlie the reservoir sand.

(vi) Depth/potential reservoir factor (average depth of potential reservoir sand occurrence/total thickness of unit's potential reservoir sand).

Brown and Reid's maps 1 through 3 can be used to predict certain geologic factors. They indicate the regional trend for depth of burial, sandy facies in a unit, and areas where increased thickness of individual sand units can be expected.

Maps 4 through 6 are designed to determine the extent and effectiveness of seals in areas that have established reservoir sands and to try to project that trend regionally. Map 6 also indicates the relationship between thickness of overburden per foot of potential reservoir sand.

Record Number:

Well Number: Well Name:

State: County: Latitude: Longitude:

Depth of Well		Depth of Well (SLD)		Elevation of Measuring Point		Elevation of Ground Level	
(ft)	(m)	(ft)	(m)	(ft)	(m)	(ft)	(m)

Basic Data - Potential Reservoir Sand Determination	Unit A		Unit B		Unit C		Unit D	
	(ft)	(m)	(ft)	(m)	(ft)	(m)	(ft)	(m)
Depth to top of Unit (SLD)								
Thickness of Unit								
Unit's total sand thickness (ft/% & m/%)								
Unit's total shale thickness (ft/% & m/%)								
Unit's sand-shale ratio								
Number of potential reservoir sands in Unit								
Total thickness of Unit's potential reservoir sands								
Average thickness of Unit's potential reservoir sands								
Maximum thickness of a potential reservoir sand layer in Unit								
Ratio - Unit's potential reservoir sand thickness:Unit's total thickness								
Ratio - Unit's potential reservoir sand thickness:Unit's total sand thickness								
Thickness - Immediately underlying shale seal - potential reservoir sand - immediately overlying shale seal								
Ratio - Thickness of immediately underlying shale seal:thickness of potential reservoir sand:thickness of immediately overlying shale seal								
Depth to top of uppermost potential reservoir sand (SLD)								
Depth to top of lowermost potential reservoir sand (SLD)								
Average depth to top of Unit's potential reservoir sands (SLD)								
Percent of potential reservoir sand in upper third of Unit								
Percent of potential reservoir sand in middle third of Unit								
Percent of potential reservoir sand in lower third of Unit								
D/PR factor (average depth of potential reservoir sand occurrence/total thickness of Unit's potential reservoir sand)								

Geophysical logs:

Table 1. Data sheet for geologic parameters to be calculated from geophysical logs.

To supplement the maps, Brown and Reid also used a series of 5 graphs depicting the following geologic parameters within each unit:

(i) ratio of potential waste-reservoir sand thickness to total thickness.
(ii) ratio of sand thickness to shale thickness.
(iii) number of potential waste-reservoir sands.
(iv) maximum thickness of potential waste-reservoir sands.
(v) occurrence of potential waste-reservoir sands in upper third, middle third, and lower third of unit.

These graphs are designed to give quantified information in determining which unit, if several are under consideration for waste storage, has the more positive aspects and which unit could be most economically developed.

8. POROSITY AND PERMEABILITY

The areal distribution pattern of effective porosity and permeability of a potential reservoir can be mapped by either direct or indirect methods. If porosity logs are available at the control wells, a direct method would be to construct a map showing the average per cent porosity for each chronostratigraphic unit. By combining these maps with the maps showing sand thickness, it should be possible to establish porosity trends.

If direct porosity information is not available, there are several indirect methods that can be used to determine relative porosity. If the resistivity of the formation water (R_w) has been calculated, and the resistivity of the formation (R_o) can be determined from the electric log, the formation factor (F) can be found by substituting into equation 2. Once a value for 'F' is determined, a value for porosity can be read from standard log analysis charts if local information shows a direct ϕ-F relationship.

In areas of unconsolidated sediments such as the Atlantic Coastal Plain of the United States, it may be possible to determine an empirical relationship between thickness of sand and porosity-permeability. Brown and Reid found in their study that the maximum usable porosity and permeability was present in a reservoir when the ratio of the unit's potential reservoir sand thickness (map 3) to the unit's total sand thickness (map 2) approached a value of one. Similar empirical relationship can be determined for areas of differing geologic environments.

The whole purpose of the discussion of Brown and Reid's paper is to point out what can be done with geophysical logs in a predictive sense. With the exception of samples for the determination of lithologies (and even this can be fairly accurately approximated with the proper suite of logs) all the maps and graphs can be derived using geophysical logs. The purpose of the maps and graphs is to provide a step-by-step method to delineate areas that appear to warrant further investigation, to eliminate areas that appear unsuitable for waste storage, and to provide management with decision making tools in the expenditure of the exploration budget.

9. SUMMARY

Geophysical logs have a proven value in the job of monitoring the movement of effluent from waste storage areas. The underground movement of contaminants from deep-well disposal sites or surface storage areas can be detected in observation wells using a variety of downhole geophysical tools. The gamma spectrometry log is especially versatile in monitoring radioactive wastes because it can detect and identify gamma-emitting isotopes in both cased and uncased wells. The presence of possible vertical fractures that may have been induced by drilling can be detected by running an acoustic borehole televiewer log prior to setting casing in an injection well. Injection wells may be periodically checked by current-meter traverses and the acoustic borehole televiewer to detect the cause and effect of any changes in injection flow patterns.

Perhaps an equally important application of borehole geophysics to the waste disposal field is in delineating and predicting areas suitable for liquid waste storage. If an acceptable disposal site can be defined in geologic terms such as porosity, lithology, depth of burial, and water quality, geophysical logs can be used to select areas that will satisfy the site requirements.

The techniques initiated by Brown and Reid supply a means of quickly evaluating large areas that have limited subsurface data. The step by step evaluation rejects from consideration, areas that do not meet predetermined criteria. The final result is a series of maps showing areas that require further investigation. New criteria can then be applied that will further define the requirements of a disposal site and the process repeated. The end result is to determine areas that meet a maximum set of limits so that an active drilling programme can be initiated. The drilling of test holes is the ultimate method to determine the suitability of a potential deep-well injection site. By using this technique, the selection of the drilling sites can be made in the most efficient and economical manner.

ACKNOWLEDGEMENTS

In this paper, the discussion concentrates on the use of geophysical logs in the field of subsurface waste disposal. Many of the techniques presented here are condensed from a USGS Prof. Paper by Brown and Reid (1976).

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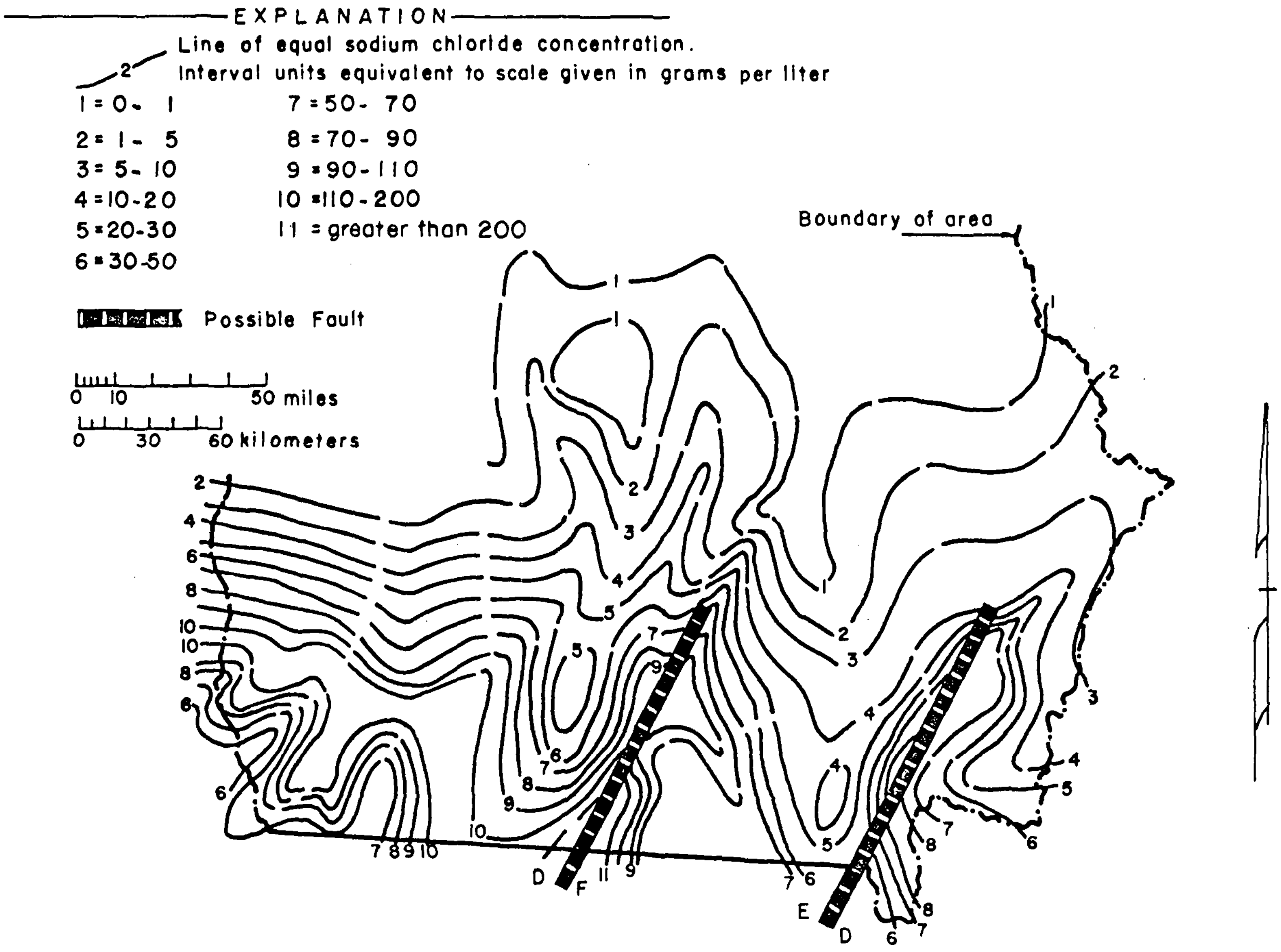

Figure 1. Formation water salinity for Lower Cretaceous sand calculated from geophysical logs.

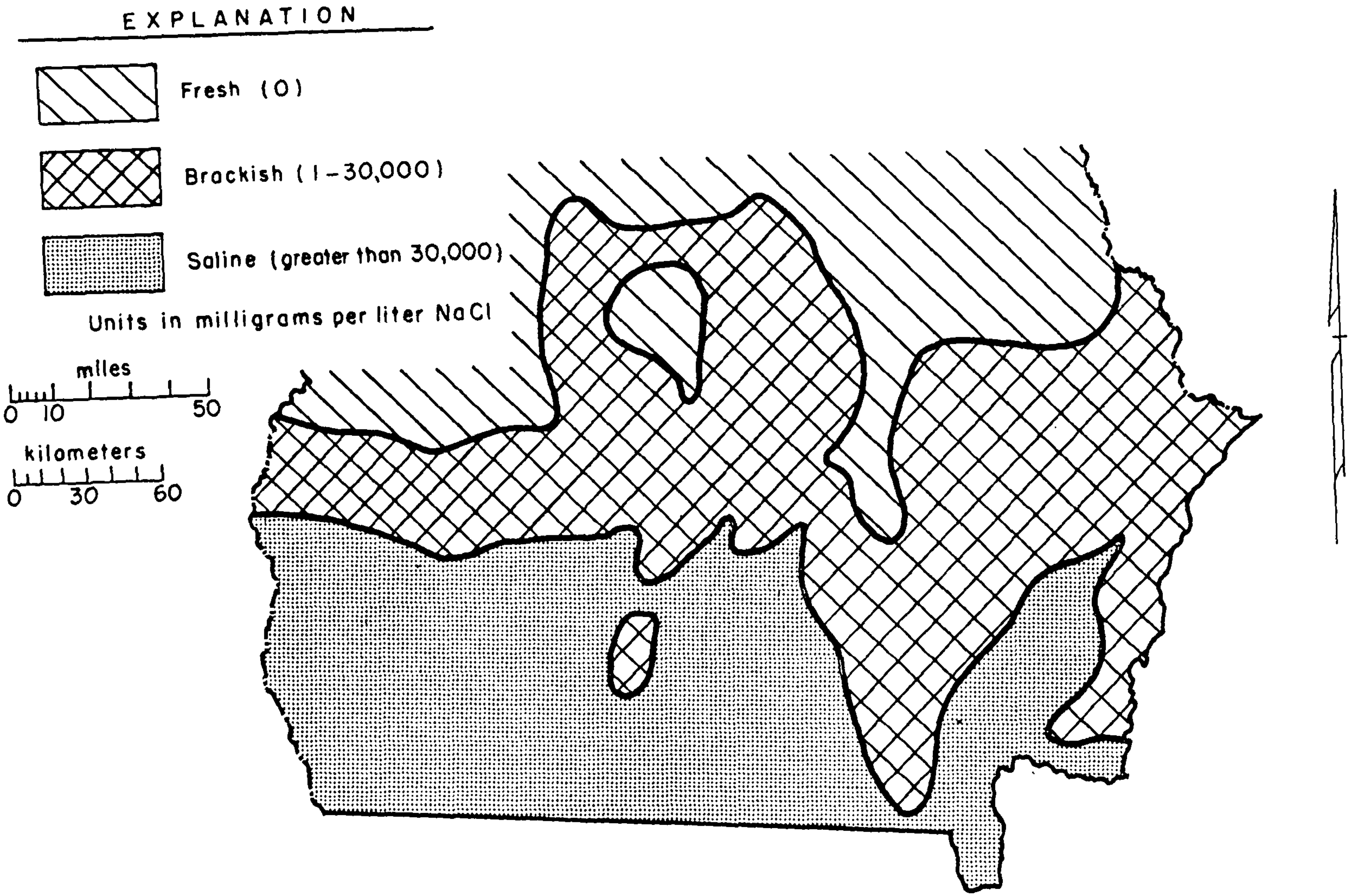

Figure 2. Major water types, Lower Cretaceous sand.

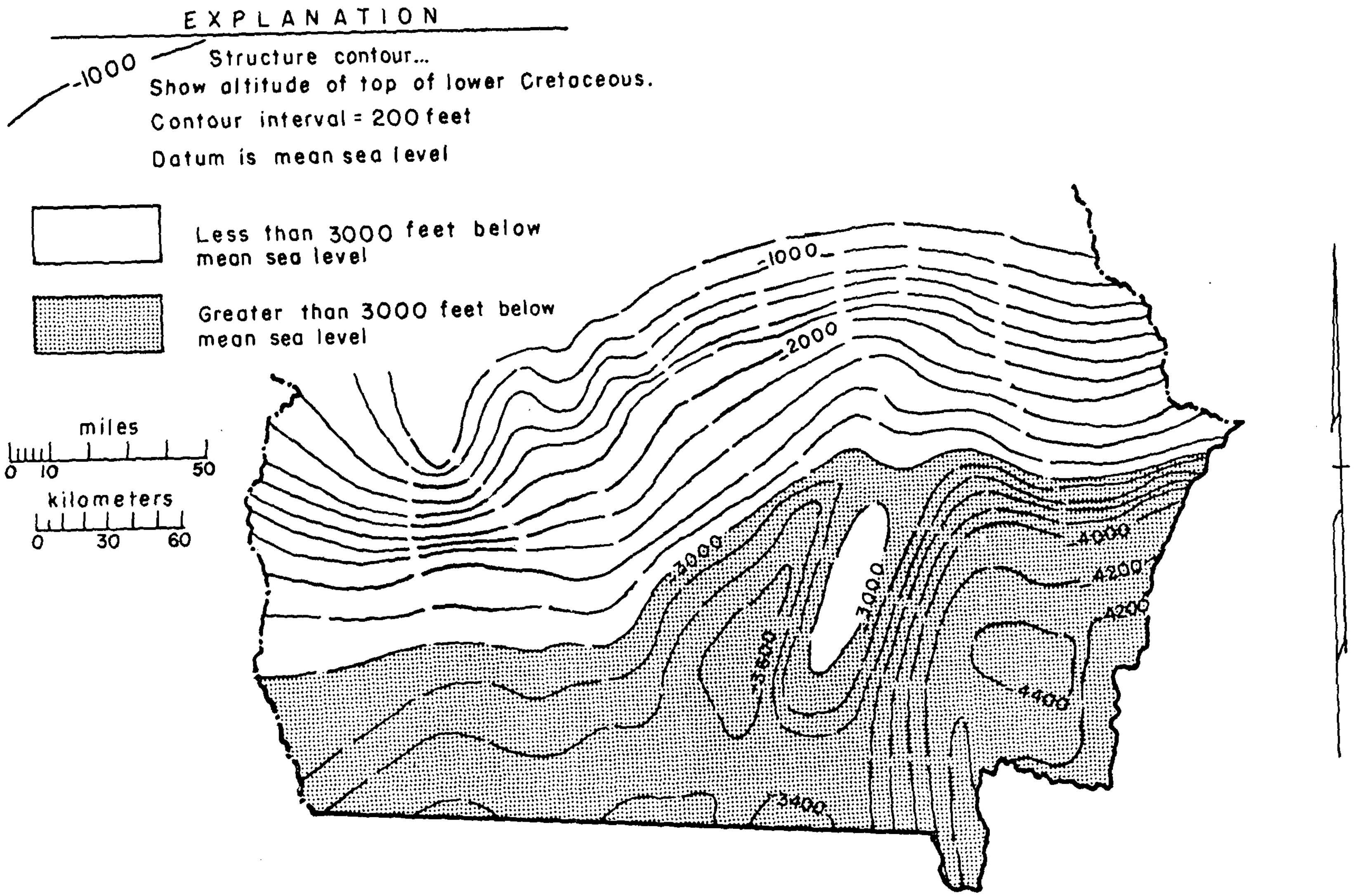

Figure 3. Structure on top of the Lower Cretaceous.

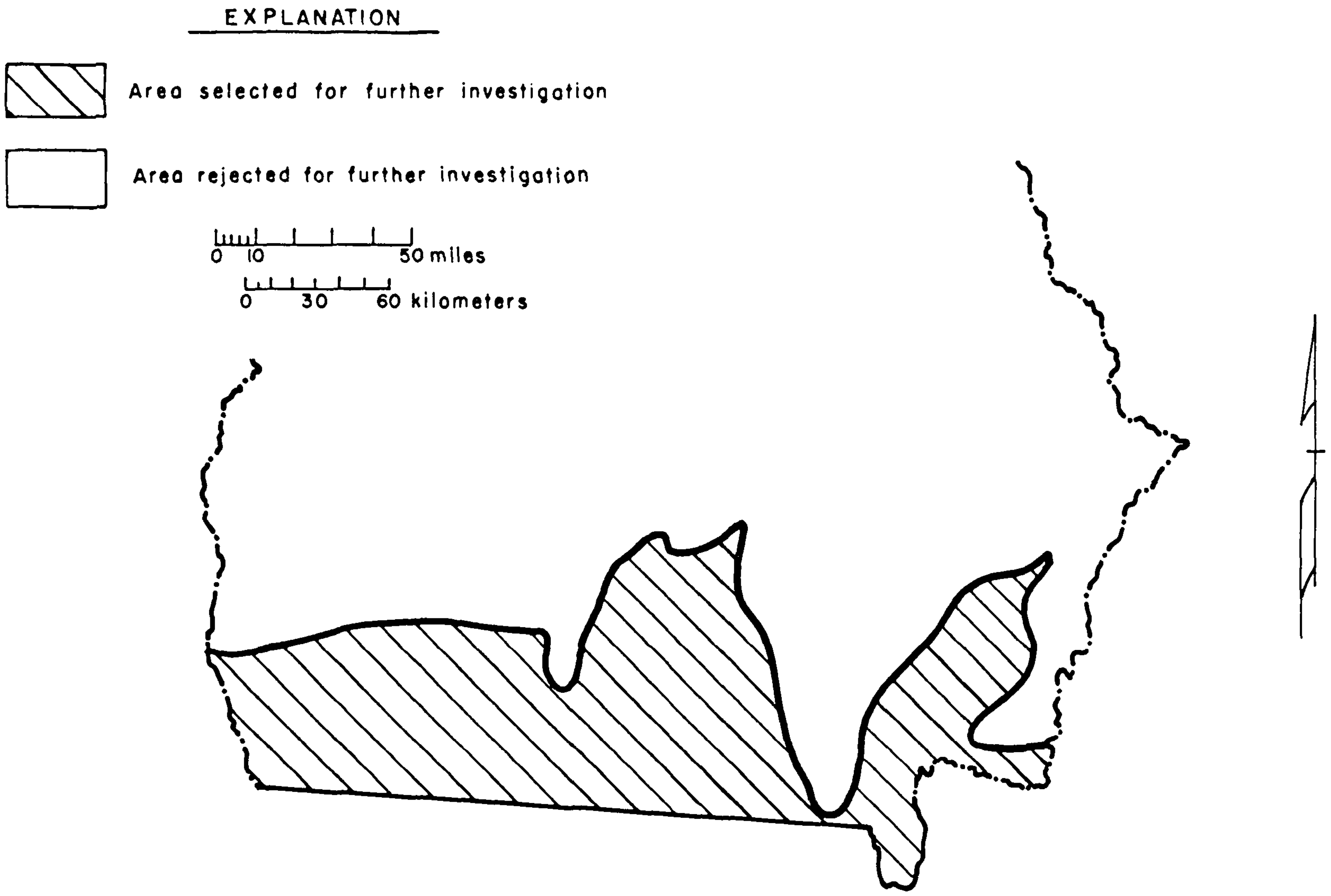

Figure 4. Area of waste storage potential, phase 1.

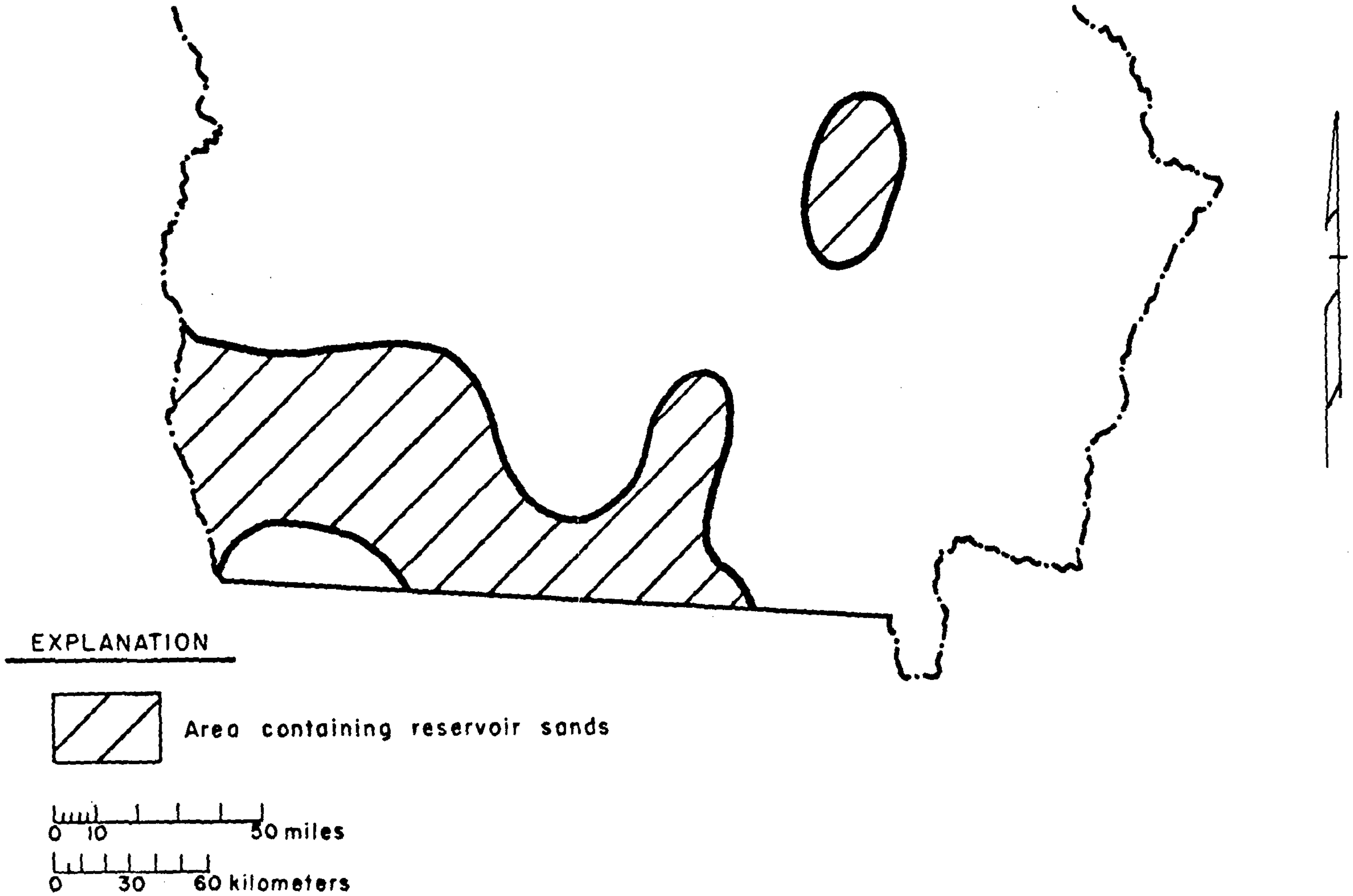

Figure 5. Areas with lower Cretaceous reservoir sands.

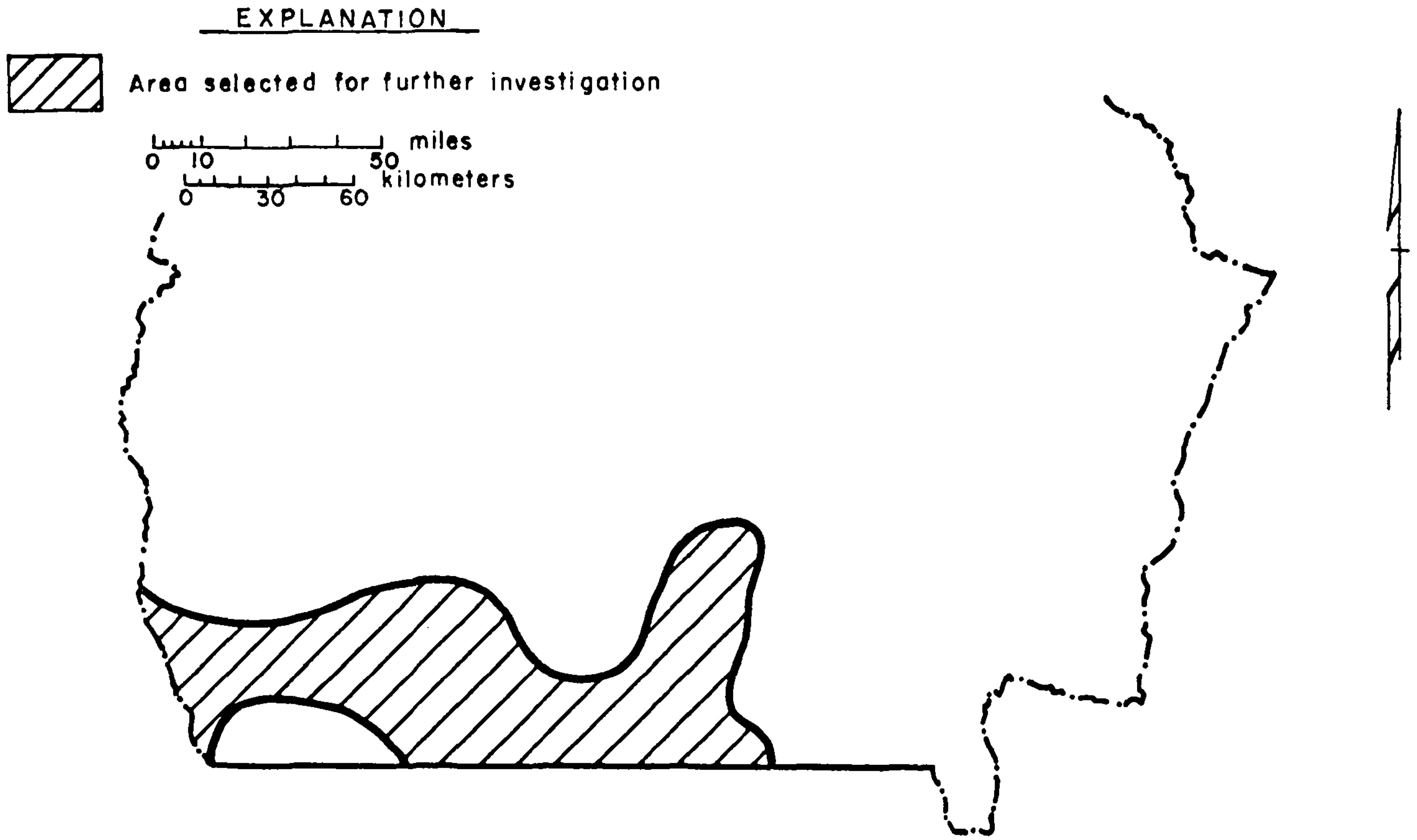

Figure 6. Area of waste storage potential, phase 2.

PAPER 11

TRACER METHODS FOR THE DETERMINATION OF GROUNDWATER RESIDENCE-TIME DISTRIBUTIONS

K. E. White

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1. INTRODUCTION

Tracers are used to determine the direction of movement of groundwater, its dilution and residence-time in an aquifer, and its spatial dispersion. Usually the hydrogeologist has little information about the detailed geological structure in the area of interest and will, therefore, require assurance that a given tracer accurately represents the behaviour of water or substances in solution or suspension.

The purposes of this short review are to compare the behaviour of chemical, radioactive and biological tracers, illustrated by examples selected from the literature, and to offer information which should prove useful to anyone planning tracer tests. Some of the data have been obtained from pilot-scale experiments and these are often of great value, but the uncertain composition of natural strata means that field and model tests must always complement each other. Theoretical concepts are not dealt with; the physics of liquid dispersion through porous media and the hydrodynamics of groundwater movements have been extensively described in the literature and may be referred to in the book by Fried (1) published last year.

In most applications a 'gulp' or 'slug' of tracer is introduced as a point, line or disc source and its appearance at natural or artificial points of outflow is monitored. Some examples of tracer curves from experiments conducted by WRC during 1975 are shown in Figure 1. These illustrate that valuable information can be obtained for the expenditure of only a few grammes of chemical or a few millicuries of radiotracer. Tracer curves of the type illustrated in Figure 1(c) usually indicate 'plug' flow whereas those of the type illustrated in Figure 1(d) and, to a lesser extent, in Figure 1(a), suggest that three-dimensional dispersion in the aquifer has taken place within a zone or pool, the volume of which can then be estimated as outlined elsewhere (2). Figure 1(b) illustrates the very slow percolation of tracer through an unsaturated zone. When part of the dispersion process takes place in an unsaturated zone, the tracer curve may be complex particularly where the depth to the water table varies. Tracer may then be released in stages to the saturated zone, giving a multi-modal curve difficult to distinguish from that caused by multiple pathways through the strata. It must also be remembered that non-appearance of tracer may not be taken as proof that an underground connection is impossible under other circumstances.

Naturally-occurring variations in the deuterium and oxygen-18 content of waters may reveal pathways and residence times in subterranean systems. Stable isotopes have not been dealt with here, but they have been adequately discussed at a recent symposium (3) where papers on gathering environmental data using the isotopes of hydrogen, carbon, nitrogen, oxygen and sulphur were presented. Some earlier papers of interest are those by Vogel and Ehhalt (4) on the use of carbon isotopes in groundwater studies; by Münnich and Roether (5) comparing carbon-14 and tritium ages of groundwater; by Tamers (6) on carbon-14 dating, and by Ericksson (7) on oxygen-18, deuterium and tritium.

2. TRITIUM

This radioisotope is of unique importance in groundwater studies. The dating of groundwater by comparison of tritiated water concentrations in samples with the levels in rainwater, following the massive injections of tritium into the atmosphere from thermonuclear explosions, was described by Smith (8). The partial test ban treaty has been effective and levels in rainwater are now only an order of magnitude or so above the pre-nuclear age level and about two orders below the peak levels that occurred during 1962-63. Figure 2(a), provided by AERE Harwell, shows the tritium content of rainwater over the past 20 years and its seasonal fluctuations (1 TU = 3.26 pCi/l). Because of the broad peak of activity spanning two decades and the seasonal fluctuations, it is not possible to 'date' a single water sample - a series of samples with time or depth are required to eliminate ambiguity by comparing profiles.

It is important to recognize that the period left for the determination of accurate date profiles using fall-out tritium is limited. This is illustrated by Figure 2(b) from a report, commissioned by the EEC, by Kelly and others (9) of the National Radiological Protection Board. The inventories of tritium in the environment from bomb-testing and natural processes with their respective bands of uncertainty are shown with the predicted quantities arising from nuclear power stations. These indicate that concentrations of bomb tritium are now approaching natural levels. It might thus be worth considering an intensive programme over the next 5 years, logging as many groundwater profiles as possible, particularly in areas likely to be of interest for water sources or waste disposal over the next few decades. Even if the counting equipment is not currently available, sampling could be carried out while establishments develop the expertise for counting tritium in the 5-100 TU range using techniques already described (10-13).

When the determination of low levels of tritium becomes too expensive, tritiated water can be used as a tracer, but it cannot be introduced in the same manner as that provided by natural climatic conditions. Injections of tritiated water for tracer purposes are relatively trivial compared to natural levels, and it is of interest to compare the minute radiation dose rates arising from tritium in the environment, Figure 2(b), with the level of several microrads per hour due to natural background gamma radiation. Tritium may thus be used as a tracer with little hazard to the public, but it should only be applied where the length or complexity of the study justifies its use as it may contaminate the system for decades.

When tritiated water is applied to assess the residence-time of water in the unsaturated zone, it should be injected below the grass or plant root zone to prevent losses by evapotranspiration. The depth and method of injection needs to be selected with care because migration rates may be less than one metre per year. A method for applying tritium in controlled quantities over an area would be to lift turves and implant a thin sheet or disc of frozen tritiated water prepared in the laboratory, replace the surface layers, and give the area a gentle watering.

3. OTHER RADIOACTIVE TRACERS

The most useful radiotracers for groundwater investigations are the halide ions, but the possibilities are limited by availability, price, and half-life. The essential properties of readily available tracers are shown in the table below.

Radioisotope (Stable Product)	Half-Life ($T_{\frac{1}{2}}$)	Use
I-132 (Xe-132)	2.3h	Short-term connection tests. I-132 may be repeatedly generated in mCi quantities from Te-132 generator ($T_{\frac{1}{2}}$ = 78 h). Excellent in situ detection.
Br-82 (Kr-82)	35.4h	Studies lasting up to about 10d. Cheap in curie quantities. Systems over 10^8 m^3 may be investigated. Excellent in situ detection.
I-131 (Xe-131)	8.0d	Studies lasting up to about 2 months. Expensive in curie quantities. Fair in situ detection.
I-125 (Te-125)	60.2d	Studies lasting up to about 1 year. Available in pre-packed quantities of 1 to 30 mCi. In situ detection by flow-through plastic scintillation head. X-ray emitter.
Cl-36 (Ar-36)	3.10^5 years	Pilot scale studies. Recovery and re-use possible. Available in vials of 0.25 mCi. In situ detection by Geiger or flow-through plastic scintillation counter. Cerenkov counting possible.

The use of iodide may be limited by a tendency for it to be adsorbed on organic matter so that results obtained in areas of unknown strata should be treated with caution. In pilot-scale tests at Grenoble, reported by Molinari and others (14), this year it was shown that iodine-131 and stable iodide behaved satisfactorily in comparison with tritium (Figure 3(a)), over a 13 m path-length of a laboratory aquifer made with alluvial material and operated under saturated conditions. Kaufman and Orlob (15) have stressed the importance of incorporating a sufficient non-active form of tracer as a carrier (Figure 4(a)). If, as their data suggest, the concentration of carrier needs to be in the mg/l range then the carrier itself could be detected under the right conditions (see Section 4) using an ion-specific electrode, making the need for the radionuclide questionable. However iodine-131, being a gamma-emitter has the advantage of detection when the tracer is contained within cores of solid material.

Several relatively long-lived isotopes which are readily available and may be applied in anionic form are sulphur-35 used as sulphate; cobalt-56, cobalt-58 or cobalt-60 used as cobalticyanide; sulphur-35 ($T_{\frac{1}{2}}$ 87 d) is relatively cheap but emits low-energy beta rays and must therefore be assayed by liquid scintillation counting. Cobalt-56 ($T_{\frac{1}{2}}$ 77 d) is expensive even at millicurie quantities but is one of the most prolific gamma-ray emitters known and is thus highly suited to in situ detection. Cobalt-58 ($T_{\frac{1}{2}}$ 71 d) is cheaper than cobalt-56 but less readily detectable. Cobalt-60 ($T_{\frac{1}{2}}$ 5.3 years) is cheap at curie quantities and readily detectable in situ. Sternau and others (16) have reported that potassium cobalticyanide is not absorbed to any appreciable extent in formations containing significant amounts of clay or in limestone, but Baetsle and Souffriau (17) found that both this compound and iodine-131 as iodide travelled at a velocity 5 to 10 per cent lower than that of water.

The technique of incorporating a cation into a stable complex anion offers a wider choice of half-lives and energy, and has been widely exploited using chromium-51 ($T_{\frac{1}{2}}$ 28 d) as the EDTA complex, although chromium-51 is a poor emitter of gamma rays. Knutsson and Forsberg (18) compared the behaviour of this tracer with tritium percolating through mixtures of 90 per cent sand and 10 per cent of a variety of minerals. They obtained good recovery except in the presence of iron-bearing material, when some delay was noted. The stability constants of some metal-EDTA complexes shown below are very high and therefore warrant further investigation as candidates for groundwater tracers.

Fe^{3+}	25.1	Cr^{3+}	24.0	Hg^{2+}	21.9	Lu^{3+}	20.0	Ni^{2+}	18.6
In^{3+}	24.9	Sc^{3+}	23.1	Ga^{3+}	20.5	Cu^{2+}	18.8	Y^{3+}	18.2

In particular those radionuclides that are cheap in curie quantities include:

indium-114 m ($T_{\frac{1}{2}}$ 50 d), scandium-46 ($T_{\frac{1}{2}}$ 84 d), mercury-203 ($T_{\frac{1}{2}}$ 47 d), gallium-72 ($T_{\frac{1}{2}}$ 14 h), lutecium-177 ($T_{\frac{1}{2}}$ 6.7 d), copper-64 ($T_{\frac{1}{2}}$ 12.8 h), and yttrium-90 ($T_{\frac{1}{2}}$ 69 h). In situ detection would be readily feasible with scandium-46, mercury-203, gallium-72, and copper-64. Iron-59 ($T_{\frac{1}{2}}$ 45 d) is readily detectable but expensive. Nickel-63 ($T_{\frac{1}{2}} \sim 100$ years) is a low-energy pure beta emitter.

Most uncomplexed cations suffer ion-exchange delays and probably the only cation worthy of consideration is sodium-22 ($T_{\frac{1}{2}}$ 2.6 years); this is readily detectable in situ but very costly at over £100 per millicurie. Sodium-24 ($T_{\frac{1}{2}}$ 15 h) is cheap in curie quantities and readily detectable, thus affording an alternative to bromine-82 in short studies of large systems of high permeability.

The disposal of effluents containing radioactive waste to the ground as practised at Hanford and Oak Ridge in the USA and Chalk River in Canada, has provided a wealth of information on the relative behaviour, in various strata, of many radioelements. In particular the nuclide ruthenium-106 ($T_{\frac{1}{2}}$ 1 year) has been shown to be worthy of consideration as a water tracer since it is difficult to contain in natural strata when released in the presence of nitric acid. This is a waste product of nuclear reprocessing so could be available in quantity, but ruthenium-103 ($T_{\frac{1}{2}}$ 40 d) which is very readily detectable in situ and cheap at millicurie levels is also available as a stock item as the chloride or nitrosyl complex.

It is worth remembering that many of the radionuclides found unsuitable as water tracers because of facile adsorption on solid surfaces, may be applied to indicate the direction of groundwater flow away from a borehole by location of the radial surface where the isotope has lodged. Suitable isotopes (for labelling solids), with data on their maximum permissible concentrations in water, main radiations and costs, have been listed elsewhere (2); this publication also includes data for many of the aqueous-phase tracers considered above. Details of the methods have been described by Fried (1) and by Halevy and others (19) in their review of borehole dilution techniques.

4. CHEMICAL TRACERS

When a chemical tracer is used, samples may be analysed in the laboratory by procedures developed to realize greatest detection sensitivity, or concentrations may be determined in situ by a device such as an ion specific electrode or conductivity probe. A third approach, that of neutron activation analysis, is suitable for some elements. It is, for example, possible to detect 10^{-8} mg bromine or sodium, 10^{-7} mg iodine or potassium and 10^{-6} mg chlorine in a sample. Cost or interference from other elements which may be activated are the main disadvantages but naturally-occurring trace elements, if their concentrations vary with time, could be exploited.

Since mineral lattices are negatively charged, anions are the obvious candidates for chemical tracers. In most groundwater investigations, fluoride, chloride and bromide ions may be considered of equal choice regarding their proven conservative properties, whereas iodide requires critical assessment. Fluoride and iodide concentrations down to about 0.02 mg/l are detectable by ion specific electrodes under ideal conditions. Samples may have to be treated to reduce the effects of interfering substances, but this could be carried out continuously using ionic buffers and precipitants for interfering substances. The logarithmic response of electrodes over several orders of magnitude in concentration is reliable, but a large portion of the working day may be taken up in calibration. However, new electrodes are being developed which promise greater stability or sensitivity and the present state of the art on a worldwide basis has been reviewed (384 references) this year by Buck (20).

Chloride concentrations below 0.1 mg/l are readily detectable, but applications of chloride will be of little benefit where background levels are high or variable. Fisher (21) found that levels in rainwater greater than 1 mg/l were confined to areas close to the Atlantic seaboard of the USA; levels greater than 0.5 mg/l being confined to areas within about 100 miles of the coast with a steady decrease in concentrations inland. Levels of sodium followed a similar pattern in absolute terms yielding a much higher ratio of sodium:chlorine than that found in sea water. At the Stevenage Laboratory, the analysis of rainfall since February 1975 has indicated a mean value of 11 mg/l with a standard deviation of 8.4 mg/l and range from 2.4 to 35 mg/l. Clearly, residence-times of chloride in the unsaturated zone might be quantifiable where such variations occur in a regular manner, so that concentration profiles may be compared.

The use of cations is probably limited to lithium, which is not readily absorbed, probably because it is the largest of the simple hydrated ions. Adsorption losses will depend on the dimensions of the crystal lattice and the particle-size distribution of the deposits concerned because of the larger specific surface areas of the smaller particles. An example was quoted by Levi and Miekeley (22) for the adsorption of caesium (Cs-137) on vermiculite. The exchangeable fraction was found to be only 10 per cent for a specific surface area of 7 m^2/g but 51 per cent for an area of 43.5 m^2/g. They also found that lithium ions in the same apparatus exchanged to the extent of 10 per cent whereas the figure for potassium ions was 40 per cent.

Studies on the behaviour of various pollutants, although they may well be lost by biological oxidation if oxygen is present, have shown that some, such as phenol, can give reasonable indications of water-retention times, as illustrated by Figures 3(b) and 5(b) (the latter reported by Gaillard and others (23)) where phenol compares well with tritium and iodide. Dextrose is another organic material which appears to be conserved, as shown in Figure 4(b), whereas the pesticide Lindane is delayed considerably - Figure 5(a). These curves also serve as a reminder that the residence-time of any particular substance, even nitrate, cannot be inferred from results using established water tracers. If it is important to be able to predict the fate of a substance, then that substance or a labelled form of it, should be used directly.

5. FLUORESCENT TRACERS

Fluorescent dyes radiating various colours are available, but the one most often used in hydrological work is fluorescein (or uranine). Since its fluorescent spectrum peaks at green wavelengths where the colour response of the human eye is at its most sensitive, this dye is very suitable for direct observation in clear water, although it is sometimes difficult to detect at low concentrations against a green background. Under these conditions it may help to place something white in the water (or withdraw a sample) and to view the water by transmission. Where the intensity of daylight is low or there is darkness, the fluorescence may be excited by using ultra-violet lamps. Schwille and others (24) employed this technique to trace the course of the infiltration front continuously from the soil (fine sand) surface to the water-table in laboratory columns. The uneven advance of the tracer fronts and their horizontal dispersion through the capillary zone, which in one case prevented the tracer from reaching the water table, were recorded in detail. Quantitative measurements are taken with fluorimeters provided with filters to accommodate dyes which fluoresce at different wavelengths, and facilities to allow a continuous flow to be monitored. Wilson (25) has described a system, powered by a portable generator, which can be used in the field.

Detection of radiotracers does not depend upon the state of the sample, but quantitative work in fluorimetry needs close control of temperature and composition. For example, it is essential that standards are made up in the same water as that being traced. It is particularly important to avoid the use of chlorinated tap-water which may quench the fluorescence considerably. Fluorescence displays a negative temperature coefficient and the effect may be as high as several per cent per degree centigrade for the rhodamine dyes. Precise temperature control is therefore required and the equilibrium working temperature of a fluorimeter may take some hours to achieve. Temperature correction data for rhodamine B, Pontacyl and fluorescein dyes have been given by Feuerstein and Selleck (26). One advantage of fluorescein over the rhodamine dyes is that it has a temperature coefficient almost an order or magnitude lower. It suffers higher photochemical decay but this should not be important for subterranean tracer work. Rhodamine B and fluorescein were found to be satisfactory over a range of pH values from about 5 to about 10 with rapid decrease in fluorescence below a pH value of 5. Pontacyl gave stable readings to a pH value of about 3. Feuerstein and Selleck investigated a range of environmental effects, including sorption by suspended solids and algae, and concluded that Pontacyl was the most suitable choice since it displayed a negligible uptake by suspended solids.

In one of their technical reviews, G.K. Turner Associates (27) report that Pontacyl is not manufactured now but that a comparable product, Sulpho Rhodamine B Extra* (C. I. Acid Red 52), is available. They found the cost ratio to be about 3:2:1 for Pontacyl, rhodamine WT and rhodamine B and the adsorption tendency to be in the ratio of about 1:1.5:4 respectively. Examples of the recovery curves of dyes passing through fine soils, shown in Figures 3, 4(b) and 5(a) indicate that dyes may fail to represent accurately the time-scale of water movement through such materials.

The stability of twelve fluorescent dyes was tested by Reynolds (28) under conditions of alternate saturated- and unsaturated-zone conditions, and he concluded that pyranine was most suitable to trace drainage water in acid soils provided sufficient was used to overcome lag effects. However, the dyes tested did not include Pontacyl or rhodamine WT. Pyranine was detectable for several months in a field test and was photographed in ultra violet light to trace drainage profiles. In the discussion of Inoue's paper (29), describing the use of 3 kg fluorescein to check the predictions of groundwater movement at an atomic energy site, two cases were reported where fluorescein and rhodamine B had been found after several years in the ground.

Fluorescent tracers have been assumed to be safe in use, but doubts as to whether they are carcinogenic may restrict their use in systems connected to drinking-water sources. Rhodamine WT is in widespread use in the USA and Canada and to date the only problem appears to be that pointed out by Wright and Collings (30), that the residues from the degradation of rhodamine dyes can cause an astringent taste in chlorinated drinking waters. An example of human intake restrictions has been given by Wilson (25), i.e. 0.75 mg/d for rhodamine B dye. This standard was set on a 'temporary' basis by the US Food and Drug Administration.

6. BIOLOGICAL TRACERS

In concept, the use of a bacterial tracer is attractive because the ability to isolate a single cell from a large volume of sample yields a sensitivity of detection which may exceed that possible with radioisotopes.

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*Lissamine Red 4B (supplied by ICI) is a second comparable product.

Wherever waters have been polluted by sewage, the direction of flow can be inferred by the enumeration of micro-organisms, including coliform bacteria, which can contaminate wells a considerable distance from the source of pollution. In cases where the source of such pollution must be identified, a tracer organism such as Serratia marcescens may be used. The Centre has used this tracer (31) to identify individual sources in pollution studies of coastal waters. Serratia produces red, pigmented colonies which are readily identifiable and a strain has been selected which has resistance to certain antibiotics which are applied to reduce the growth of other micro-organisms during incubation. It is possible to grow 10^{14} Serratia cells per day to a concentration of about 10^{13} per litre. Bacterial tracers need to be used with care and while the risks to health are usually low, they should not be ignored. For example, Serratia has often been used for demonstrations in colleges but has been implicated in cases of septicaemia by Dobson (32).

Wimpenny and others (33) have pointed out that the specificity of a bacteriophage for its host means that different phages can be used as tracers simultaneously to identify possible sources without any health hazard, as the organism is completely inert in the absence of its host. They compared Serratia marcescens with a lambda-like phage of E. coli and two yeasts for tracer work in the R. Taff and found the phage to be the most suitable. This phage is produced at concentrations of 10^{16} plaque-forming units per litre and visible plaques are incubated in about 5 h, so that rapid appraisal of dispersion in a sampling programme is possible. As bacteriophages have a covering which makes them insensitive to chloroform, the latter may be used to eliminate more sensitive natural populations of micro-organisms in the samples.

Gerba and others (34) have reviewed the survival of waste-water bacteria and viruses in soil. They found that the survival period of bacteria increases with decreasing temperature and decreases with acidity of the soil. They may survive for several months (even multiply if organic matter is present) but the factor most difficult to predict is the antibiotic activity of other soil microflora. In one case, coliforms in sewage pumped underground were isolated from observation wells up to 5 miles away for 3 months after they were introduced. The adsorption of bacteria and viruses was greater the higher the cation concentration, and the percolation of viruses through soil was no more reliable than that of bacteria although the antibiotic effect of other microflora was practically absent. In the range of pH values of most natural waters, enteroviruses retain a net negative charge.

Probably the cells of greatest size that have been used are lycopodium spores, which have a diameter of about 25 μm. These may be coloured by dyeing and used to investigate cavernous and fissured limestone, as reported by Smith and Atkinson (35). The survival of living cells depends, to some extent, on their ability to move towards or stop at sites presenting favourable nutrients, temperatures, surfaces, etc. Blakemore (36) reported that some bacteria even have lines of iron-containing cells, making them capable of magnetic-field detection and it is suggested the purpose may be to enable them to 'swim' downwards where the supply of nutrients might be higher. These considerations suggest that bacteria cannot always be regarded as impartial tracer units in the same way as lifeless ions, particularly in groundwater where water movements may be too slow to carry them along.

7. DISCUSSION

It is agreed that tritium in the form HTO is the outstanding water tracer, challenged only by water containing deuterium or oxygen-18, but these heavy atoms may not constitute the 'perfect' water tracer under all conditions. In chemical terms, the presence of one or two additional neutrons in the nucleus of one of the three atoms of the water molecule makes little difference, but the physical properties may be changed significantly. For example, heavy water may become concentrated in lakes due to preferential evaporation of the lighter molecules as reported by Tongiorgi in the discussion of the paper by Vogel and others (37) which gave data on the deficit of deuterium and oxygen-18 in rainwater compared to ocean water. The isotopic enhancement of deuterium levels in soils has been discussed in detail and some valuable experimental data were presented by Zimmerman and others (38). Also the fact that tritium may be concentrated by electrolysis shows the slight differences in physical properties.

When one end of the symmetrical water molecule is twice (DHO) or three times (HTO) its normal mass, the modes of vibration, illustrated by Figure 6(a), will clearly be more perturbed than when the central atom is heavier than normal (H_2O^{18}) and tritiated water in particular is less likely to represent the behaviour of normal water molecules in situations where evaporative losses are high, where near-freezing temperatures exist or dispersion takes place by the movement of monomolecular layers of water. Kaufman and Orlob (15) compared the passage of tritium with chloride in sandy loam columns and their results, shown in Figure 6(b), serve as a caution in regarding any tracer as 'perfect'. Tritium lagged and they interpreted the area between the chloride and tritium fronts as the volume of 'exchangeable water' or 'solid water' associated with the medium (their terminology). Chloride tracer was assumed to have entered all connected pores containing free water and they thought it probable that tritiated molecules had entered the media granules, replacing water adsorbed on the surface of clay minerals present or between the unit-cell layers of the clay colloids. Also, exchange probably occurred between the tritiated water and water adsorbed as dipoles on the exchangeable cations. These are valuable and thought-provoking results with regard to the acceptance of HTO as the 'standard' water tracer, as HTO will exchange with H_2O, T^+ ions will exchange with H^+ ions, and OT^- ions will exchange with OH^- ions.

It is not being suggested that when differences are detected between tracers, the one which lags is more suspect than the leading tracer - rather that it might be considered prudent, whenever clay is present or suspected, to use at least two and possibly three of the least-sorbable tracers available. Careful thought should then be given to the possible interactions between the tracers themselves as well as between the tracers and the groundwater or minerals present, in order to decide whether a mixed tracer 'cocktail' should be injected or sequential injections applied, separated for example by intervals of one per cent of the estimated mean retention-time.

The mass, structure and approximate size of some chemical, fluorescent and biological tracers (shown in Figure 7), suggest that water molecules may be able to diffuse into zones where few of the tracers can penetrate. It is clear that even phage tracers may be readily trapped in fine media and the bacterial tracers can form a partial seal in fine soil to delay another tracer in any subsequent investigations. The dye molecules are more than two orders of magnitude smaller than coliphages and are relatively large compared to the simple ions but comparable in size to some of the hydrated ions. Sizes of hydrated and bare ions are illustrated as the ion may be released from its hydration sheath to diffuse at the crystal surface.

The percolation rate of even the best tracers will depend on the environmental conditions as well as the soil or matrix type and results must cite the conditions. For example, in northern countries the percolation of groundwater in similar soils depends upon the severity of weather conditions, particularly diurnal or seasonal variations in periods of frost, and results cannot therefore be applied to predict behaviour at sites where environmental conditions may not match those where experiments were conducted.

The tracer recovery curves presented and the information reviewed allow certain conclusions to be drawn with regard to the selection of tracers for various media and various kinds of test. One aspect which ought perhaps to be given more attention is that of care in using long-lived tracers, whether radioactive or otherwise, which have any doubt at all attached to them with regard to their safety in the local environment. There is doubt about the safety of bacterial tracers and fluorescent dyes and the latter may certainly be as long-lived as tritium in the ground. Long-lived isotopes, bacteria, dyes and some chemicals should not be used in quantity unless preliminary tests give adequate evidence that a system of long residence-time is under study and only then after checking with interested parties that long-term contamination will not cause problems later. There have been many reports of the use of long-lived materials in systems having residence-times of a few days, even hours in some instances, and this should be regarded as irresponsible, not only on health grounds but from the point of view that contamination of the system may prevent further studies. The very short-lived radioisotopes are ideal for preliminary tests as they are completely self-cleansing within the system. It may be prudent in some situations to carry out several preliminary tests using such tracers, increasing the quantity of tracer in stages. Otherwise, established harmless substances such as common salt, iodide or lithium might be used prior to the application of the other tracers.

8. CONCLUSIONS

(i) There are only a few more years during which advantage can readily be taken of the enhanced tritium in rainfall levels caused by nuclear-bomb testing (Figure 2). New programmes should therefore be considered to cover the next 5 years or so in order to collect ground-water age data, as revealed by the tritium profile, particularly for any areas likely to be of interest over the next few decades.

(ii) The unique value of tritium has been established but it cannot be assumed that it (or deuterium and oxygen-18) will faithfully represent the behaviour of normal water molecules under all conditions. It may be important to obtain evidence from other tracers, particularly when strata containing clay are being examined or where severe evaporative or freezing conditions occur.

(iii) When the use of two or three tracers are considered necessary to determine residence-time distributions, for example in clay, careful thought should be given to the alternatives of injecting mixed tracer 'cocktails' and sequential applications because some tracers may interact with each other or the components of the aquifer to cause misleading results.

(iv) When tracer studies are contemplated in systems of capacity, such that kilogrammes of dyes or chemicals, curies of radioactivity or very high numbers of bacteria have to be used, preliminary tracer experiments should be regarded as essential to indicate the rate of movement away from the injection zone and to check that no rapid transit paths to the open local environment exist.

(v) The most suitable tracers for preliminary studies, or short-term connection tests, are the short-lived radioactive tracers because their trivial mass and self-cleansing properties leave the system exactly as it was in every way. Otherwise relatively harmless materials such as common salt or iodide can be used, provided measures are taken to avoid density effects. Attempts to avoid the use of short-lived radioisotopes for emotive reasons may result in the use of materials which are potentially more hazardous or which may cause long-term local contamination.

(vi) Prediction of the residence-time of chemical compounds may not be possible from the results of experiments using water tracers alone.

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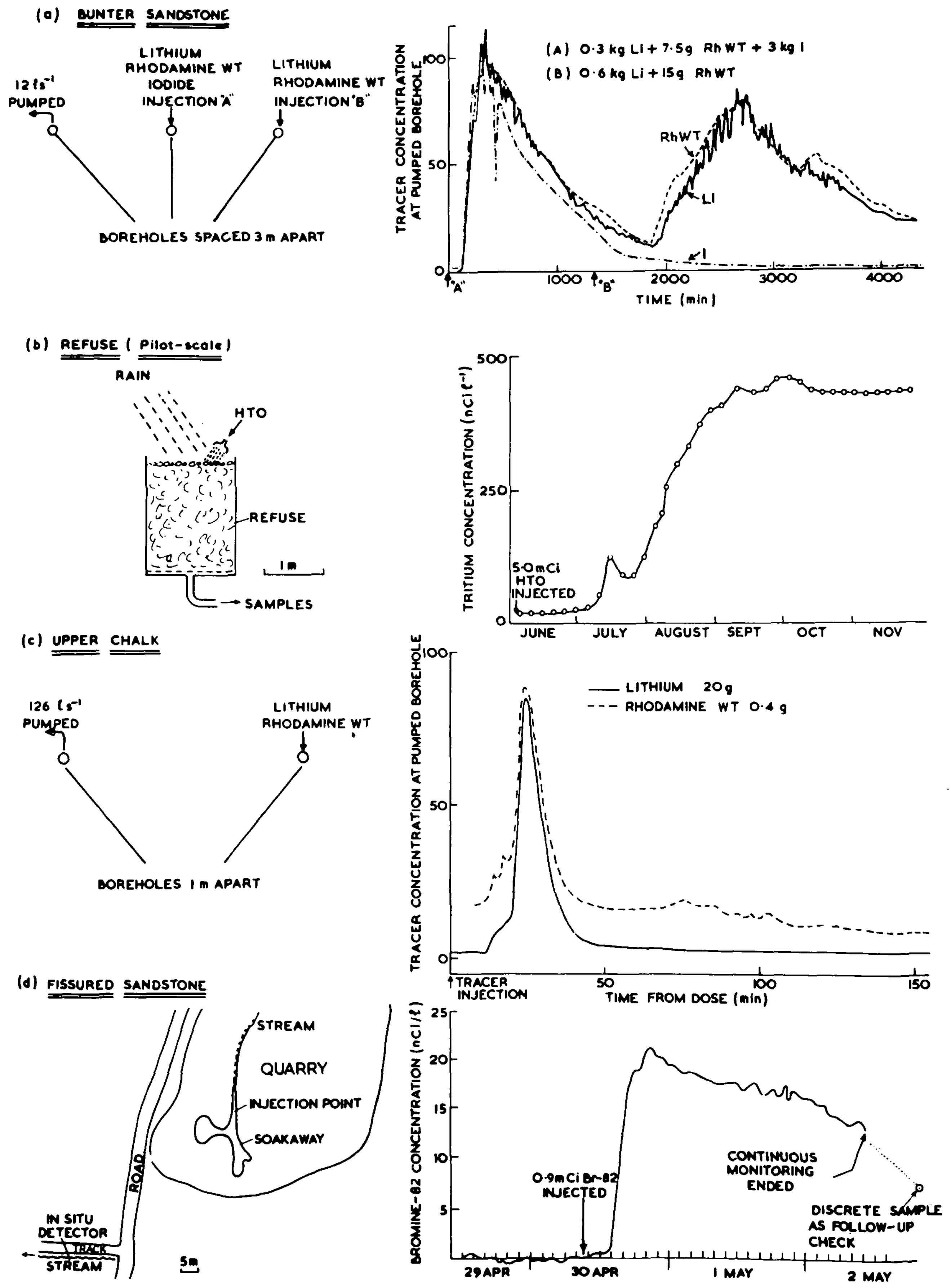
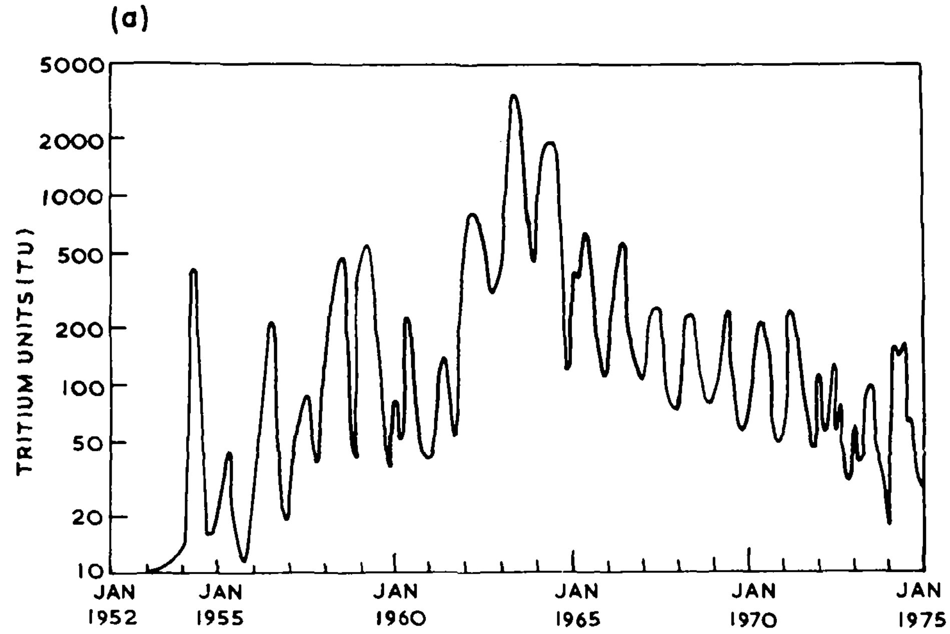


Figure 1. Examples of groundwater tracer experiments carried out by WRC during 1975



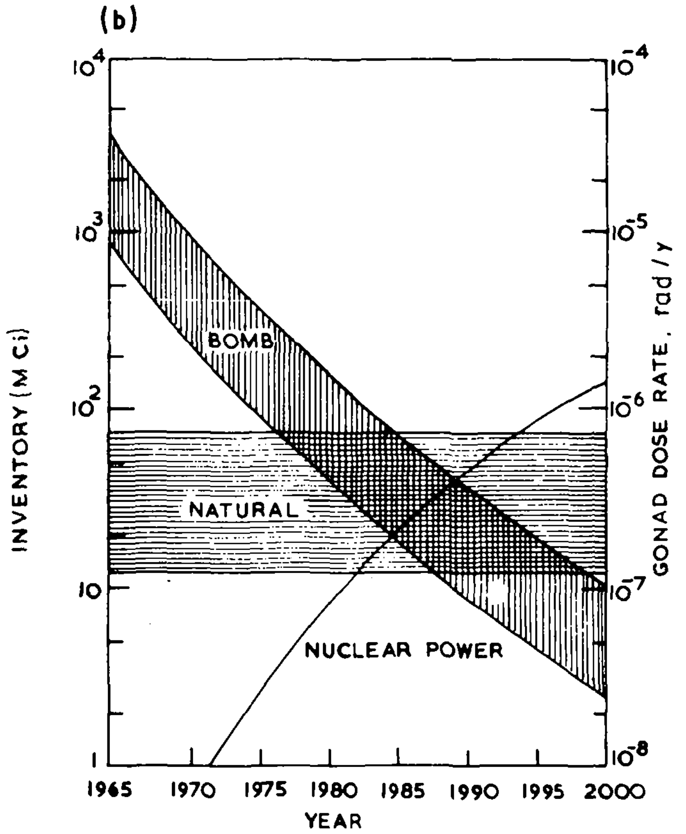


Figure 2. Tritium data. (a) Concentration in UK rainfall.
(b) Inventory in waters of the Northern Hemisphere. (Ref. (9).)

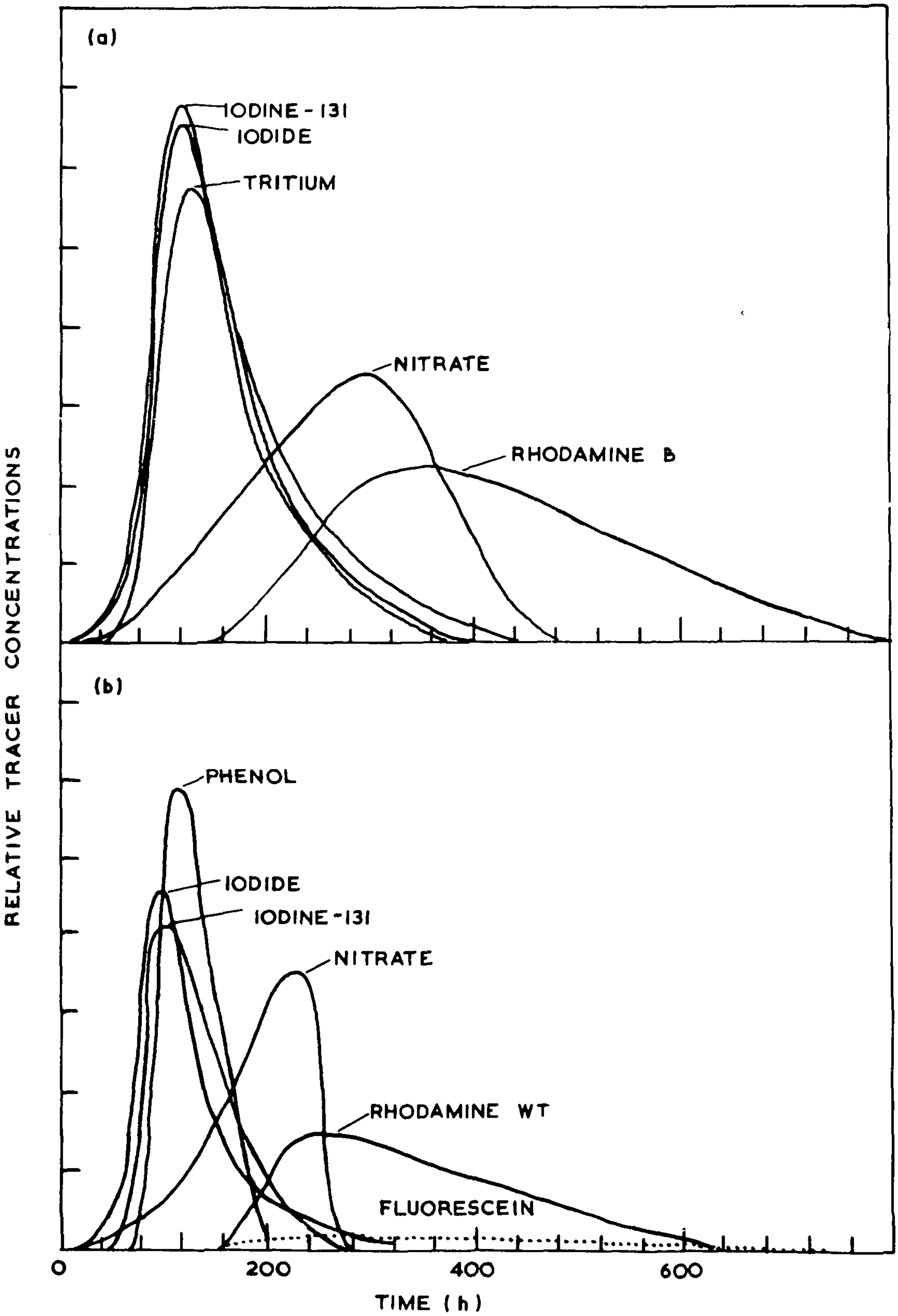


Figure 3. Comparison of residence times of various tracers and pollutants in alluvial deposits (Ref. (14)).

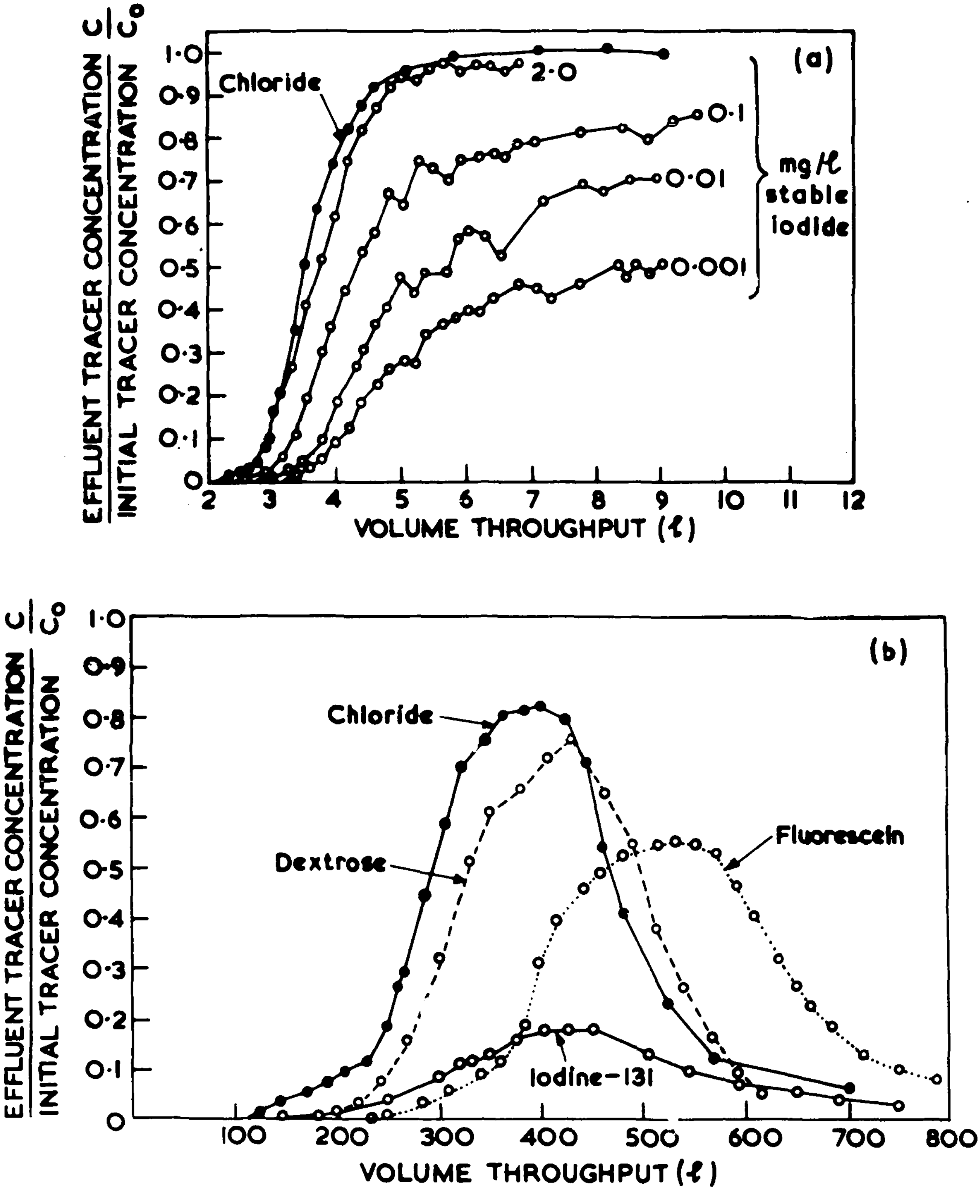


Figure 4. (a) Influence of stable iodide on the passage of iodine-131 through loam.
(b) Passage of several tracers through loam (Ref. (15)).

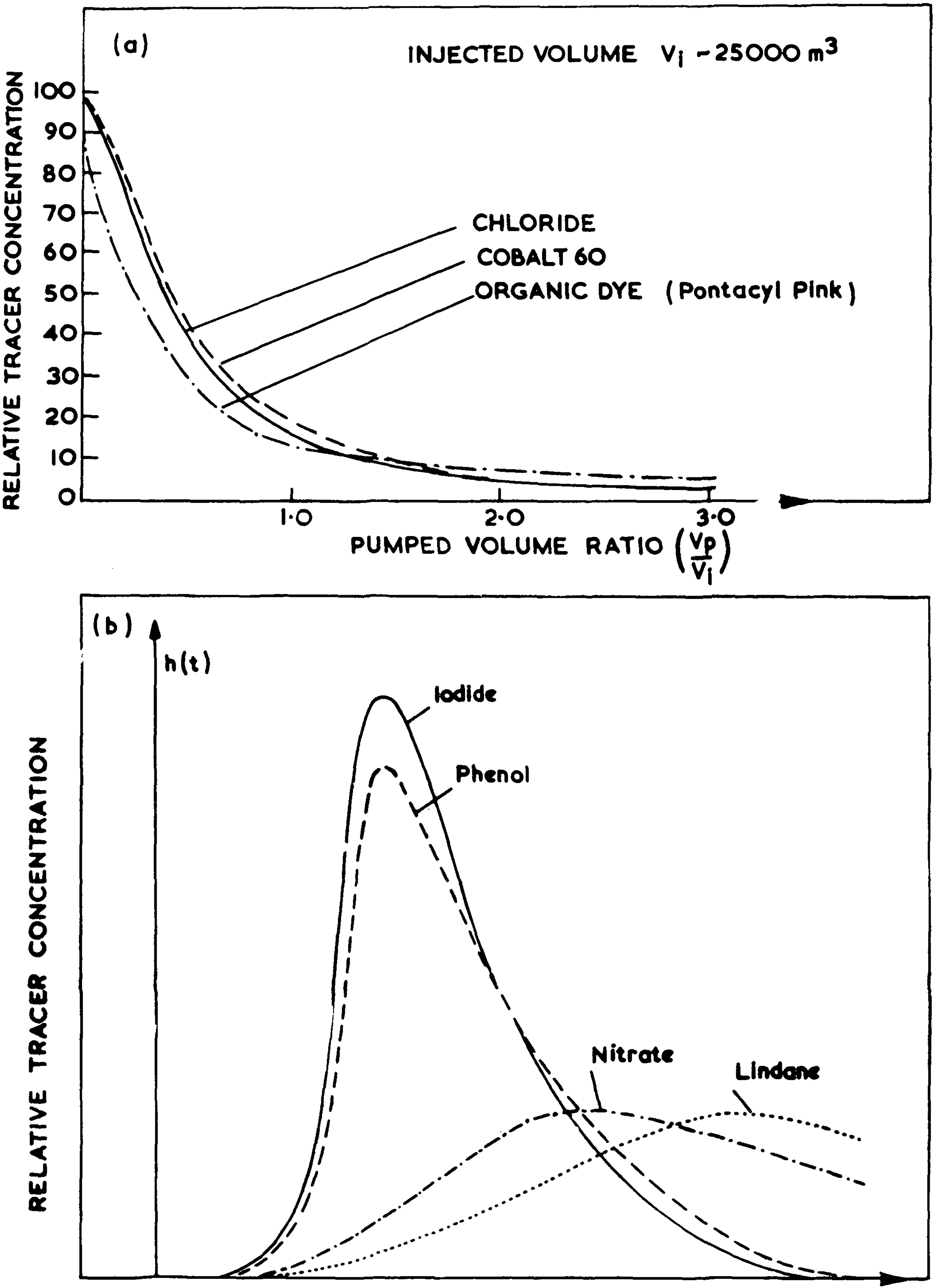


Figure 5. (a) Breakthrough curves from an injection-pumping test in a well in limestone formations (Ref. (16)).
(b) Passage of three pollutants through alluvial deposits compared with iodide (Ref. (23)).

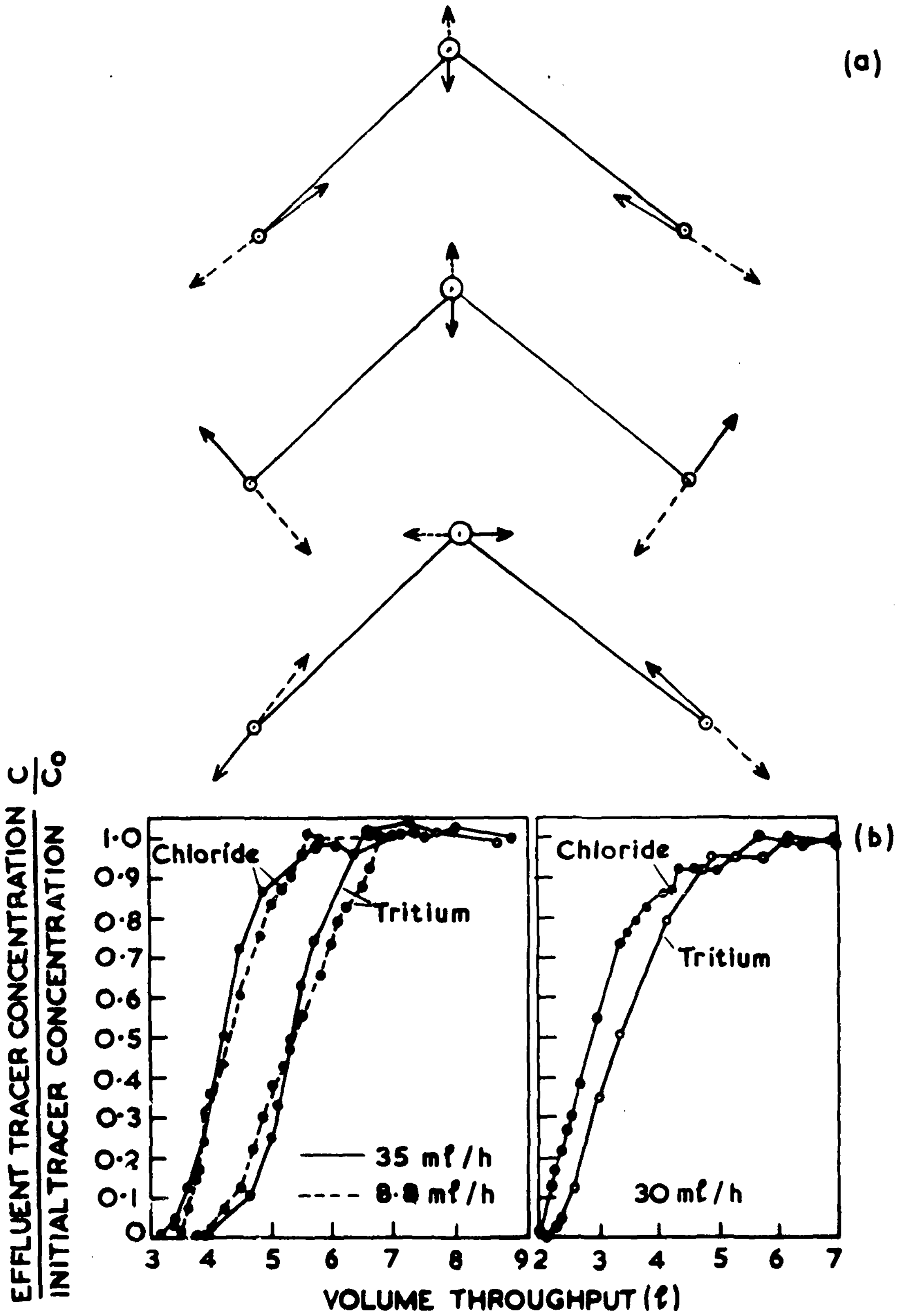


Figure 6. (a) Modes of vibration of the water molecule.
(b) Passage of chloride and tritium through loam (Ref. (15)).

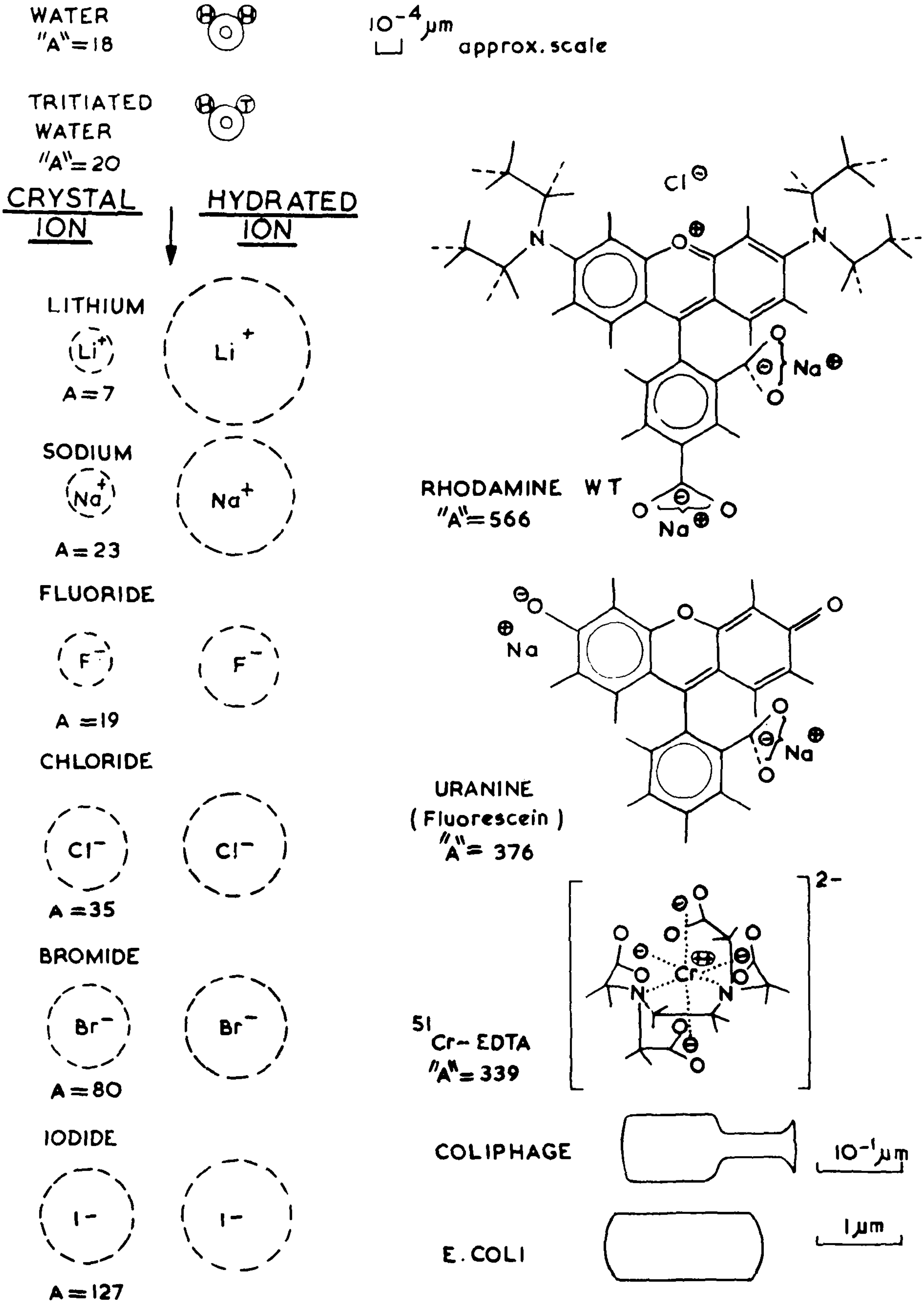


Figure 7. Comparison of the structure, mass and approximate scale of various tracers with the water molecule.

PAPER 12

FIELD MEASUREMENTS OF DISPERSION COEFFICIENTS IN THE UNITED KINGDOM

D. B. Oakes and K. J. Edworthy

1. INTRODUCTION

The techniques of groundwater quality modelling to predict the movement of pollutants through aquifers are well established (1, 2). The application of these techniques to real problems has been limited in the past by the very demanding data requirements of such models. Two processes, convection and dispersion must be described in any study of pollutant transport. The convective flux of contaminant results from groundwater seepage, so that a quality model requires pre-knowledge of groundwater flows, which may be obtained, for example, from a groundwater flow model. Dispersion is the mixing of miscible fluids resulting principally from the variability of fluid particle velocities which occurs in flow through porous media.

The dispersivity of an aquifer material may be measured in laboratory or field tracer experiments, or may be estimated by matching model response to observed regional quality variations. The latter technique requires reliable estimates of regional groundwater flows which will depend on the accuracy of the groundwater flow model. In some instances regional history matching has led to the estimation of very large dispersivities, and the question must be asked whether these values are realistic or whether they are related to deficiencies in the groundwater flow model. The estimation of aquifer dispersivity by carefully controlled field experimentation must be considered a pre-requisite of quality model studies. This paper describes two experiments in the Triassic Sandstone aquifer of Nottinghamshire to investigate the mechanism of dispersion, and to provide values of dispersivity for use in regional quality studies. Additionally, it was intended that some comparison of the suitability of the various tracers used might be made.

For a description of other field techniques available, the reader is referred to Fried (2). In general, however, field estimation of dispersivity requires the observation of tracer movement in a well defined flow field so that techniques will often need to be tailored to meet particular field conditions.

2. MECHANISMS OF DISPERSION

Fried (2) attributes to dispersion 'all the physical phenomenon governing the evolution of a transition zone when one fluid in a porous medium is displaced by a second, miscible fluid'. More generally, the mechanism of dispersion is described on a microscopic scale as shown in Figure 1. Dispersion results from the variability of molecular velocities through the pore space, and the tortuosity of the flow paths. This process may be described on the macroscopic scale by an equation of the form:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x} \qquad \ldots\ldots\ 1$$

valid for one-dimensional flow and dispersion where

c = concentration of pollutant or tracer (ML^{-3})
u = mean pore velocity (LT^{-1})
D_L = longitudinal dispersion coefficient (L^2T^{-1})

Experimental evidence has suggested (1) that in general groundwater flow problems D_L may be expressed:

$$D_L = \alpha_L u \qquad \ldots\ldots\ 2$$

where α_L = longitudinal dispersivity (L) and is a property of the medium.

On a regional scale the microscopic dispersion effects will be enhanced by large scale heterogeneities of the aquifer. For example, consider a layered medium as shown in Figure 2 in which groundwater flow is strictly horizontal under an imposed gradient i. There is no mixing between layers and, for the purposes of this analysis, no longitudinal dispersion within each layer. A slug of tracer injected over the full saturated depth will be convected without dispersion as shown in Figure 2. If the porosity θ is uniform, and the distribution of horizontal permeabilities is normal with mean $\bar{K}$ and variance σ^2, then it may be shown that the movement of tracer to a fully penetrating observation well is described by Equation 1 with an equivalent dispersivity given by:

$$\alpha_L = \frac{1}{2} \theta \sigma^2 i t/\bar{K} \qquad \ldots\ldots. 3$$

Fried (2) has derived an expression for the asymptotic form of the longitudinal dispersivity in a layered medium with mixing between layers. As the mixing between layers, described by the transverse dispersivities, tends to zero, Fried's formula for equivalent longitudinal dispersivity tends to infinity, in agreement with Equation 3. As transverse dispersivity increases in Fried's model, so does the equivalent longitudinal dispersivity tend towards the depth averaged longitudinal dispersivity of the layers. In a similar fashion, the dependence in Equation 3 of α_L on time is expected to decrease as interlayer mixing increases. This dependence is important because when dispersivity is time-invariant the dispersion effects become less and less important compared to convective effects as time increases (2), so that when large times are considered dispersion may often be ignored. This will not be the case when a relationship such as Equation 3 holds.

It is clear that dispersivity is a function of scale and possibly of time, so that the values of dispersivity used in groundwater quality models must be related to the scale of problem studied and the mechanisms of dispersion active in the aquifer. In a 2-d representation of pollutant transport, the appropriate values of dispersivity will depend on the depth of contamination. In a 3-d model, the dispersivity values used should relate to the dimension of the spatial discretization. To obtain suitable data for use in groundwater quality models, and to investigate the importance of large scale heterogeneities, the Water Research Centre undertook some experiments in the Bunter Sandstone aquifer at Clipstone, near Mansfield. The site, which is particularly well instrumented is described below.

Two experiments were carried out, one to measure dispersivities in narrow, well defined layers of the sequence, and the other to measure the effective dispersivity of the full penetrated depth.

3. WATER RESEARCH CENTRE EXPERIMENTS

The Clipstone experimental site near Mansfield is situated within Forestry Commission land (NGR 603 623) and was used by the Water Resources Board during 1971 - 73 for a series of artificial groundwater recharge experiments (3). To monitor groundwater level changes in sufficient detail during these experiments, eleven observation wells were constructed in the vicinity of the recharge well (see Figure 4). A recharge supply of up to 53 l/s of treated potable water was available and the recharge well was equipped with a submersible pump capable of abstraction at a rate of up to 19 l/s.

The site is underlain by the Lower Mottled Sandstones and Pebble Beds of the Triassic Bunter Sandstone formation. These rocks are typically fine-to-medium-grained, poorly cemented orthoquartzites (4). This is true at this site where the above lithologies predominate; also within the 65 m succession penetrated here are thinly-bedded micaceous silty sandstones and siltstones, and in the coarser range some medium to very-coarse grained slightly pebbly sandstones with clay pellets. Cross-bedding, common in the Bunter Pebble Beds, does not appear to be an important feature here. All the sandstones have a small ferruginous clay content which ranges in colour from pale pinkish-brown to dark red-brown, and may constitute up to 2% or more by weight.

Texturally the sands are sub-rounded to sub-angular and generally well-sorted. Grain-size analyses carried out on samples from the recharge well and observation boreholes 5 and 10 indicate that the typical sandstone at this site is positively skewed and leptokurtic with a mean grain size of 1.43 ϕ (0.37 mm). This is slightly larger than the average size of a range of sandstones taken from drilling samples at Edwinstowe nearby, where average grain size is significantly less than 0.3 mm. That part of the succession penetrated at the Clipstone site to 65 m depth shows relatively wide lithological differentiation so that the finer-grained deposits tend to be slightly more argillaceous and the coarser-grained lithologies slightly coarser with a smaller clay content.

Selected sedimentary parameters determined from grain-size distribution are compared in Figure 5. The properties themselves are of intrinsic interest in indicating the textural uniformity of the succession penetrated, and are also of value in allowing more complete comparison with values of dispersivity obtained by other workers. It can be seen that the ϕ-deviation measure (5) is centred on about 0.6.

Physical and hydraulic properties of selected core samples were measured by the Institute of Geological Sciences for the Water Resources Board. There is a range in horizontal hydraulic conductivity between 0.21 m/d and 11.92 m/d, and the average value (graphic mean) is 2.70 m/d. Similarly the mean porosity is between 27 to 28%. Aquifer tests show that the transmissivity of the aquifer here is about 190 m^2/d and that the long-term specific yield is of the order of 18%.

Natural groundwater level was about 38 m below ground surface (approximately 68 m A. O. D.) at the start of the experiments. Groundwater flow is towards the east at a gradient of 0.01. The aquifer is essentially phreatic but contains a number of less permeable strata which act as partial aquicludes as the lithologic description will have indicated.

The outline plan for the first experiment was as follows:

(i) Recharge, using the potable mains supply water previously used for recharge experiments, would be started about two weeks before tracer injection to allow equilibrium to be attained in and around the recharge well. The pump would be tested at the same time.

(ii) Using geological and geophysical log information, intervals of relatively low and relatively high 'apparent' permeability would be selected in boreholes 3 m and 6 m from the recharge well.

(iii) Instruments to measure the tracer concentration in the pore water during the course of the experiment would be placed in the boreholes adjacent to each of the intervals (selected as in ii).

(iv) During pumping the discharge would be monitored to allow the recovery of the injected tracer to be assessed.

3.1. RADIOISOTOPE TRACER EXPERIMENT

To allow in situ measurement in the observation wells, Harwell Laboratories advised the use of a γ-emitting radioactive tracer and Br-82 was selected. Laboratory tests at Harwell had shown that bromine as an anion was taken up to the extent of 4% only at concentrations of 0.5 to 1.0 mg/l, when shaken with a slurry of Bunter Sandstone for 8 hours. In natural groundwater, with 50 to 60 mg/l of chloride, it was felt that losses under recharge conditions would be minimal. Estimates of the rate of migration of recharged water into the aquifer indicated that by using observation wells at 3 m and 6 m distance from the recharge well, the field-work could be completed in about 3 days, the period agreed with the Forestry Commission and the Severn-Trent Water Authority. In relation to this also, with a half-life of about 36 hours, Br-82 was ideally suited as tracer.

Intervals suitable for monitoring were selected at the levels shown in Figure 6. The objective was to determine the change in tracer concentration in the pore-water immediately about the borehole so that the influence of the annulus of free water around the counting instrument in the borehole was to be avoided as far as possible. To ensure this, polyurethane foam cylinders were cast around the counters, moulded by polythene bags, and shaped by a thin-wire frame. The counters could just be moved in the boreholes, but the remaining annulus was reduced, it is estimated, to less than 10 mm. Counters were sodium iodide crystal scintillation units housed in 100 mm diameter brass containers, with internal collimation.

Background natural γ-activity profiles were measured in boreholes 1, 5, 7 and 10 and the counters set to the depth shown in Figure 6. Only the counter in borehole 1 lacked a polyurethane foam shield, and from this counter and the one in borehole 10 periodic measurements were made; at the other holes, Nos 5 and 7, continuous chart records were taken.

Approximately 500 m Ci Br-82 as 10 g of KBr was used dissolved in 3.03 l of water after sequestering any free bromine with 5 g of sodium thiosulphate. Two 1 ml samples were retained for detector calibration and injection of tracer at a constant rate was carried out over a period of 8 hours. A recharge rate of 26 l/s was maintained throughout the injection and recharge at this rate was continued for a further 14.13 hours.

Abstraction at the rate of 1230 m^3/d was started 25 minutes after the end of recharge and the activity of the abstracted water was measured by diverting some of the pumped water, at the rate of approximately 0.4 l/s, through a 0.22 m^3 cylindrical plastic container in which the counter was suspended centrally. The pump was shut-down after 22.6 hours as agreed with the landowners, when significant amounts of tracer were still being recovered. Recovery of tracer was estimated at 28%.

Measurement of activity was carried out in boreholes and abstracted water during both recharge and abstraction.

3.2. DYE AND CHEMICAL TRACER EXPERIMENTS - JULY 1975

In a second period of field experimentation during Summer 1975, the organic dye rhodamine WT, lithium as the chloride and potassium as the iodide was used. It was intended that these experiments should continue until most of the injected tracer had been recovered. The plan for the experiment was as follows:

(i) To pump at a constant rate of about 1000 m^3/d for 10 days before the start of injection to attain equilibrium conditions as near as practicable.

(ii) Inject a mixture of the above three tracers in an observation well at 3 m radius.

(iii) After the tracer arrival from 3 m had been satisfactorily identified, it was decided to inject a mixture of rhodamine WT and LiCl only at 6 m radius. In this way tne '3 m' tail could still be identified.

By using these three tracers under identical conditions it was hoped that some comparison of performance might be made. A bulk value for dispersion was sought to augment the values measured for thin layers under recharge conditions.

The first injection of 6 g of rhodamine WT, 4 kg of KI and 2 kg of LiCl in aqueous solution, was made over a period of 15 minutes with borehole No. 7 . Groundwater and dye were mixed thoroughly using a simple plunger system. A second period of injection lasting 10 minutes was made 22.5 hours after the end of the first into borehole No. 5 at 6 m from the pumped recharge well. Twelve grams of rhodamine WT and 4 kg of LiCl was added to the groundwater, and mixed in the same way.

Dye concentration in the abstracted water was measured using a flourometer linked to a continuous chart recorder. Discrete samples were taken for later laboratory analysis, for Li^+ and I^-.

The abstraction rate was maintained at 1025 m^3/d for the duration of the experiments. Tracer recovery estimated for lithium was 97% and for iodide ions was approximately 67%.

Dispersion data for the other principal British aquifer, the Chalk, has also been sought. Tracer tests in the Chalk aquifer have proved more difficult to undertake since existing abstraction wells are generally acidized during development. Experiments have, however, been run at two sites in Sussex where this was not done, using rhodamine WT and lithium. Flow through fissures between the specially-drilled tracer dosing boreholes, each 6 m from the pumped well, was extremely rapid and at neither site was it reasonable to calculate dispersion values which could be considered representative. Experiments using larger volumes of the aquifer are in hand.

3.3. RESULTS AND INTERPRETATION

An interpretation of the experiments is obtained by comparing the field results with results generated by a conceptual model of the flow system. The conceptual model is necessarily a simplification of the real system but should incorporate all the important flow mechanisms of the prototype. In this case, the model assumed horizontal, radial flow, equivalent to recharge to, or discharge from, a fully confined aquifer. Changes in saturated thickness were therefore ignored. Under these conditions the equation describing the movement of a tracer is given by:

$$\frac{\partial c}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (\alpha_L r u \frac{\partial c}{\partial r}) - \frac{1}{r} \frac{\partial}{\partial r} (ruc) \qquad \ldots\ldots\ 4$$

where r = radial distance (L) and the other parameters are as already described.

Under steady flow conditions, as were established in the field experiments, we have:

$$u = \pm \frac{Q}{2\pi b \theta} \frac{1}{r} = \pm \frac{A}{r} \qquad \ldots\ldots\ 5$$

where $\pm Q/b$ = the discharge (-) or recharge (+) per unit depth.

It is apparent that in the recharge experiments the discharge per unit depth will not be known for the horizons of investigation, although the mean value will be known.

An approximate analytical solution has been obtained for Equations 4 and 5 under recharge conditions (6), and has been used by a number of workers to derive dispersivity values from field experiments (2, 7). However, it may be shown that the approximations used in the derivation of this analytical solution limit its usefulness to cases where $\alpha_L/r < 0.025$, r being the radius of observation. It is apparent that the analytical solution of Hoopes and Harleman is of little use in the majority of field investigations.

Equations 4 and 5 were, therefore, solved numerically by the method of characteristics (8) which prevents the numerical dispersion introduced by other methods. The two mechanisms of convection and dispersion are treated separately in this method with the convective transport handled by moving the grid points according to the groundwater flow velocities. The problem is most conveniently treated by using a grid of mesh points as shown in Figure 3. The grid disposition is such that during one time interval each mesh point is convected to the exact location of an adjacent mesh point. The mesh points therefore appear stationary with new points being introduced into the system at the well face under recharge conditions and at the outer boundary under discharge conditions. Mesh points are removed from the system at the well under discharge conditions and at the outer boundary under recharge conditions. Redistribution of concentration due to dispersion is estimated at each time step by solving the equations:

$$\frac{\partial c}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (\alpha_L r u \frac{\partial c}{\partial r}) \qquad \ldots\ldots\ 6$$

$$u = \pm \frac{A}{r} \qquad \ldots\ldots\ 7$$

The method of solution is illustrated in Figure 7. As with the analytical solution of Hoopes and Harleman, the numerical solution depends on two parameters, α and A. These parameters were estimated for each experiment by matching the numerical solutions to the field results. Essentially α determines the shape of the breakthrough curve, and A its time of arrival. The time of arrival is also dependent on α, however, a fact which does not appear to be widely recognized. Indeed, many workers (2, 9, 10) have used the time of travel of a tracer between injection and detection wells to estimate the mean pore velocity without regard to the effects of dispersion. The effect of dispersion on estimated time of travel is illustrated by considering the movement of a thin slug of tracer in one-dimensional linear flow for which there is an analytical solution, given by Bear;

$$C = \frac{C_o}{(D_L t)^{\frac{1}{2}}} \exp\left[-\frac{(x - ut)^2}{4D_L t}\right] \qquad \ldots\ldots\ 8$$

where C_o is a constant dependent on the initial conditions,
and x is distance travelled from the site of injection.

The breakthrough curve at a given distance, say X_o, is readily obtained from equation 8 and the time at which the breakthrough curve reaches its maximum value is given by

$$t_{max} = \frac{-D_L + (D_L{}^2 + u^2 X_o{}^2)^{\frac{1}{2}}}{u^2} \qquad \ldots\ldots\ 9$$

It is seen that

$$t_{max} = \frac{X_o}{u}$$

when $D_L = 0$

and $t_{max} \rightarrow 0$

when $D_L \rightarrow \infty$

The pulse peak travels in the groundwater system at velocity u, and the time required for the peak to move distance X_o is X_o/u. However, concentrations at the observation point represent point values on a continually decaying tracer distribution curve so that the peak value at the observation point will be recorded before the peak of the tracer curve has reached the observation point as shown in Figure 8. If Equation 9 is expressed in terms of dispersivity it becomes, after rearranging terms:

$$\frac{t_{max}}{X_o/u} = -\frac{\alpha}{X_o} + \left(\left(\frac{\alpha}{X_o}\right)^2 + 1\right)^{\frac{1}{2}} \qquad \ldots\ldots\ 10$$

The left hand side is the time of arrival of the observed peak at X_o as a ratio of the time of arrival of the actual peak of the tracer pulse at X_o. When α/X_o = 0.2, this ratio has value 0.82 so that the effect of dispersion is to significantly reduce the apparent arrival time of the tracer peak. This effect is enhanced in tracer movement to a pumping well because the dispersion coefficient increases as the pulse moves nearer the observation point. Runs with the numerical model have indicated that with tracer injection at 3 m radius and a dispersivity of 0.6 m we obtain a ratio equivalent to that in Equation 10 equal to about 0.6. Under recharge conditions the ratio is close to unity, and Hoopes and Harleman's solution also gives unity. It is apparent that in this instance, decrease in the tracer peak is dominated by convective effects and the divergence of stream lines.

3.4. RECHARGE EXPERIMENTS

The breakthrough curves for the radiotracer are shown in Figures 9 and 10 togethe with the 'best fit' profiles generated by the numerical model. The 'best fit' values of the parameters are given in Table 1.

Table 1.

Obs. borehole No.	r (m)	Background γ (cps)	α (m)	A (m^2/d)
5	6	29	0.16	35.9
7	3	40	0.31	28.9
10	6	36	0.38	23.7

The higher background γ radiation indicates intervals of higher silt/clay content within the sequence which should correspond to lower permeabilities. The lower values of A computed for boreholes 7 and 10 could also result from lower permeabilities. It is also to be expected that horizons with a higher silt/clay content will give higher dispersivity values than 'cleaner' horizons due to the wider grain size distribution. This is confirmed by the results. An analysis of the field data based on Hoopes and Harleman's analytical solution yielded dispersivities between 1/3 and 1/2 of the numerically derived values.

3.5. DISCHARGE EXPERIMENTS

The rhodamine WT dye tracer was used as an on-site indicator of tracer movement and was invaluable. The main analysis under discharge conditions was however, carried out using the lithium and iodide tracers.

The breakthrough curves for lithium and iodide are shown in Figure 11 together with the 'best fit' profiles generated by the numerical model. As with the recharge case the fit is quite sensitive to variations in A and α. The best fit values of the parameters are given in Table 2.

Table 2.

Well No.	r (m)	α (m)	A (m^2/d)
7	3	0.60	10.93
10	6	0.60	14.74

The dispersivity values are larger than the values obtained for the discrete layers under recharge conditions. In addition, there is little difference between the values for the 3 m and 6 m injection radii suggesting that large scale stratiform heterogeneity is significant, but that there is mixing between successive layers. A dispersivity of 0.5 m was obtained from tracer experiments in the sandstone aquifer of the coastal plain of Israel (7) in close agreement with the Clipstone analyses.

The numerically derived A values may be interpreted in terms of depth of flow and interconnected porosity.

Using Equation 5 with an estimated depth of flow of 31 m (based on the depth of the recharge well) the following values of porosity are derived:

Table 3.

Experiment	Observation/injection well no.	θ
Recharge	5	0.32
"	7	0.39
"	10	0.48
Discharge	7	0.48
"	10	0.36

The ratio Q/b will not be known for each horizon of investigation in the recharge experiments, and the depth-averaged value has been used. The difference between the porosity estimates for the discharge experiment may be due to azimuthal anisotropy or the influence of regional flow. Laboratory measurements of porosity gave values between 0.19 and 0.31 for 14 core samples, with an average value of about 0.28. The mean of the 5 values in Table 3 is reduced to about 0.28 by assuming a flow depth of 44 m which would suggest that 13 m of aquifer below the base of the recharge well may be contributing to the flow regime.

The presence of a confining layer close to the bottom of the recharge well was indicated by the results of aquifer tests carried out during 1973, but this clearly requires substantiation by drilling.

4. CONCLUSIONS

(i) Field experiments were devised to investigate the mechanism of dispersion in the Bunter Sandstone at Clipstone. A numerical model of tracer movement was able to reproduce the tracer breakthrough curves under both recharge and abstraction conditions.

(ii) The calculated dispersivities are in close agreement with measurements in an Israeli sandstone aquifer. A value of 0.6 m was obtained for longitudinal dispersivity of the full depth of flow. This value is relatively small compared with values reported in the literature for other aquifers (11,12). Further experimentation is needed at the Clipstone site and in other UK aquifers to provide reliable estimates for use in groundwater quality models.

(iii) The presence of large scale heterogeneities is evident in the results presented in this paper, and there appears to be transverse dispersion between layers.

(iv) The numerical model has confirmed the importance of dispersivity to the estimation of aquifer thickness or porosity by time of travel experiments. In general, the convective-dispersion equation must be solved to interpret time of travel data.

(v) Lithium and iodide tracers appear to be equally suitable as tracers in the Bunter Sandstone.

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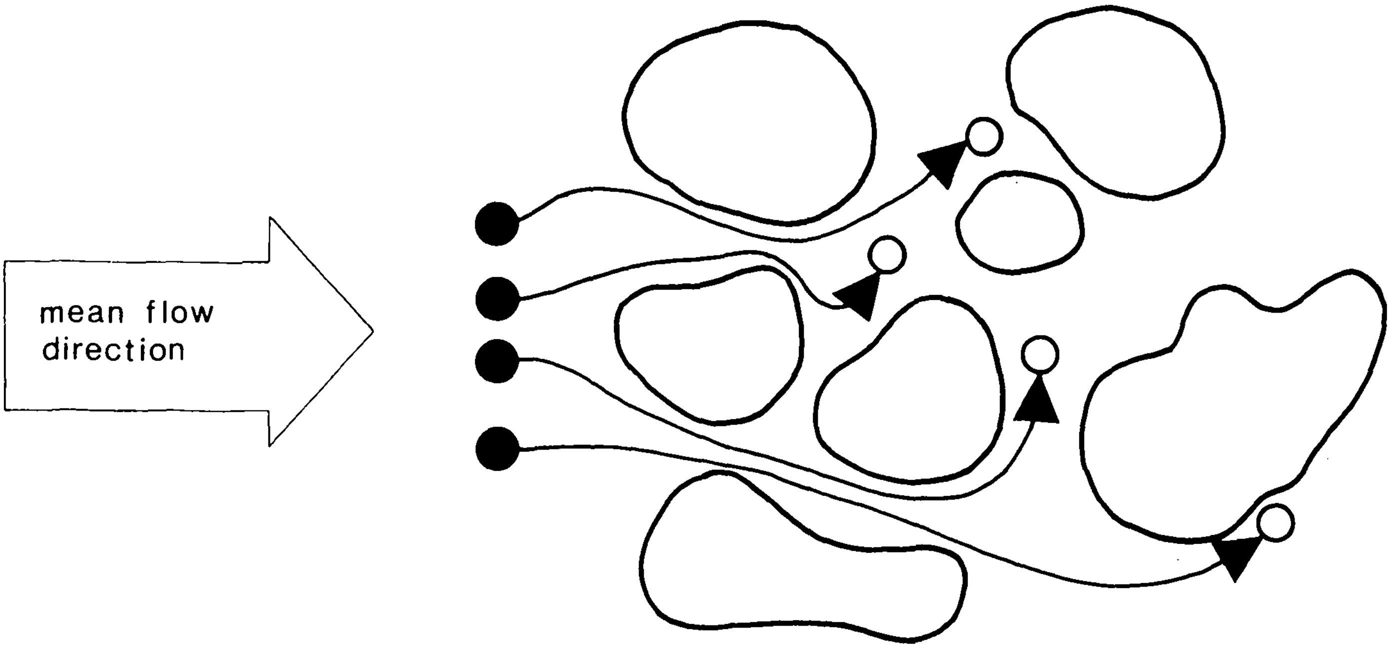


- ● Labelled water molecules at time o
- ○ Labelled water molecules at time t

Figure 1. Dispersion on microscopic scale

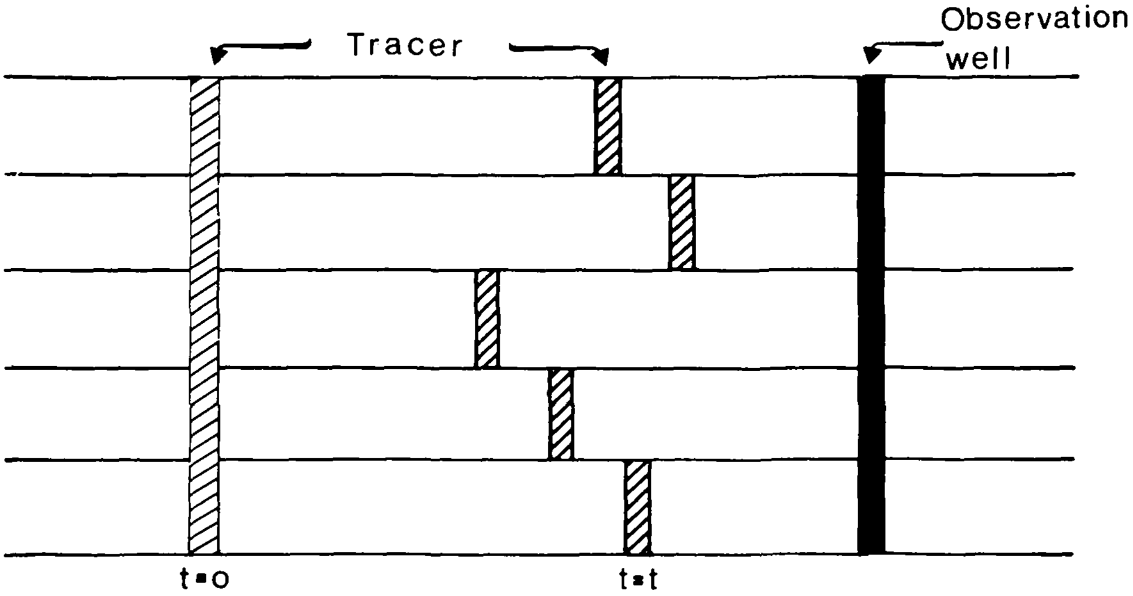


Figure 2. Dispersion on macroscopic scale

$$r_n{}^2 = r_w{}^2 + 2\ (n-1)\ A.\ \Delta t$$

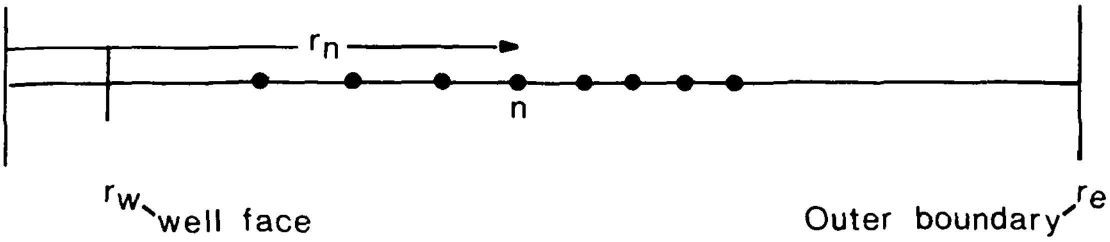


Figure 3. Mesh point layout for radial flow solution by method of characteristics

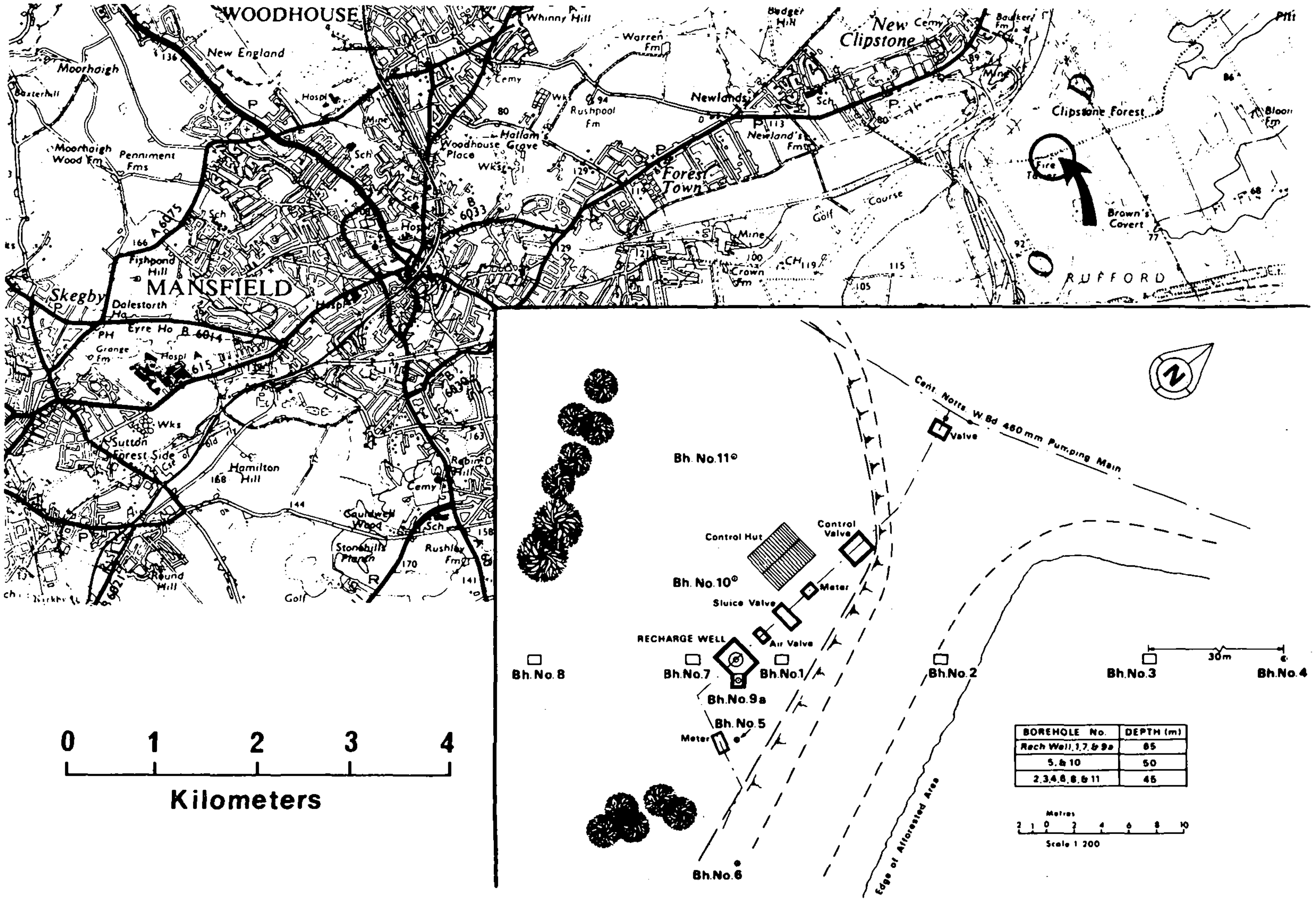


Figure 4. Clipstone Forest artificial recharge site, Notts

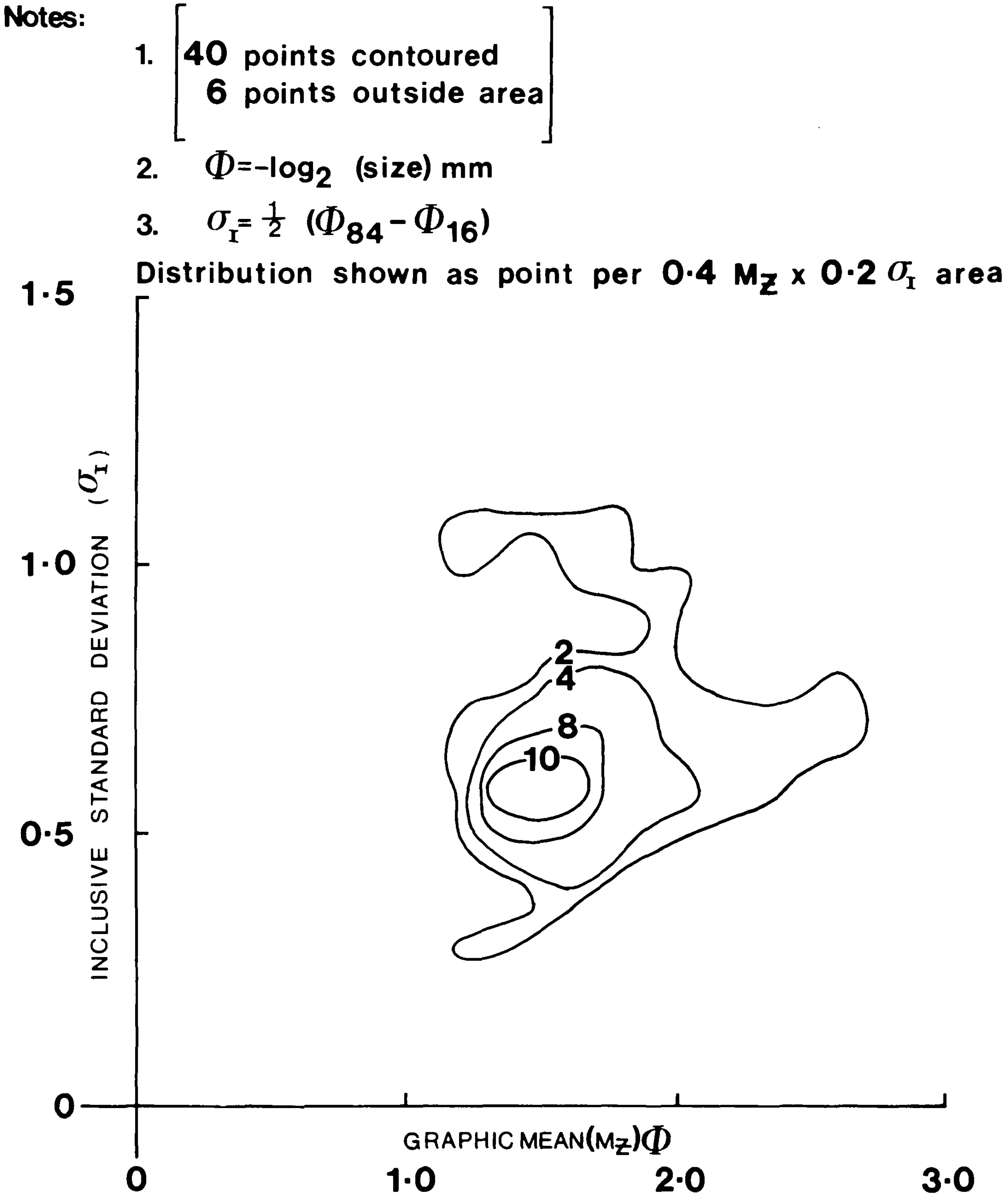


Figure 5. Clipstone Forest - grain size properties of Bunter Sandstone aquifer

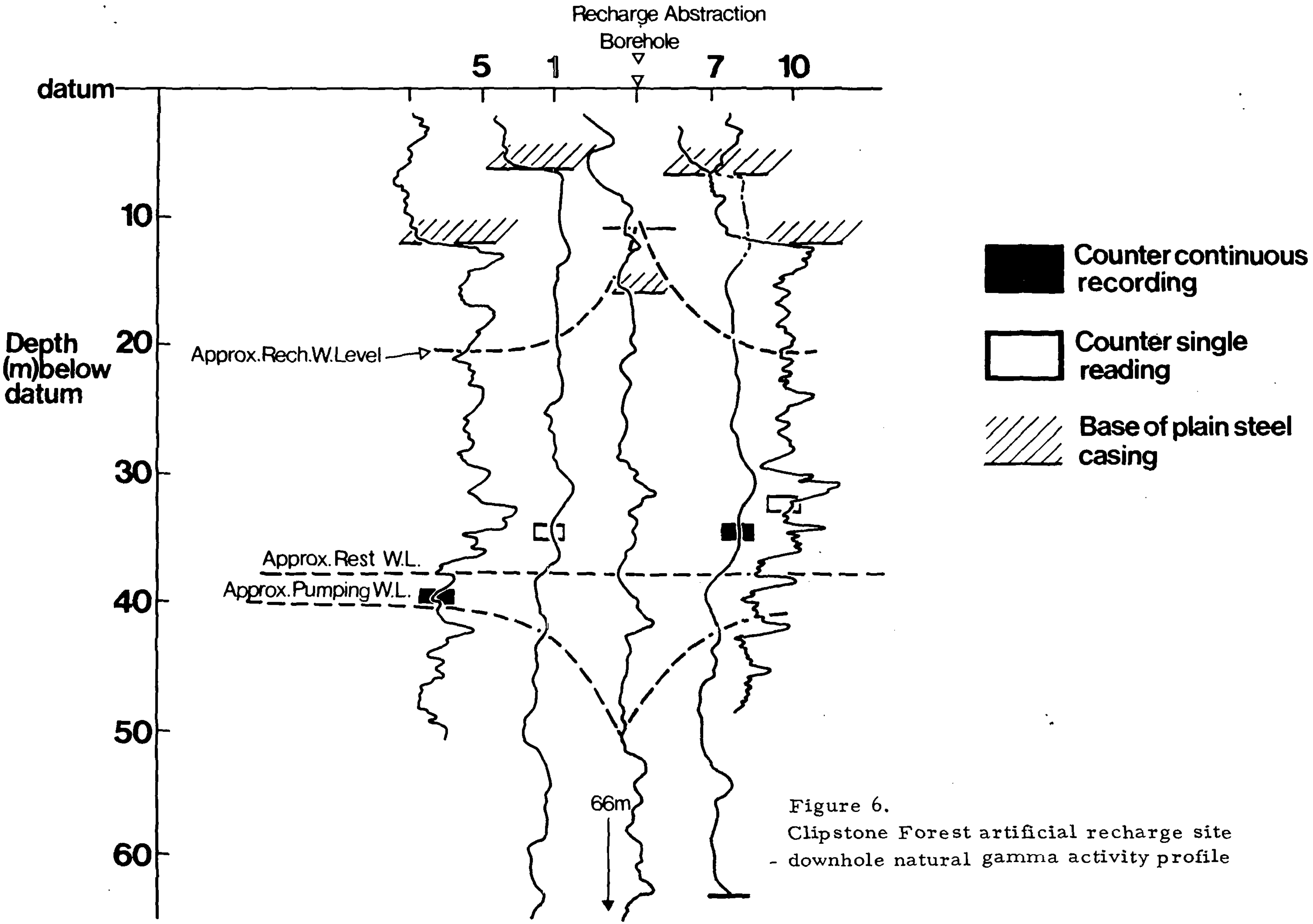
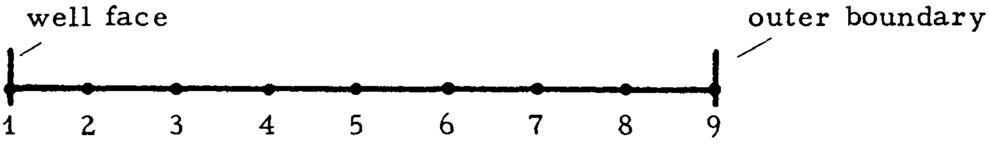
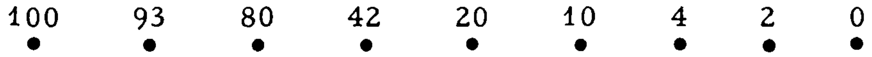


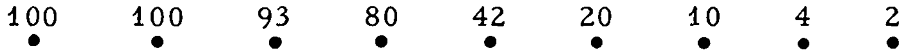
Figure 6.
Clipstone Forest artificial recharge site
- downhole natural gamma activity profile



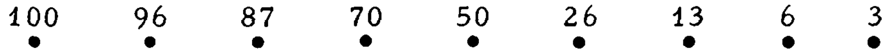
(a) mesh layout



(b) concentration distribution at time t

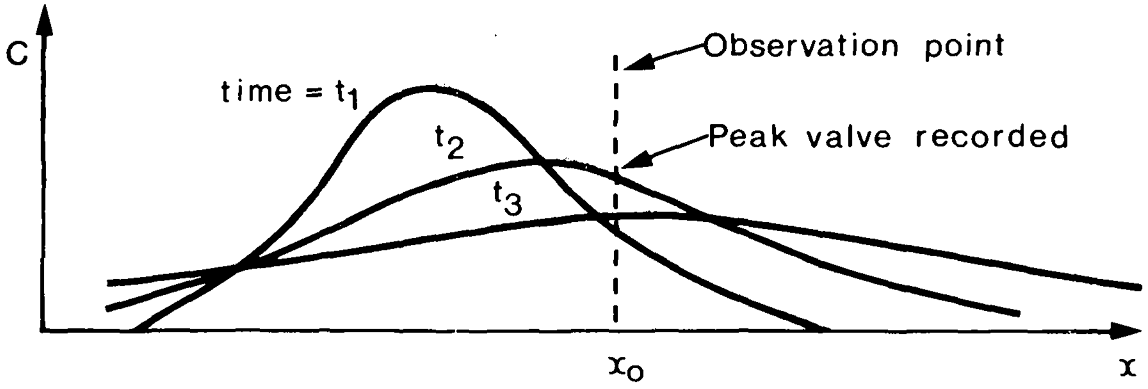


(c) concentration distribution at time t + convective transport



(d) concentration distribution at time t + convective transport + dispersion = concentration distribution at time t + Δt

Figure 7. Example of solution under recharge conditions.



Time of arrival of peak at observation point = t_3
Time of observed peak at observation point = t_2

Figure 8. Relationship between arrival times of observed and actual concentration peaks

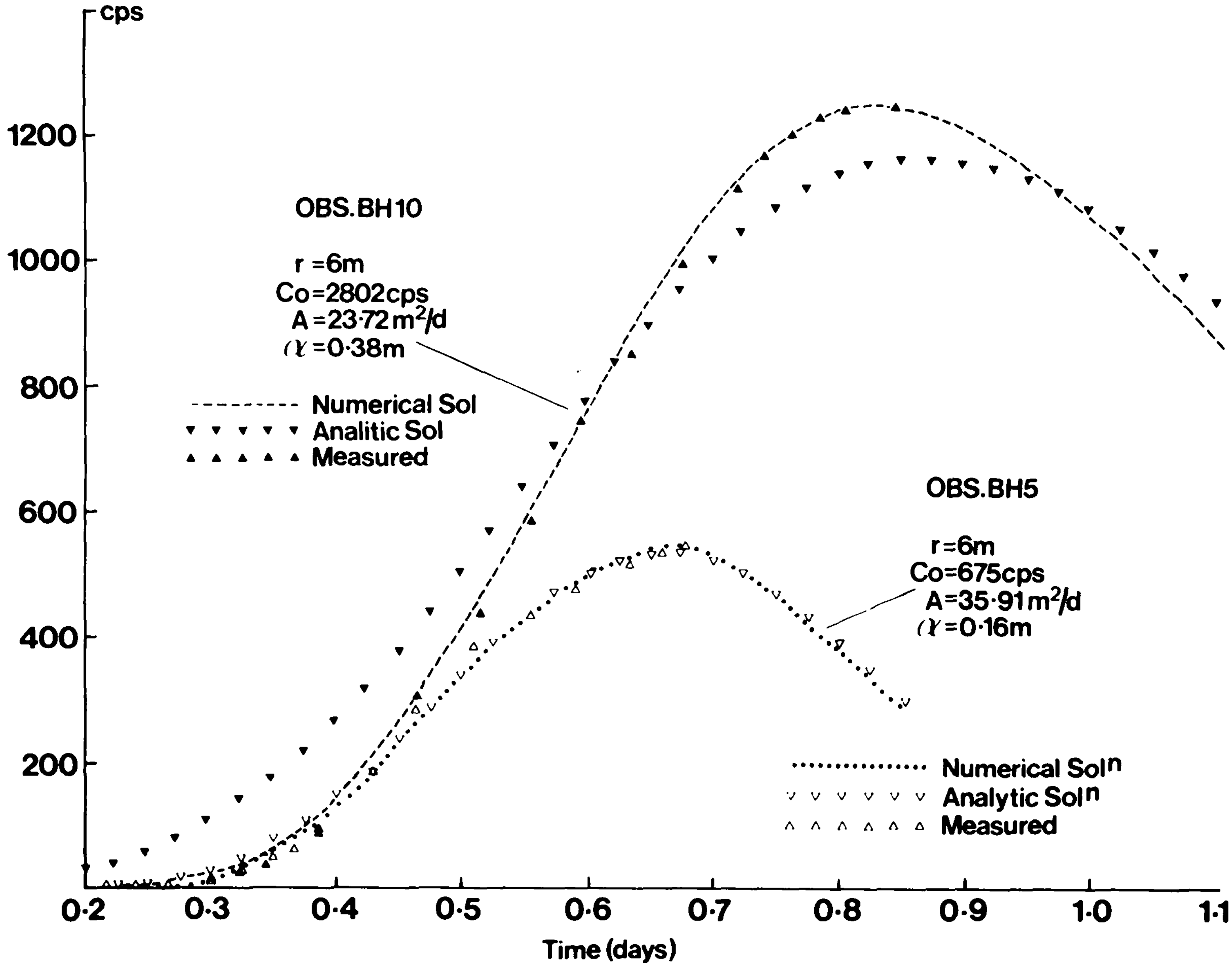


Figure 9. Comparison of observed and computed breakthrough curves during recharge experiment

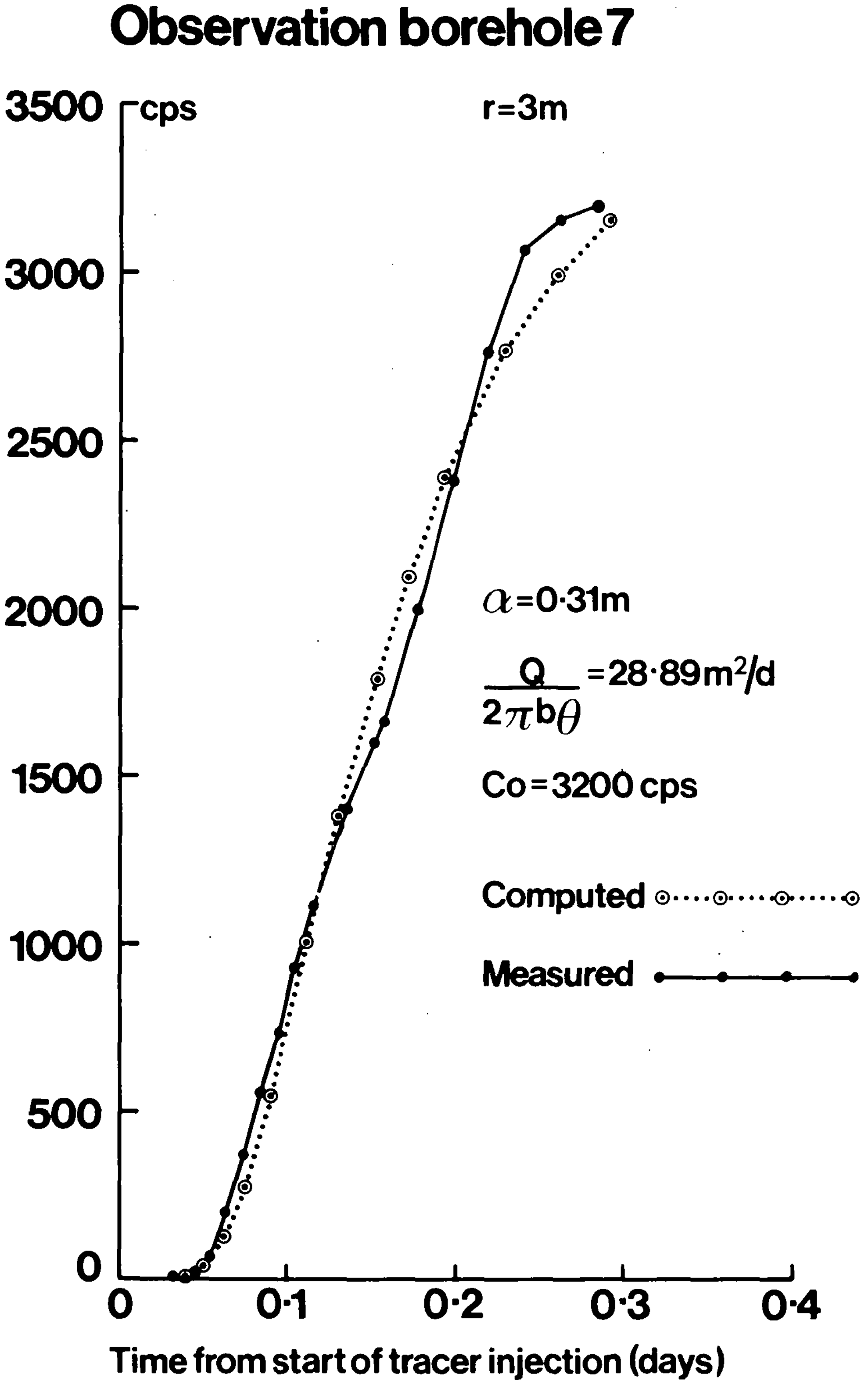


Figure 10. Comparison of observed and computed breakthrough curves during recharge experiment

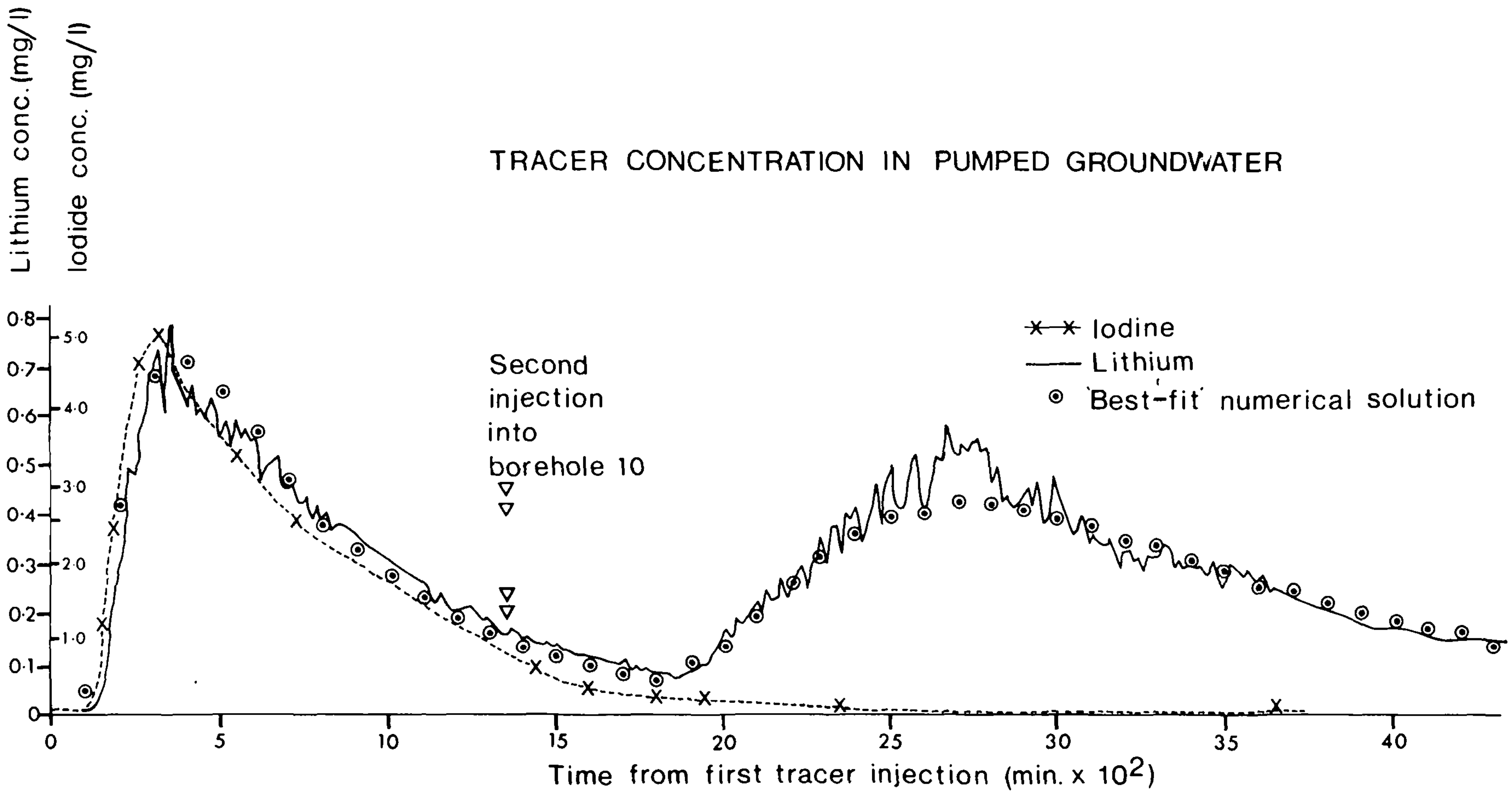


Figure 11. Tracer concentration in pumped groundwater

SUPPORT PAPER B

TRACE ELEMENT DETERMINATION IN WATERS USING FIELD CONCENTRATION TECHNIQUES AND X-RAY FLUORESCENCE

J.M. Marsh and J.W. Lloyd.

1. INTRODUCTION

Accurate analyses of trace elements in natural waters may be required for many reasons such as the delineation of hydrochemical facies in groundwater, pollution etc. As prior knowledge of the trace element content may not be available, multi-element anlaysis techniques can be used to advantage. Of those in use x-ray fluorescence spectrometry provides a comprehensive technique but requires some form of sample preconcentration.

For preconcentration various methods have been used(1), of which coprecipitation has been selected here on the basis of speed, simplicity and its adaptability for field use. Field precipitations avoid trace element losses inherent in carriage and storage of samples.

2. COPRECIPITATION METHODS

Coprecipitation followed by x-ray fluorescence analysis was first proposed by Luke(2). The mechanism of coprecipitation is complicated but the concept is simple. A soluble compound is added to the water to form an insoluble complex with trace elements. However, if the solubility product of the complex is not exceeded because of the very low trace element concentration, it will not precipitate. If a comparatively large amount of a suitable carrier element is introduced into the solution the formation of sufficient complex is ensured and the carrier and trace elements will coprecipitate. The carrier element must have similar properties to those of the elements being studied. Organic or inorganic precipitants may be used such as sodium diethyldithiocarbamate (carbamate), hydroxides and carbonate.

In this study carbamate, cupferron and hydroxide have been used. Previous authors(2) (3), performed their analyses using sample volumes up to 50ml, and Watanabe (3) gives a lower detection limit of 0.02-0.06 μg for Fe, Zn, Cu and Co with a precision of ± 0.3 μg for 5 μg of element. To obtain this order of weight of element for analysis from most natural waters, a sample volume of one litre has been chosen for this study. Watanabe showed that with samples > 300ml, carbamate precipitation efficiency decreased, however Sear(4), reports complete recovery of 1 μg Co from one litre using carbamate.

For the element analyses described below, three sets of precipitating conditions (methods) were originally selected and are listed in Table 1.

Table 1. Precipitation conditions

	Method 1 (pH9)	Method 2 (ph5)	Method 3 (ph4)
Elements	Y, Cr^3, Mn, La, Ni, Zr	Pb, Hg, Zn, Se, Cu, Cr^6, Fe, Co	Al, Sn, Ti, Sb
Coprecipitant	150 μg Fe^{++}+ 150 μg Cu^{++}	300 μg Ni^{++}	150 μg Cu^{++}+ 150 μg Fe^{++}
Complexing agent	Carbamate + hydroxide	Carbamate	Cupferron

Reagent quantities have been optimized by trial precipitations on identical weights of element in 50ml and one litre of water. Where statistically equivalent results have been obtained, precipitation has been regarded as being complete.

3. FILTRATION

Collection of the precipitate has been carried out by pressure filtration through a membrane filter of nominal pore size 0.45 μm under pressure. The apparatus has been based on a design by Skougstad and Scarbo(5). Pressure is applied by a standard tyre pump.

Precipitates normally adhere to the filter on natural drying without fixing. If the concentration of trace elements, however, exceeds lmg/l, flaking of the precipitate may occur. When the excess concentration is provided by one element such as Fe or Cu, masking techniques may be used. In the case of high concentrations, analyses are made on smaller volumes of water.

4. X-RAY FLUORESCENCE ANALYSIS

Analyses have been carried out using a Philips PW 1450 AHP x-ray spectrometer under the conditions listed in Table 2. The spectrometer is operated under vacuum at a voltage of 60kV and a current of 30mA. The intensity of diffracted radiation is measured by a scintillation detector, gas flow proportional detector, or both.

To minimize instrumental drift effects, each sample is analysed in two cycles, each of which measures a peak and background count for each element. If a sloping background is present in the peak region, then two background measurements are made. To compensate for slightly different machine conditions between batches, a standard reference sample is measured with each batch. The results obtained for all the samples are divided by the results of the reference.

5. CALIBRATION

Calibrations have been made for the elements as listed in Table 1. One calibration has been made for each method and the elements in each precipitated simultaneously. Calibrations have been made depending upon the expected element concentration in water. In the tested ranges (see Table 2) the calibration equations are linear. Throughout calibration, made-up solutions consisted of distilled de-ionized water with standardized spectrographically pure metals or compounds.

Sixty samples have been analysed for each calibration. The amounts of each element added have been arranged in order so that the total weight

Table 2. X-ray fluorescence spectrometer operating conditions and calibration results

Element	X-ray Tube	Line	Crystal	Colli-mation	Detec-tion	Background 2θ° from peak	Sensitivity c/s/μg	Blank net c/s	Background c/s	Limit of Detec-tion(μg)	% error at 95% level
Al	Cr	Kα	PET	550 μ	F	-0.48	25.0	83	88	0.25	2.0
Ti	Cr	Kα	PET	150 μ	F	+3.16	180	64	22	0.02	7.0
Cr	W	K$\alpha_{1,2}$	LiF(200)	150 μ	F	-0.79	89	36	60	0.50	8.8
Mn	W	K$\alpha_{1,2}$	LiF(220)	150 μ	F	-0.61	2.0	17	34	1.60	178.0
Fe	W	K$\alpha_{1,2}$	LiF(200)	150 μ	F	-0.74	134	1042	181	0.12	13.0
Co	W	K$\alpha_{1,2}$	LiF(220)	150 μ	S	+0.61 -0.69	6.2	1	8	0.22	23.0
Ni	W	K$\alpha_{1,2}$	LiF(200)	150 μ	F	-0.81	153	242	326	0.07	14.8
Cu	Mo	K$\alpha_{1,2}$	LiF(220)	150 μ	F	+1.04	9.5	89	74	0.64	8.0
Zn	Mo	K$\alpha_{1,2}$	LiF(220)	150 μ	F	+0.93	8.5	33	66	0.55	30.0
Se	Mo	K$\alpha_{1,2}$	LiF(200)	150 μ	S	+0.50	5.7	10	124	0.96	370.0
Y	Mo	K$\alpha_{1,2}$	LiF(220)	150 μ	S	+0.93	11.5	22	111	0.47	22.0
Zr	W	K$\alpha_{1,2}$	LiF(220)	150 μ	S	-0.94	5.6	18	119	1,93	84.6
Sn	Cr	L$\alpha_{1,2}$	LiF(200)	550 μ	F	-1.95	236	950	48	0.06	12.0
Sb	Cr	L$\alpha_{1,2}$	LiF(200)	550 μ	F	-1.20	21.0	49	9	0.17	40.0
La	W	Lα_1	LiF(220)	550 μ	F	-2 27	56.2	3	568	0.09	10.8
Hg	Mo	Lβ_1	LiF(220)	150 μ	S	+0.39	2.5	3	54	1.43	23.0
Pb	Mo	Lα_1	LiF(200)	150 μ	F+S	-1.00	13.7	0	358	0.65	43.3
Pb	Mo	L$\beta_{1,2}$	LiF(200)	150 μ	F+S	+0.59	8.7	27	463	1.2	65.0

PET = Pentaerythritol
LiF = Lithium fluoride

F = flow detector
S = scintillation detector

of trace elements in each case was about 300 μg. Thus the possibility of inter-element absorption and enhancement are randomized. The precipitates have been analysed and the results, shown in Table 2, obtained using a linear regression.

The results are not of the same precision as obtained by Watanabe et al(3), when precipitating from a small volume. However, the results for Ti, Cr, Fe, Co, Ni, Cu, Sn, La, Y yield errors $<25\%$ and Al, Zn, Hg yield errors $<30\%$. Assuming complete precipitation, errors will be controlled principally by the slope of the calibration line as in the work of Watanabe et al.(3). Additional errors are, however, introduced if the first assumption is not always fulfilled. It is noted that the variance of results of test precipitations from 1 litre was greater than from 50ml, indicating a greater uncertainty of complete precipitation from 1 litre. Thus the extra error is accounted for by the greater variability of extraction due to reduced concentrations.

Mn does not precipitate completely with carbamate. Difficulty was also experienced with Se and Sb.

After calibration the technique was assessed for precipitating trace elements from natural waters. Samples of four different waters were obtained and to 1 litre aliquots of these, and distilled de-ionized water, were added known amounts of Cr, Ni, Pb, Cu and Zn. Precipitations were carried out on these and on samples to which no addition had been made. The natural waters were of various chemical types ranging in total dissolved solids concentration from 282 to 1274mg/l. Recovery at pH5 was satisfactory within the calibration error.

Adjustment of the pH for precipitation at pH9 can cause waters with bicarbonate alkalinity to become oversaturated with respect to carbonates. In testing, this has resulted coprecipitation of trace elements with carbonates. The filter is too coarse to remove the carbonate precipitate, and this has caused the abandonment of 'method 1' for most natural waters. The elements covered by this method are now being recalibrated using a different precipitant. The method is still a useful one for waters with very low alkalinity.

6. APPLICATION TO NATURAL WATERS

Values of trace element concentrations determined using this technique in a number of different hydrochemical situations are shown in Table 3. Maps of distributions of many trace elements may be made simultaneously, and one for Fe in groundwater of the southern Lincolnshire Limestone is illustrated on Figure 1. Comparison of maps may show differing assemblages of elements which identify differing water types. Their actual distribution may be compared with their theoretical distribution if pH and Eh values are known, and the oxidation reduction stability assessed.

Care must be taken to ensure that samples are representative of the aquifer, otherwise results may be affected by contamination by well materials.

The assemblages shown in Table 3 are distinctive for each water and can be seen to be related to pH and Eh where values of these are available. The higher concentration of Zn and Cu, and the dominance of Cu in the granite waters, indicates contamination of the acid waters by brass well fittings.

Groundwater recharge may be identified if an assemblage is found to contrast with the background. Sample 19 is an example of a river water entering a gravel aquifer. The distinctive elements, Ti, Al and Sb may be present in suspension as they may also be in the Coal Measures water which was sampled within a mine, however the results may be legitimately used in tracing studies.

The use of the technique in identifying surface water pollution is well illustrated in Table 3. The very high levels of metals associated with the mine tip is due to the oxidation of sulphide minerals. This causes a lowering of pH with a consequent increase in stability of elements in solution.

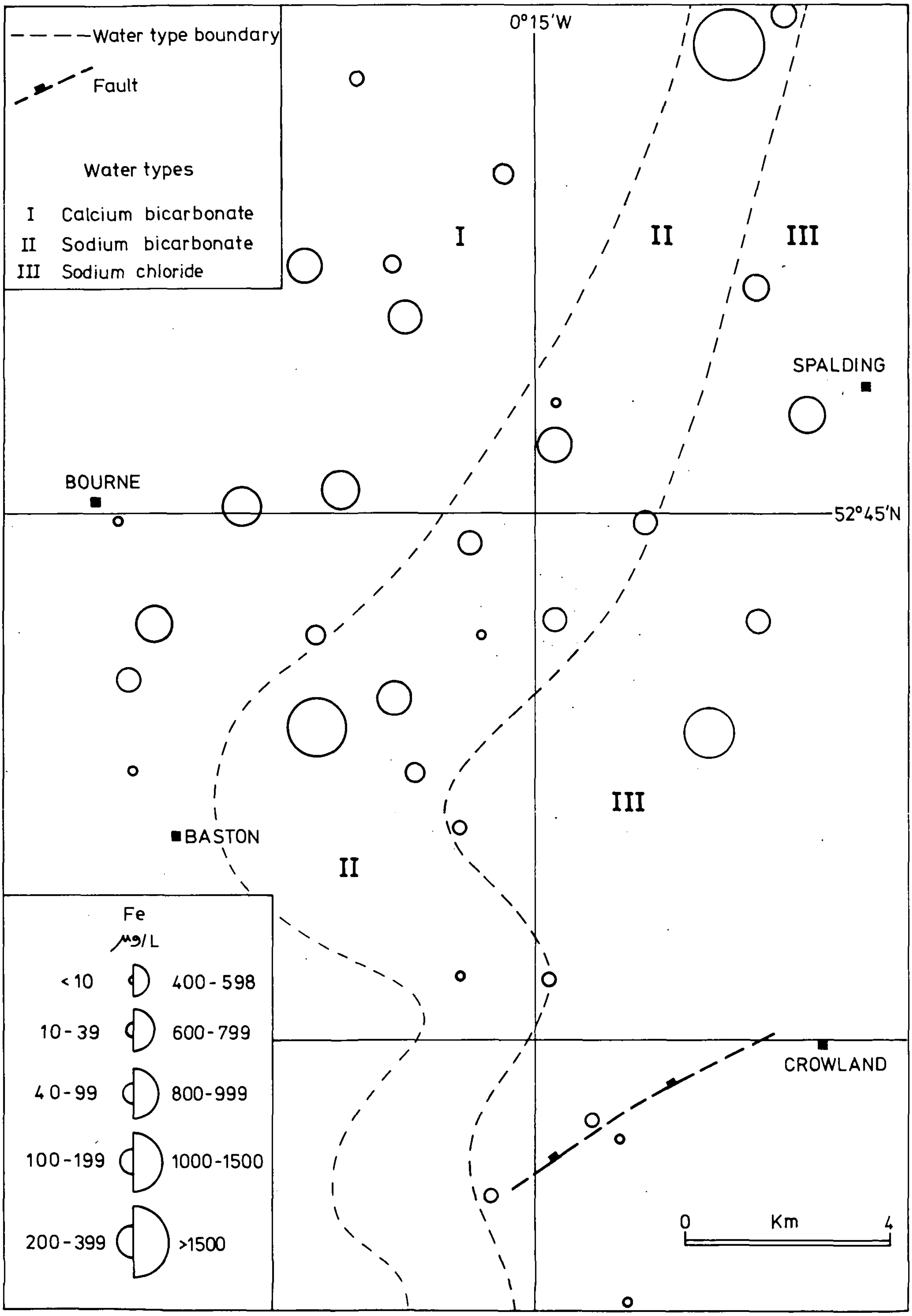


Figure 1. Distribution of Fe in Lincolnshire Limestone aquifer

Table 3. Representative trace element analyses (g/l)

	No.	Ti	Al	Sn	Sb	Pb	Zn	Cu	Cr	Fe	Co	pH	Eh (mV)
South Lincs. Limestone	1	0.21	16.6	-	-	-	9.1	1.3	-	156.9	-	7.75	-20
	2	-	1.3	-	-	-	7.1	0.6	-	134.0	-	7.75	+10
	3	-	2.2	0.2	-	-	8.3	2.8	-	3.6	-	7.33	+288
	4	0.3	12.5	-	-	-	8.6	0.8	-	184.1	-	7.60	-50
	5	-	0.4	0.6	-	-	9.6	3.5	-	475.7	-	8.13	-88
North Lincs. Chalk	6	0.5	15.0	-	-	-	11.9	11.1	-	7.1	-		
	7	1.4	50.9	-	1.3	0.1	8.4	9.3	-	76.4	-		
	8	0.2	10.4	-	-	-	12.0	8.7	-	1.4	-		
	9	-	10.0	-	-	-	24.8	1.8	-	3.7	-		
	10	-	4.6	-	-	-	43.2	13.0	-	2.1	-		
Scilly Isles Granite	11					1.0	182	426	0.2	110.0		5.40	
	12					-	62	346	0.1	13.0		5.70	
	13					1.0	125	920	0.1	190.0		5.80	
Coal Measures	14	65.1	2318	-	83.0	1.6	26.0	18.4	0.4	259.8		7.55	
	15					7.9	853.3	23.0	0.5	660.8		8.30	
Trent River Gravels	16	0.1	3.2	-		5.8	18.0	16.5		945.9		6.74	
	17	0.0	2.3	-	-	-	5.7	15.0		54.8		6.70	+30
	18	0.2	2.3	-	-	0.6	13.4	14.6		9.2		6.71	+65
	19	41.0	754.4	-	84.1	1.2	25.1	11.0		190.0		6.50	+40
Coal mine tip pond Refuse tip pond	20	5.0	371	-	15.4	1.8	7837	28.6		90	3.5	6.50	
	21	4.0	158	-	7.7	82.0	306738	1223		10197	2960	5.40	
	22	0.2	6.2	-	-	-	1861	5.8		0.7		7.00	
	23	0.3	34.6	-	-	1.6	58	9.3		1027		7.30	
	24	3.1	263	-	5.6	27.5	239	31.0		146		7.00	

- : not detected Blank space : not determined

7. CONCLUSIONS

The technique described provides a rapid method of determining a range of trace elements. Preparation of samples suitable for x-ray fluorescence analysis in the field avoids risk of contamination and problems associated with sample carriage and storage.

At present the technique has been developed to analyse fourteen elements to acceptable precisions. Work is in progress to expand the range and to increase precision.

Field studies have shown that the method can be conveniently used in hydrochemical mapping and tracing studies. The detection limits are well within inorganic pollution standards so that the method is eminently suitable for this type of work.

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SUPPORT PAPER C

DATA BASED GROUNDWATER QUALITY PROTECTION AND SURVEILLANCE IN NORWAY

Knut Ellingsen.

ABSTRACT

The infiltration area and part of the surrounding precipitation area of groundwater wells for public water supply in Norway, is subject to a graded protection which is to a large extent standardized. Four main zones are generally used:

00: The very close area, 10-30 m from the well(s).
01: The certain infiltration area.
02: The probable, but not certain, infiltration area, and
03: Safety zone, sometimes being extensive.

The main zones may be divided into subzones, for instance based on variable thickness of the unsaturated zone, or presence of relatively impermeable strata in the profile. The restrictions are grouped as follows:

01: Buildup and constructions.
02: Outlet.
03: Waste deposition/accumulation/cleanup.
04: Agriculture.
05: Industrial activity.
06: Traffic.
07: Recreation, and
08: Storing - chemical compounds.

These main restriction groups are divided into several sub- and sub-subgroups. Generally the most frequently used combinations of zone/restrictions are:

00: 01 - 08
01: 01 - 03, 08 and partly 04 - 06
02: 02 - 03, 08 and partly 01, 04 - 05
03: Partly 01 - 03 and 08

The zone- and restriction-specifications are fed into a data file which also contains other essential information and serves as a tool to the control of the waterworks. The groundwater set-up is part of a more comprehensive system, which also includes surface water.

1. RESTRICTION ZONES

Groundwater for public water supply in Norway is generally taken from Quaternary glaciofluvial or fluvial sand and gravel deposits that are in contact with surface water, or (quite seldom) are totally self supplied with water.

Even though groundwater at present plays a minor role in Norwegian water supply compared to surface water, the relative share of groundwater is increasing, especially in certain parts of the country.

The total depth of the water yielding profile including the unsaturated zone is often small. As the groundwater's exposition towards pollution from surface activity in these cases is marked, the groundwater's infiltration area is subject to a graded protection which is to a large extent standardized. In general, disinfection of the water is not used if the activity in the infiltration area is satisfactorily regulated.

The surface water, very often a river, is usually a positive hydrologic barrier. The infiltration area on land is then divided into four main zones.

Zone 00 embracing the nearest area around the well, usually within a distance of 10 - 30 m from it.
Zone 01 embracing the certain infiltration area
Zone 02 embracing the probable, but not certain infiltration area

Zone 03 embracing a safety zone including catchment areas that may have influence under special conditions, etc.

The area of the zones varies greatly from place to place according to the hydrogeologic conditions. But generally the magnitude of the areas will be as follows (1 daa = 1000 m^2):

The area of zone 00: 0, 3 - 2, 5 daa
The area of zone 01: 10 - 60 daa
The area of zone 02: 20 - 400 daa
The area of zone 03: Less than one and up to several square kilometres

Often the restriction zones also embrace areas situated at the other side of a neighbouring surface water course if the water course's function as a positive hydrologic barrier is not complete.

Investigation of the hydrogeologic conditions in connection with a well is as a rule unsatisfactory and often totally lacking. The zone borders are then drawn according to assumptions made mainly on the basis of what can be observed on the surface. The areas of the zones will then often become much larger than objectively necessary. In these cases it is the owner of the waterworks duty to carry out investigations which might show that diminishing of the zone areas can be made without risk for the water quality.

The reason for the general lack of satisfactory investigations is mainly of economic nature. The land in the well area is often low-interest and low-price land. It becomes cheaper to pay for restrictions than to hire a group of specialists. Obviously simple, standardized and cheap techniques concerning the discovery of groundwater movement are needed, e.g. its direction and speed, within relatively small areas and not great depths.

2. RESTRICTIONS

In general, restrictions in the groundwater influence area of a well should be regarded in close connection with the treatment process that the water is subject to. But it is regarded as essential for hygienic reasons not to introduce complex water treatment procedures. This accentuates the need for relevant restrictions on activity and installations in the vicinity of the well.

The restrictions have been standardized and divided into eight groups. The grouping made is a result of the experience that is available at present, and may be changed in the future. The main groups are: (number in brackets indicates the number of subgroups)

01	Buildup and constructions (4)
02	Outlet (3)
03	Waste deposition/accumulation/cleanup (6)
04	Agriculture (7)
05	Industrial activity (4)
06	Traffic (5)
07	Recreation (4)
08	Storing - chemical compounds (5)

The subgroups assign objects, and sub-subgroups a prescript to the objects, e.g. a more precise description. The following example illustrates this: Restriction No. 080301 belongs to main group 08; Storing - chemical compounds, subgroup 03; presticides, and the sub-subgroup 01, total prohibition of such substances. Instead of total prohibition, the storing of pesticides might have been allowed in especially secured tanks, a description of which is given under sub-subgroup 02. Often several 'description' sub-subgroups are practised.

In addition to the three general information boxes included in the six-digit number above, special restrictions suited to local conditions may occur. These are indicated by an additional '-1' mark in addition to the six digits, indicating special circumstances.

3. STORING AND USE OF INFORMATION

The restriction zone data and the restrictions applied are stored in an electronic computer data file, together with other relevant data of the waterworks, such as technical equipment, hydrogeologic description of the aquifer, water quality analyses and other data from the operation and maintenance of the waterworks that we receive.

Generally the most frequently used combinations of zone/restrictions are:

00: 01 - 08
01: 01 - 03, 08 and partly 04 - 06
02: 02 - 03, 08 and partly 01, 04 - 05
03: partly 01 - 03 and 08

The system is at an introductory level and little experience has been collected until now. However, it is expected to become a useful tool in the control of groundwater plants in Norway.

SUPPORT PAPER D

ENVIRONMENTAL TRITIUM AS AN INDICATOR OF POTENTIAL GROUNDWATER POLLUTION FROM LANDFILLS

J.D. Mather, D.B. Smith, D.A. Gray and E.W. Clipsham.

ABSTRACT

A full hydrogeological investigation of all existing and potential industrial and domestic waste landfills would be prohibitively expensive. In an attempt to identify a relatively cheap indicator of potential pollution problems, the Department of the Environment financed a research programme, undertaken jointly by the Institute of Geological Sciences and the Harwell Laboratory, to assess the value of environmental tritium measurements on groundwaters adjacent to landfill sites. The principle of the method is outlined, and complicating factors such as the tritium content of waste liquids themselves are emphasized.

The results from some 27 individual field studies, undertaken over a wide range of hydrogeological environments, are reviewed, and some of the landfill sites where tritium measurements made a significant contribution to the assessment of potential pollution are discussed in detail. It is concluded that environmental tritium can provide a relatively inexpensive 'worst risk' indicator, providing hydrogeological conditions are simple and there are no complicating factors such as saline intrusion or induced infiltration from adjacent rivers.

1. INTRODUCTION

The potential pollution of groundwater supplies by leachates and liquid wastes from landfill sites and spoil heaps is a problem of some economic importance, and over the past few years this has received considerable publicity. In the assessment of existing and proposed sites, it would be extremely valuable if a relatively cheap indicator of potential pollution risk could be defined. The present paper describes a pilot study undertaken for the Department of the Environment by the Institute of Geological Sciences (IGS) and the Harwell Laboratory, to assess the value of environmental tritium measurements in estimating the potential pollution risk to groundwaters adjacent to landfill sites.

Tritium is a radioactive isotope of hydrogen and forms part of the water molecule. It is, therefore, an almost perfect tracer for water and is of particular value in following the movement of groundwater where it is not susceptible to loss by sorption or chemical reaction. Measurements of the thermonuclear tritium can indicate whether groundwater consists of water which has recently originated as rain or whether it contains a component of such recent water. This aspect can be used to examine groundwaters in the vicinity of landfill sites to assist in the assessment of the pollution risk to the groundwaters from the landfills. The basis of site selection was principally the acquisition of relevant data from sites covering a wide range of geological conditions. Site selection was undertaken by IGS staff and sample collection and analysis by Harwell personnel. The results were interpreted jointly in terms of the known hydrogeology.

2. CONCEPT OF THE TRITIUM METHOD

Prior to 1954, cosmic radiation was the principal source of tritium in the atmosphere and in rain. The tritium concentration was between 5 TU and 10 TU (1 Tritium Unit, TU, represents 1 tritium atom to 10^{18} hydrogen atoms and produces 7.2 disintegrations/minute/litre of water).

Thermonuclear tests resulted in a marked increase of the tritium content of the rain. Peak values occurred following the thermonuclear test series in 1954 and 1958, with a major peak after the extensive 1962/63 tests (1). Since that time, mean tritium levels have reduced to be fairly constant since 1972. Due to an exchange which takes place between the stratosphere (where the tritium is stored) and the troposphere each spring, tritium levels show an annual cycle. High values occur in the summer months when groundwater recharge is at a minimum and lower values occur during the winter period. The ratio of the summer to winter tritium values is about four to one.

Tritium has a half-life of 12.26 years so that the overall concentration in any body of water is reducing with time.

It is of interest to note that in 1974, the tritium content of groundwater consisting entirely of water which has recharged since 1954 has a nominal value of about 100 TU. This is evaluated by using monthly values of the tritium concentration during the period, estimating the amount of recharge (from the rainfall less the evaporation for each month) and allowing for radioactive decay.

The concept of applying tritium measurements to assess the degree of risk of pollution to a groundwater supply is based on interpretation of the individual results in the light of the known geology of the area and of the hydrogeology, if any relevant data are available. The basic premises are:

(a) Very low tritium values (0-5 TU). Water essentially of pre-1954 origin. Not susceptible to short term pollution and unlikely to show a rapid rise of pollutant concentration.

(b) Intermediate tritium values (5-30 TU). Contains a significant fraction of post-1953 water. The geology of the area and the depth of the water table will assist in interpreting the meaning of the measurement.

(c) High tritium values (30-120 TU). Contains a high proportion of post-1953 water, at risk from local surface or river contamination. If the water is adjacent to a long-established landfill site and has not become polluted, then it is unlikely to be at risk from the established site. However, an extension of the landfill or change in the type of waste might produce problems. Essentially hydrogeological work would be needed before allowing any change of the tipping practices.

Several additional factors have to be considered in relation to some of the measurements. As mentioned above, in an area where landfills were established well before 1954, then even very low tritium measurements cannot exclude the possibility of pollution. In general, the water will move more rapidly than the pollution, so that a safety factor exists, but this does not prove that pollution will not occur in due course, although some pollutants may be permanently retained. A further complication can occur where there is extensive discharge of waste liquids since these could saturate the strata beneath the landfill and rapidly increase the rate of transport of effluent to the water supply.

3. SITE SELECTION AND SAMPLE COLLECTION AND ANALYSIS

Samples for tritium analysis were taken from groundwater abstraction points where it was considered that there was a possibility that leachates from a landfill site located nearby could have moved towards the groundwater source. For the obvious reason that landfill sites are not commonly located in groundwater recharge areas, such sites are difficult to identify. However, a total of 27 individual studies were selected where it was thought that the tritium technique might provide valuable additional data.

The waste disposal sites were selected after a study of the published literature on suspected groundwater pollution from waste disposal sites in the United Kingdom, together with a detailed analysis of those sites assessed by IGS during the DOE Review of Waste Disposal Sites in England and Wales (2). After a potential waste disposal site had been selected, reference was made to the National Well Record Collection stored at IGS to locate nearby groundwater abstraction points. If, on general hydrogeological grounds, it appeared that there could be movement of leachates from the site to the groundwater abstraction point, the site was considered for inclusion. An attempt was made to cover as many different hydrogeological environments as possible so that the results of the study could be widely applied. Some of the landfills were inspected and, where necessary, the local Water Authority was approached for information.

The water samples from springs were normally taken at their uppermost point of discharge and the borehole samples from a rising main before chlorination. If the supply was not in use the water was run to waste for fifteen minutes before taking the sample. The bottle was rinsed three times with the sample then filled to the top; the screw-caps had polythene liners and were wrapped in parafilm to exclude air. Measurements of temperature and pH were taken in the field on flowing water. Samples were brought back to the laboratory for tritium analysis, each sample in a 1 litre glass bottle.

On receipt of a water sample, the sealed glass bottle was opened in a laboratory where the tritium level of water vapour in the atmosphere was kept low by an air conditioning plant incorporating water scrubbing, which was operated with low level tritium water. A sample of approximately $\frac{1}{2}$ litre was distilled to dryness in a closed distillation system to remove solids. This was repeated if the distillate was of poor quality and activated carbon could be used to remove traces of organic materials.

One hundred millilitres of the distilled sample was then converted to an electrolyte by the addition of 0.75 g of sodium peroxide. This solution was electrolysed at low temperature to a volume of 5 ml. In the process, 90% of the tritium remained in the electrolyte, thus reconcentrating the tritium by 18 times.

After distillation, this water sample was passed through a magnesium furnace at 600°C and the resulting hydrogen was reacted catalytically with petroleum product ethylene (containing no tritium) to form ethane gas. This gas was used to fill a proportional counter (1.7 litres) to 2 atmospheres pressure and the low-energy particles from the tritium were recorded in an anticoincidence counting system. Using this system and a refined heavy steel and plastic shield, the background of the detector was reduced to 2 counts/minute in the absence of tritium. A sample containing 4 TU before electrolysis would then produce an additional 1 count/minute above the background. The overall accuracy of measurement is considered to be ± 2 TU or ± 10% at higher concentrations.

4. RESULTS

From the results it is possible to make a general assessment of the value of tritium measurements relating to the susceptibility of groundwater to pollution from landfill sites. Of the 27 individual studies undertaken, tritium made a positive contribution to the appreciation of the pollution risks in over half the cases. In some of the other studies, no positive contribution occurred. The results are discussed in terms of the value of the tritium measurements for selected sites and general conclusions are drawn to provide guidance to further use of the technique. The following examples illustrate the positive contribution groundwater measurements have made to the assessment of pollution risk and some of the conclusions which these measurements have made possible.

Example 1.

An area of approximately 7.3 ha in the South of England has been used for the disposal of trade refuse and construction wastes since 1963. The southern part of the landfill is located on the mottled clays and silty sands of the Reading Beds which are up to 15 m in thickness and overlie Upper Chalk. However, Reading Beds are absent from the northern part of the site where tipping takes place directly onto Chalk. A Chalk abstraction point with a yield of 50 l/s lies 1 km east-south-east of the site with a probable hydraulic gradient towards it from the landfill. However the tritium content of 5 TU suggests that little post-1954 recharge is contributing to the yield from this source and it is concluded that there is no immediate risk from the landfill.

Example 2.

A group of disused fluorspar workings in the Midlands were used between June 1971 and July 1972 for the disposal of industrial solid wastes. The old workings were in an area where limestones overlie basaltic lavas; groundwater within these limestones is perched and discharges from springs at the limestone/lava junction. The tritium concentrations of two springs approximately 300 m north and south of the disposal site were 109 and 105 TU respectively suggesting a very short residence time for groundwater within the limestones. Thus there is a major risk to these springs from the disposal site.

Example 3.

A pit in the Lower Chalk of Yorkshire has been used for the disposal of domestic waste for over 35 years. The Lower Chalk, at this locality, is about 30 m in thickness and overlies Kimmeridge Clay. Groundwater discharge takes place at springs on the Chalk/Clay junction and a series of springs 400 m to the south-west form a village water supply. A rapid flow time to these springs was confirmed by the groundwater tritium concentration of 88 TU and on basic hydrogeological considerations it might be expected that the spring would be polluted. The fact that no pollution has been detected implies that dilution and chemical processes, such as sorption and precipitation, are sufficient to attenuate leachates before they reach the spring. However the high tritium groundwater concentration suggests a higher risk if wastes with a greater pollution potential were to be deposited at the landfill.

Example 4.

Waterton (3) suggested that large increases in sulphate concentrations in Magnesian Limestone sources used for public supply in the northeast of England had been caused by adjacent colliery spoil heaps. One of these sources was a mineshaft and Waterton noted that a burnt out pyritic colliery spoil heap was situated within a few metres of the shaft and suggested that the intense heat had created fissures in the glacial clays, allowing percolation of acid leachates, derived from the roasting of pyrites into the limestone. A sample taken for tritium analysis showed a concentration of 50 TU which suggests the rapid fissure transport of water. Thus although the tritium data cannot confirm Waterton's conclusions, they do not conflict with them.

Example 5.

Two gravel pits about 5 km apart, overlying Lower Chalk in the south of England have been used for the disposal of industrial solid and liquid wastes since the late 1940s . At both sites there is a significant unsaturated zone, 22 m thick at the northern pit and 45 m thick at the southern one. There is a borehole 400 m away from the northern site and the southern site has a borehole close to the disposal area which is drilled through the Lower Chalk into the underlying Upper Greensand. Groundwater tritium measurements gave 30 and 2 TU for the northern and southern borehole sites respectively. Thus the data suggest that the groundwater source 400 m away from the northern site is at more immediate risk from pollution by landfill leachates than the source immediately adjacent to the southern site. However, without much more detailed hydrogeological analysis, it is not possible to define whether this is because of the thicker unsaturated zone at the southern site, or because the bulk of the abstraction is from the Upper Greensand rather than the Chalk, or simply because there is a relatively steep hydraulic gradient away from the southern landfill in the opposite direction to the borehole.

Example 6.

The Bunter Sandstone aquifer is polluted in the area around a colliery in South Yorkshire (4) and a number of sources for this local pollution have been suggested as follows:

1. recirculation of mine drainage and/or coal washing water;
2. seepage from spoil heaps;

3. development of mining subsidence fissures allowing groundwater to move from the Magnesian Limestone into the Bunter Sandstone;
4. faulting of the sequence bringing Magnesian Limestone into contact with Bunter Sandstone;
5. connate water in the Bunter Sandstone,

or 6. saline intrusion from the River Don.

Tritium analysis of the main polluted groundwater source gave a value of 45 TU which suggests that the pollution has a high level rather than a deep-seated origin. Thus pollution mechanisms 1, 2 or 6 are favoured. The groundwater used for coal washing has a tritium concentration of 17 TU and if this were being recirculated, it might be expected that the polluted borehole would have a similar tritium concentration. The fact that it is much greater favours pollution mechanisms 2 or 6 and of these, seepage from spoil heaps, the solution advanced by Nicholls (4), appears the more likely.

Example 7.

Domestic waste is deposited in a disused sand quarry in easterly-dipping Bunter Pebble Beds in the English Midlands. A groundwater source lies 1.5 km to the south-east and was considered at possible risk from the landfill. The groundwater tritium concentration of 62 TU is unexpectedly high and warns of a potential high risk of pollution and the need for further hydrogeological investigations.

In few of the studies can the tritium data be said to have contributed nothing to an understanding of the potential pollution problems from adjacent landfills. These studies were generally those where there was an additional source of potential pollution whose tritium content was not determined. In two of the investigations the assessment of pollution risk was complicated by saline intrusion from adjacent estuaries. Their tidal nature meant that tritium contents and salinities varied with the state of the tide. When high tritium results were obtained, it was not possible to determine if this was the result of estuarine infiltration or was indicative of local rapid infiltration which could indicate a significant pollution risk from an adjacent landfill. However, even in these situations a negligible tritium content was still a useful result as it indicated the lack of post-1954 recharge and could be interpreted to imply that a rapid rise in the pollution load was unlikely. One of the studies revealed the probability of infiltration to the groundwater body from an adjacent canalized river and this again made meaningful interpretation of the tritium data in terms of potential landfill leachate pollution an impossible task.

5. DISCUSSION

The results of the research project indicate that under certain conditions analysis of environmental tritium concentrations can provide a relatively inexpensive general appraisal of the susceptibility of groundwater to pollution from adjacent existing landfills. These conditions can be summarized as follows:

1. Geological and hydrogeological conditions need to be simple with a relatively homogeneous aquifer.
2. The abstraction points used for groundwater tritium determinations should be down hydraulic gradient from the landfill and within 2 km.

3. Sites where there are complicating factors such as saline intrusion from an estuary, or induced infiltration from an estuary, or induced infiltration from an adjacent river, are likely to provide ambiguous results.
4. When liquid wastes are being discharged into a landfill their tritium content needs to be determined.

If these conditions are met, tritium measurements should provide a valuable 'worst risk' indicator in the preliminary assessment of pollution problems at existing landfill sites. However, it must be emphasized that tritium is only an indicator and to be most effective it must be used to supplement traditional hydrogeological analysis and not as a definitive parameter in its own right. Any deductions made from the tritium data will refer to landfill conditions as they were at the time measurements were made. Thus if for instance tritium data indicated very slow groundwater movement between a solid waste landfill and an abstraction point, this situation might completely change if a decision was taken to deposit liquid wastes at the site. In the present study single tritium measurements have been made, but more valuable data would be obtained if the tritium concentration of a groundwater source was monitored regularly over a longer period of time.

6. APPLICATION TO THE SELECTION OF NEW LANDFILL SITES.

Although the present study concentrated on existing sites, the results allow conclusions to be drawn with regard to the use of the technique in the preliminary assessment of potential landfill sites. The principles are the same but the results need to be interpreted much more cautiously. This is because the process of landfilling may significantly change the hydrological and hydrogeological regimes in the immediate area of the landfill. Infiltration might be increased or decreased depending upon the type of waste being deposited and the nature of the cover material used. This is particularly the case where liquid wastes are to be lagooned or mixed with solid wastes. In these cases a recharge mound might be formed beneath the site increasing hydraulic gradients and groundwater flow rates. However, providing these difficulties are considered when making assessments, thermonuclear tritium measurements of groundwaters provide a useful additional tool in the prediction of possible pollution hazards to local abstraction points from new landfill sites.

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SUPPORT PAPER E

CONSTRUCTION AND INSTRUMENTATION OF LYSIMETERS TO STUDY POLLUTANT MOVEMENT THROUGH UNSATURATED SAND

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and A. Parker.

ABSTRACT

As part of the Department of the Environment sponsored Landfill Research Programme being undertaken by a joint Institute of Geological Sciences/ Harwell team, a group consisting of four lysimeters has been constructed to investigate the movement of potential pollutants from landfill sites through unsaturated sand. The concepts involved in the work and the reasons for choosing a lysimeter technique are discussed. Three of the lysimeters are being irrigated, one with a synthetic leachate containing metallic cations, organic and inorganic acids and phenol, the second with an aqueous solution of organic compounds and the third with a solution of the common anions found in industrial and domestic waste leachates. Multi-outlet drip irrigation has been used and the progress of moisture fronts has been followed using tensiometers and a neutron moisture probe. Liquid samples from the unsaturated sand have been obtained using section probes installed at various depths in the lysimeters. The geology and hydrogeology of the experimental site and the techniques and problems involved in constructing the lysimeters are described.

1. INTRODUCTION

At the beginning of 1973 the Department of the Environment (DOE) authorized the expansion of an existing limited research programme on the behaviour of wastes in landfill sites, which was centred at the then Water Pollution Research Laboratory. This original research programme had been initiated on the recommendation of the Technical Committee on the Disposal of Toxic Solid Wastes which reported in 1970.

The expanded programme is divided between two research teams, one from the Water Research Centre (WRC) and the other a combined team from the Institute of Geological Sciences (IGS) and the Harwell Laboratory. The ultimate object of the work is to provide the scientific basis for a proposed Code of Practice on the selection of landfill sites for the disposal of various types of waste. In order to achieve this objective, the research teams are concentrating on experimental work within three principal fields:

(i) site investigations at selected industrial landfills;
(ii) laboratory studies under controlled conditions, and
(iii) controlled field experiments into the movement of pollutants through the unsaturated zone.

This paper concerns one aspect of the unsaturated zone studies which are the responsibility of the IGS/Harwell team.

Except when waste is tipped directly into standing water, there is an unsaturated zone beneath every landfill. This zone warrants particular attention as it is here the first contact occurs between leachates and rock minerals. Also within this zone groundwater flow is much slower than through the saturated zone, as only when all available pore space has been saturated will the maximum potential permeability of the material become effective. It thus constitutes a valuable buffer zone between the base of a landfill and the water table. It is appreciated that North American literature tends to regard the unsaturated zone as being of little significance; however, this probably results from the differing geological conditions in North America where over 90 per cent of groundwater abstracted for public supply and industry comes from unconsolidated deposits of sand and gravel in which the water table is relatively close to the surface. In the United Kingdom the majority of groundwater resources are contained within bedrock aquifers where the water table may be at a significant depth. Thus the unsaturated zone plays a much greater role in the potential attenuation of leachates and aquifer protection.

Because of the diversity of unsaturated zone conditions, pollutant movement within three different lithological types - chalk, sand and gravel - is being studied. A number of techniques are being used including laboratory columns, spray irrigation and monitoring of radioisotopic tracers and lysimeters.

For the investigations in sand, where groundwater flow is intergranular, lysimeter techniques are being used. These lysimeters include both monolithic cores containing approximately 0.65 m^3 of sand and field lysimeters which isolate approximately 50 m^3 of sand. The object of using field lysimeters is to isolate bulk samples of sand in an undisturbed condition so that pollutants will move under conditions approximating to those encountered in the field. The effects of permeability variations between sand layers, the presence of layers rich in clay minerals and any discontinuities can then be assessed and a much more realistic picture built up of unsaturated zone flow. It is appreciated that the basic chemical processes, such as ion exchange and precipitation, which occur between leachates and sand could be obtained from laboratory experiments. However, it is difficult to extrapolate from a laboratory to a field situation and by working with field lysimeters it is hoped to reduce some of the problems.

The geological requirement for such a lysimeter site is approximately 3 m thick layer of sand underlain by an impermeable clay. A series of sand masses can then be isolated by the construction of impermeable vertical walls through the sand into this underlying clay. Clearly the walls need to be constructed so that disturbance of the sand is kept to a minimum and the continuity between sand and walls must be such that edge effects are not significant. In order to instrument the lysimeters, access must be provided to one wall. The present paper describes the construction and instrumentation of four such field lysimeters at a site in Oxfordshire.

2. GEOLOGY

The site selected lies on an outlier of the Lower Greensand which at this non-conformable locality uncharacteristically overlies Kimmeridge Clay.

Four lysimeters have been constructed, two on either side of a central trench which allows access to one wall of each of the lysimeters (Figure 1). The clay/sand interface dips towards the northeast, so that the lysimeters to the east of the access trench contain 3.0 to 3.5 m of sand compared with 2.5 to 3.2 m of sand in those to the west (Figure 2).

The Lower Greensand consists of slightly clayey fine sands with more clayey beds occurring approximately every 0.5 m and correlates with the middle unit of the Lower Greensand of the Fernham area(1). Twenty-three discrete sedimentary units have been differentiated within these sands (Figure 3) and almost all are bioturbated with burrows up to 0.5 m in length. These sedimentary units are thought to be generally continuous across the four lysimeters although those above unit 4 thin towards the east.

Grain size analysis using the methods of Folk(2), including wet-sieving and pipette analysis, reveal that all the layers of sand contain approximately the same two fractions of material - a fine sand fraction averaging about 130 microns in size and a clay fraction averaging less than 1 micron in size - mixed in different proportions. The mineralogy of the sedimentary units was examined using X-ray diffraction techniques and the results are given in Figure 3. Material finer than 4 microns in size is mostly a smectite, probably calcium montmorillonite.

As a guide to relative smectite abundance, the area under the 14-15 Å diffraction peak is given in Figure 3. Comparison was made with standard diffractometer traces of known mixtures of quartz and Surrey fullers earth and these suggest that where smectite is most abundant it may form 30 to 35% by weight while it probably forms 5 to 10% where it is least abundant. There are subordinate amounts of clay-mica throughout the sequence and optical examination suggests that much of this is glauconite. The calcite and aragonite occur as shell debris. The sand is not cemented except locally within unit 1 where hard sandstone doggers occur. Prior to lysimeter construction there was only a transient water table which appeared a few cm above the sand/clay interface after significant infiltration had occurred.

3. CONSTRUCTION OF LYSIMETERS AND SUPPORT FACILITIES

Prior to the construction of the lysimeters an access road was laid to the research site and connections were made to the nearest water main and electricity and telephone cables. The walls of the lysimeters were constructed by driving sheet piling in parallel drives 0.5 m apart, excavating out between the piles, placing concrete in the resulting trenches and then withdrawing the piles before the concrete hardened. Two firms submitted tenders for the work and a contract was awarded to Cementation Construction Limited on a prime cost basis.

Unfortunately, once work commenced it soon became apparent that this construction technique was not satisfactory. The cohesive nature of the sands and the sandstone doggers made pile driving extremely slow and this was discontinued. An experimental trench was excavated to below the sand/clay junction and left for over a week. This trench proved to be stable and there was no sign of slumping even at the sand/clay junction. It was therefore decided to proceed by excavating trenches to the required depth, breaking sandstone doggers with a pneumatic hammer operated from within a safety cage, quickly lowering preformed reinforced steel mesh cages into the trenches followed immediately by the insertion of concrete. In this way the walls of all four lysimeters and the access trench were constructed during a period of 5 weeks. The work continued with the excavation of the access trench and the concreting of its floor slab. The bond between the sand and concrete proved to be excellent.

After discussion of the alternatives it was decided to cover the whole of the four lysimeters and the immediately surrounding area used for support facilities with an agricultural barn (Figure 2). This is 3 m in height at the eaves and will be used for agricultural purposes at the end of the project.

The liquids used for irrigation are stored in four 4550 litre tanks from whence they are fed via constant head tanks to the irrigation networks on individual lysimeters. These storage tanks are in turn supplied from a 13 600 litre tank fed direct from the mains. Effluent which is recovered from the lysimeters is fed to a sump from whence it is pumped to a 13 600 litre effluent tank which is periodically emptied by tanker. The sump will also collect any liquid spillages from within the whole of the barn so that there is no chance of contaminating the Lower Greensand outside the lysimeter walls.

4. INSTRUMENTATION

(a) Irrigation

An irrigation system has been developed for the application of artificial leachates to the surface of the lysimeters in an even and controlled manner. This consists of a grid of 100 jets, 40 cm apart, which are fed from a supply tank via a peristaltic pump giving a constant irrigation rate of 2 mm per day. To obtain even irrigation of the area between individual jets, and so minimize concentration gradients, the grid is rotated at one revolution per hour so that each jet describes a circle of 20 cm diameter. This rotation is obtained by the use of two motors attached to opposite corners of the grid by steel struts attached to their spindles.

(b) Suction probes

Liquid is extracted from the unsaturated sand by suction probes set at various depths below the surface to monitor the rate of downward movement of the artificial leachates and any concentration attenuation. Each probe consists of a slightly tapered ceramic thimble 12 cm long and 3.5 cm maximum diameter with a pore size of less than 5 μm, whose open end is sealed with a brass plate cemented by 'Araldite' to the thimble. A stainless steel tube is mounted off-centre through the end plate thus enabling liquid to be extracted before the thimble has been filled. The steel tube is attached by a length of plastic tubing to a peristaltic pump continuously running at low speed which enables liquid to be extracted at a rate of 0.005 ml per minute. To install a probe, a hole is drilled through the concrete retaining wall of the lysimeter from the access trench and extended by augering into the sand to a total distance (sand and concrete) of 2 m. The hole is inclined at a 10° slope to the horizontal such that the probe tip is below the tube exit. The performance of the probes improves with decreasing suction potential which is dependent on the degree of saturation and the grain size of the water-yielding material. Thus care has been taken to install them within the sand layers avoiding the clay-rich layers which are present in the lysimeters.

(c) Tensiometers and neutron probe access tubes

Tensiometers have been installed at various levels in two lysimeters to monitor suction potentials within the unsaturated sands. Modifications have been made to the design of commercially available instruments to enable installation at about 10° to the horizontal. The design used consists of a small 5 x 1 cm ceramic thimble (5 μm pore size) cemented by 'Araldite' to a 2 m length of stainless steel tube. It incorporates a side arm connected to a water manometer, a sight glass to check for entrapped air and a water reservoir containing 'soil moisture blue' which prevents algal growth.

To obtain a continuous profile of total water content, a neutron probe is being used. A vertical aluminium access tube was emplaced in each lysimeter using a modification of the method of Eeles(3). These tubes are installed throughout the whole thickness of the sand sequence and into the underlying clay.

(d) Other instrumentation

Probes for taking gas samples from the lysimeters, and thermocouples for temperature measurement have also been installed.

5. COMPOSITION OF IRRIGANTS USED ON LYSIMETERS

Of the four lysimeters available three are being irrigated with artificial leachates. These consist of:

(i) a solution containing heavy metal ions, alkalies, alkaline earths, chloride, lower straight chain carboxylic acids and phenol;

(ii) phenol, 2:4 dichlorophenol, aniline, trichloroethylene, 1:2 dichloroethane and m-xylene at a nominal 100 mg/1 level together with acetate,

and (iii) a solution containing various anions e.g. sulphate, chloride, acetate, nitrate, phosphate and bromide.

In deciding upon the composition of the first of these leachates, previous work on leachate composition was examined in detail. Both industrial and domestic waste leachates generally consist of a base of acetic, propionic and butyric acids which are produced by bacteriological breakdown of organic matter. In addition they may contain heavy metal cations such as chromium and cadmium together with sodium, potassium, calcium and magnesium as well as anions such as chloride and sulphate. Usually, iron is also present. After carrying out laboratory experiments to check its long-term stability, an artificial leachate of the following composition was selected.

Cadmium	100 mg/l	Nickel	100 mg/l
Calcium	500 "	Potassium	900 "
Chromium	100 "	Sodium	1000 "
Copper	100 "	Zinc	100 "
Iron	100 "	Chloride	1600 "
Lead	100 "	Acetic Acid	5000 "
Magnesium	100 "	Propionic Acid	3000 "
Mercury	10 "	Butyric Acid	2000 "
Lithium	20 "	Phenol	20 "

pH 5.0

The metal ion concentrations for Ni, Cd, Cr, Cu and Pb have been increased to ten times the maximum reported for leachates, for two reasons. In addition to facilitating analysis, these concentrations will be sufficient to saturate an appreciable fraction of the measured cation exchange capacity of the sands within the lysimeter. Although some of the metals will be precipitated as carbonates or basic carbonates, the movement of others may be influenced by the cation exchange capacity of the sand. Concentrations of Na, K, Ca and Mg have been kept near the maxima found in leachates. Lithium has been added as a tracer together with phenol which is a contaminant commonly associated with organic industrial waste. Because of the difficulties encountered in keeping appreciable amounts of iron in solution, a concentration of only 100 mg/l was chosen. Sulphate and phosphate have not been added since they may cause precipitation of lead and calcium.

The introduction into landfill of some organic compounds, particularly if they are significantly water soluble, may give rise to potential pollution hazards. For this reason, the behaviour of phenol, dichlorophenol and aniline at concentrations of 100 mg/l is being studied on a second lysimeter. Two halogenated hydrocarbons and xylene have also been incorporated into the aqueous solution since these are representative of dry cleaning solvents and paint constituents. However, owing to volatility and absorption losses, trouble is being experienced in maintaining these compounds at a reproducible level.

Leachates from landfills containing industrial and domestic waste, also contain inorganic anions as well as organic acids. The levels of sulphate and chloride may reach up to some thousands of mg/l as well as other anions at lower levels. For this reason the behaviour of a solution containing these components is being studied on a third lysimeter. The principle anions in the solution are SO4 (2500 mg/l), Cl (2100 mg/l), NO_3 (100 mg/l), PO4 (100 mg/l) and Br (40 mg/l) as a tracer. 1000 mg/l of acetate is also included.

6. PRELIMINARY RESULTS

Irrigation of the lysimeters with mains water commenced in June 1975. This preliminary irrigation was undertaken in order to attain equilibrium conditions, with a constant discharge from the base of the lysimeters, before irrigation with artificial leachates commenced. The hydrogeological regime established in one of the four lysimeters is illustrated in Figure 3. Attention is drawn to the presence of two unsaturated zones - A and B. The lower of the two owes its existence to the presence of the clay layer comprising unit 12.

Irrigation of the first of the lysimeters with the artificial leachate containing metal ions commenced in October 1975 and liquids from suction probes at different depths are being analysed regularly. The composition of the liquid reaching the probe 62 cms below the surface in lysimeter 4 during the first 130 days of irrigation is shown in Figure 4. It can be seen that the nitrate ion concentration present initially dropped steeply after some 50 days irrigation with the nitrate free synthetic leachate, and the alkali metal and alkaline earth ions also commenced to rise around this time, but had not all reached their concentration in the applied solutions. On the other hand the heavy metal ions had not yet appeared at the suction probe and the analyses for them are all less than 1 mg/l, most being near to the detection limits (they show considerable scatter and for clarity have not been plotted).

Cores of sand taken from the top surface after 54 days show that the heavy metal ions are being absorbed or precipitated in the top 10 cms of sand. After 120 days irrigation even the most mobile metals have only penetrated as far as 20 cms. The limited data on the total organic carbon (TOC) content of the solution at the 62 cms probe have shown maximum after 90 days which coincided with the coldest part of the winter months. It must be emphasized that data is still being collected and that it will be some years before the experiment is completed, since even the fastest moving front is only moving at 1 cm per day.

ACKNOWLEDGEMENTS

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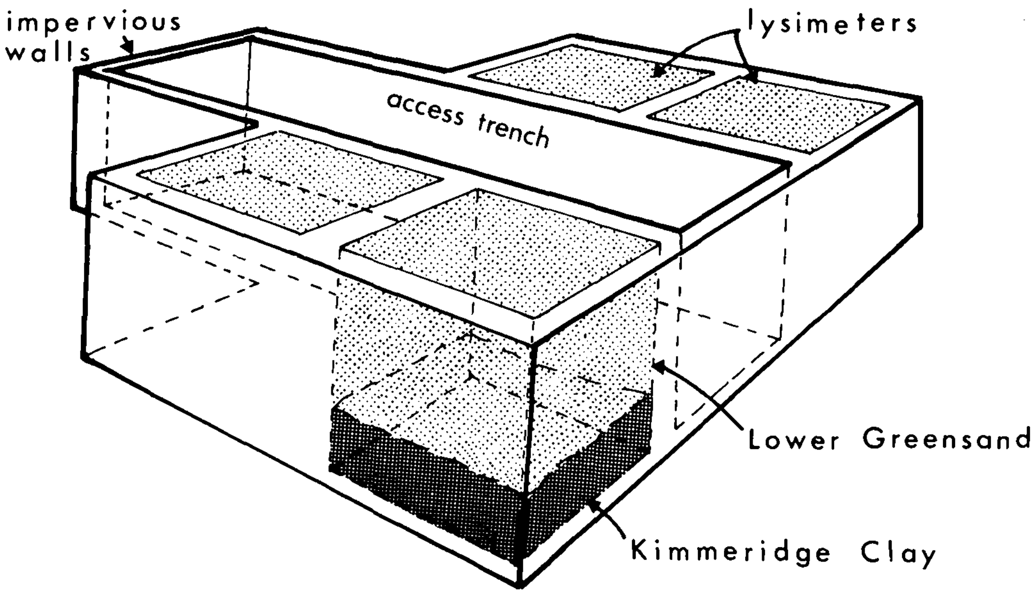


Figure 1. Basic configuration of the four lysimeters and access trench

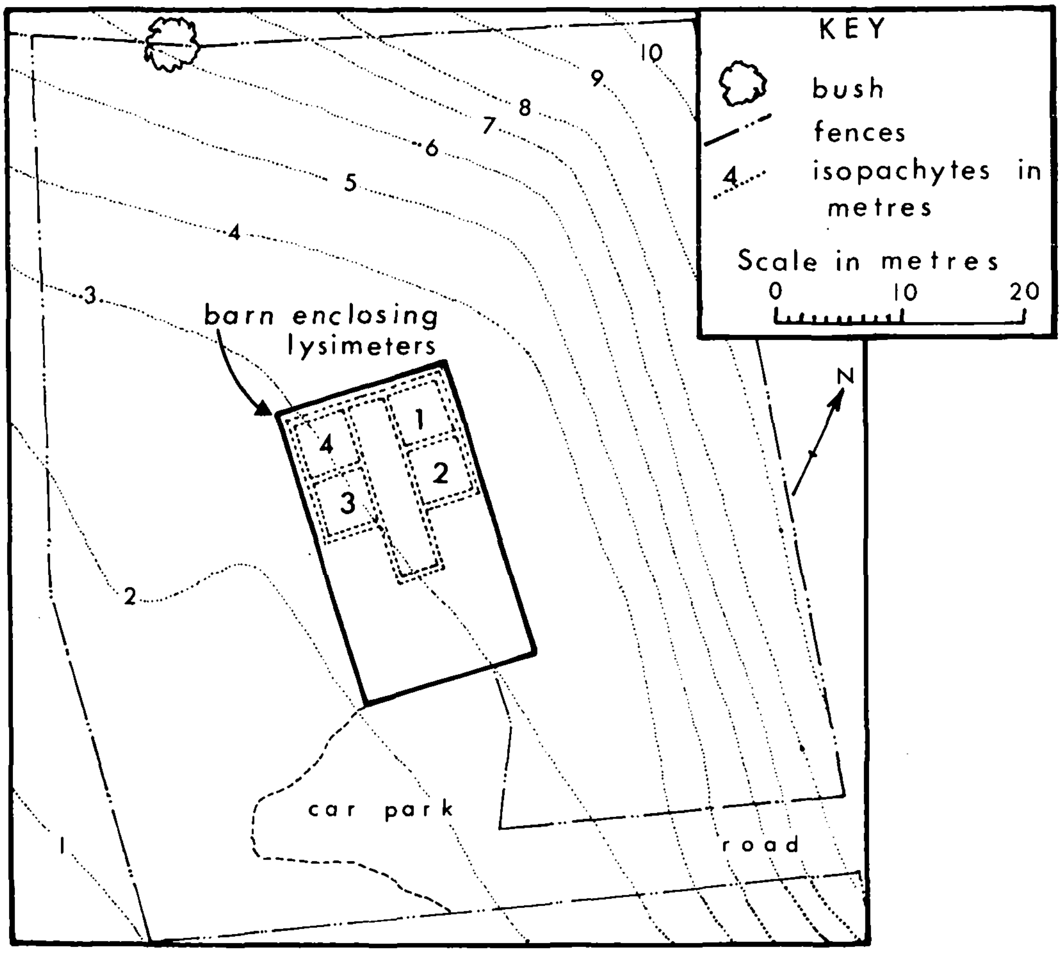
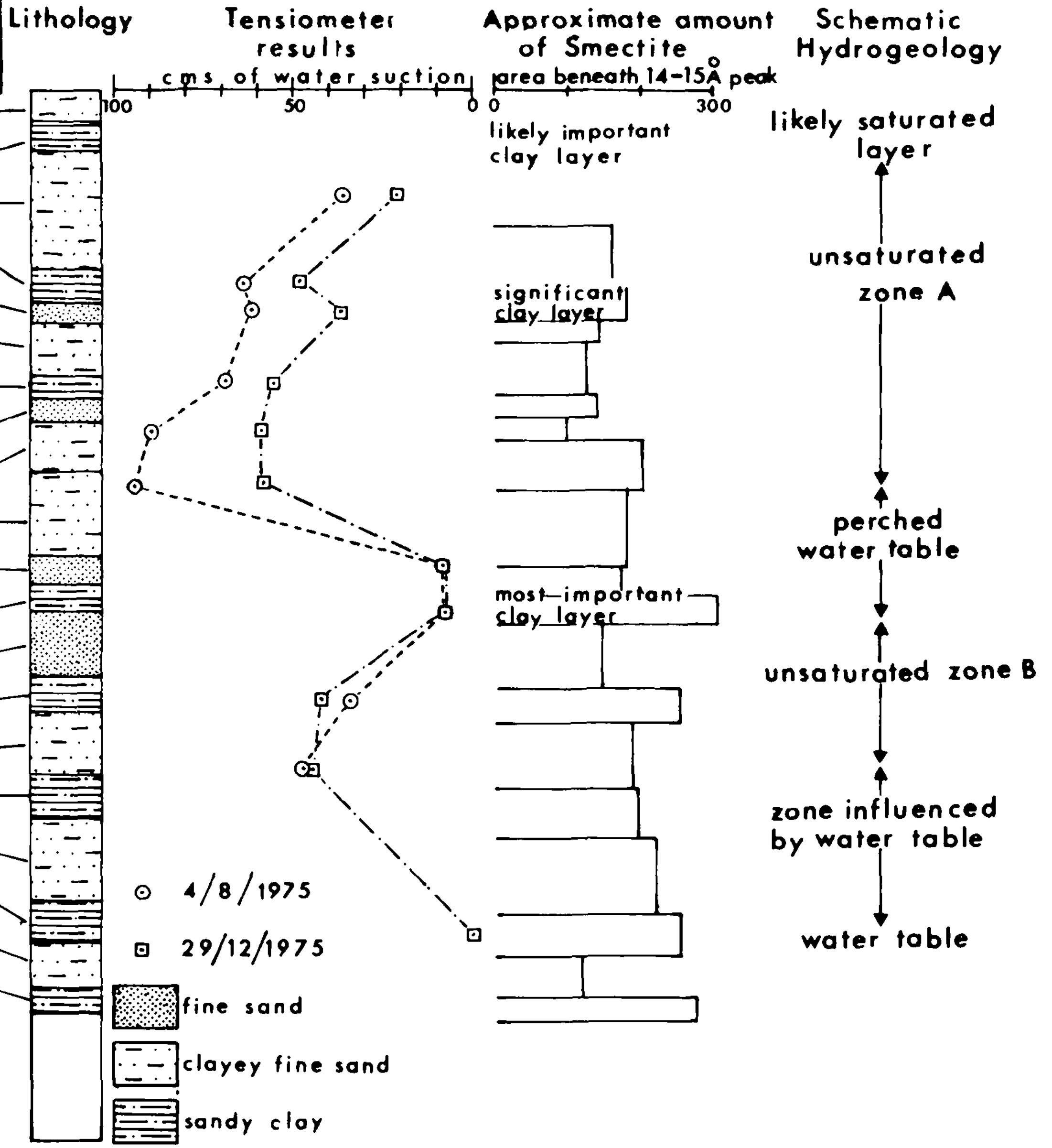


Figure 2. Location of the lysimeters in relation to the thickness of Lower Greensand

Mineralogy (2)				Unit No.
Quartz %	Feldspar %	Calcite %	Other Minerals (3)	
-	-	-	-	23
-	-	-	-	22
55	1-5	8	a p	21
70	1	4	a p	20
60	1	5	a p	19
60	1-5	5	p	18
55	0	6	p	17
70	5-10	6	p	16
60	5-10	6	a	15
60	0	10	a	14
65	1	6	a	13
40	1	7	a	12
50	10-15	3	a p *	11
45	1-5	4	a p	10
55	5-10	0	a	9
60	1	5	a	8
40	1	4	a	7
50	5-10	3	a *	6
60	1-5	0	a p	5
40	1-5	0	a p	4
65	1	0	a p	3
60	0	0	a	2
55	15-20	0	*	1



(2) Smectite and clay-mica also occur in each unit
(3) a ≡ aragonite, p ≡ pyrite, and * increased background count indicating 1-2% of amorphous iron-rich material

Figure 3. Correlation of the mineralogy, lithology, and hydrogeology within Lysimeter 4

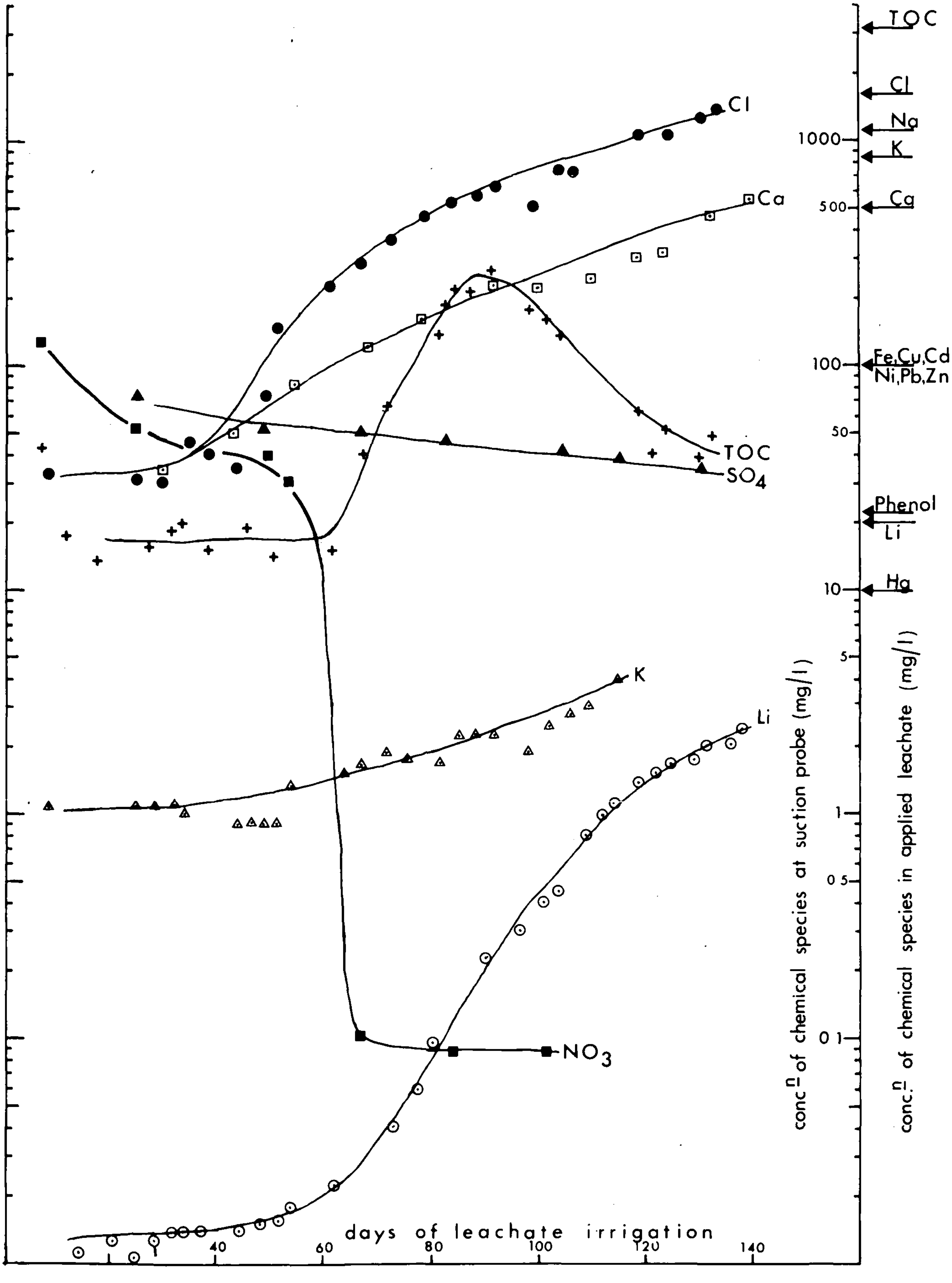


Figure 4. Selected chemical results from a suction probe 62 cms deep in Lysimeter 4

SUPPORT PAPER F

GROUNDWATER QUALITY MONITORING STRATEGY

Lorne G. Everett and Richard M. Tinlin

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1. INTRODUCTION

Groundwater serves as a major source of water supply in the United States. Public water supplies for one third of the nation's 100 largest cities are derived from groundwater. It is estimated that in rural areas 95 per cent of the domestic water and over half of the water for livestock and irrigation are obtained from underground resources. Furthermore, most of the day-to-day base flow of the nation's rivers and streams originates from groundwater discharge.

The natural quality of groundwater tends to be degraded by activities of man. Wastes which are not discharged into lakes, streams, or the ocean are deposited on land and from there may migrate downward to pollute groundwater. The extent of this pollution has grown in recent decades concomitantly with increases in population, agriculture, and industry; however, information as to the magnitude of the problem is meagre.

Currently, the United States Environmental Protection Agency (EPA) has an investigational programme of groundwater pollution under way on a regional basis. From the reports already issued (Fuhriman and Barton, 1971; Scalf, et al, 1973; van der Leeden, et al, 1973, 1975; Miller, et al, 1974), it is apparent that there are literally millions of point sources of pollution in existence.

Four basic types of monitoring have been defined by the EPA. In terms of groundwater quality, these may be interpreted as follows.

(a) Ambient trend monitoring. This concerns measurements of groundwater quality and deviations in relation to standards, and involves temporal and spatial trends within a groundwater basin or area.

(b) Source monitoring. This involves the measurement of effluent quantity and quality for pollution sources which may affect groundwater.

(c) Case preparation monitoring. This serves to gather evidence for enforcement actions of past, existing, or anticipated groundwater pollution situations; implied are carefully documented measurements within a circumscribed area.

(d) Research monitoring. This contributes to research investigations on groundwater quality and pollution occurrence and movement.

Of the four above types, the monitoring methodology listed herein is directed largely towards source monitoring. Case preparation and research monitoring, while providing valuable data, are clearly specialized needs which do not lend themselves to a national programme. Ambient trend monitoring provides background quality information on groundwater resources (such as the ongoing programmes of the U.S. Geological Survey). Thus, a national programme to protect groundwater quality relative to those activities of man which pollute groundwater will focus primarily on measurements relating to pollution sources and methods of waste disposal which contribute to pollution. Furthermore, because it is unfeasible to monitor all sources and causes of pollution, the strategy concentrates on identifying the most important sources and methods of disposal. In essence then the strategy becomes a resource allocation problem with the goal of developing a cost-effective monitoring programme which will contribute the maximum to the protection of the nation's groundwaters.

2. PURPOSE AND CONCEPT

The monitoring strategy described in this paper is intended to serve as a set of guidelines for developing and implementing a groundwater quality monitoring programme. It should be apparent that factors such as climate, hydrology, population, pollution sources, and water use vary from place to place; therefore, the design of an appropriate monitoring programme will also vary accordingly. No one set of guidelines can cover all situations; however, with judgement the approach presented herein can be extended and interpreted to meet most other situations which will be confronted in the field.

The physical, chemical, and biological mechanisms governing groundwater pollution are reasonably well understood. Yet, applying this knowledge to the many different situations which can result from superimposing a given groundwater pollution source upon a particular hydrogeologic environment is difficult. The strategy is expressed in a generalized form so that it can be usefully employed by regional, State, and local water pollution control agencies and is applicable to all types of groundwater aquifers, areas, and basins. Alternatives in the decision-making process leading to the final monitoring programme are considered throughout the strategy.

Monitoring may be defined as a scientifically designed surveillance system of continuing measurements and observations, including evaluation procedures. The EPA is currently involved in establishing, in co-operation with the States, a national groundwater quality monitoring system as part of the legislatively directed programme to prevent, reduce, and eliminate groundwater pollution.

3. GROUNDWATER MONITORING APPROACH

The monitoring strategy is presented in the form of a series of procedural steps arranged in chronological order. In this way, a straightforward sequence of actions is outlined which can lead to a groundwater quality monitoring programme in a given area. The monitoring strategy consists of 15 steps, listed below:

Step 1 - Select area or basin for monitoring.
Step 2 - Identify pollution sources, causes, and methods of waste disposal.
Step 3 - Identify potential pollutants.

Step 4 - Define groundwater usage.

Step 5 - Define hydrogeologic situation.

Step 6 - Study existing groundwater quality.

Step 7 - Evaluate infiltration potential for wastes at the land surface.

Step 8 - Evaluate mobility of pollutants from the land surface to the water table.

Step 9 - Evaluate attenuation of pollutants in the saturated zone.

Step 10 - Prioritize sources and causes.

Step 11 - Evaluate existing monitoring programmes.

Step 12 - Establish alternative monitoring approaches.

Step 13 - Select and implement the monitoring programme.

Step 14 - Review and interpret monitoring results.

Step 15 - Summarize and transmit monitoring information.

Each of the above steps has been fully developed in a recent TEMPO report (Todd, et al, 1976). Expanded discussion and site-specific examples are given for each of the steps in the strategy. To remain within the page confines allowed by the Conference, only Step 10 will be presented.

3.1. STEP 10 - PRIORITIZE SOURCES AND CAUSES

The monitoring strategy consists of a sequence of monitoring objectives or steps which must be performed in order to prioritize the identified sources and causes of groundwater pollution for monitoring within each of the selected monitoring areas. These monitoring objectives are presented not only in a chronologically preferred order for accomplishment but also in an order of increasing difficulty, both in terms of the monitoring methods available to accomplish these objectives and in terms of capability to interpret the data obtained from using these methods. Concomitantly the costs increase with implementation of these methods and the analytical procedures used in their evaluation. A recent TEMPO report (Everett, et al, 1976) describes the majority of groundwater monitoring methods and provides a generalized cost breakdown of the major cost factors for each method.

In the early stages of a monitoring programme it will not be possible to make an accurate prioritization of the pollution sources because of incomplete data and knowledge regarding the fate and transport of pollutants in site-specific situations, unless considerable monitoring is already under way. The prioritization scheme is dynamic in nature and with time will tend towards an optimum as more information is gained from a monitoring programme.

Each objective of the strategy has been carefully selected to identify and build up the prioritization scheme which follows. In Step 1 criteria for selecting the monitoring areas are set forth. Step 2 prescribes that each monitoring area should be fully inventoried for known or potential sources and causes of groundwater pollution, and the method of waste disposal associated with each source determined. Completion of Step 3 will result in the identification of the biological, chemical, physical, and radiological characteristics of the pollutants associated with each source and as a result will allow a trial ranking to be made of the sources and causes in terms of the potential of the various pollutants to violate drinking water standards. Completion of Step 4, which has as its objective identification of groundwater usage in the vicinity of each source will allow a further refinement of the trial ranking of the sources and causes made in Step 3, based this time on their threat to existing groundwater usage.

Of the possible uses of groundwater, it is commonly held that usage for potable water supplies stands out as paramount. Therefore, sources and causes which pose a health threat to potable water supplies will have priority over nonhealth-related damages to potential users. Of foremost concern then in the prioritization will be pollution sources expected to result in the presence of pollutants exceeding the U. S. Public Health Service mandatory drinking water limits. For other sources of pollution the damage to users can be estimated on a monetary basis and the prioritization carried out based on the cost of anticipated damages to existing or potential users. The cost of groundwater quality degradation has been estimated, in areas such as the Los Angeles Basin in Southern California, in terms of the following considerations.

(a) Quality-related consumer costs, i.e., the cost of various treatments such as water softening or chlorination.

(b) The cost of removing the pollutant to the background level of the groundwater resource.

(c) The cost of removing the pollutant in the groundwater to the limits of drinking water standards.

In another instance a detailed investigation was made of an incident where a freshwater aquifer had been polluted by accepted disposal of oilfield brine through an 'evaporation' pit and later a faulty disposal well (Fryberger, 1972). Several rehabilitation methods were evaluated in detail, including controlled pumping to the Red River and deep-well disposal. Although real economic damage both present and future resulted from this brine pollution, rehabilitation was determined to be not economically justified.

With completion of Steps 2, 3 and 4 of the methodology a much improved appreciation of the potential for groundwater quality degradation at the land surface will be realized.

One of the more difficult tasks facing an agency charged with monitoring groundwater pollution sources will be to gain an accurate understanding of the fate and transport of pollutants associated with particular sources in site-specific situations. The presence of a pollutant at the land surface does not necessarily demonstrate a threat to groundwater quality. In most situations important data deficiencies will exist relative to pollutant mobility. The application of generalizations regarding the fate and transport of pollutants subsurface should be used with great care. Sometimes under tight budgetary constraints no other choice will exist. In such cases the application of rule-of-thumb generalizations should be left only to the specialist.

The objectives of Steps 5 and 6 are to gain a site-specific appreciation of the hydrogeology and existing water quality in relation to the pollution sources. In general, it will not be an objective of Steps 5 and 6 to require that regional appraisals of hydrogeology and groundwater quality be conducted, unless a diffuse source covering many square miles is involved.

Steps 7, 8 and 9 comprise the basis for estimating pollutant mobilities and their ultimate presence at a point of groundwater discharge. Based on the estimations of pollutant mobilities determined as a result of the analyses carried out in these three steps, it will be possible to make a more accurate revision of the prioritization made in Step 4. The final three-phase adjustment in the prioritization will be made by considering first the potential pollutants at the land surface (Step 7), secondly, pollutants potentially reaching the water table (Step 8), and lastly, pollutants potentially reaching water supply wells (Step 9).

The refinement in the prioritization carried out as the result of Step 8 will have particular significance in terms of the nondegradation mandates of U. S. PL 92-500 and for the protection of sole source aquifers as required under U. S. PL 93-523. The refinement in the prioritization carried out as the result of Step 9 will have particular significance in demonstrating whether or not existing usage is being threatened and for estimating potential damages to these users. Solute transport models will play an increasingly important role in the years to come as a means for estimating the damage potential to the groundwater users.

Completion of the procedural steps and resulting prioritization scheme suggested above will allow a monitoring agency to direct its monitoring resources in a most effective manner toward the primary goals of PL 92-500 and PL 93-523. The prioritization obtained will need to be re-evaluated on at least a yearly basis as pollution controls are implemented and as new sources of pollution are detected.

It should be understood that the strategy presented herein must of necessity be somewhat generalized. There are a large number of combinations of pollution causes, hydrogeologic situations, and monitoring methods, among other variables, that can govern the implementation of a monitoring programme.

Therefore, persons involved in a monitoring programme will be required to exercise professional judgement in order to interpret and to apply this strategy to the specific local situations which they encounter. Site-specific examples of the application of the strategy are presented by Tinlin, 1976.

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SUPPORT PAPER G

TRACER TESTS IN GROUNDWATER

Dr Jan Sidenvall

ABSTRACT

Uppsala city relies for its water supply on natural groundwater and recharged river water. The recharge plants have a total capacity of 700 l/s and the groundwater well galleries 1200 l/s.

To ensure a supply for the next 30 years, large-scale investigations have been made and two new recharge plants and two groundwater well galleries have been constructed. The area concerned is shown in Figure 1.

Different tracer tests were carried out as follows.

(a) The velocity of natural groundwater flow in the esker of Uppsala was determined. The complex Cr-EDTA was used.

(b) At Vallskog, test recharging was started. During recharge oxygen and temperature were determined <u>in situ</u>, by means of sampling from special test well galleries. At different depths water samples were collected for chemical analysis.

Only 500 m from the recharge basin recharged water had dispersed to become indistinguishable from natural geoundwater. To confirm the results, one curie of ^{51}Cr-EDTA tracer was added to the recharge basin. Chromium-51 was determined in situ, and dispersion coefficients determined.

(c) Groundwater velocities were determined during recharge. Twelve kg of Cr in Cr-EDTA was added to the recharge water. It was possible to follow the tracer all the way from recharging to the abstraction well-field at Storvad, a distance of 2600 m.

About 10 km to the north of Uppsala a new large recharge plant (Vallskog) will be built. From this plant recharged water will flow through eskers to three different groundwater well-fields at Svista, Fullero and Storvad. Only Storvad has been constructed in this area at the moment.

1. GEOLOGY

The esker of Uppsala is deposited on the western slope of a fairly large north-south trending valley near the town. The coarser parts of the esker are deposited in the lower part of the valley, so that groundwater is readily available here. The rest of the valley is filled with clay and some glacial till.

Figure 2 shows a profile of the geology at Skediga. Here the esker can be sub-divided into a very coarse part, intersected in boring No. 7314, and a more normal part.

1. 1. VELOCITY OF NATURAL GROUNDWATER

At test well No. 7314 at Skediga, 1 kg of Cr, in a solution of Cr-EDTA, was pumped into the esker. Groundwater samples were taken every day at the Storvad well gallery 1300 m down gradient. During the whole test the groundwater gradient remained at 0. 2%.

As previous experience told us that we might expect a velocity of 10 to 15 m a day, the result, shown in Figure 3, was very surprising to us. The test was therefore repeated, but with the same result. There were two different plumes of tracers probably following different paths in separate parts of the esker. One moved with a velocity of 120 m a day. The main cloud, however, moved with a velocity of 60 m a day, which means that the esker material here must be very coarse and permeable. The borings show coarse material only.

If the velocity was the same from the proposed recharge plant to the proposed well-field at Storvad the situation would be very serious. River water would not disperse adequately into the groundwater system. Further tests will be necessary to confirm the preliminary results.

1.2. RECHARGE TESTS AT VALLSKOG

An experimental recharge basin was constructed at Vallskog, and around the basin three different observation wells were drilled. In Figure 4 parts of these wells are shown with groundwater levels during recharge.

In May 1974 pumping of water from the river Fyris was started at the rate of 180 l/s. The recharged water was analysed frequently and some especially relevant details are shown in Figure 5. Total hardness in German degrees (dH^{o}) and temperature (^{o}C) are according to an arithmetic scale, the rest is according to logarithmic scale (for example specific conductivity (H)). Other ions were determined also, but they did not provide much information as tracers. At the bottom of the figure the recharge period is shown. Temperature has already been used as a tracer, and it was known that the temperature of recharged water varied between $0^{o}C$ and about + $25^{o}C$ (Figure 5). Natural groundwater has a temperature of between 7 and $8^{o}C$. The temperature was therefore determined daily at the test wells and at different depths before and during the test. Figure 6 shows a few examples of temperature curves from test well No. 7401 at Vallskog. The vertical axis gives the depth and a separate column shows the stratigraphy.

The temperature curves show how recharged water reached well No. 7401 around the 28 June 1974. After that time the temperature rose quickly indicating that recharged water reached this well in the beginning of July. Note that the warm and less dense recharged water entered the well at a depth of 26 m.

After another month recharged water was detected at the groundwater level (6 m). This shows clearly how the velocity at the depth of 26 m is much higher than that at the groundwater level although the density of natural groundwater is higher than that of recharged water.

At test well No. 7416, recharged water reached the well first at a depth of 12 m (Figure 7). Later there were two different intervals of recharged water at this location, one at a depth around 12 m and another at a depth of 25 m.

Figure 8 shows temperature, oxygen and water chemistry at a depth of 26 m for well No. 7401. During April and May, 1974, the curves reflect the composition of natural groundwater, then around 10 June the concentration of most constituents changed. After a few weeks the groundwater was virtually identical to the recharged water. At the beginning of July the temperature rose rapidly and this was also found to occur in the other test wells.

These tests were followed by a tracer test. One curie of ^{51}Cr in the complex ^{51}Cr-EDTA was put into the recharge basin during recharge and daily during the test ^{51}Cr was measured in situ at all test wells. Eventually it appeared that the tracer had moved towards well No. 7401 only. The tracer was detected in the interval 18 to 20 m in this well.

From these observations we can make the following interpretations, where the distance from the recharge basin to well No. 7401 was 165 m and the groundwater gradient remained the same.

(i) Velocity interpreted from temperature was 3 m/d.
(ii) Most ions had a mean velocity of about 4 m/d.
(iii) The velocity of ^{51}Cr-EDTA dosed water was 8 m/d.

Some of these tests were repeated under the same circumstances with the same results.

This indicates that groundwater as well as recharged water in an esker flows in a complex way, and moves preferentially through the most coarse material, often of a lenticular form.

From the experiments at Vallskog we have determined a dispersion coefficient, and calculate that recharged water should disperse completely into natural groundwater less than 500 m from the recharge basin.

At a test well-field at Ensta 800 m from the recharge basin there has been no change in the water composition or temperature during 1974 and 1975 that could be connected with recharge.

1.3. LARGE-SCALE TRACER TEST WITH Cr-EDTA (Vallskog to Storvad)

As it was now clear that the rate of water movement changed very much from Vallskog to Storvad we wanted to know where the change took place. Figure 9 shows the area in question, the distance between Vallskog and Storvad being 2600 m. Shaded areas show parts of the Uppsala esker, most of which is covered by clay. Circles show where a few important groundwater observation wells are placed and these are just some of more than one hundred wells in this area. The map also shows the groundwater level contours during the tracer tests and the solid circles show examples of wells in different observation well-fields.

Twelve kg of Cr as the Cr-EDTA-complex was put into the recharge basin at Vallskog during recharge. Water samples were taken at different well-fields and at different depths.

The different velocities determined by this experiment were:

from recharge basin to well No. 7401 at Vallskog	8 m/d
from recharge basin to well No. 7418 at Ensta	7 m/d
from recharge basin to well No. 7314 at Skediga	11 m/d
from recharge basin to well No. 7412 at Faxan	12 m/d
from recharge basin to wells at Storvad	15 m/d

The following results were also obtained:

from basin to well No. 7401	8 m/d
from well No. 7401 to well No. 7418 at Ensta	6 m/d
from well No. 7401 to well No. 7314 at Skediga	12 m/d
from well No. 7314 to well No. 7412	9 m/d
from well No. 7314 to Storvad well gallery	24 m/d

2. RESULTS

These results show that it is possible to follow groundwater over a very long distance. On the other hand the results must be used with care. The first tests (Skediga to Storvad) gave a medium velocity of 60 m/d at a gradient of

0.2%. The tracer flowed through a thin, permeable interval not typical of the full groundwater system. But for the whole groundwater flow over the same distance and the same gradient the medium velocity was about 24 m/d.

Locally temperature and some naturally-occurring ions are good tracers if the dispersion coefficients are known. On the other hand special tracers such as Cr-EDTA are fairly cheap and very easy to use and to detect.

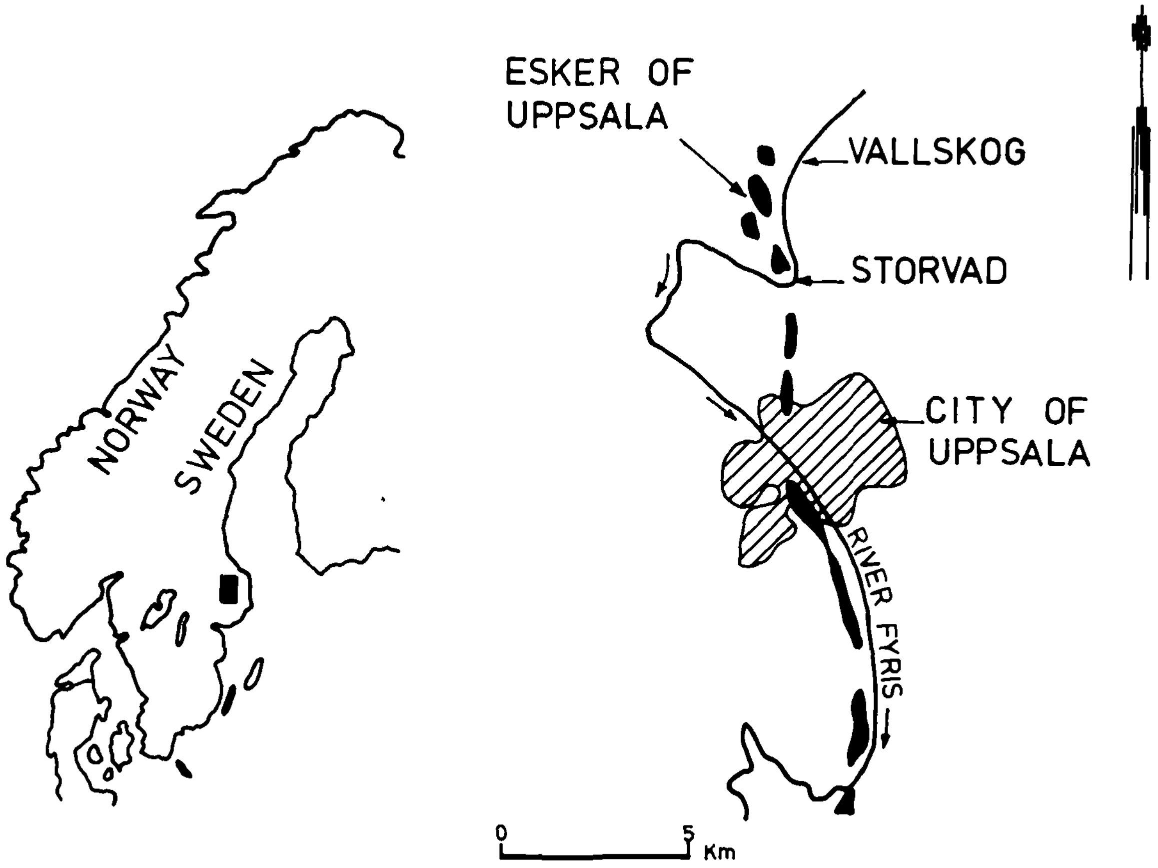

Figure 1. Location maps

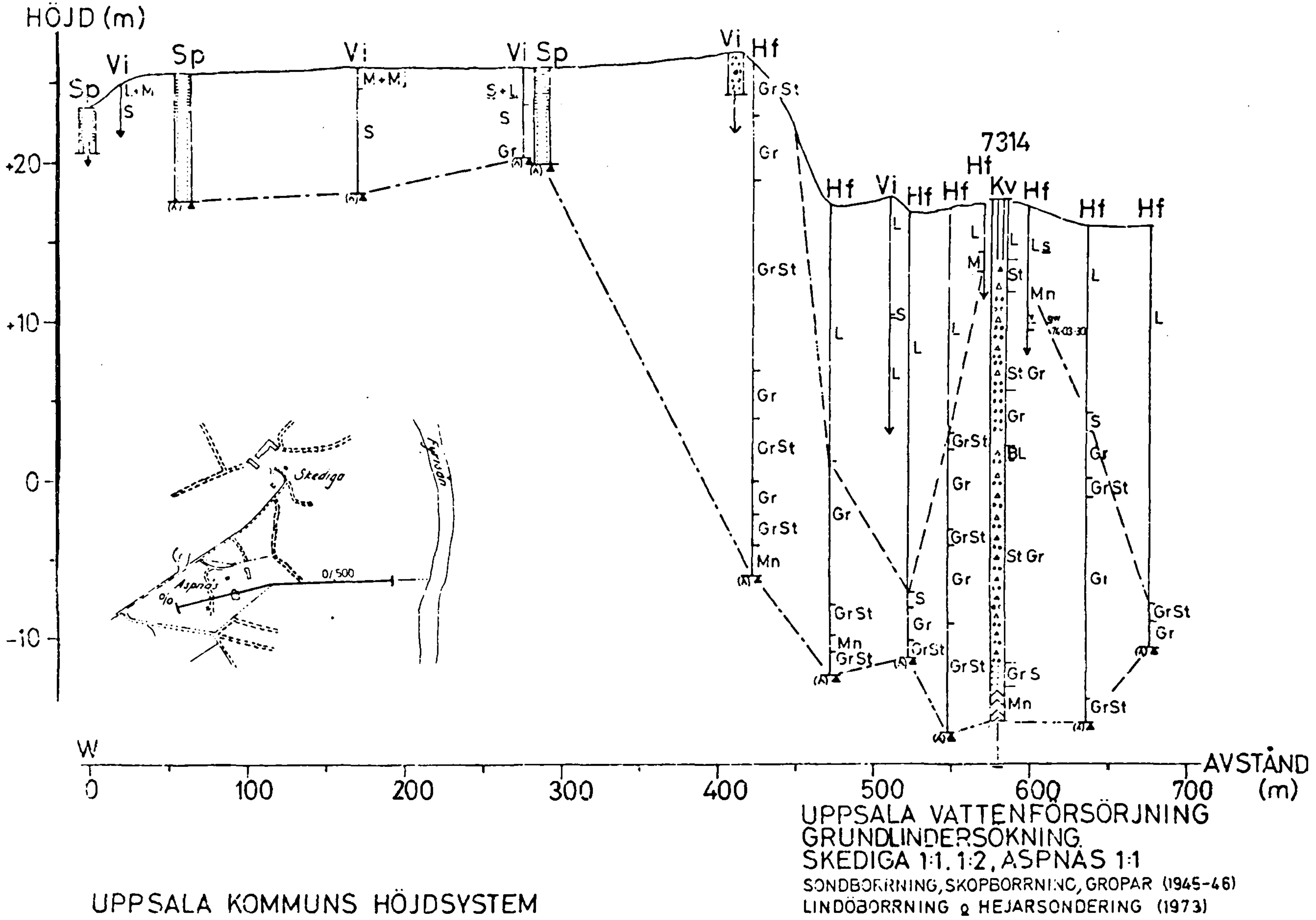

Figure 2. Concentration of Cr-EDTA at Storvad groundwater well-field

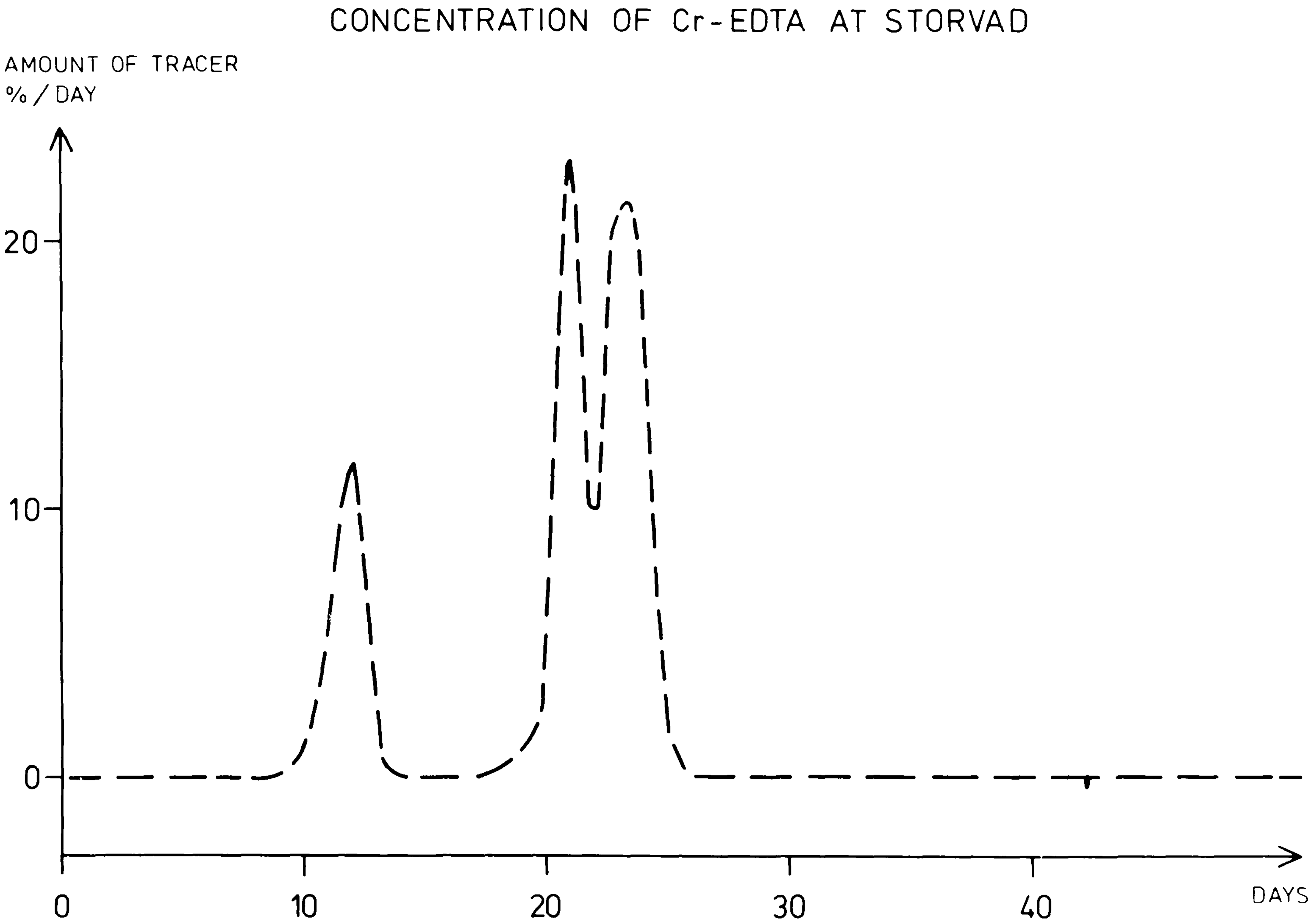

Figure 3. Geological section at Skediga.

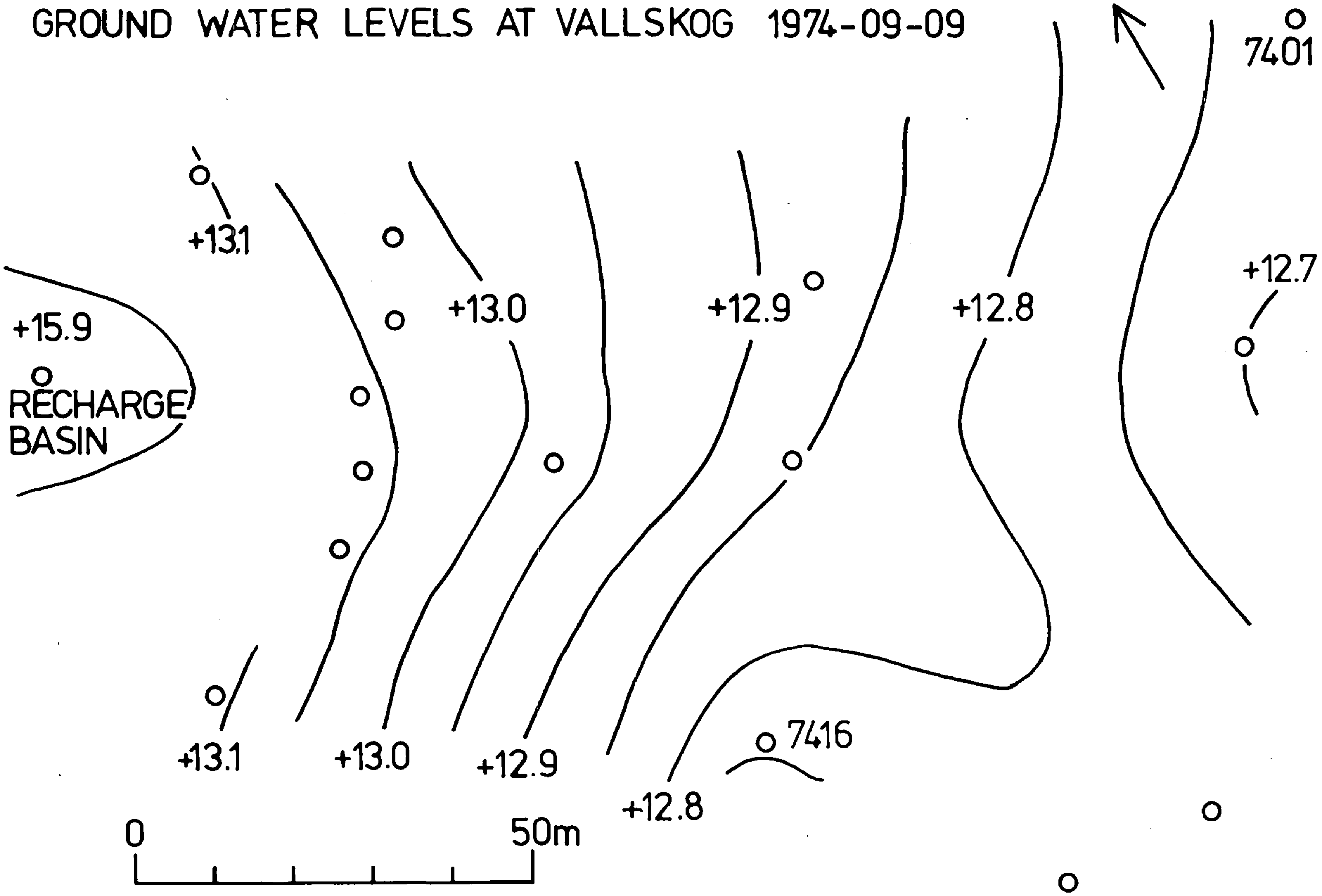

Figure 4. Test well-fields at Vallskog recharge basin. The map also shows groundwater levels during recharging.

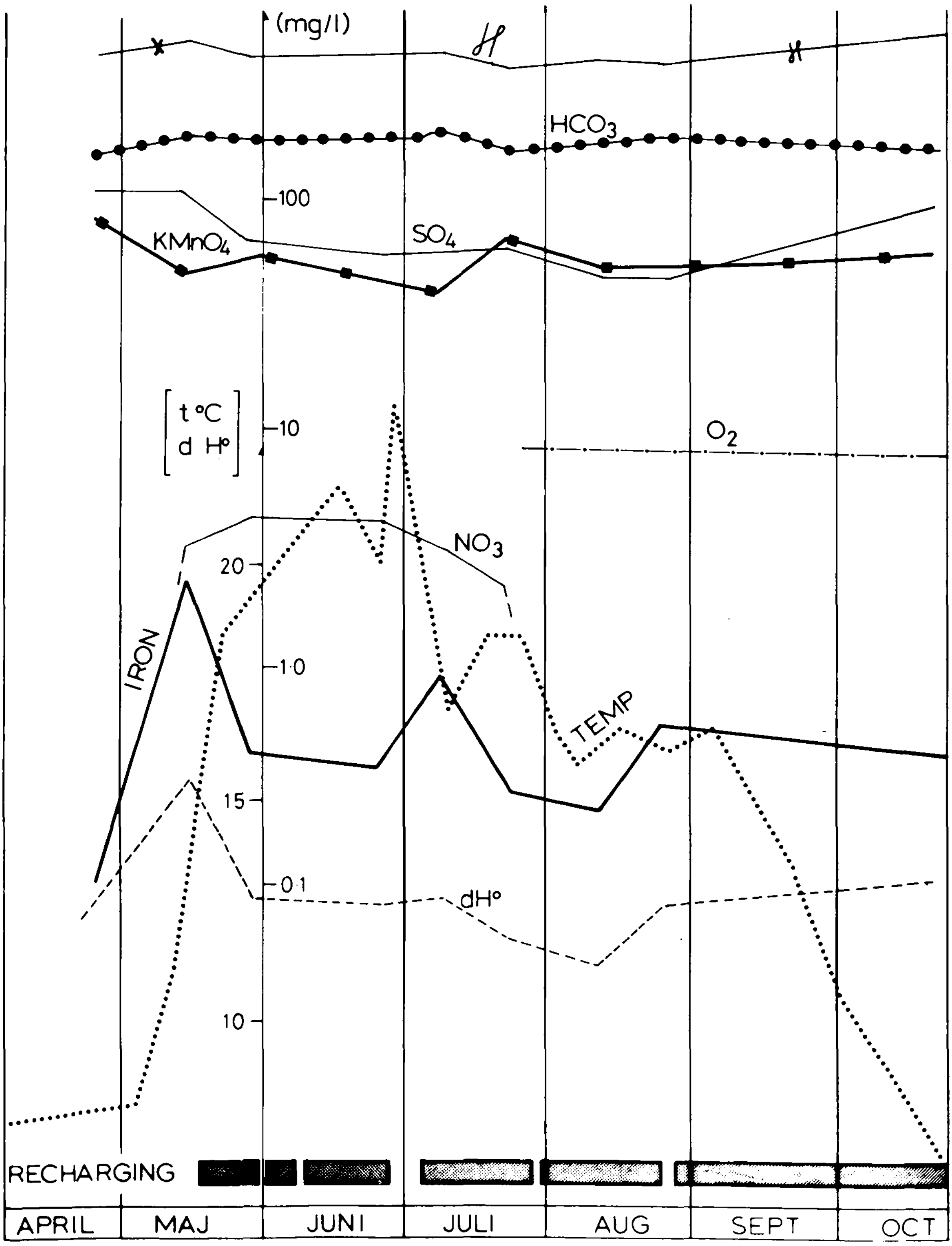

Figure 5. Waterchemistry, River Fyris, 1974.

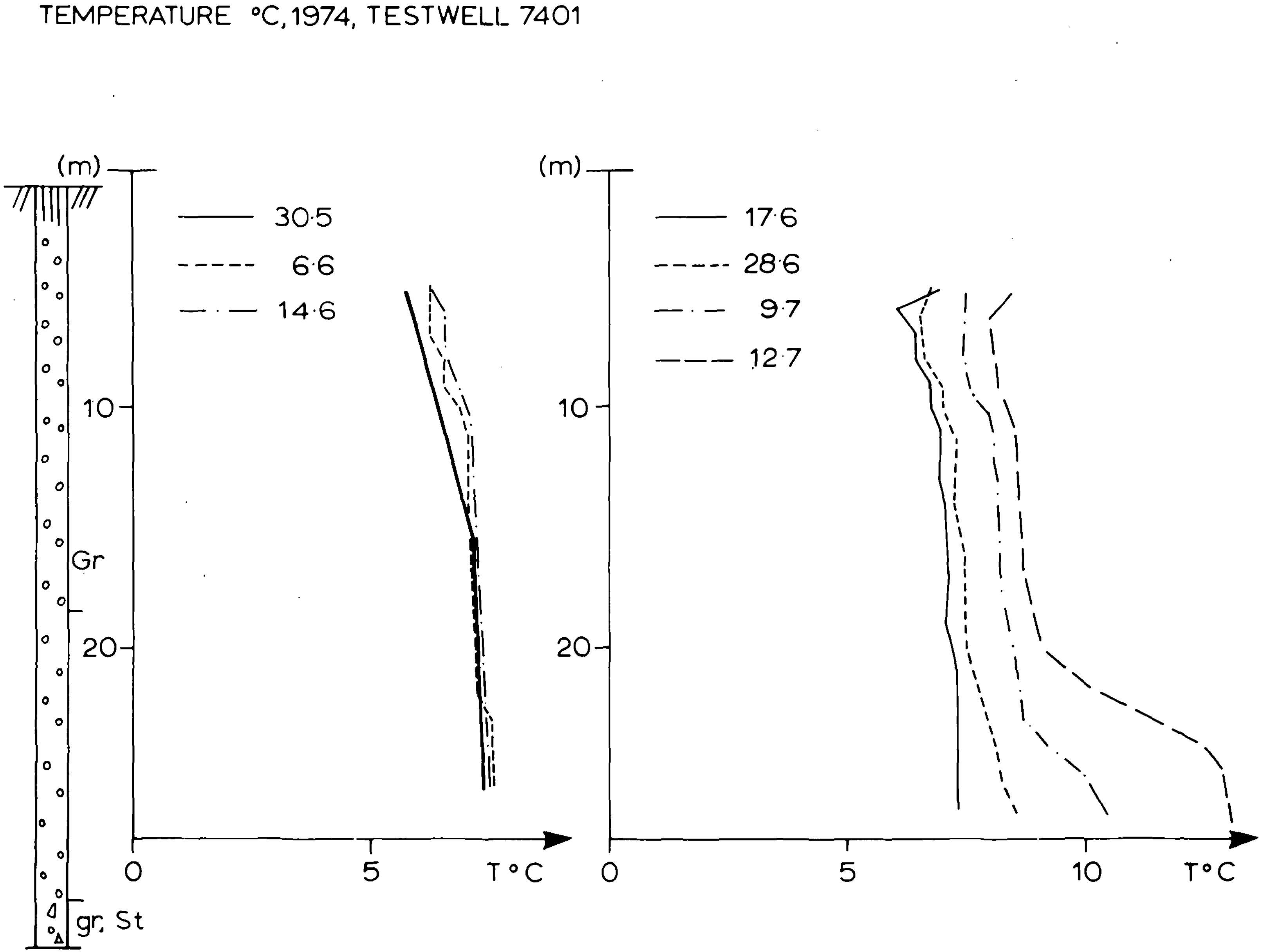

Figure 6. Water temperature curves at well No. 7401.

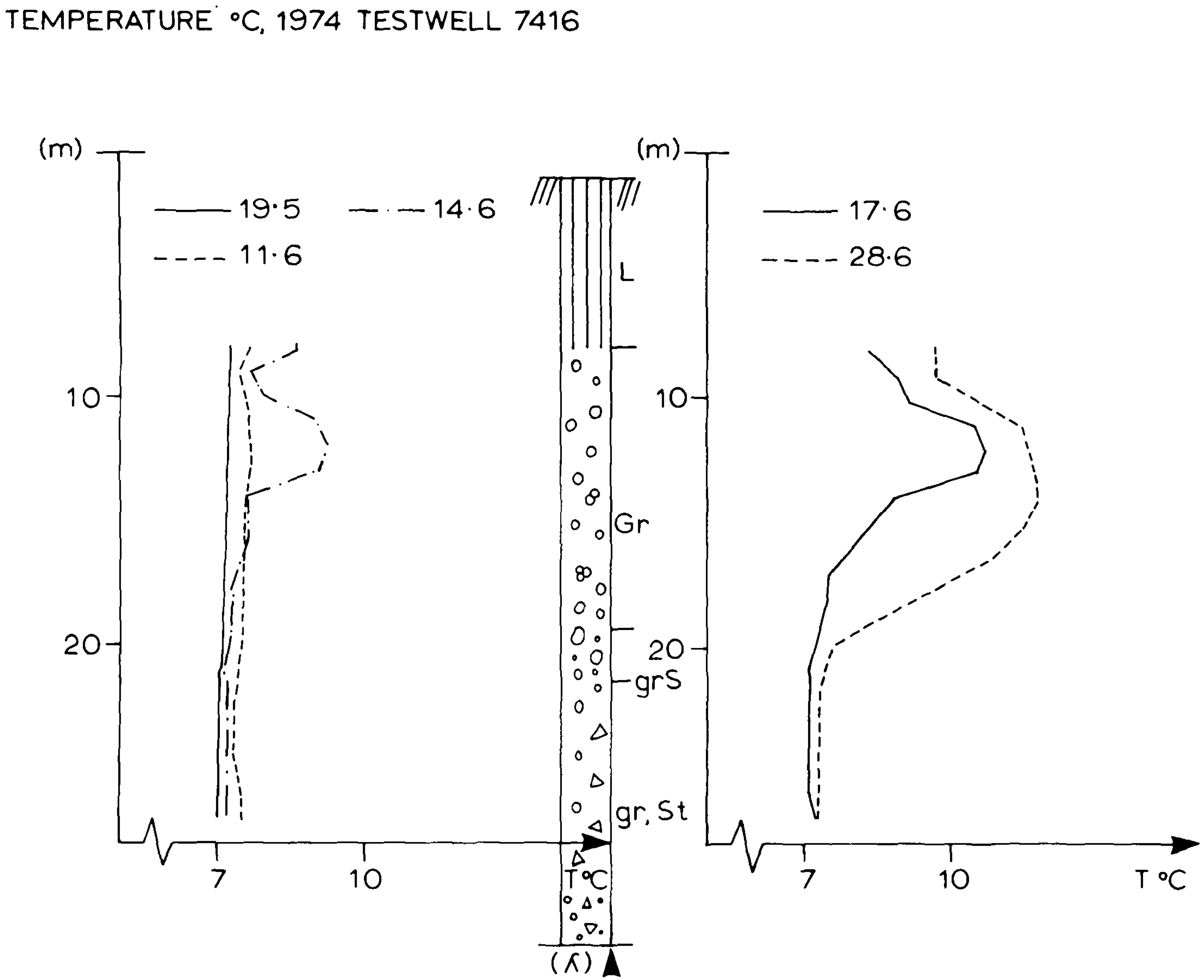

Figure 7. Water temperature curves at well No. 7416.

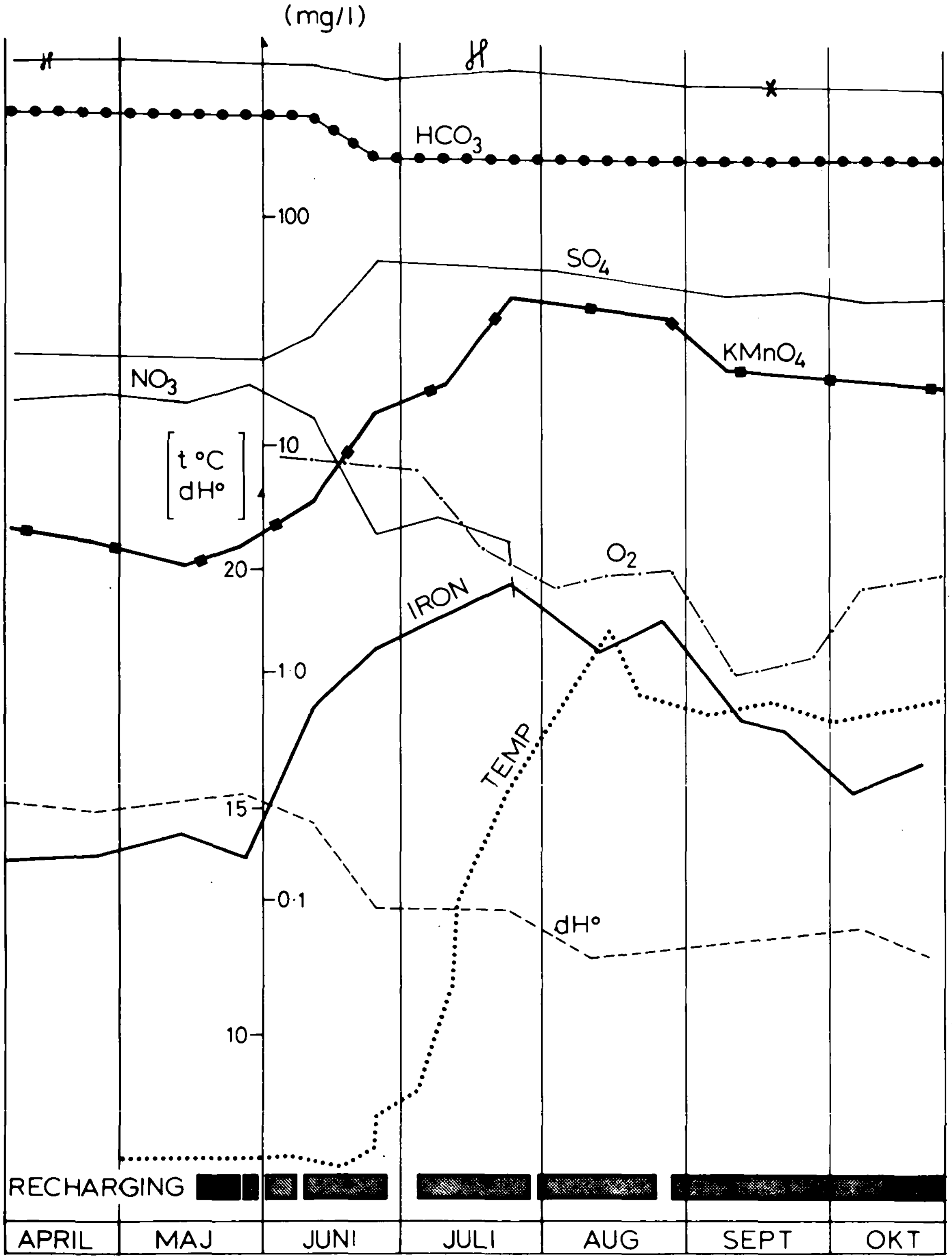

Figure 8. Water chemistry at well No. 7401.

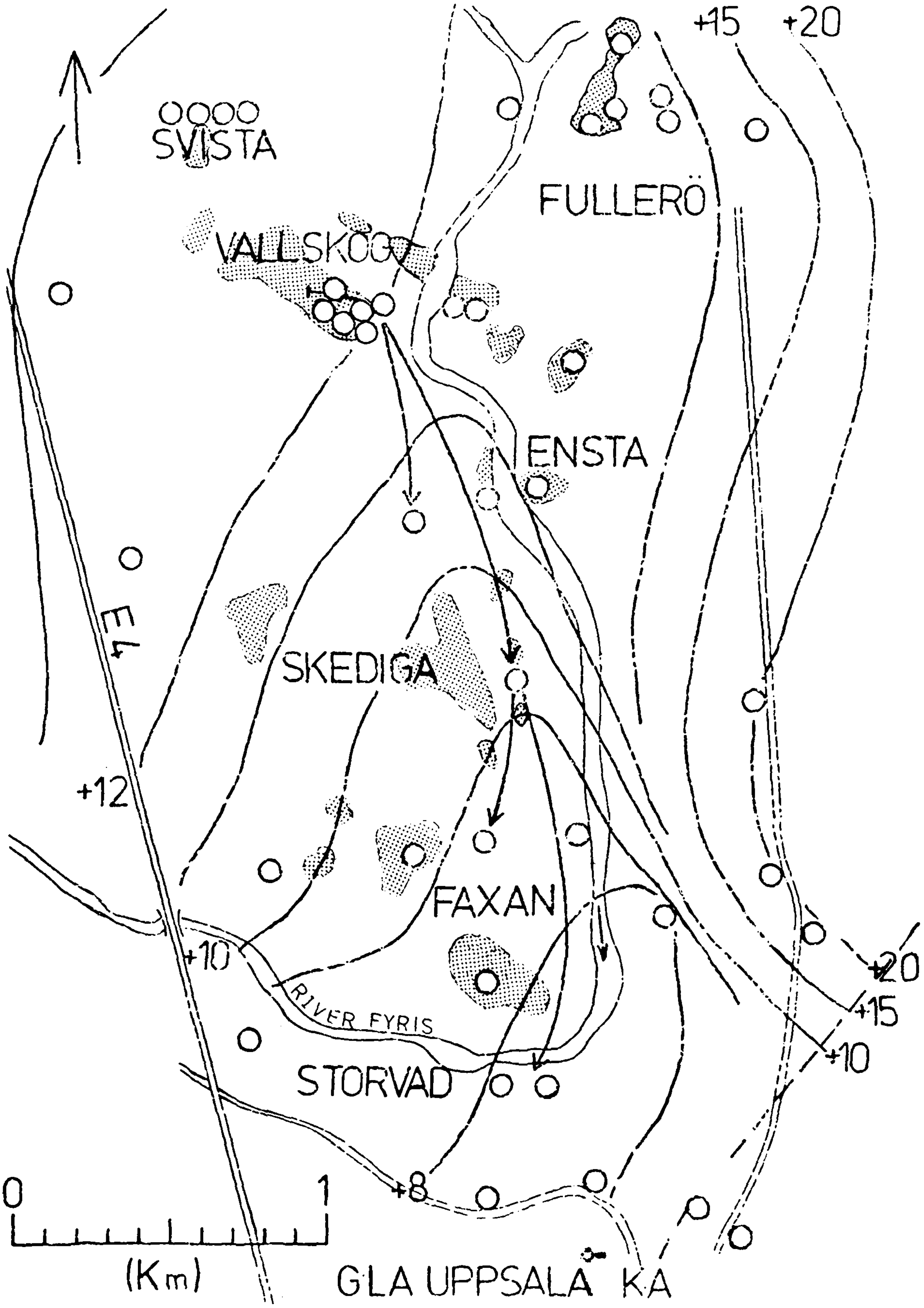

Figure 9. Map showing how the tracer Cr-EDTA moves during the large tracer test

SUPPORT PAPER H

THE DETECTION OF CONTAMINATED GROUNDWATER IN THE NOTTINGHAMSHIRE TRIAS BY GEOPHYSICAL TECHNIQUES

J.W. Finch and D.H. Griffiths

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1. INTRODUCTION

At the request of the Severn Trent Water Authority the Department of Geological Sciences, Birmingham, has recently been investigating the possibility of detecting polluted groundwater in the Trias in Nottinghamshire using geophysical methods. As the aquifer is being increasingly developed there have been a number of occurrences in which boreholes have begun to show greater concentrations of dissolved solids. In some cases these increases have been considerable, leading to increases on occasions of more than 25 times in the electrical conductivity of the groundwater, reaching a maximum of 13 000μmho/m. Sodium chloride is the main contaminant, and possible sources are old coal mine tips and diluted mine effluent, which is discharged locally into rivers and ditches. However, other sources cannot as yet be ruled out.

The area chosen for the preliminary survey was one where severe contamination of one borehole had been observed, though adjacent holes within distances of 1 km showed little or no trace of pollution. The Bunter Pebble Beds constitute the aquifer, here mostly medium to coarse grained sandstones, containing numerous pebbles and thin layers and lenses of mudstone and siltstone. There is no drift and the beds outcrop. Maximum thickness is 138 m, the dip being gently to the east. The Pebble Beds are underlain by the sandstones, marls, limestones and dolomites of the Permian. No faults are shown on the geological maps, but this may be due to the difficulty of recognizing such features when mapping such a uniform succession, rather than to their absence.

There is a history of increasing depth to water table in the area and it now lies between 10 and 100 m. Williams et al (1) considered that fissure flow was four times more important than intragranular flow in the part of the aquifer they studied. There is no reason to doubt that similar conditions occur in the area under study. This seems to be borne out in the region generally by the random and fairly sparse distribution of contamination in wells, suggesting local sources and flow mainly through fissures to nearby wells.

The nature of the problem suggested immediately the electrical resistivity method as being the most likely to succeed. One of the earliest uses of the method in this context was in coastal areas where there had been incursion of sea water into aquifers (2, 3). Subsequent applications have been to an increasing variety of problems of this type. There have, for example, been investigations at inland sites where natural contamination has occurred as a result of formations containing rock salt being brought into the proximity of an aquifer, usually by faulting (4).

Recently increasing attention has been paid to the problem of sites where there has been contamination due to industrial discharge. Successful geophysical approaches to such problems have been described, mainly from the United States (5, 6, 7).

In the successful surveys the contaminated water has always been significantly more conducting than the 'normal' pure water. In addition the thickness of the contaminated layer has been about the same as, or greater than, the depth to its top. These two factors have made it relatively easy to detect and map from the surface. In the area under consideration borehole data have indicated that the contaminated groundwater has in places a relatively high conductivity. Absence of drift at the surface was a simplifying factor, as was the uniform nature of Trias. The considerable depth of the water table over part of the area (as much as 30 m) indicated that contamination would have to be on a considerable scale to be detected. An even more difficult problem was posed by the possibility that a major part of the contaminated water might flow through a few widely spaced fissures, perhaps only diffusing a small way into the surrounding sandstone. The origin of these fissures, which in places reach to the surface, is uncertain. If natural they may well have opened in places as a result of mining disturbance.

Detection in such instances would depend on the width of the diffusion zone relative to depth to water table and the ratio of the conductivities of the contaminated and natural groundwater. The survey described below may be regarded as a feasibility study. It outlines an approach that is fairly simple, not too expensive and, since effective, likely to be successful elsewhere in the region where the same problem is being met.

2. THE SURVEY

The site was chosen because of the strong contamination of a local well. The total area covered by the survey is about 18 km^2. The land surface is gently undulating but the survey was considerably hindered by the fact that it is either afforested or under intensive arable cultivation. Fissures had been noted in the area as sometimes appearing. One in particular had apparently appeared during the previous year, trending east-south-east and having a surface width of more than 3 m at one point. It is relevant to note that it passes to the south-east of a nearby working colliery.

It was decided firstly to try and map the electrical resistivity of the saturated sandstone over the area, the water table being at a depth of between 10 and 30 m. Thirty-three soundings were made, the locations of which are shown in Figure 1. An expanding Wenner array was used in conjunction with the tripotential method in an effort to reduce the effect of lateral variations (8). The formation resistivity at depth was contoured, this also being shown in Figure 1. Assuming no marked variation in porosity in the aquifer this map may be taken to reflect the variations in pore water resistivity below the water table. It shows an area of marked low resistivity in the west of the area, with two lobes extending eastwards. The low resistivity area includes the coal mine and the effluent discharge site.

These results thus indicated a general area of contamination of the groundwater. Following this, surveys were carried out with the particular aim of defining any fissures and determining whether they were associated with a zone of particularly highly conducting water, as might be expected in the circumstances. The likely position of one fissure was in the first place recognized from an inspection of the sounding data. Traverses were then made along the line AB of Figure 1, which was believed to cross the fissure at right angles. Three different types of array were used, normal Wenner, asymmetrical Wenner and dipole-dipole, to determine which had the best resolving power. Only single traverses were made with the first two, separations being chosen to give a response from the upper part of the saturated aquifer, and were based on an examination of adjacent soundings. The normal Wenner (Figure 2b) appeared to have very little resolving power, the traverse showing no very obvious anomaly. The asymmetrical Wenner array gave a large amplitude anomaly indicating a localized body of higher resistivity than the surroundings. This array has a smaller depth of penetration than either the normal Wenner or the dipole-dipole and the high resistivity anomaly is interpreted as being due to the dry part of the open fissure situated between the water table and the surface.

In the case of the dipole-dipole array a number of traverses with increasing electrode separation were made. The results are plotted in Figure 2a in the form of a 'pseudo section', i.e. a cross-section which shows in a semi-quantitative manner the vertical and lateral variations in the apparent resistivity. A very obvious zone of low apparent resistivity (marked with an arrow) can be seen. This has been interpreted as due to a thin (about 10 m) near-vertical body of low resistivity (circa 20 ohm/m). The most likely source of this anomaly would seem to be a fissure containing highly conducting water, and having a diffuse zone extending outwards on either side in which there is a gradation from contaminated pore water to normal groundwater.

Dipole-dipole traverses were made along three other lines and pseudo sections drawn up. Two of these which showed low resistivity anomalies (lines CD and EF of Figure 1) are given in Figure 3. These anomalies are less pronounced than those of Figure 2 and probably more typical. It is not possible to interpret these results quantitatively. They merely demonstrate the presence of a low resistivity body. It is possible that pumping at a nearby borehole causes more mixing of the contaminated groundwater and thus the anomaly is more subdued.

3. CONCLUSIONS

Contaminated groundwater flowing along the lines of fissures and in intra-granular spaces has been detected by surface resistivity methods. This success must be largely due to the comparative uniformity of the aquifer and to the low resistivity of the contaminated groundwater. The low resistivity anomalies allow the extent of the contamination to be defined and traced back to indicate the source of the contamination.

Although each site must be considered on its individual characteristics, the success of this survey demonstrates that geophysical techniques can play an important part in the investigation of groundwater pollution. The techniques utilized in this survey might reasonably be expected to be successful if applied to similar problems in other aquifers.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the Severn Trent Water Authority for providing funding for this project. The views expressed in this paper are those of the authors and do not necessarily reflect those of the Water Authority. Thanks are due to all members of the University of Birmingham and Severn Trent Water Authority who have assisted with this survey.

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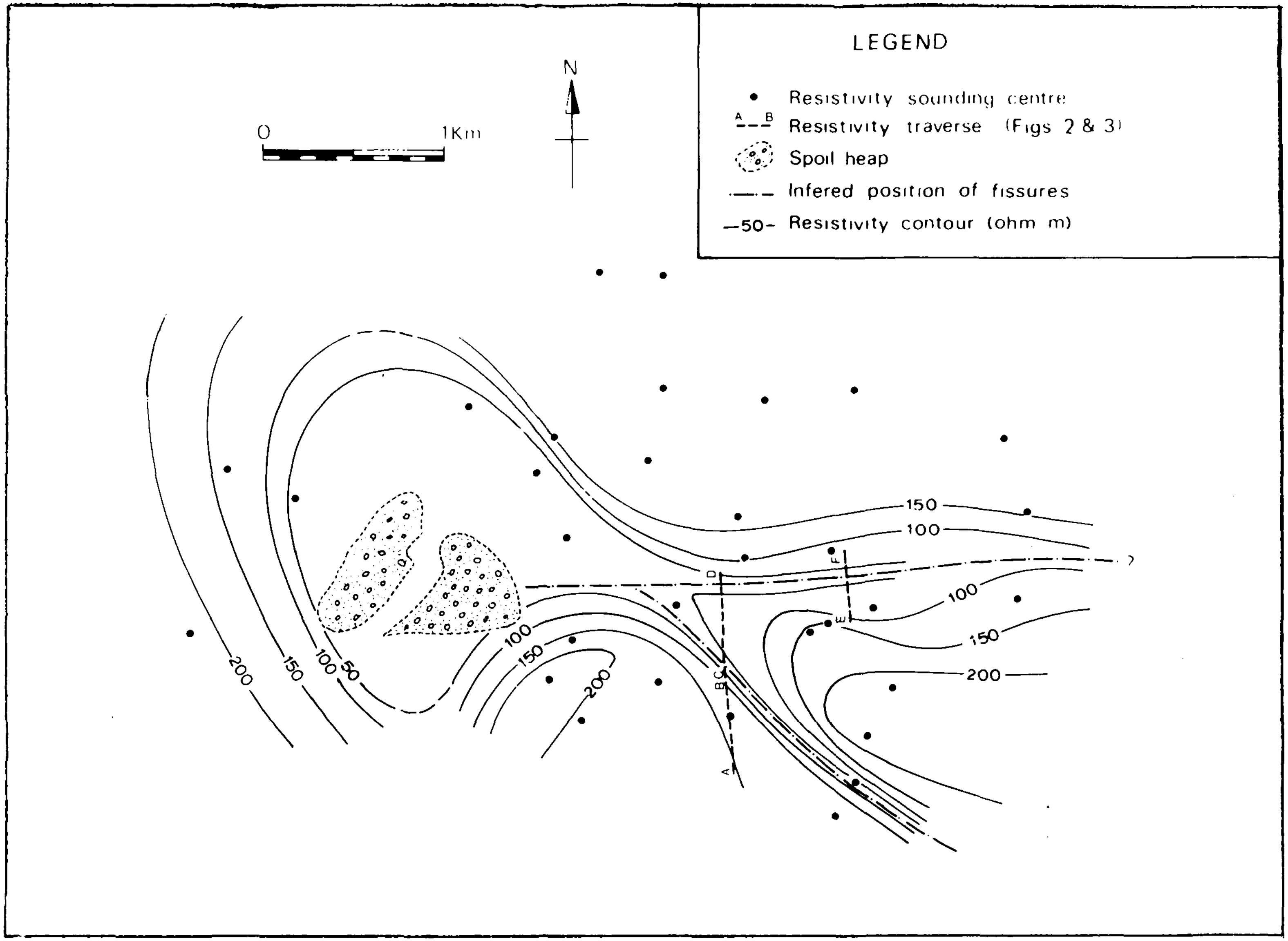

Figure 1. Sub-water table unit resistivity contour map

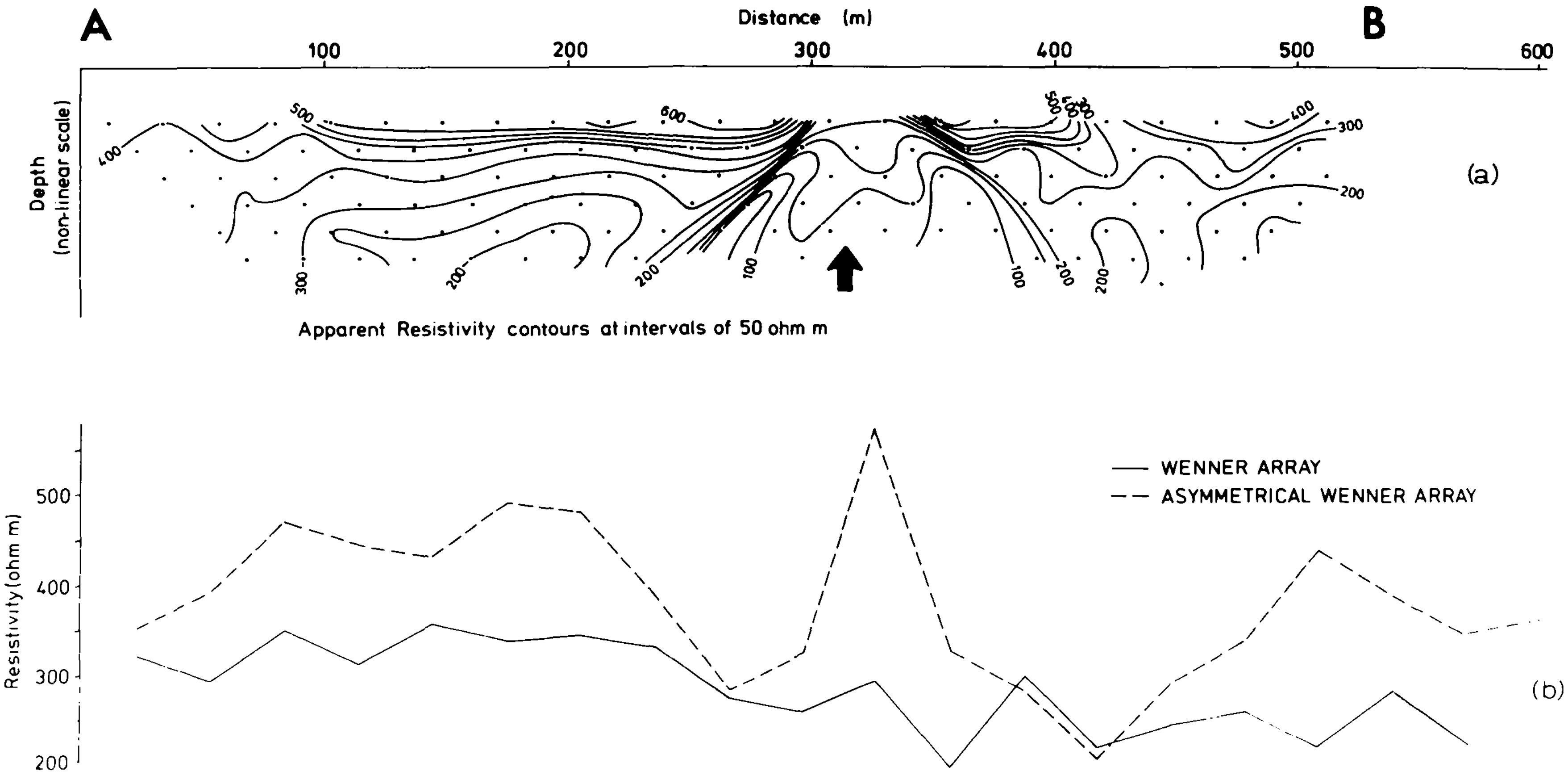

Figure 2. Comparison of resistivity array anomalies

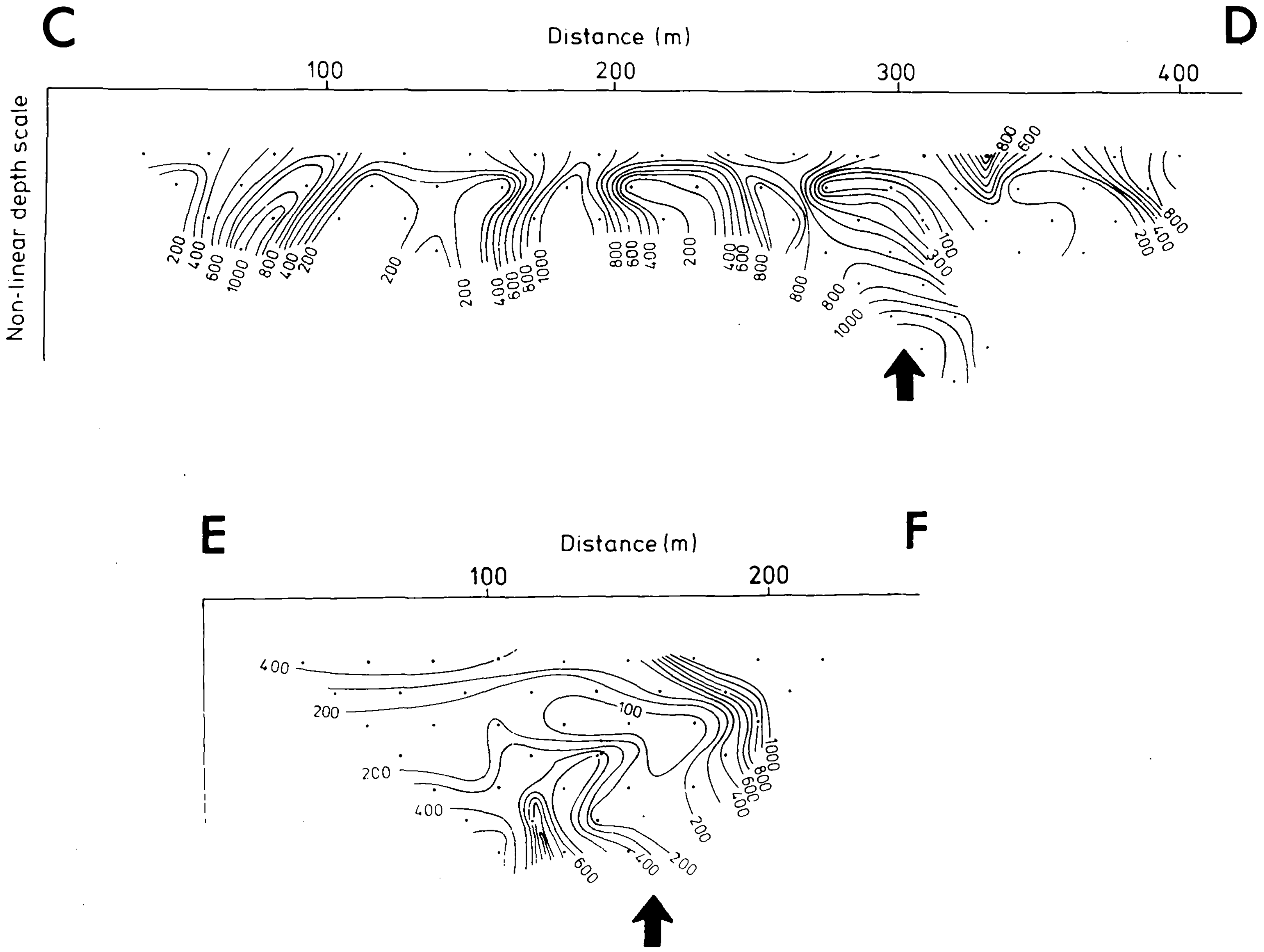

Figure 3. Dipole-dipole pseudo-sections

SUPPORT PAPER I

NITRATE IN GROUNDWATER - PROCEDURES IN THE COLLECTION AND PREPARATION OF ROCK AND WATER SAMPLES

Mrs E. Gray, Mrs J. Holland, Miss J. Breach and C. Rowland

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1. INTRODUCTION

Rising concentrations of nitrate in many groundwaters in Britain over the past ten years have caused concern to the Water Authorities. In response to this nationwide concern a programme of research was initiated in late 1974 by the Water Research Centre. This research is co-ordinated with other complementary research programmes being carried out by the Institute of Geological Sciences (IGS) and the Water Authorities, through the Nitrates Sub Group Committee of the Department of the Environment. The Centre's investigation has been reported in papers by Young et al (1976) (1) and Young and Hall (1976) (2).

In this research, attention has been directed mainly towards the movement of water and its solutes through the unsaturated zones of the aquifers to the water table, and this paper concentrates on the techniques used to obtain representative samples of the rock and pore water for analysis.

2. SITE SELECTION

Investigations have been carried out at twelve sites on the two most important British aquifers, the Cretaceous Chalk and the Triassic Bunter Sandstone. The sites have in most cases been chosen to fulfil the following criteria:

(i) They should be on exposed Chalk or exposed Bunter Sandstone. Exposed strata are being investigated first because the increasing nitrate concentrations have been observed mainly in areas where the strata are at outcrop.

(ii) The water table should be between 20 and 60 metres below surface. Initially sites were selected where the water table was more than 30 metres below the surface, but the programme has developed to include sites where the water table is nearer the surface, and investigations of the saturated zone are now undertaken.

TABLE 1A - CHALK

Drilling Method		Accuracy of Depth	Possible Contamination	Other Effects	Estimated costs for 30m borehole	Estimated time for 30m borehole
Flight auger		Method developed to give samples approximately 1m apart	No flushing medium used, but smearing of samples at other depths in hole	Sample structure destroyed	Using WRC's own B 30 S mobile drilling rig £200	3 days
Percussion drive coring	Cable tool	Very accurate measurements obtainable, depending on core recovery	No flushing medium, but top 5 cm of core discarded as it may be rubble which has fallen in from higher levels	The percussion effects break up Chalk sample	Using WRC's drilling rig, £700 Using contractor £1,070*	15 days
	Pneumatic hammer			Greater percussion effects than cable tool	not known	not known
Rotary air/water/mud flush		Very accurate measurements obtainable, depending on core recovery	Flushing medium may intrude up to 3 cm into core (9), (10).	Abrasion of core by rotation	£1,900*	not known

* including moving on to site, not including wear on bits due to flints

Drilling Method	Accuracy of Depth	Possible Contamination	Other Effects	Estimated costs for 30m borehole	Estimated time for 30m borehole
Flight auger	Method developed to give samples approximately 1m apart	No flushing medium used, but smearing of sample on sides of borehole	Sample structure destroyed. Friction heating dried sample noticeably	Using WRC's own rig* £200 Using contractor £1, 220*	3 days 7 days
Percussion drive coring: Cable tool Pneumatic hammer	Very accurate depth measurements depending on core recovery	No flushing medium used. Top 5 cm of core discarded as it may be rubble fallen in from higher levels	Not possible to use these methods in cemented sandstone	Can only be used to depth of c. 6m, as the coring equipment breaks on meeting cemented sandstone	not applicable
Rotary Air flush	Very accurate depth measurements possible if 100% core recovery obtained	Penetration of air 3-4 cm into core (9), (10). Inner core used for nitrate and tritium samples. Effect on tritium count not known, but contamination is possible	Air pressure very high if required below 80m	£4, 500 ϕ	10 days
Reverse circulation water flush		Inner core used for nitrate and tritium samples. Effects and extent of penetration being investigated	Formation water used to prevent external contamination	£4, 500 ϕ	10 days
Rotary mud flush			Method used only when the formation is unconsolidated at depth, as nitrate content of mud may be up to 12 mg/l NO$_3$-N	£4, 500 ϕ	10 days

ϕ includes moving on to site, and wear on bits.

*Augers abraded by sandstone. Costs of moving to site included but not costs of wear on bits and auger flight.

(iii) The land use history of the site location in which the borehole is to be drilled should be available for about 20 years.
This history is obtained from the farmer, and details of the long-term history of the area are obtained from the records of land use collected annually by the Ministry of Agriculture Fisheries and Food (MAFF).

The twelve sites investigated so far have been selected with the assistance of the staff of the Agricultural Development and Advisory Service of MAFF, the Water Authorities and Water Companies.

Preliminary drilling has been carried out at most sites, followed by detailed drilling at those sites where the nitrate profile obtained was found to be of interest. At two sites boreholes were drilled to 150 metres and 200 metres respectively through the Bunter Sandstone, to ascertain the nitrate profile below the water table adjacent to public supply boreholes with differing nitrate concentrations in the abstracted water. At three sites on the Chalk, boreholes have been positioned to allow areal estimations of variations in the nitrate content of water in both the unsaturated and saturated zones of small groundwater catchments.

Work at most of the sites has been undertaken with the co-operation and assistance of the various Water Authorities and Companies, and in some areas the Centre's role has now evolved to that of consultation.

3. EXTRACTING THE ROCK AND WATER SAMPLES

(i) Drilling Methods.
Various methods were used to investigate the different formations (Table 1), and to obtain representative cores from which the pore water could be extracted. The cable tool percussion drive coring method was preferred for detailed drilling of the Chalk and the unconsolidated sandstones. Rotary air flush was preferred for consolidated sandstone, but it was necessary to use water and mud flush drilling at depths below 80 metres.

Preliminary and supplementary site investigations have been carried out by auger drilling to depths of up to 30 metres. The depths of the unconsolidated samples could not be estimated as accurately by augering as they could be by other methods, but comparison of the analysis of samples from an augered borehole and of samples from an adjacent cable tool percussion borehole showed that the augered samples gave a realistic estimate of the nitrate profile, (Figure 1).

(ii) Sampling Intervals.

The sampling intervals depended on the type of site being investigated but were generally as follows:

Table 2. Sampling intervals

Site type		Nitrates (metres)	Tritium (metres)
Chalk			
Preliminary sampling	Unfertilized	2.0	-
	Fertilized	1.0	-
Detailed sampling	Unfertilized	0.5	5.0 m, except from 8 - 15 m where samples taken every 0.5 m.
	Fertilized	0.5	
Bunter Sandstone			
Preliminary sampling	Unfertilized	2.0	-
	Fertilized	1.0	3 m if no detailed drilling is to follow.
Detailed sampling	Unfertilized	not yet decided	5 m except from 8 - 15 m depth where samples taken every 0.5 m
	Fertilized	1 m to water table or to 30 m if lower, then every 2 m.	

This basic pattern has been altered to cover known variations in geology, and to elucidate details from the profiles obtained in the preliminary drilling. Extra samples have been taken where the borehole penetrates the saturated zone.

(iii) Water Samples.

The water in each borehole has been sampled as soon as possible after penetration of the saturated zone to prevent changes in the sample due to aeration.

Water samples have been collected from all accessible boreholes and springs in the vicinity of the site to measure the chemical variability of the local groundwater.

The water samples are generally analysed for nitrate, nitrite and tritium. The nitrate and nitrite samples have been preserved by the addition of mercuric chloride to a concentration of 40 mg/l immediately they are collected, to prevent changes in nitrate concentration due to bacterial activity.

4. SAMPLE HANDLING

A - Drilling

A particular effort has been made to prevent contamination of the samples at all stages, special attention having been paid to cleanliness of the drilling and sample extraction equipment. As far as possible, all drilling equipment which came into contact with the sample was dry, free of oil, grease and water, and not allowed to come into contact with the soil. Drilling crews were instructed that no extraneous material should be allowed to enter the boreholes, and the boreholes were kept covered when drilling was not in progress. Boreholes were always lined to below the soil/rock interface to prevent contamination from the soil.

B - Withdrawal of core samples

(i) Drive core samples

Following recovery of a filled core barrel from the borehole, the core was extruded into 250 gauge polythene layflat tubing, sealed at one end. About 5 cm of core were discarded from each end of the core before wrapping to avoid contamination of the sample. As much air as possible was extruded from the wrapping and the open end was sealed. The sample was then labelled and enclosed in a second, heavier gauge wrapping.

(ii) Auger samples

Auger runs were generally of 0.5, 1.0 or 2.0 metres length depending on the length of sample interval required. The augers were withdrawn from the borehole and the samples collected only from the lowest auger flight, to ensure minimal contamination from loose materials entering the borehole from higher levels. Personnel collecting these samples wore clean rubber gloves and pushed the rock into a polythene bag with a clean spatula. The samples were double wrapped and labelled in a similar way to the drive core samples. Augered samples of sandstone were often warm on extrusion due to frictional heating and were sealed as soon as possible in order to limit the evaporation losses, which would have increased the apparent nitr te content of the remaining formation water.

(iii) Rotary Cores

Rotary coring was confined to sampling from the Bunter Sandstone. The cores were contained in the core barrel by flexible plastic core barrel liners which provided support and a layer of protection to the core prior to wrapping. The samples were double wrapped in polythene as soon as possible. Attempts to remove the outer 5 cm of core before wrapping have not been successful due to the consolidation of the sandstone cores.

5. TRANSPORTATION AND STORAGE OF SAMPLES

In the initial stages of the programme core samples were returned to the laboratory daily and stored in a refrigerator at about 4°C until prepared for analysis. Freezing was not considered suitable as fractionation of the water and its dissolved solids could occur. Samples were transported to the laboratory in double walled insulated boxes. On occasions samples have remained in these boxes or in an unheated garage for periods in excess of 24 hours. As bacterial activity is generally minimal at temperatures below 4°C, storage under these conditions in winter was considered satisfactory. It is recognized that storage in cold boxes may not be an ideal system but until there are data available to allow comparison of possible alternative methods, this method will be used.

6. PREPARATION OF SAMPLES FOR ANALYSIS

The techniques of sample preparation were tested by the analytical laboratory of Water Research Centre at the start of the programme.(3) For the two methods used, a leaching method and a centrifuge method, the results obtained were comparable and therefore the leaching method was discontinued in favour of the faster centrifuge method which also involved less sample handling. To extract the pore water for analysis using the centrifuge method of extraction, approximately 300 grammes were removed from the centre of the sample, taking care to exclude any of the outer 5 cm of rock core. This was placed in one of the specially designed extraction pots and spun for one hour at 6000 rpm at 12°C in an M. S. E. Highspeed 18 Mk3 refrigerated centrifuge with a 6 × 300 ml angle rotor. The water was removed from the base of the extraction vessel and put into a small clean glass bottle, then stored under refrigeration at 4°C whilst awaiting analysis. The centrifuged core sample was sealed in polythene and stored under deep freeze conditions for later carbohydrate analysis. The amount of water obtained was found by weight difference. A portion from each core sample was kept in a sealed jar for analysis at a later date for carbon dioxide, and a solid piece of approximately 25 cm^3 was retained for bulk density, porosity and permeability determinations. Total water content is determined by weight difference after drying overnight at 110°C (3).

7. PHYSICAL ANALYSIS OF ROCK SAMPLES

The dry bulk density and porosity were determined for samples of undisturbed core from which interstitial water samples were obtained.

The rock samples of approximately 25 cm^3 were dried, weighed and their bulk volume measured by total immersion in mercury using a Ruska porometer. The porosity and grain densities are determined using a method based on the Kobe method (4). The vertical and horizontal permeabilities were measured on a few selected samples using a Ruska liquid permeameter, using methods developed by IGS (5).

8. CHEMICAL ANALYSIS

Nitrate and nitrite determinations have been made using a Technicon Auto-Analyzer (II) with a method adapted from that of Kamphake, Hannah and Cohen (6) being used to prepare the samples. Chloride was also measured using the Technicon AutoAnalyzer (7).

Methods for these and other analyses have been described by Young et al (1).

9. RADIOACTIVE ANALYSIS

The samples for environmental tritium analysis were transported to the Atomic Energy Research Establishment laboratories at Harwell, as soon as possible, and stored in the tritium controlled atmosphere until analysed. The method of analysis has been described by Otlet (8).

10. CONCLUSIONS

The continuing nitrate investigation programme depends to a large extent on the care with which the samples are prepared and analysed. In the work done so far it has been shown that:

1. The auger method of drilling is satisfactory for obtaining Chalk samples from which preliminary profiles can be obtained.

2. The pore water can be extracted satisfactorily from the samples using a centrifuge method.

3. Care must be taken at all stages of the sampling procedure to prevent contamination.

There are still a number of techniques which need to be checked or improved, in particular:

(i) the method of obtaining representative samples from the Bunter Sandstone;

(ii) possible changes in the samples, as a result of bacteriological activity or chemical reactions, during transportation and variable length storage under differing conditions;

(iii) the distribution of the determinands within the core.

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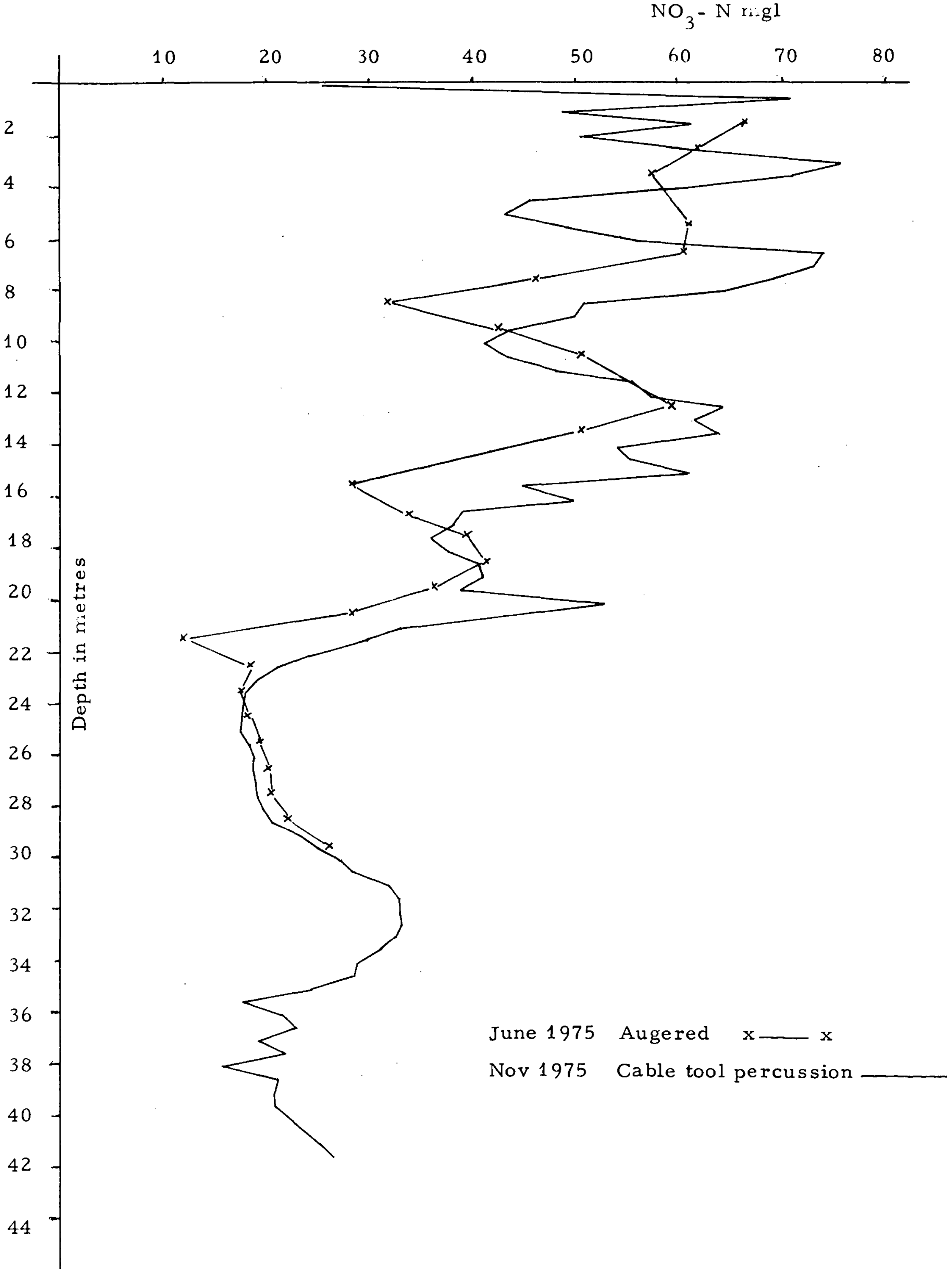

Figure 1. Comparison of results of Nitrate analyses of samples obtained from an augered borehole and an adjacent cable tool percussion borehole

SUPPORT PAPER J

GROUNDWATER QUALITY SURVEILLANCE NEAR A LANDFILL SITE - COMPARATIVE STUDY OF GROUNDWATER SAMPLING TECHNIQUES

Miss S. Brown

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1. INTRODUCTION

The Water Research Centre (WRC) has been involved together with the Anglian Water Authority and Aspinwall and Co. in the investigation of groundwater quality in the vicinity of a landfill site on the East coast of England.

A series of seven investigation boreholes were drilled in February and March 1975 and piezometer tubes were installed in five of these boreholes. Prototypes of groundwater samplers designed at the WRC were installed in the remaining two, two samplers in each. The configuration of the boreholes is shown in Figure 1. Samples for chemical analysis were taken on a monthly basis by the Water Authority and the WRC from April to October 1975.

This Paper summarizes the results from these six months of sampling and analysis by the WRC with special reference to the significance of the different sampling methods employed.

1.1. GEOLOGY AND HYDROGEOLOGY

Boulder clay overlies glacial sands and Red Crag deposits in the vicinity of the site and for a considerable distance inland. The base of the boulder clay locally has been proved to lie between 10 and 12 m AOD. The base of the excavation for the landfill is at 7.99 m AOD, well below the base of the clay and within the glacial sands, which are between 3 and 5 m thick. The glacial sands and the Red Crag can be considered a single hydrogeological unit with a total thickness of more than 50 m. The base of the Red Crag is not penetrated by any of the observation boreholes.

Gamma-logging of the boreholes (see Figure 2) was undertaken by the WRC and the logs show the very variable nature of the Red Crag deposits. These consist of sands, silty sands and relatively thin clay bands. Two clay lenses have been identified at 4 m AOD and - 10 m OD both of which may act as a control on groundwater movement around the landfill site. The 4 m clay extends from the coast inland to borehole 7 and the - 10 m clay over the same area, although it is absent in borehole 6. This lower clay is only 1½ m thick in borehole 7 but increases in an easterly direction attaining 5 m in borehole 1.

Minor clay intervals of local significance only also occur as in borehole 4.

The Red Crag is described (Woodland, 1945) as greyish and greenish sands of varying degrees of coarseness, the colour being due to disseminated ferrous salts. However, these have been oxidized in the upper horizons of the Crag to a yellowish brown to deep reddish brown. The water table lies at approximately 2 m AOD and slopes east north-eastward with an average gradient of 0.0005, although this is locally increased to approximately 0.0015 by the enhanced recharge due to the landfill. The rate of groundwater movement will therefore be slow and will be mainly within the sandier horizons at 0 to 2 m AOD and - 4 to - 10 m OD at rates which are estimated at between 1 and 4 m/day.

1.2. INITIAL GROUNDWATER QUALITY

In order to evaluate the influence of the landfill site on the groundwater composition it is clearly necessary to know as much as possible about the natural hydrogeological situation. Unfortunately there is very little historical chemical data from wells in this area, so background values have been calculated from those boreholes which lie to the west of the landfill and from two wells, wells 4 and 5. Table 1 gives the mean values, standard deviations and probable natural range of various chemical parameters. Some of the wells, however, may have been polluted from sources other than the landfill and show relatively high mean values for either nitrate, chemical oxygen demand or phenols, for example, and these have been treated with caution.

The chloride results indicate that there may have been some coastal saline intrusion to the east of the landfill site. The results for Zone B (see Table 1) have been calculated from results from wells 4 and 5 to the East. The mean chloride value is 147 mg/l compared with a value of 63 mg/l for wells to the west of the tip. Chloride results from boreholes 4 (20 m) and 5

Table 1. Background (natural) groundwater quality in vicinity of landfill site

(Calculations are based on data provided by the Anglian Water Authority from wells 1, 2, 4 and 5 and boreholes 6 and 7)

Chemical parameter	No. of observations	Mean	Standard deviation	Probable natural range
pH units	30	7.47	± 0.39	7-8
Electrical conductivity µmhos	31	1002	±216	750-1250
Ammonia mg/l of N	30	0.07	± 0.11	0-0.2
Nitrate mg/l of N	6	0.36	± 0.09	0-0.5
Alkalinity mg/l of $CaCO_3$	27	239	± 51	175-300
Chloride Zone A/	17	63	± 8.6	50-80
mg/l of Cl Zone B	13	147	± 35.8	100-190
Total hardness mg/l of $CaCO_3$	12	398	± 78	300-500
Sulphate mg/l of SO_4	14	156	± 64	80-240
Chemical oxygen demand	23	11.1	± 7.8	0-20
Calcium mg/l of Ca	16	142	± 28	100-180
Magnesium	12	13.2	± 6	5-20
Sodium	7	50.4	± 8	40-60
Potassium	3	1.5	± 0.8	0.3 ?
Total iron	12	2.7	± 2.8	0-6
Phenols*	20	0.025	± 0.037	0-0.06*

Concentrations in mg/l unless stated otherwise.

/Zone A is that area to the west of the landfill site.

Zone B is the area to the east of the landfill site which encompasses wells 4 and 5 and boreholes 4 and 5.

*Natural levels of phenol in groundwater should be zero. These wells may have been slightly polluted by sources unknown.

(20 m) also show relatively high chloride concentrations (100 mg/l). The results from the - 3.6 m OD piezometer in borehole 1 are extremely variable and are not definitely indicative of saline intrusion, although it is nearest the coast.

High chloride values may alternatively come from the landfill site. Very high levels of chloride ion (>1000 mg/l) have been measured in borehole 9 adjacent to the tip and it is possible that the 'pollution front' may have reached the nearest boreholes which are wells 4 and 5 and boreholes 4 and 5.

1.3. ERRORS IN SAMPLING AND ANALYSIS

Differences in groundwater composition can be the result of a number of factors, the most important of which are perhaps (a) The variability of the aquifer, in both physical and chemical composition, and (b) The time of sampling with respect to groundwater stage and its relationship to natural recharge.

These are natural factors; in addition to these there are artificial factors due to the establishment of sampling points. As well as the disturbance of the aquifer caused by drilling, there may be actual contamination by drilling water, cement or perhaps bentonite. Having obtained a sample there still remains a further analytical error to take into account.

Particularly under conditions of pollution, the changes which can take place in the well or borehole due to interaction with the atmosphere may be significant. The presence of oxygen and nutrients such as nitrogen, phosphorus and soluble organic compounds can cause a considerable difference between the water within the aquifer. A shallow water level, large diameter borehole situation presents conditions most susceptible to these effects. In the present situation, where the open holes are very narrow (50 mm i. d.) and the water level is relatively deep, effects were expected to be correspondingly small, even if polluted conditions existed.

2. METHODS

2.1. DRILLING AND 'OPEN HOLE SAMPLER' INSTALLATION

The seven observation boreholes were drilled using a percussion rig. Open hole samplers were installed in boreholes 1, 2, 4, 6 and 7. The samplers consist of a porous pot which is connected to the surface by 50 mm internal diameter uPVC tubing. Three samplers were installed at different depths below the water table in both boreholes 1 and 7. Two open hole samplers were placed in each of the remaining three boreholes. The boreholes were back-filled with excavated material to 2.5 m below ground level, and then grouted to the surface (see Figure 3).

2.2. GROUNDWATER SAMPLER INSTALLATION

WRC groundwater samplers were installed in boreholes 3 and 5 at the same depths as the porous pots in boreholes 2 and 4 respectively. (See Table 2). Each sampler was placed at the required level in the borehole and the temporary lining pipes slowly withdrawn to allow the Crag deposits to collapse around it, thus tending to retain the original subsurface environment. The samplers consist of a small ceramic pot through which the groundwater infiltrates and which is then collected in a 250 ml chamber. The water sample is ejected from the sampler by passing pressurized gas through the plastic tubing which connects the sampler to the surface. (Edworthy, 1976, in preparation.)

Table 2.

50 mm dia. open hole		Corresponding groundwater sampler	
Borehole 2 (24 m)	- 6.13 m OD	- 6.13 m OD	Borehole 3 (24 m)
Borehole 2 (36 m)	-17.73	-18.36	Borehole 3 (36 m)
Borehole 4 (20 m)	- 1.35	- 1.35	Borehole 5 (20 m)
Borehole 4 (30 m)	-11.48	- 9.19	Borehole 5 (30 m)

2.3. SCHEDULE OF SAMPLING AND ANALYSIS

Sampling from the site was undertaken at monthly intervals. The WRC only took samples from those sites listed in Table 2, with the aim of comparing the two methods of sampling. Samples were collected from the porous pot samplers with a stainless steel depth sampling device, and from the groundwater samplers as described. The first sample from each groundwater sampler was rejected.

The Anglian Water Authority collected water samples from boreholes 1, 2, 4, 6 and 7 and from some local wells. Standing water in boreholes 1, 2, 4, 6 and 7 during the month was removed before sampling by blowing high pressure nitrogen into the bottom of each hole. WRC samples were taken prior to the blowing out of each hole.

The chemical parameters analysed by the WRC for each sample were ammonia -N, nitrate -N, nitrite -N, sodium, potassium, calcium, magnesium, alkalinity, chloride, sulphate and total organic carbon. The pH and dissolved oxygen content of the samples were measured on site. Analytical methods used are described in Appendix 1.

3. ANALYTICAL RESULTS

From the seven months of data obtained, only chloride shows a consistent difference. Concentrations from the open boreholes are 6 to 20 mg/l higher than those from the groundwater samplers; this is well outside analytical error and therefore significant.

Sulphate levels in the porous pot samplers have been higher than those from the groundwater samplers except at 20 m in Bhs 4 and 5 (see Figure 4). A 'significance of difference' test for non-independent samples was conducted on the data available, to establish whether the apparent differences were mathematically significant. Table 3 lists for each pair of samplers the mean of the differences for the seven months of samples ($\bar{X}_D$), the estimated standard error of the differences, and the t-value, which compares the two latter values. The level of significance which can be applied to the t-value is shown in the last column.

$$t = \frac{\bar{X}_D}{\sigma_{\bar{X}_D}}$$

where $\sigma_{\bar{X}_D}$ is the estimated standard error of $\bar{X}_D$

Table 3. Significance of difference of sulphate analyses

Pair of samplers	No. of paired observations	Mean of differences	Estimated stand error of $\bar{X}_D$(%)	t	Level of sig.
<u>A</u> Bh 2(24m) Bh 3(24m)	7	39.6	17.12	2.3	.05 - .1
<u>B</u> Bh 2(36m) Bh 3(36m)	5	32.4	3.38	9.59	.001
<u>C</u> Bh 4(20m) Bh 5(20m)	6	-21.5	14.24	-1.5	Not significant
<u>D</u> Bh 4(30m) Bh 5(30m)	7	20.6	10.66	1.93	.05 - .1
All samplers	25	18.16	7.87	2.31	.025- .05

This test shows that there is a 90 to 95% chance that the differences noted between the sulphate concentrations in pairs A and D are significant, a 99% chance for pair B, and a 95 to 97.5% chance that the differences are significant when all four pairs of samplers are considered. Possible reasons for these differences are discussed in Section 4.

Several of the chemical parameters measured on samples from the open holes showed a very large variation during the first three or four months of sampling, but have since stabilized close to the values obtained from the corresponding groundwater samplers (see Figure 5). The diagram only shows sodium and calcium, although the same effect was noted with potassium, magnesium and sulphate. Bh 4 (20 m) and Bh 2 (24 m) are strongly affected. Samples from the groundwater samplers, however, have maintained an almost constant composition since the start of the sampling.

Total organic carbon (TOC) analyses have not proved helpful in illustrating any trends. Samples taken from the groundwater samplers show a much greater variation than those from corresponding open holes (except Bh 2, 36 m, which has produced very erratic results).

The upper part of the aquifer in the vicinity of boreholes 4 and 5 at 20 m is the only interval which has noticeably higher values of concentration for most of the chemical parameters. The nitrate, nitrite, calcium, magnesium, alkalinity, chloride and sulphate concentrations are all well above the background levels in these two boreholes. Concentrations of these parameters measured at borehole 9, only a few tens of metres down the hydraulic gradient from the landfill, are 7 to 10 times the background concentration.

Calcium concentrations have increased in all the samples, except Bh 2 (36 m) during the sampling period. The only anion to show a similar trend in concentration is alkalinity. To help establish whether the increase in the calcium ion concentration was directly related to an increase in bicarbonate concentration, which would have suggested solution of calcium carbonate from the aquifer, graphs were drawn (see Figure 6) comparing measured alkalinity values with the alkalinity which would be expected from corresponding calcium concentrations, assuming alkalinity can be accounted for in the form $CaCO_3$ (i.e., Calcium-determined Alkalinity = Calcium ion concentration $\times \frac{100}{40}$). Figure 6 shows that in some cases the calcium-determined alkalinity is unrelated to the measured alkalinity values, i.e., boreholes 4 and 5 (20 m and 30 m).

High ammonia, nitrate and nitrite levels also indicate contamination in borehole 2 which is not reflected in borehole 3. Unlike sodium and calcium, the concentrations of these three constituents have not fallen with time i. e., there has been no 'flushing-out' of the system.

The parameters measured in the field, i. e. pH and DO have not varied significantly after initial fluctuations in borehole 4 (20 m) and borehole 2 (24 m). All pH values are between 7 and 8. Dissolved oxygen measurements taken at the bottom of the water column in the open holes indicate that oxygen concentration is between 0. 25 and 0. 65 ppm in all cases. This rises to approximately 1. 5 to 2 ppm just below the water surface, illustrating the measurable though perhaps unimportant, amount of surface aeration.

4. DISCUSSION

The results of the analyses have been outlined in the preceding section and interpretation of the main observations is presented.

(a) Chloride concentrations. The higher concentrations of chloride ion in the open holes cannot be related to changes in the concentration of any of the cations, and the cause of the difference has not been ascertained.

(b) Sulphate concentrations. The 'significance of difference' test conducted on the sulphate analyses showed that there was a 95 to 97. 5% chance that the higher concentrations of sulphate in some of the open hole samples was significant. There are two possible explanations:

(i) that since a slightly more oxidizing environment exists at the water surface in the open hole samples bacterial oxidation of traces of sulphides might occur; it is also possible that diffusion of oxygen from the water surface to the lower layers may occur, and further

(ii) that different rates of sulphate reduction are occurring, taking place more efficiently in the aquifer (as represented by the groundwater samplers) due to the absence of either oxygen or nitrate. It is believed that either of these constituents might act as a preferred source of energy and thus inhibit any sulphate-reducing bacteria.

With reference to Figure 4 the samples with the most obvious difference in sulphate concentration are from boreholes 4 and 5 at 30 m, and boreholes 2 and 3 at 36 m. These are the deeper sampling points and therefore further beneath the water table (15 m and 20 m respectively) where the environment would perhaps be expected to be more anaerobic.

The upper pairs of samplers in boreholes 4 and 5 at 20 m and boreholes 2 and 3 at 24 m, show 'converging' concentrations, so that after four months the analytical differences between the two different methods of sampling are small. It is believed likely that the initial difference was due to pollution of the open hole samplers (or just disturbance of the strata) during drilling, which was dispersed only slowly from around the drilled hole. This is discussed in further detail below.

(c) Sodium and Calcium results. Figure 5 shows that samples from both boreholes 2 (24 m) and 4 (20 m) had large initial differences in sodium and calcium concentrations. Similar variations occurred in the magnesium, potassium and, as noted above, sulphate concentrations. The time taken for the open hole samples to reach the equivalent values in the groundwater samplers was approximately three months. The disturbance of the strata during drilling and the possibility of a small amount of pollution occurring at the same time, is thought to be responsible for these initial differences. An attempt was made to eject the standing water in the open hole samplers each month, by passing compressed nitrogen gas at high pressure to the bottom of the hole. It would appear, however, that most of the water remained within the PVC tubes so that only a small inflow of fresh groundwater occurred through the porous pot. Three months elapsed before most of the water left standing in the tubes after drilling had been replaced.

However, the groundwater sampler is completely evacuated before samples for analysis are taken and is thus replenished with fresh groundwater.

(d) Calcium and Alkalinity results. The graphs in Figure 6, which compare field alkalinity with alkalinity determined from the calcium concentrations, illustrate two main points:

(i) the results for boreholes 4 (20 m) and 2 (24 m) again indicate pollution and possible disturbance during drilling as shown by the convergence of the field alkalinity and calcium determined alkalinity after three months.

(ii) in all boreholes after the initial three months of sampling, the calcium determined alkalinity is higher than the field determined alkalinity. This suggests perhaps that calcium is either being removed in solution from non-carbonate minerals in the aquifer or that the increase in calcium concentrations, noted in all boreholes except borehole 2 (36 m), is related to the influence of the landfill.

(e) Total Organic Carbon results. The greater variability of TOC concentration in samples taken from the groundwater samplers was thought to be due to solution of the 'Oroglas' sample chamber. Laboratory experiments have been undertaken by the WRC to determine the extent to which the samplers are affected by solution under similar temperature conditions to those prevailing at depth using Chalk derived tap water. Only a slight increase in the TOC levels was detected (i.e., from 0.4 to 1.3 mg C/l over three months) but not sufficient to account for the variability in the results. It is possible that microbial action on the Oroglas or the plastic tubing connecting the samplers to the surface may increase the reaction rate; however, at present it is not possible to determine the cause of the variability.

(f) Boreholes 4 and 5 (20 m). The analysis of samples from boreholes 4 (20 m) and 5 (20 m) shows that the concentrations of nitrate, nitrite, calcium, magnesium, alkalinity, chloride and sulphate are all well above the background levels (see Table 1). These are the two closest observation boreholes to the landfill site, just over 100 m from the most easterly part of the excavation. In this area the dominant lithology in the Crag is a silty sand which would be expected to have a permeability of 1 to 4 m/day. Since the local hydraulic gradient around the tip is .0015 the rate of flow of water through the aquifer would be very low - 0.5 to 2.5 m/yr. However, slight contamination in boreholes 4 (20 m) and 5 (20 m) suggests that zones of higher permeability exist in the sandier horizons of the Crag through which water will move with a higher velocity, and that the 'average lithology' concept is not valid.

The high calcium concentrations in boreholes 4 (30 m), 5 (30 m), 2 (24 m) and 3 (24 m) may be indicative of a change in the composition of the groundwater resulting from the establishment of the landfill site.

5. CONCLUSIONS

In this experiment the main advantage of the groundwater samplers was the retrieval of representative samples of the groundwater immediately after installation, which was not achieved with the open hole piezometers.

After the initial period of three months required for stabilization of the open hole samplers, the observed differences in the chemistry of samples from the two types of samplers was relatively small. This is probably due in part to the small diameter of the open hole piezometers, which do not have a large water surface area exposed to the atmosphere; also the ends of the PVC tubes are sealed with a cap, so there is minimal movement of air in the air column. This means that only a small amount of oxygen will be dissolved from the atmosphere. Chemical reactions within the water column standing in the open hole sampler will, therefore, be limited. In a larger diameter borehole open to the atmosphere this may be different; however, this would need further experimentation.

The results from boreholes 4 and 5 (20 m) (Section 4) appear to indicate that there is a slight contamination of groundwater within this interval, most probably associated with movement of pollutants down gradient from the landfill site. However, this does not appear to have reached any of the other WRC sampling points. The last to be affected, if at all, should be boreholes 2 and 3 (36 m) which are below the - 10 m OD clay horizon.

The groundwater samplers functioned satisfactorily throughout the experiment except for the clogging of the porous pot in one sampler. This problem has been solved by two different methods (a) surrounding the sampler in the borehole with a clean washed sand or fine gravel, and (b) changing the porous pot section to a perforated plastic cover with fine mesh gauze to prevent the entrance of most of the fine material.

ACKNOWLEDGEMENTS

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APPENDIX 1

ANALYTICAL TECHNIQUES

AMMONIA	Automated analysis using a Technicon AutoAnalyzer II. The ammonia is determined by reaction with alkaline phenol and hypochloride in the presence of nitroprusside.
NITRATE	Technicon AutoAnalyzer II. Nitrate is reduced to nitrite using hydrazine in the presence of copper sulphate. The nitrate is reacted with n-naphthylenediamine and sulphanilamide.
NITRITE	As for nitrate, but omitting the hydrazine reduction.
CHLORIDE	Technicon AutoAnalyzer II method. Chloride is reacted with mercuric thiocyanate to release thiocyanate ions which, in the presence of ferric iron, forms the highly coloured ferric thiocyanate.
SULPHATE	By titration with Barium chloride solution using Thorin as indicator according to BS2690:Part 6:1968.
ALKALINITY	Either by manual titration to BDH pH 45 indicator or using a Technicon AutoAnalyzer II method involving reaction with buffered methyl orange.
SODIUM	By flame photometry - results corrected for interferences.
POTASSIUM	
MAGNESIUM	By Atomic Absorption Spectrophotometry.
CALCIUM	
T.O.C.	Using a Beckman T.O.C. analyzer.

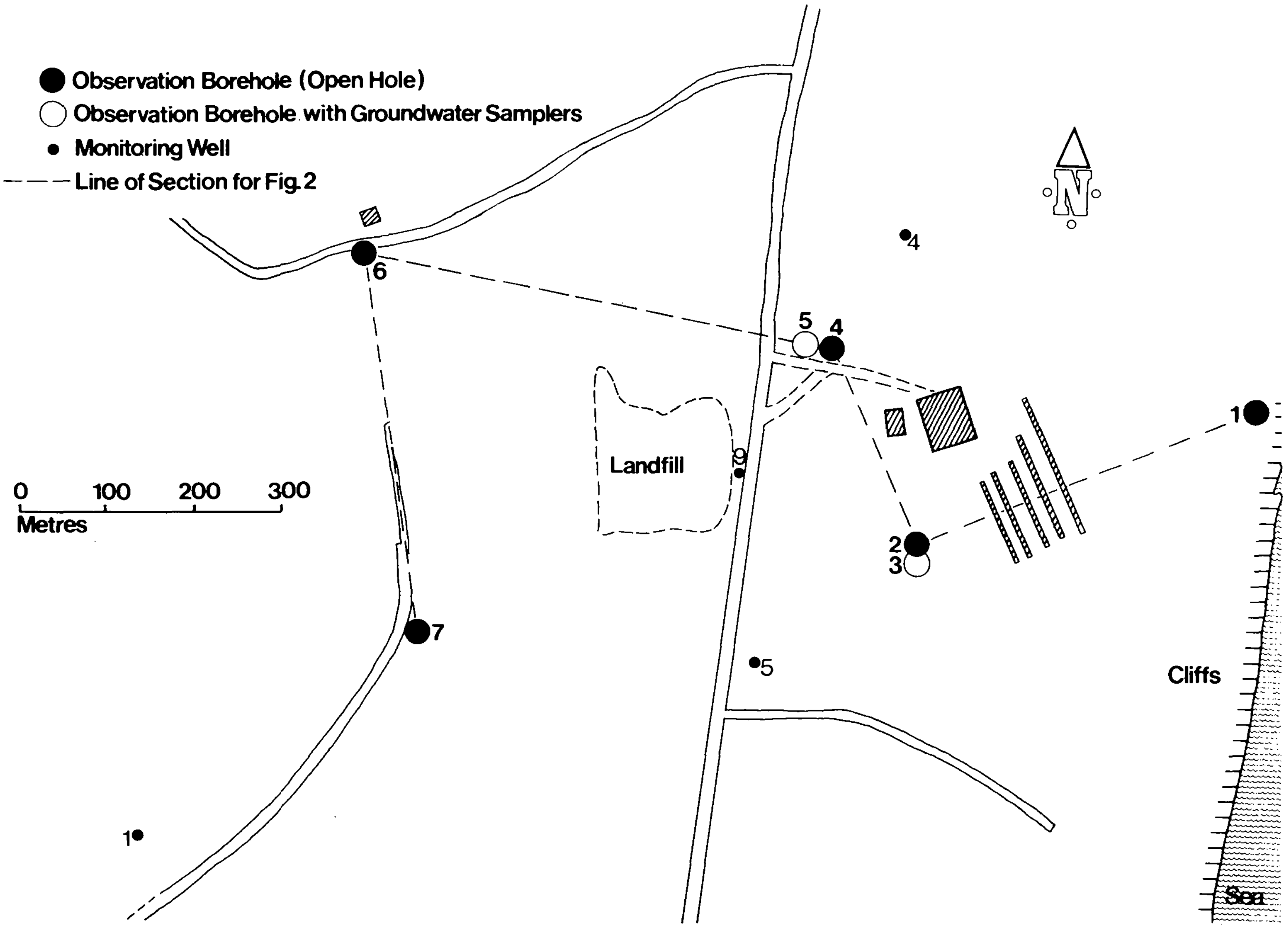

Figure 1. Site Map

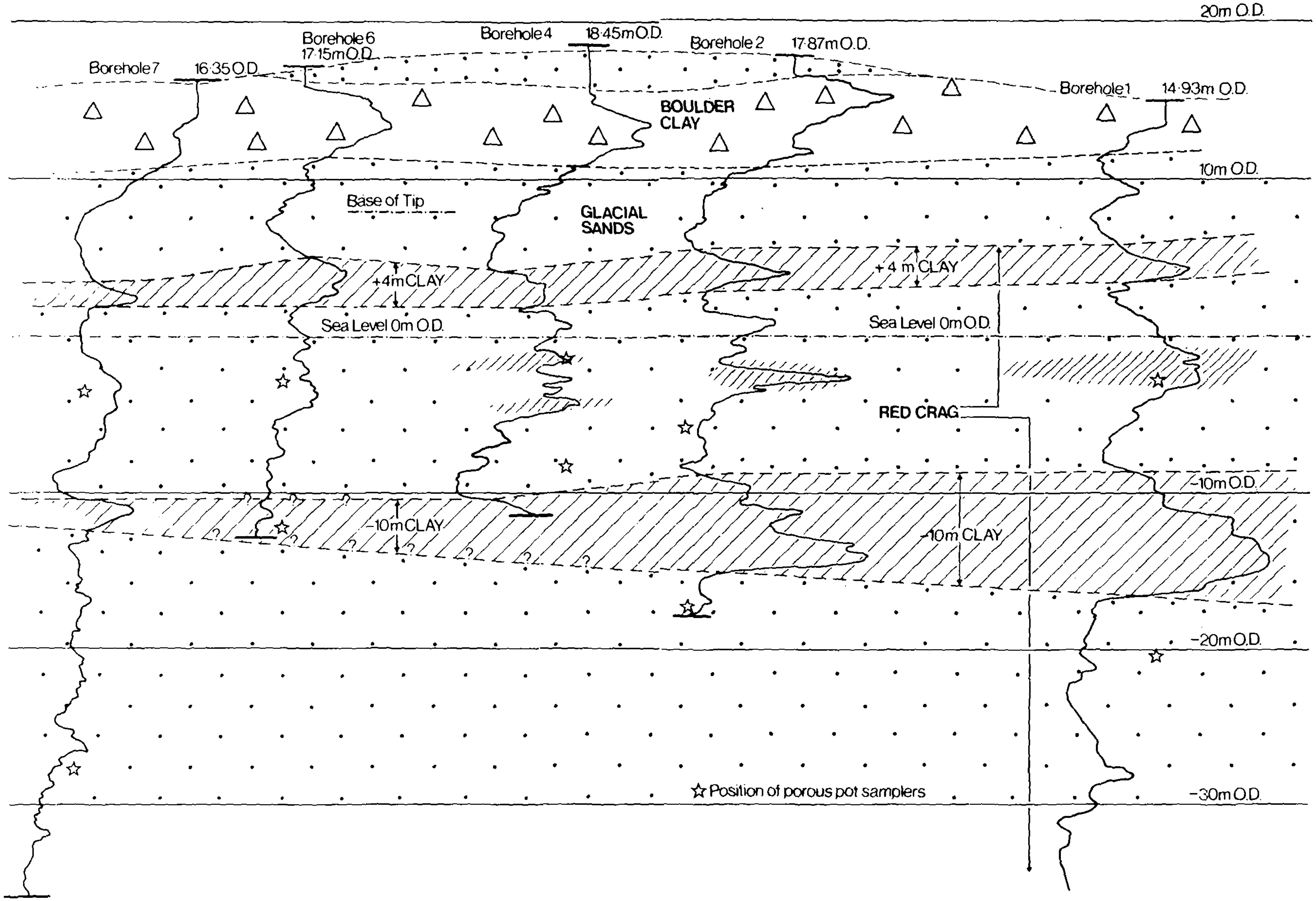

Figure 2. Gamma-Ray logs of observation boreholes 1, 2, 4, 6 and 7

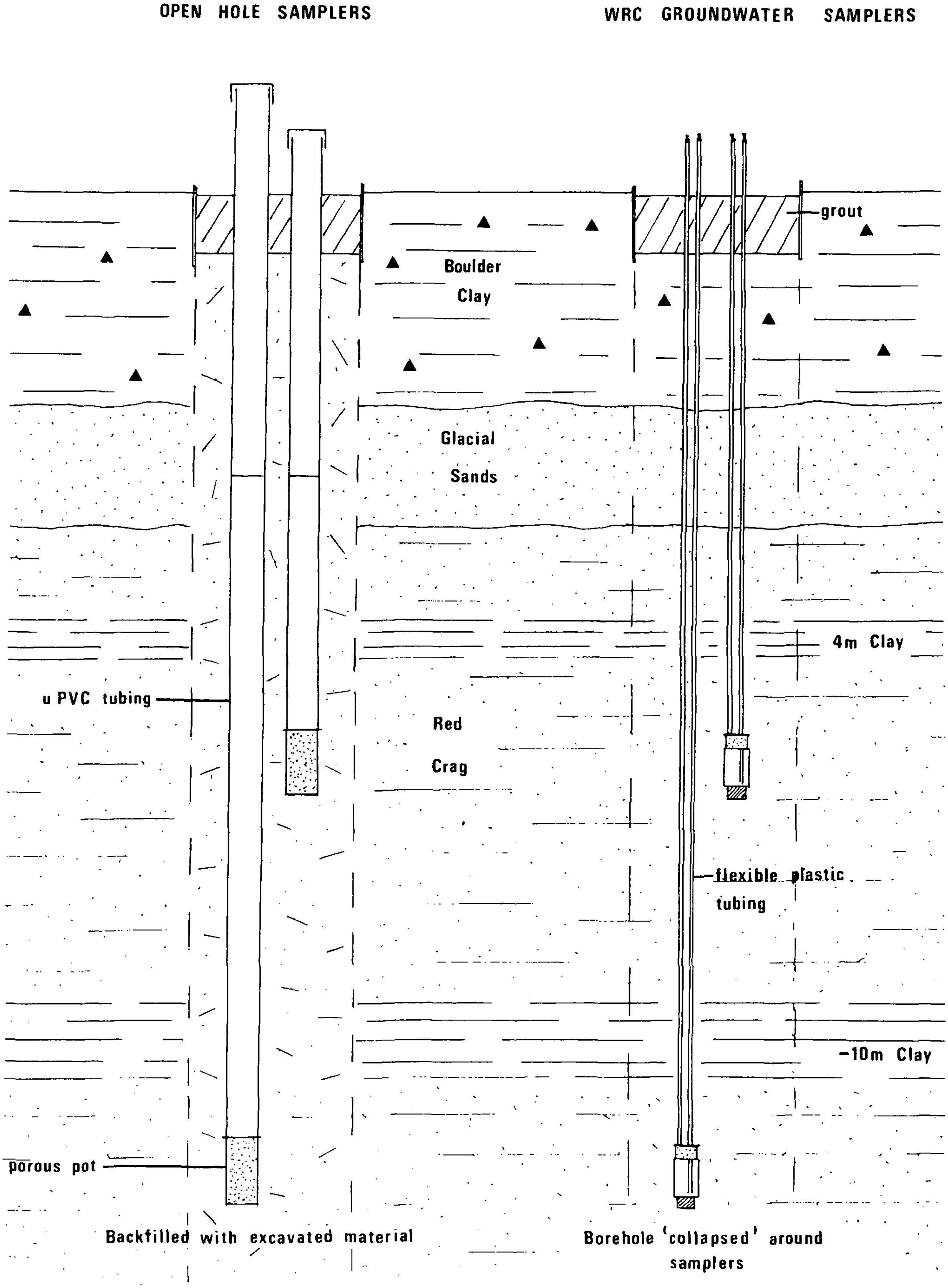

FIG 3 COMPARISON OF THE INSTALLATION OF THE TWO TYPES OF SAMPLER

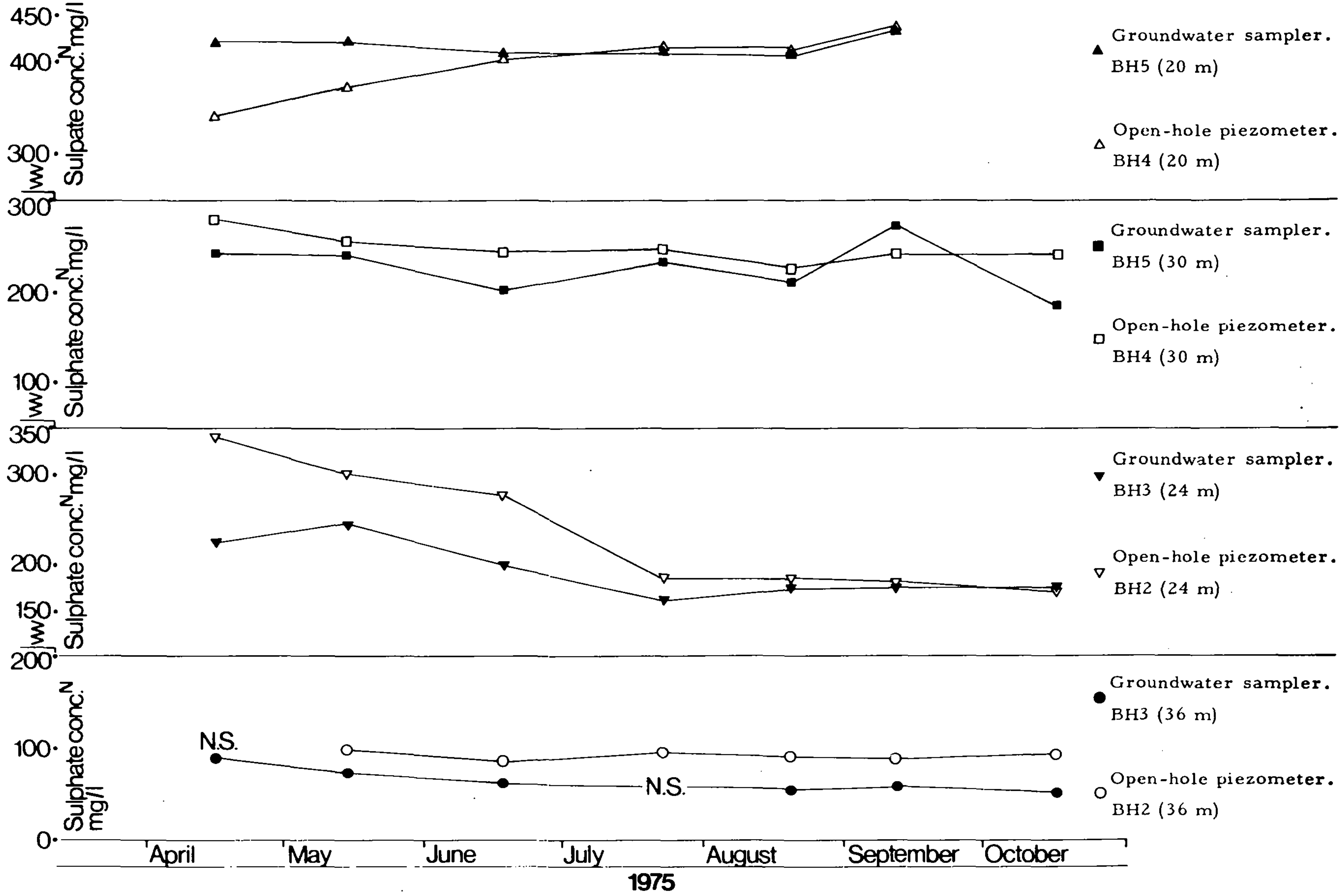

Figure 4. Comparison of sulphate determinations between open-hole and groundwater samplers

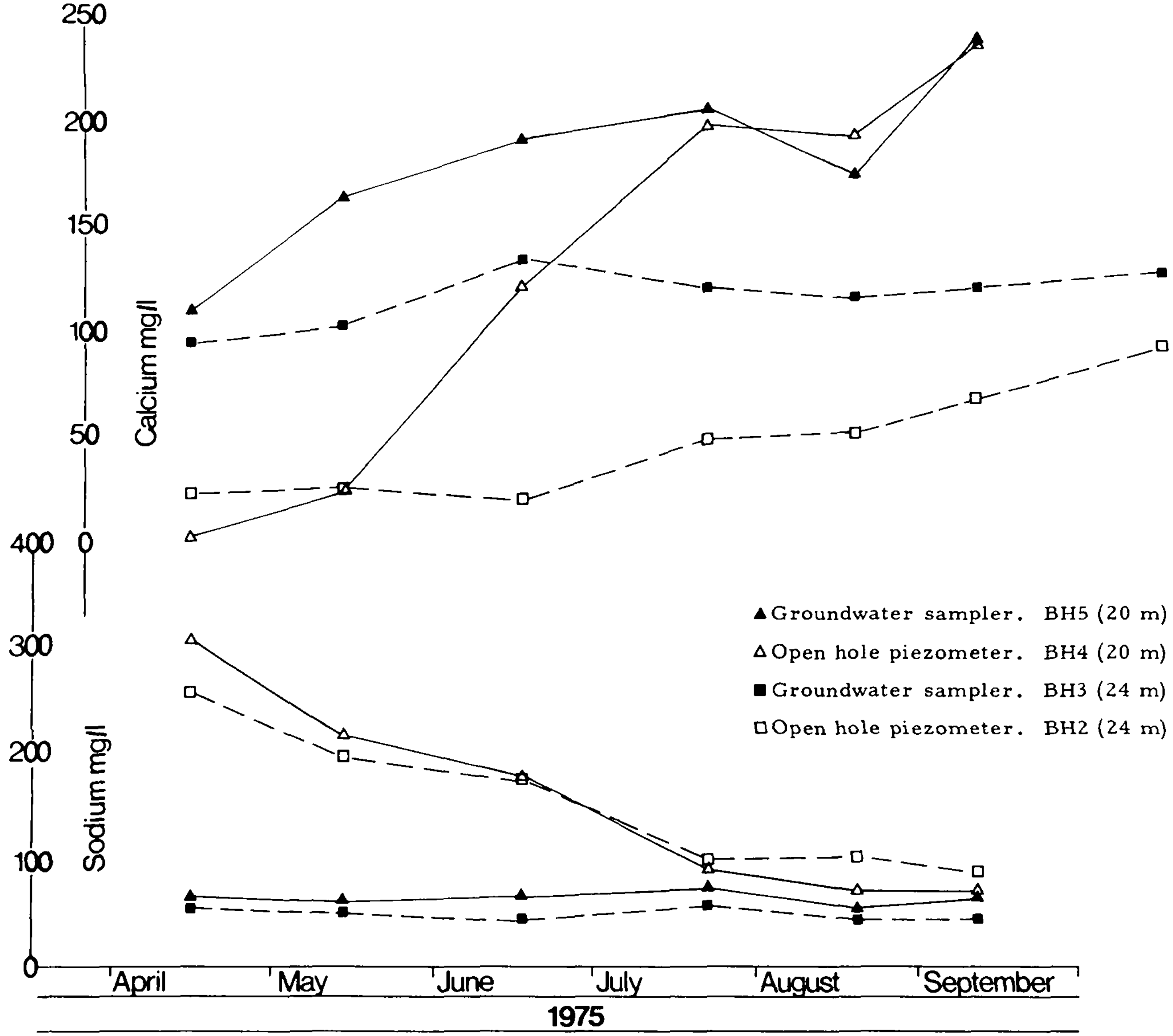

Figure 5. Comparison of sodium and calcium determinations for open-hole and groundwater samplers

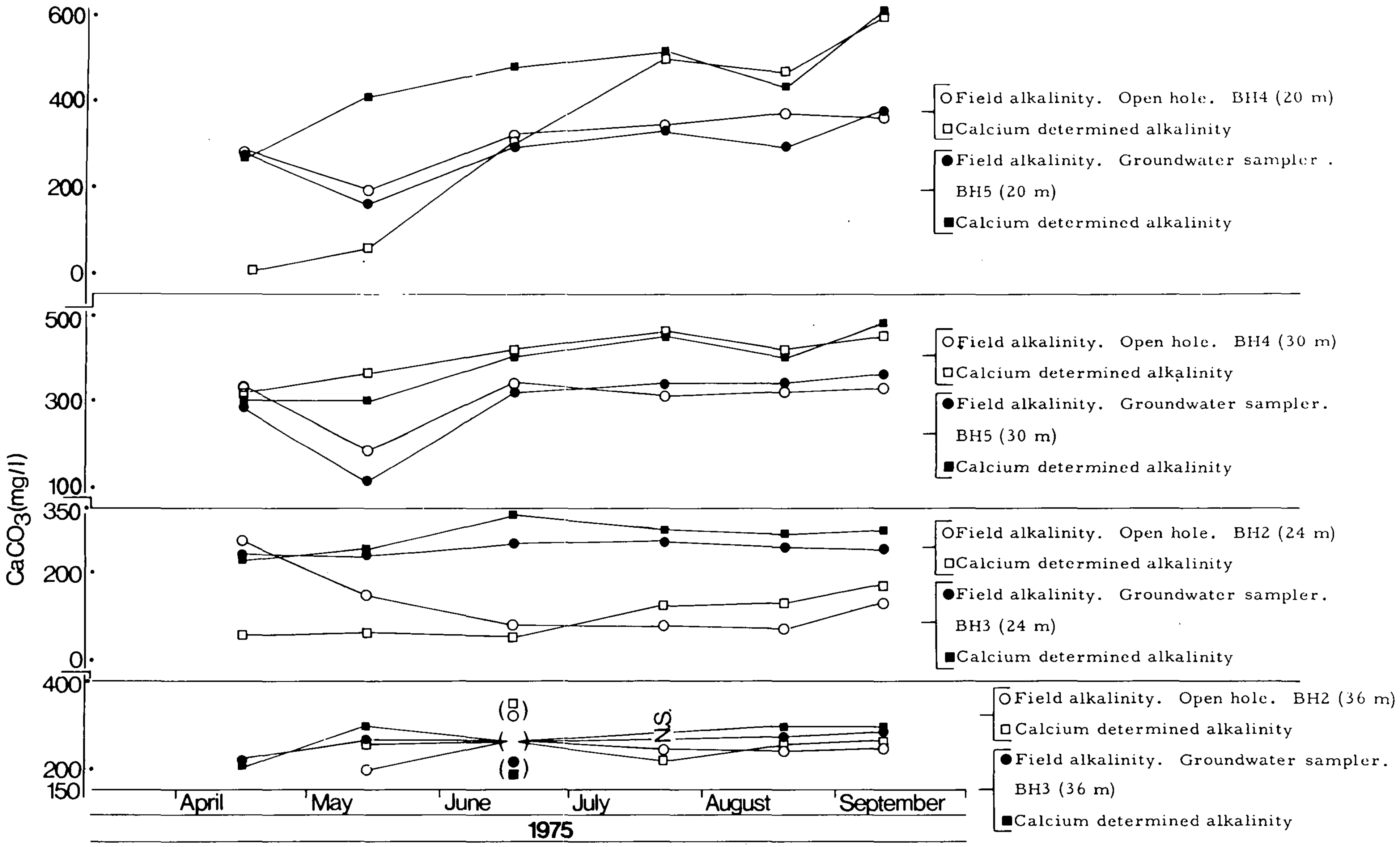

Figure 6. Field alkalinity and calcium determined alkalinity

DISCUSSION - SESSION 3

In opening the discussion, Dr I. HARRISON commented that the first problem for specialist investigations, e.g. of landfill sites, is that the data available from records are often very sketchy, even for major British aquifers. It is necessary to collect the basic hydrogeological data before the specialist data that are required. Various speakers had commented that drilling costs were now so high that any borehole must be made to yield as much data as possible. Where boreholes more than 50 metres deep are needed for preliminary hydrogeological analysis, funding may not permit the logical extension of the study to include estimation of the parameters need for, say, modelling techniques. In these circumstances it is vital that every possible piece of information is used; if, for example, previously unsuspected pumping effects are observed in a borehole, then estimates of aquifer constants and the leakage of any confining layer can be made, even though the sophisticated techniques normally used for a full-scale pumping test may not be available.

Sampling and analysis are becoming increasingly expensive and it is generally necessary to concentrate on a few varieties, rather than try to analyse for large numbers of species. In the case of landfill studies, it is necessary to select the particular species of interest in advance, perhaps phenols or heavy metals, and then to concentrate on these. The complexity of the whole range of compounds forming leachates is really too great for the analyst to handle effectively.

Dr Harrison wondered if the authors of the various papers would like to comment on the compatibility of the data now being accumulated on landfills. Recently a substantial body of information has been published on landfills, principally from industrial sites in the UK. Both government and private agencies are involved in these field studies. However, there is as yet no concensus of opinion on (a) the investigation techniques to be used, (b) the most appropriate sampling and analytical methods, (c) which are the best ions to indicate the movement of leachate, or (d) what is the likely outcome of siting a landfill on a particular formation.

As far as the local authority is concerned the most important question usually relates to the proximity of a borehole to a landfill site, and what is going to happen in the future. An immediate answer is usually required but is rarely forthcoming, especially in the case of domestic landfills. In fact, while a lot of information is being sought on industrial landfills, little work is being done on domestic sites.

Some of the questions may be answered by the Department of the Environment's landfill programme, but should there not be some concensus between all the interested parties on the basic questions outlined above?

Dr Harrison went on to say that he could see problems in translating the results of the borehole dispersion tests, described by Oakes and Edworthy, to large scale practical problems. During the test a relatively large head is generated over a small distance, while in the latter case dispersion may be occurring very slowly over a large distance. Mr Edworthy, in his introduction, said that there was not a great deal of information on this point. Was the reason for the relatively low dispersivities that Oakes and Edworthy measured due to the small distance between the recharge and observation boreholes resulting in a predominance of fissure flow at a local level?

Dr Harrison finally asked whether anyone thought that the expense of drilling extra boreholes, for example in a landfill study, was warranted in view of the problems of scale that had been discussed in the previous session.

Messrs OAKES and EDWORTHY gave the following reply to Dr Harrison. Although there is evidence for considerable fracturing and fissuring of the Bunter Sandstone in some parts of Nottinghamshire, which is partly due to working of underlying Coal Measures, there is no sign of important fracturing at Clipstone. It is not felt, therefore, that fissure flow exerts a significant effect on the experiments. Dispersivity is scale-dependent, however, and the results obtained must reflect the scale at which the experiments were conducted.

In reply, Dr C. BARBER, Mr J.A. NAYLOR and Mr P.J. MARIS agreed with Dr Harrison that it is often difficult to select determinands which may be useful indicators of groundwater pollution from landfills, and it is often practical to concentrate on the determination of only a few substances in groundwater in the vicinity of a site. This is due to the complexity and general lack of knowledge of the composition of landfill leachates, particularly where hazardous substances are involved.

The techniques of sampling and analysis of groundwater in landfill site investigations have not been fully developed, although now we probably have acquired sufficient experience to determine which technique is appropriate in a given situation. The authors' paper indicated some of the more useful techniques as well as some of the 'grey areas' where knowledge is lacking. With the accumulation of information from reports of laboratory studies of landfill, as well as landfill site investigations, it may become more apparent as to the appropriateness of different techniques, as well as the 'compatibility' of data collected using different techniques.

Preliminary hydrogeological assessment forms an important part of any site investigation, and ideally maximum use should be made of any boreholes drilled during this phase. Detailed evaluation of aquifer properties may not be possible due to the constraints of time and availability of staff required to carry out this work. An indication of aquifer properties may be obtained from laboratory analysis of recovered samples, from standard constant head or falling head tests in the boreholes, and from the response of water levels to infiltration.

Dr M. FLEET, in addressing his comments to Mr Brown, said that the Water Research Centre's geophysical borehole studies are primarily related to water supply, although the Centre is also involved in monitoring the contamination derived from landfill sites. The resulting problems at such sites are not dissimilar to those caused by deep well disposal methods, as described in Mr Brown's paper. He had found the description of the acoustic borehole televiewer and the gamma spectrometer particularly interesting. Bearing in mind that the Centre works principally in clean, potable water, and already possesses closed-circuit television, would Mr Brown recommend either of these other tools and in which order of preference?

Dr Fleet had also noted Mr Brown's use of downhole flowmeters and wondered what sensitivities had been obtained. He noted that the Centre used a heat pulse flowmeter, which is much more sensitive than the impeller type, and can record flows down to 1 mm/sec.

In reply to Dr Fleet, Mr D.L. BROWN said that although WRC is dealing essentially with clear water, the acoustic borehole televiewer has the advantage that it can work at greater depth than closed-circuit television. The main problems with closed-circuit television are that below about 300 metres water naturally becomes cloudy, and also light sources tend to fail because of the pressure. The acoustic televiewer allows the breadth and depth of fractures, and hence their volumes to be determined empirically. He used the device in conjunction with an acoustic caliper which was currently under development by the USGS.

The gamma spectrometer is a very useful tool, especially for work on landfill studies. If leachates have not reached the water table they cannot be detected by conventional downhole geophysical instruments in observation boreholes, but this tool is able to detect them behind the casing and above the water table. The gamma spectrometer may not be available for purchase, but one company in the USA will undertake surveys on a commercial basis. It is a very expensive tool but, in relation to the cost and problems of radio-active wastes disposal that expense is probably insignificant.

Mr Brown said that the current-meters with which he was familiar were of the vane type, and the work described was in mega-volumes so the sensitivity was unknown. However, readings of 1 rpm could be made which were equivalent to a flow of about 0.14 l/s. The flow meter was used principally to determine relative changes in velocity in the borehole and so identify the contributing zones. At low flow rates the thermal flow meter or spinner surveys would certainly be preferable; the scale of operation must be the deciding factor.

Professor J. BEAR said that the unsaturated zone was very important in many studies and asked if there was an instrument which could continually log the passage of either a natural or artificial tracer within this zone. To some extent it can be done using neutron devices to measure water content changes, but are there any other methods? He believed that the gamma spectrometer could not be used because it examined only that part of the aquifer immediately outside the casing and, due to wall effects, this is uncharacteristic of what happens within the body of the rock.

Mr D.L. BROWN agreed with Professor Bear that it was a difficult problem. The USGS had attempted to measure the movement of artificial isotopes in the unsaturated zone at Maxey Flats, and had found that it was only possible to detect them at a relatively short distance beyond the casing.

Mr K.E. WHITE, in reply to Professor Bear, said that when high-energy gamma-ray emitting tracers were used, a detector, such as a sodium iodide crystal, in a borehole could 'see' a sphere of the surrounding aquifer, and it could be advantageous to use narrow boreholes, the diameters of which were small relative to the 'infinite' radius beyond which, in a uniformly distributed tracer field, spherical volume shells did not contribute to the probe reading because of the shielding effect of the medium. Figure D 1 indicates the dependence of this radius on gamma-ray energy; Figure D 2 illustrates the transmission of a broad beam of gamma rays from various radionuclides through concrete (density 2.35 g/cm^3). He said that, as the detection efficiency of the crystal in the probe increased with its radius, a suitable compromise would probably be the use of a borehole of about 50-mm radius with a close-fitting probe which had a long crystal (at least 100 mm) to compensate partly for the restricted radius.

Mr White reported that tests to indicate the effective infinite radius for Br-82 have been carried out by WRC Stevenage. Under saturated conditions, in sand,

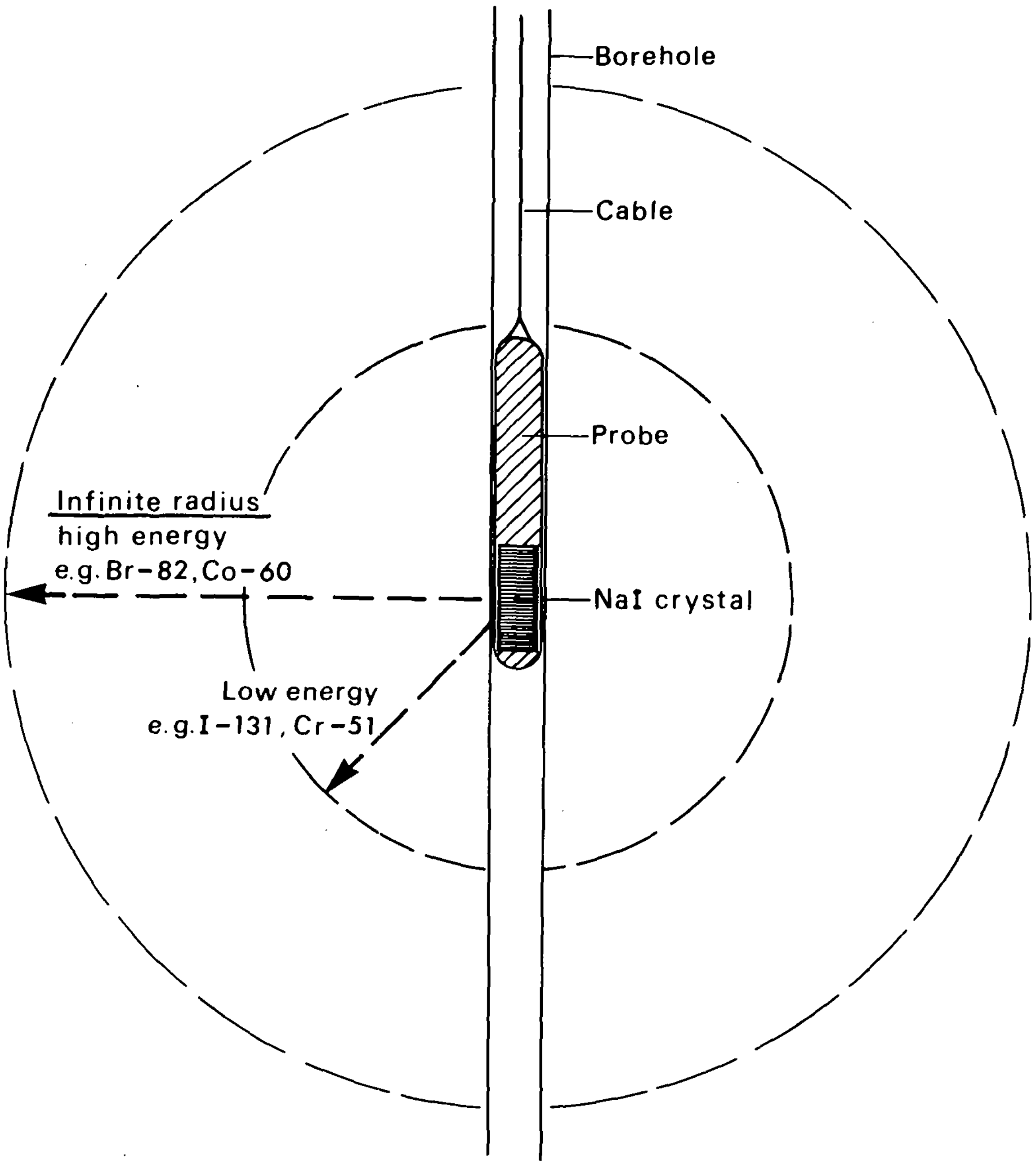

Figure D1 Dependence of effective radius on gamma-ray energy of tracers

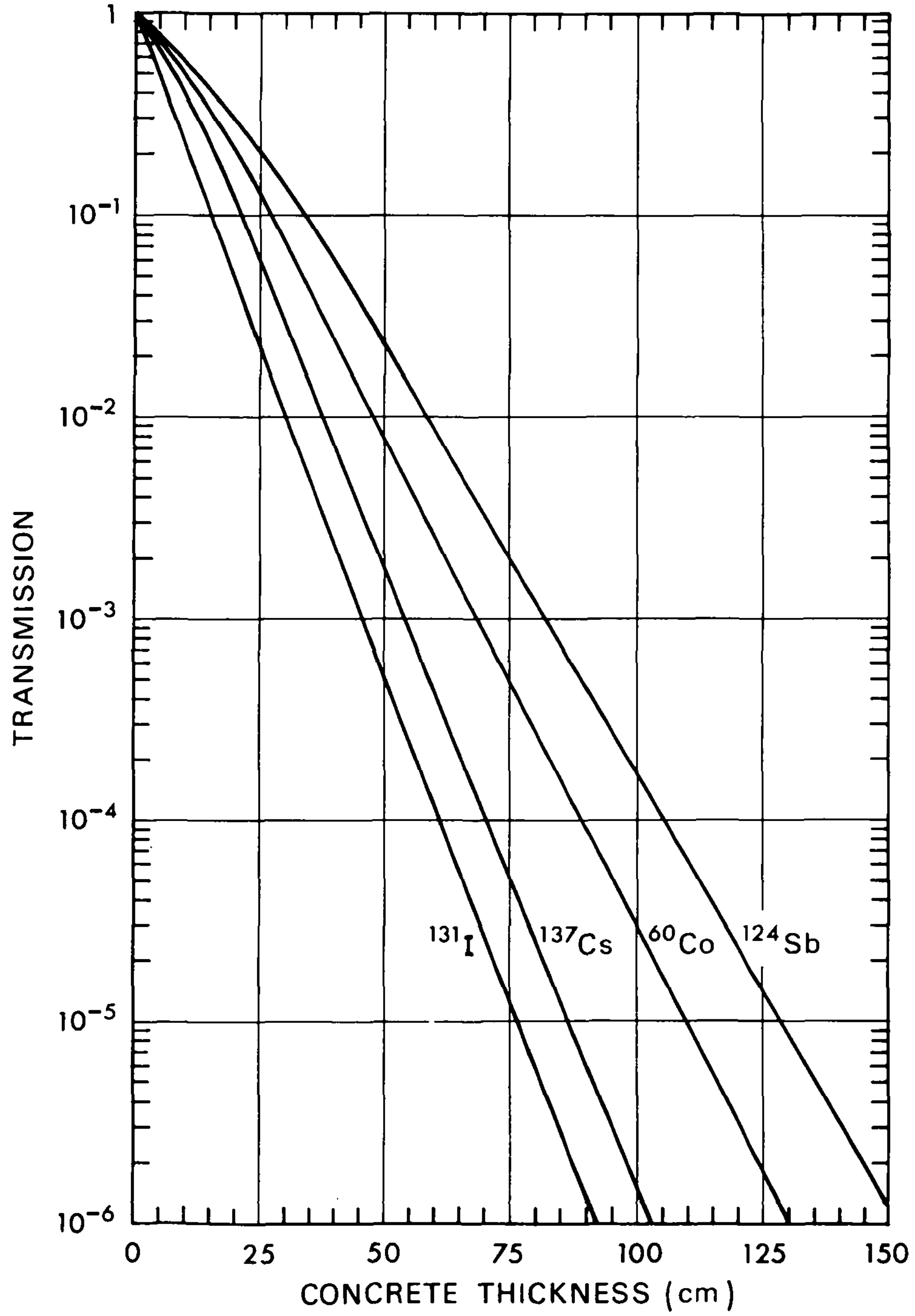

Figure D2 Transmission of a broad beam of gamma rays from various radionuclides through concrete. (From Radiation Protection ICRP Pubn. 21. Figure 47.)

this was found to be about 34 cm, and in water alone about 54 cm, so that for the unsaturated zone some intermediate radius could be expected. The volumes 'viewed' might not, therefore, be too dissimilar from those applicable to the neutron moisture meter provided that high-energy emitters were used. However, for pilot-scale studies, crystals and boreholes of smaller diameter could be used with lower energy emitters to obtain better resolution on tracer dispersion.

Dr L.J. ANDERSEN asked Mr Brown whether it was necessary to run a caliper log of a borehole in order to interpret the results of a flowmeter survey, as the rate of flow is governed by the borehole diameter?

Mr D.L. BROWN agreed with Dr Andersen, but explained that he had been discussing a screened well of known diameter. It was necessary as a first step to calibrate a flowmeter, and this was usually done by pumping at a constant rate with the current meter in the solid casing immediately above the screen. Counts and flowrate could then be related. The flowmeter could then be lowered to the bottom of the borehole and raised a foot at a time. A curve showing percentage increase in flow with decreasing depth was obtained and the contributing zones are marked by slope changes in the line. Vertical sections of line represent zones where there was little or no inflow.

Dr L.J. ANDERSEN noted that Dr White, in his presentation, had suggested that tritium analysis should be intensified during the next five years as the concentrations of 'bomb' tritium were now approaching natural levels.

Dr Andersen agreed that much information could be obtained about the movement of water in the unsaturated and saturated zone by intensifying the tritium profiles, but believed that the use of the bomb tritium for the age determination of groundwater may be possible for some decades rather than for some years. Groundwater with no tritium content must originate from precipitation before 1952. The 1963 to 64 precipitation with a high tritium content (concentrations from 500 to 4000 TU) may be present in deep aquifers for many years. If the input concentration is 1000 TU or greater it should still be possible to measure the tritium content even 100 years after precipitation.

Mr K.E. WHITE, in reply to Dr Andersen, agreed that deep aquifers existed where tritium concentrations below 1 TU could be found, and that possibly decades were left for dating. However, there were areas in many countries where the water tables were not very deep, possibly as low as a few metres in places. He said that if these shallow systems were not sampled before the readily identifiable fallout peaks reached the water table, then accurate dating information would be lost. He thought, perhaps, the alarm on tritium had been sounded too early; however, it should be remembered that isotope decay and dispersion continually degrades tritium profiles, and also that interference of waste tritium in the environment because industrial uses and activities could well increase with time, affecting the aquifer directly, the samples collected, or the analytical laboratories, equipment or materials.

Mr White said that water samples in storage for dating should be kept in glass bottles. Weiss et al (1) had found that 1-litre glass bottles gained tritium at a rate of 0.01 TU per year compared to 0.20 TU per year for polyethylene bottles, for an ambient level of 200 TU. These results from Heidelberg, which were not published when the present paper was written, demonstrated great expertise in this field, quoting a detection limit, for a single analysis, of about ±0.08 TU (1σ). Such remarkable detection sensitivity would clearly extend the period over which dating could be carried out in deep systems or those where percolation was extremely slow. It was interesting to note that these workers found levels below 0.1 TU in deep north-east Atlantic waters, this level being about 1% of that for ocean surface waters.

Mr J.H. BLACK said that as part of the Department of the Environment landfill research programme, bromine-82 had been used in tracer experiments in the unsaturated zone. The tracer had been irrigated on to a prepared surface of the Chalk and its movement through the unsaturated zone was being monitored by 60 to 75 mm diameter boreholes. A major problem occurs where there is local irrigation or rainfall as the borehole may act as a short-circuit. To overcome this, the anulus between the borehole casing and the chalk was lined with polyurethane foam. The foam contains a small proportion of hydrogen ions, which precludes some neutron moisture measurement. The concentration of the bromine-82 tracer could easily be read off a depth correlated instrument, the time scale being limited solely by the amount of bromine-82 used and the activity levels obtained.

When polyurethane foam is to be used in boreholes, it should be remembered that it has a pressure breakthrough level. At the depths at which it was used by Oakes and Edworthy, for instance, some of the cells would tend to break, which would lead to the absorption of the surrounding water at a rate proportional to the pressure. The foam should thus be used with great care below the water table.

Dr H.A.C. MONTGOMERY, in referring to the paper by Mr White, said it was suggested that the heavy atoms, i.e. tritium, deuterium and oxygen-18, might not constitute the perfect water tracer in every circumstance. Mr White had quoted an example taken from a paper by Kaufman and Orlob (2) where the behaviour of tritiated water and the chloride ion was very different indeed. In a previous session anomalous behaviour in the Chalk was discussed,and a paper to be heard later would probably produce evidence of further peculiarities of the movement of tritium through the chalk. Under what conditions, therefore, is tritium a perfect tracer for groundwater ?

Mr K.E. WHITE, in reply to Dr Montgomery, said that he had an open mind about the 'Chalk ground-water tritium anomaly' and thought there was no reason why two or more modes of dispersion should not take place simultaneously, with the initial and subsequent vertical profiles dependent on the fissure characteristics and the frequency and intensity of precipitation. Elucidation of tritium profiles was likely to take a long time to allow for sufficient field studies to be completed in various chalk aquifers of different fissure and block-size distributions. A series of repeat studies on boreholes positioned in close proximity could help in deciding what aquifer properties might be deduced from the tritium data.

He said there were no strict conditions for the use of tritium as a groundwater tracer but until proved otherwise, it can be regarded as the best tracer available, provided that the essential interest was in the rate of movement and dispersion of the water molecules rather than a pollutant - actual or anticipated. For prediction of the fate of pollutants in general, the use of a back-up tracer in addition to tritium might be prudent; and for specific pollutants a labelled form of the substance might be necessary. The best approach was to commence with jar tests in the laboratory to determine adsorption isotherms and the kinetics of any tracer uptake on material taken from the aquifer, and then to carry out pilot-scale percolation tests using columns, and finally to proceed with experiments at field sites. He said that labour and cost restraints were such that field tests were sometimes started without such preliminary studies, which nevertheless could be needed later to account for anomalous results or very poor tracer recovery.

On the question of the chloride v tritium results for loam, studies were needed concerning the behaviour of 'normal' water molecules in various matrices, while tritium dispersion was also being investigated. Some conclusions might only be reached by using techniques such as nuclear magnetic resonance combined with simultaneous use of tritium, deuterium and 0-18.

Dr R.E. JACKSON said that his department in the Directorate of Environment, Canada, used an ion-selective fluoride probe for their groundwater tracer work. This avoided the use of radiotracers and the resulting public disquiet.

Mr K.E. WHITE, in reply to Dr Jackson, said that in problems which would yield to tracer application, the appropriate tracer should be chosen after consideration of factors relative to the individual case; one such factor being public reaction. He pointed out that each proposed use of radioactive tracer in the UK involved an application which was considered by the Department of the Environment (DOE) and the Ministry of Agriculture, Fisheries and Food, and if the proposed tests were approved the DOE notified local district councils, the county council, and other interested parties. He said there had seldom been official objections because it was usually realized that potential benefits of the study far outweighed conceivable risks. There were, of course, always a few objectors to any action such as borehole drilling or introduction of any substance, whether radioactive or not, into the local environment. As mentioned in the present paper, the acceptance of unreasonable objections could result in a tracer or method being used to solve the problem which was potentially more harmful. Fluoride, although of infinite half-life, might well be preferable to, say, tritium of half-life 12 years, if it could be introduced in the required amounts without density effects. Its advantages should be balanced against those of other tracers for convenience of use, cost, background variations, and the probability of obtaining meaningful results, for reasons which the following comments of his colleague, Mr Smith illustrated.

Mr B.D. SMITH contributed the following written discussion:
The use of fluoride and a specific ion electrode as an alternative tracer system to radioisotopes for groundwater studies. As with most chemical analyses, the limit of detection for the electrode technique was controlled by, amongst other things, interferences from other elements. Thus, for a fluoride electrode, iron and aluminium could interfere by producing fluoride complexes and a pH value below 4 produced hydrogen fluoride. These reactions could also occur within the aquifer leading to an apparent loss of tracer. With electrodes, there was also the need to control the ionic strength of the solution under test. These interferences could be reduced by the addition of various reagents. For example, CDTA would complex more readily than fluoride with iron and aluminium, a sodium acetate/acetic acid mix would buffer the pH and sodium chloride could be used to adjust ionic strength. Therefore, although the electrode technique was sensitive (0.02 mg F^-/l) and had, like the use of radiotracers, the advantage of continuous in situ detection, the electrode technique might require a flow-cell to mix in the required reagents.

Mr ANDERSEN asked Messrs Oakes and Edworthy if the peak concentration measured in an observation well would be observed before or after the real peak of the tracer pulse had reached the well.

Messrs Oakes and Edworthy replied that when tracer is moving from an injection well to a pumped well, only the variation with time at a few points where observation wells are located can be measured and not the complete distribution in the aquifer. The analysis in the paper shows that the concentration measured in an observation well between injection and pumping wells will reach a peak value when the real peak of the tracer distribution in the aquifer is still moving towards the observation well. This is because the tracer distribution is continuously decaying under the effects of dispersion. The observed peak is, therefore, recorded before the passage of the actual peak. The median of the measured tracer distribution in the observation well will indicate the time of passage of the actual peak of the tracer distribution in the aquifer. However, the median is generally difficult to determine because the measured tracer distribution will have a long slowly decaying tail.

Mr D. OLIVER submitted the following written discussion. Mr Brown's description, when introducing his paper, of borehole logging being a 'Cinderella' exactly matched his own experience. Too often he had found that the earlier application of borehole geophysics would have saved money, or led to the revision of a drilling programme. However, he believed that this attitude to the early use of geophysics was changing as more engineers became aware of the value of logging results. The number of requests that the WRC had received to run logs had doubled over the past year, and had doubled again during the current year. He thought this indicated that an awareness of the value of geophysical logging was spreading. The increase for requests had been mainly for the more sophisticated types of logging. Many of the water authorities in the UK now had their own equipment which enabled them to undertake the simpler logging techniques.

Engineers who are involved in the design of new boreholes and wells should consider at the planning stage the place and value of borehole logging during and subsequent to the drilling programme.

Mr E. COOPER submitted the following written discussion.
Since early 1968 Sir William Halcrow & Partners have been involved with investigations into the stability of spoil heaps in the South Wales Coalfield.

Although the factors affecting stability are diverse, groundwater is often a major problem, and tracing experiments have played an important role in delineating groundwater flowpaths. In any investigation of this nature the tracer should be safe, reliable, convenient and cheap (in relation to the amount of information it provides). Of the experiments carried out in South Wales using tritium, fluorescein and bacteriophage, tritium has provided the most successful and informative results.

The tritium tracing experiments, which have been carried out on our behalf by AERE Harwell, consisted of injecting tritiated water through a borehole into the base of the aquifer under investigation (usually fissure Coal Measures sandstone). Sampling subsequently takes place at preselected issues and streams which are gauged and from which background samples have previously been taken. Although the groundwater flow is demonstrated by the position of positive sampling points in relation to injection point, the non-appearance of tracer, as mentioned by Mr White in his paper, is also significant. However, because tritium experiments are quantitative, the amount of unsampled tritium which has to be accounted for is known, allowing the results to be put in better perspective.

Fluorescein has been used in small scale tests with varying degrees of success but it has been found to work only when used in large quantities; flushing up to 20 kg of dye through a borehole with the same quantity of caustic soda pellets in solution to increase the pH. For testing samples an ultraviolet lamp is used to increase fluorescence and the technique has been successful in tracing groundwater movement, again in jointed Coal Measures sandstones, over distances of up to 50 m. It has also been used successfully to trace movement of water through culverts, stream courses and rubble drains.

Bacteriophage has been used on two occasions, both of which were successful within the limits of usefulness of the tracer. Both the tests were carried out in conjunction with the Department of Microbiology at Cardiff University, and one is the subject of the paper by Martin and Thomas (3). Consideration was given to carrying out further tests with bacteriophage through a commercial outlet but were ruled out on the grounds of greater cost and relatively unproven reliability in comparison with tritium.

Mr K.E. WHITE, in reply to Mr Cooper, agreed that tritium would certainly be preferable to fluorescein or bacteriophage in most applications, but its long half-life was a problem. He said that although it was possible to determine tracer recovery quantitatively, it was never quite certain whether the remainder was going to interfere with future tracer experiments, or water dating tests using tritium concentration variations in the hydrosphere.

He thought that the kind of observation made by Mr Cooper was most valuable, and wished that others would pass on their experiences; he would be pleased to learn of the findings of any tracer tests as these were seldom described in open literature, and even information communicated internally about experiments which had been abortive would be useful. Confidentiality would be observed in all cases, even when such information was reviewed, and the results might be shown in a similar way to those illustrated in Figure 1, Paper 11.

Mr J.J. FIELD contributed the following written discussion.
In the introduction to the support paper by Black et al the following statement is made: 'The object of using field lysimeters is to isolate bulk samples of sand in an undisturbed condition so that pollutants will move under conditions approximating to those in the field'. He thought this to be a noble ideal, but was concerned that the conditions do not approximate to those in the field. If the results of these experiments are to be used to provide the scientific basis for a Code of Practice on the selection of landfill sites, it is important that the chemical and bacteriological processes taking place in the unsaturated layer below a tip be modelled.

The authors' comments would be welcomed on the following points:

(a) Each of the lysimeters has aerobic conditions at its surface. It appears that the breakdown of fatty acids causes anaerobic conditions in lysimeter No. 4 to be achieved within 1.0 to 1.5 m below the surface. However, this is still not a model of real conditions.

His limited knowledge of chemistry led him to believe that chemical and biological reactions are a function of pH which is, to some extent, dependent on the alkalinity of the leachate and the carbon dioxide evolved during bio-degradation. How will the results be related to real conditions?

(b) The rate of application of leachate at 700 mm per annum is far greater than the residual rainfall of British sites. The field capacity of refuse will further reduce the amount of rainfall available to produce a leachate by, perhaps, a further 50%.

(c) It appears that small areas of the surface of the lysimeters are beingng fed by a nitrogen-rich atmosphere to produce anaerobic conditions on the surface, and that eventually cores will be taken of the sand below these areas for analysis. Surely the log of the pollutant loads in these cores will be affected to a considerable extent by the dispersivity of the sand.

(d) As tipping continues on a real site and the lower levels of a tip are stabilized by anaerobic digestion, the strength of the leachate reaching the unsaturated zone will fall off.

Taken together, the above points would suggest that the lysimeter experiments will exaggerate the rate of movement of the constituents of the leachate through the soil and lead to over cautious guidelines in the proposed Code of Practice.

Mr J. H. BLACK replied on behalf of his co-authors as follows:
Mr Field takes issue with the paper on the question of whether or not conditions within the lysimeters approximate to those in the field. The object of the lysimeter experiments is to investigate the movement of various pollutants through unsaturated sands. No attempt has been made to model the conditions at the base of a landfill site by generating anaerobic conditions at the lysimeter surfaces. The lysimeter experiments are one of a series of studies being undertaken to characterize the chemical and bacteriological processes taking place in the unsaturated zone beneath a landfill. Other studies involve field investigations at existing landfill sites, controlled laboratory experiments and studies with smaller lysimeters. In some of the latter, anaerobic conditions

are being generated at the sand interface and Mr Field will have seen these on his visit to the lysimeter at Uffington.

Of course the lysimeter experiments will exaggerate the rate of movement of leachate constituents, as Mr Field suggests, but this will not lead to over-cautious guidelines. This is because these results will not be treated in isolation but will be co-ordinated with results from the many other research studies being undertaken to give a balanced assessment of leachate attenuation in many different geological environments.

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Session 4

FIELD INVESTIGATIONS

Chairman:

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PAPER 13

FACTORS AFFECTING THE TRANSPORT OF POLLUTANTS WITHIN AND AWAY FROM LANDFILL SITES

M. J. Stiff and C. P. Young

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1. INTRODUCTION

The transport of substances within landfills and away from landfills through soils and rock and in groundwater is dependent on and controlled by a variety of factors which are intrinsic to the substances and to the transmitting media. Because transport involves the interaction between a substance and its environment it is not always easy, if at all possible, to separate the factors absolutely.

While the intrinsic properties can be described in specific terms, a number of properties are often interlinked and interdependent. For example, the solubility of a heavy metal such as copper is directly linked with the precipitation of hydroxide or carbonate species which in turn is dependent on the composition of the environment, both aqueous and solid. Also, the observed solubility may be affected by adsorption, a property of the waste or of the minerals with which the metal is in contact. Precipitation or solution within the transmitting medium may alter the hydraulic properties of the medium.

The properties will modify the mobilities of substances, some to increase the rate and extent of movement and others to decrease them.

2. CHEMICAL INTERACTIONS BETWEEN WASTES

There are a large number of reactions in which wastes can participate and which can be manipulated to convert them to innocuous products. It is preferable for two or more wastes to mutually destroy each other, but clearly the opportunities for this are limited.

The impact of acids and alkalis is reduced by neutralization and it is quite common for acid and alkali wastes to be mixed together prior to disposal.

It has been reported (1) that, at the Coatham Stob landfill, wastes containing chromate and thiosulphate are deposited together in a lagoon. At the pH value of the lagoon, no reaction apparently takes place, but if the pH were reduced to only mildly acidic, chromium (VI) would be reduced to the sparingly soluble chromium (III), thereby decreasing the mobility of the chromium waste.

3. CHEMICAL PRECIPITATION

The factor which is usually thought of as that which limits the solubility, and hence the mobility, of inorganic substances is precipitation. Precipitants may be brought to the landfill as wastes or they may be generated within the landfill. For example carbon dioxide and hydrogen sulphide are formed as a result of anaerobic degradation. The concentration of a sparingly soluble species is limited by the solubility product. In the case of lead sulphide formed according to the equation

$$Pb^{2+} + S^{2-} \rightleftharpoons PbS_{(s)}$$

the solubility product in concentration terms is given by $K_{so} = [Pb^{2+}][S^{2-}]$. While the relationship is valid for all conditions, the value of $[S^{2-}]$ is pH-dependent because of the existence of the species H_2S and HS^- and the pH-dependency of the ratios $[H_2S]/[HS^-]$ and $[HS^-]/[S^{2-}]$. The solubility of lead in the presence of lead sulphide and at a total soluble sulphide concentration of 0.03 mg/l varies from 2×10^{-8} mg/l at pH 6, to 4×10^{-10} mg/l at pH 7, and to 2×10^{-11} mg/l at pH 8 (calculated using data from Sillen and Martell (2)).

The chemistry of carbonates is similar because of the presence of carbonic acid and bicarbonate. Not all metals can form pure carbonate precipitates but may form hydroxocarbonates such as malachite $Cu_2(OH)_2CO_3$, formed by copper.

The solubility of metals is often modified by complex formation. Many metals exist as a series of hydrous complexes as illustrated by iron (III) Fe^{3+} $FeOH^{2+}$ $Fe(OH)_2^+$ $Fe(OH)_3$. The solubility product is expressed in terms of Fe^{3+} and $Fe(OH)_3$, but depending on the pH value the solubility of iron (III) is increased by the presence of the species $FeOH^+$ and $Fe(OH)_2^+$. At pH 7 the solubility of iron (III) is increased by a factor of 10^4 over that predicted from the solubility product because of the presence of $FeOH^+$, but the effect is small in practical terms the solubility increasing from 5.6×10^{-14} mg/l to 5.6×10^{-10} mg/l.

In determining instantaneous solubilities, due account should be taken of the the rates of precipitation or of solubilization. If equilibrium is not rapidly achieved then the observed concentration may be quite different to that expected.

4. SOLUBILITY

Solubility is rather difficult to define in practical terms and it is common practice to define soluble matter as that which passes a given membrane filter (often 0.45 μm although this is not rigorous). In terms of leachate and groundwater, solubility might be defined in terms of transportability, regarding landfills and rock formations as filters.

Solubility is a function of the solvent as well as of the solute. Table 1 shows the solubility of four metals both in water in the absence of complexing agents and in a 5×10^{-3} M bicarbonate solution (characteristic of a hard water), at pH 7 (3). The effect of bicarbonate is substantial in the case of zinc and dramatic in the case of cadmium.

Table 1. Solubilities of metals in two media, buffered to pH 7

Medium	Solid phase and equilibrium solubility of metal (mg/l)			
Water	$Cu(OH)_2$	$Zn(OH)_2$	$Cr(OH)_3$	$Cd(OH)_2$
	0.7	50	0.6	10^5
5×10^{-3} M bicarbonate	$Cu_2(OH)_2CO_3$	$ZnCO_3$	$Cr(OH)_3$	$CdCO_3$
	1.3	0.7	0.6	0.07

Organic liquids possess a 'true' solubility but may also be present as stable emulsions which will enhance the effective solubility. Whether or not emulsions will remain stable during transport will depend on local factors such as the presence of stabilizers, compounds which may be present as wastes in the landfill or be naturally occurring, and whether de-emulsification will occur during passage through strata.

An example of the difficulties which may be met is the solubility of the polychlorinated biphenyl, Aroclor 1254. Values within the range <0.1 - 10 μg/l have been reported (4),(5). The higher values may represent the true equilibrium solubility or they could represent the formation of stable emulsions. A concentration of 0.5 μg/l has been found in the leachate from a landfill.

Transport of aggregates, particulate matter or liquid droplets, may also occur: this will tend to be opposed by the filtering action of the landfill and the underlying strata. It is not possible to give any size limits because, as the 'filter' becomes clogged, smaller and smaller particles are retained. In the limit no transport at all takes place but little is known about the conditions in which this might be so. Particles can also be retained on surfaces by electrostatic forces on account of the electrical double layer which exists at the interfaces between phases.

5. SORPTION AND EXCHANGE

The phenomenon of adsorption of cations on clay-type minerals, which contain exchangeable cations, is well established. The process serves to reduce the transport of heavy metals, although clays, being relatively impervious, form a physical barrier to fluid transport. The occlusion, or co-precipitation, of heavy metals by ferric hydroxide precipitates is well known to analytical chemists and might also be important in the landfill context.

The sorption of organic compounds can also occur. Water-immiscible liquids may form a film which covers particles of solid waste and refuse in a landfill and resists transport by water percolating through. Whether or not the equilibrium solubility is attained will depend at least partly on contact time.

Substances are adsorbed from solution on to solids. Experimentally, the adsorption data can often be fitted to a Freundlich isotherm of the form

$$\log Y = a \log c + \log k,$$

where Y = quantity adsorbed per unit mass of adsorbent, c = equilibrium concentration of solute in solution, and k and a are constants.

Figure 1 shows the adsorption of phenol on domestic refuse, and the differences in the behaviour of fresh and aged refuse. With the former a non-linear isotherm was obtained which is compatible with there being at least two different types of adsorption site available.

It has been postulated that, although adsorption may not lead to a permanent reduction in the quantity of phenol available for percolation, the temporary reduction might sometimes be sufficient to permit biodegradation to take place.

6. VOLATILIZATION

The temperature of domestic landfills is commonly in excess of ambient ground temperature. At a fresh tipping face, temperatures of up to 70°C may be encountered and, after 10 years, temperatures may be of the order of 25°C. There is therefore ample opportunity for the volatilization of low boiling-point compounds such as the chlorinated hydrocarbons used as dry-cleaning solvents. If these substances were deposited on the surface of a landfill they would first be absorbed by the solid wastes and would not percolate rapidly.

The process cannot necessarily be relied on to completely dissipate volatiles: it has been reported (1) that chlorinated solvents have migrated to depths of 23 m in chalk beneath a landfill but at concentrations generally below 25 mg/kg.

A second class of materials where mobility can be modified by volatilization comprises those which are converted to volatile products by reaction within the landfill or in the underlying strata. Cyanide is present as the sodium salt in certain heat-treatment metal-finishing formulations, the waste from which has been known to have been disposed to land. In contact with water at pH values of 8 and below, cyanide is present as hydrogen cyanide in large excess over cyanide ion, according to the equation

$$CN^- + H_2O \rightleftharpoons HCN + OH^- \quad (pK = 4.6).$$

At a landfill at Hammerwich, Staffs, where heat-treatment waste containing cyanide was reported (1) to have been deposited, unchanged cyanide was not visually detected in samples recovered from boreholes and nor were substantial quantities of cyanide determined analytically. However, hydrogen cyanide gas was detected in the borehole gases, which indicated that volatilization of cyanide could have been a removal process in the landfill.

7. BIOCHEMICAL FACTORS

Three types of biochemical processes can be readily identified as applicable to the landfill and groundwater fields - hydrolysis, oxidation and reduction. The reactions are catalysed by enzymes present in micro-organisms which are present either in the landfill or in groundwater. Because landfills and rock strata provide very different substrates, the populations of organisms present will be very different.

Biochemical processes lead to the production of water-soluble substances from insoluble solid materials and to the conversion of organic compounds to other, perhaps less toxic, substances. At a fresh tipping-face the refuse is well aerated and aerobic biodegradation (oxidation) takes place. Temperatures can rise to 60 - 70°C. As with any oxidation, the ultimate products are carbon dioxide, water, nitrate, sulphate and so on. The process involves the formation of acetate as an intermediate, which is then further oxidized.

As the refuse becomes covered with more refuse, the transfer of oxygen is decreased and oxygen becomes depleted. When the fill becomes anoxic, the development of an anaerobic population begins. Anaerobic bacteria use sulphate, nitrate and carbohydrate as oxygen source, or terminal electron acceptor. Sulphate becomes reduced to sulphide (whence the origin of hydrogen sulphide in landfills) and carbohydrates are reduced ultimately to carbon dioxide and methane via the intermediate fatty acids; acetic to caproic acids are present in substantial quantities in leachates. The reduction of fatty acids to carbon dioxide and methane is a slow process and thus the fatty acids are observed as persistent compounds (6). Other soluble products which have been detected include alcohols and aldehydes from carbonaceous material, and ammonia from nitrogenous material (1). All are potential water pollutants. Table 2 gives the composition of the leachate from a domestic landfill.

The groundwater underlying a landfill appears to be invariably anaerobic when the landfill is biologically active but as it flows away from the area of the landfill, oxygenated water intrudes and a plume of anaerobicity develops. If aerobic biodegradation then occurs, the aquifer can be self-purifying.

Table 2. The composition of leachate from a domestic landfill. (After Kunkle and Shade (7)).

pH	5.8-6.2
BOD	$14\text{-}17 \times 10^3$ mg/l
COD	$46\text{-}53 \times 10^3$ mg/l
TOC	$9\text{-}10 \times 10^3$ mg/l
NH_3-N	330 mg/l
Organic-N	20-30 mg/l
Chloride	1400 mg/l
Sulphate	265-410 mg/l

8. GENERAL HYDROGEOLOGICAL CONSIDERATIONS

In the same way that the transport of substances within and away from landfills is partially controlled by factors intrinsic to the materials themselves, so the hydrogeological factors may be grouped into those that are intrinsic to the transmitting medium and others which are extrinsic. Because interaction may take place between the groups of factors the properties of both the contaminating solutions and the transmitting media may change with time, leading to complex transport patterns. The intrinsic properties of the transmitting media which control transport patterns include the natural variations in permeability, porosity and pore size distribution within the zone potentially affected by contamination.

Primary, intergranular permeability may be increased by reactions between a leachate and the mineral matrix which lead to solution of either the mineral matrix or its cement, or can be decreased by precipitation from the liquid phase or by entrapment of particulate matter. Secondary permeability, developed as fissures, may be modified by similar mechanisms. If the leachate flowing through a medium remains of constant composition for a sufficient time, a new equilibrium between the solid and liquid phases may be reached. However, changes with time in the composition of the leachate from a landfill may occur because of long-term interactions between the waste or from changes in the type of deposited wastes and, under these circumstances, continued interaction between solid and liquid phases may be expected.

The total porosity of an aquifer or landfill reflects the ability of the mass to store fluids, both liquid and gaseous, whilst the effective porosity is an indication of proportion of the total pore volume which contributes to the flow of a specified fluid through the matrix. The ratio between total and effective porosity is largely dependent on the pore-size distribution. In well-sorted, coarse granular materials the ratio may be close to unity, but in fine-grained or poorly-sorted materials a significant proportion of the pores may be so small that viscosity and surface tension inhibit or completely prevent the movement of fluid under the hydraulic-head differences present in the local environment.

In addition to the variations in hydraulic properties of the main transmitting media, transport patterns may be strongly modified by the presence of localized features such as intrusive igneous bodies within sedimentary rock masses, faults bringing rocks of varying properties into juxtaposition or by the presence of zones of high or reduced permeability within a landfill. Examples of the variety of patterns of leachate transport in the groundwater zone which may arise from interaction of the many variables have been tabulated by Legrand (8) and the physical mechanisms controlling the movement of contaminated groundwater have been reviewed by Brereton and Wilkinson (9).

Pollutants entering the groundwater zone follow similar flow paths to the uncontaminated groundwater, except where modified by external factors, particularly variations in recharge rate in the vicinity of the landfill. Natural, seasonal variations in recharge would be expected to be effective over a wider area than the contaminated zone generated by the landfill and do not normally cause significant alterations to the regional flow patterns. However, increased recharge at the landfill site may occur, caused either by additional hydraulic loading in the form of liquid or sludge disposal on the site or, particularly in the case of landfills sited in excavations which penetrate low-permeability surface layers overlying aquifers, by diversion of surface drainage into the landfill from surrounding areas. In such cases a recharge mound may be generated beneath the landfill, distorting normal groundwater flow patterns and imposing a lateral hydrodynamic dispersion of the leachate into the groundwater system. The gradients around the mound represent a dynamic balance between the recharge input and outflow and alter both with variations in natural and imposed recharge and with changes in the hydraulic properties of the aquifer brought about by solution/precipitation phenomena.

9. FACTORS AFFECTING TRANSPORT WITHIN A LANDFILL

Although variations in the hydraulic properties of an aquifer may result from rock/leachate interaction, these changes are generally slight compared with those which frequently occur within the body of a landfill. All domestic waste tips, and a significant proportion of landfills receiving industrial wastes in the United Kingdom, contain a high proportion of putrescible materials. Decomposition of such material may continue after completion of the landfill and is often accompanied by a continued decrease in the ratio of voids to solids in the mass.

The mode of emplacement of solid wastes may be important in determining the hydraulic properties of the landfill during and after its active life. Two basic methods of emplacement may be considered, forming end members of a probably continuous series. In the first, and possibly older method, wastes were tipped over a face to form a slope at the angle of rest of the materials. Tipping often began at one edge of a worked-out quarry and the infill prograded across the quarry floor in a series of foreset beds, exactly analogous to a subaqueous delta. Vertical grading developed within the foreset beds, larger particles tending to roll to the bottom with fine grades remaining near the top. Foreset depth varied considerably, depending on local conditions, but the thickness of deposition was generally such that only incomplete compaction of wastes could be achieved.

Under such conditions, vertical permeability may be expected to equal or exceed horizontal permeability, and rapid vertical movement of infiltration through the wastes ensures a minimal contact time for leachate generation. In addition, the high void-to-solid ratio would be expected to maintain aerobic conditions within the greater part of the landfill, at least during its early life before decomposition aids compaction.

By contrast, the alternative method of spreading wastes in extensive, thin sheets, followed by compaction and, frequently, topping with low-permeability inert material, causes formation of a landfill with a low initial void-to-solid ratio and a sharp contrast between vertical and horizontal permeability. During the emplacement of the fill, the working surfaces may become puddled by the passage of site vehicles, further reducing their permeability, whilst slight differential compaction commonly produces depressions which subsequently act as local aquicludes within the landfill. Liquids moving vertically through the wastes tend to collect on the low-permeability layers, giving rise to lenticular, perched levels of saturation. Prolonged contact between leachates and wastes occurs and anaerobic conditions are common. Passage of leachate through the wastes is likely to be tortuous, liquids moving from one perched level of saturation to another erratically.

Wastes are deposited in two basic morphological settings. True landfills involve the infilling of existing depressions, either natural or manmade. If the landfill is within permeable beds, the leachates generated within the waste move vertically or horizontally into the host rock and have a high chance of migrating vertically towards the local groundwater zone. Landfills in strata of low permeability become saturated and leachate discharges as surface flows from low points on the landfill rim, unless precautions are taken to prevent infiltration entering the landfill or the leachate is pumped from within the wastes. Waste tips, on the other hand, are built above the existing land-surface level. Leachate generated within a layered tip may appear as surface flows from various levels around the outer faces of the tip, but may enter the groundwater zone around the periphery of the tip if it is built on permeable deposits. The hydrogeological properties of the combinations of waste-emplacement methods and situations are summarized in Table 3. Examples of three of the four combinations which have been examined during the course of the research programme sponsored by the Department of the Environment (1) are identified in Table 3.

10. HYDROGEOLOGICAL MODIFICATIONS TO TRANSPORT PATTERNS WITHIN AN AQUIFER

Leachate generated within a waste deposit may pass vertically through a zone of partial saturation of variable depth before entering the main groundwater zone. Effective permeabilities in the unsaturated flow mode are often several orders of magnitude lower than those of the same material when saturated (10) and intergranular flow rates may be very low. If secondary permeability is developed in the form of interconnecting fractures, a proportion of the leachate may move rapidly towards the groundwater zone. Vertical and lateral hydrodynamic dispersion (11), (12) within the unsaturated zone may modify the form of the recharge core whilst vertical variations in the permeability of the aquifer may create persistent or ephemeral perched levels of saturation in which dispersion by horizontal flow is dominant. In systems where rock/leachate interactions are insignificant the rate of solute displacement will be the same as the rate of solvent flow. The operation of sorption/desorption interactions between leachates and the aquifer matrix leads to retardation of pollution movement when compared with the movement of the solvent and may occur in both the unsaturated and groundwater zones. The rates of transport of non-miscible contaminants, in both unsaturated and saturated flow systems, are independent of the rates of water movement. A further solute retarding mechanism has been postulated for unsaturated flows through the Chalk - a pure, fine-grained, soft, fissured limestone of high porosity but with a media pore size of less than 5 µm. Foster (13), considering thermonuclear tritium concentrations and Young et al. (14), examining tritium, nitrate and chloride profiles measured in vertical sequences of cores obtained from the unsaturated zone of the Chalk, have suggested that water contained within the unfractured blocks is essentially immobile under the hydraulic gradients normal in the unsaturated zone but that molecular diffusion into and out of this static water phase takes place from mobile solutions moving relatively rapidly through the

Table 3. Hydrogeological comparison of waste disposals according to internal structure and morphological situation

	Subaereal Delta type						Layered type					
Type of disposal	Ratio kh:kv	Stability	Oxidation status	Passage of leachate through wastes	Discharge of leachate from wastes	Example (DOE:Ref 1)	Ratio kh:kv	Stability	Oxidation status	Passage of leachate through wastes	Discharge of leachate from wastes	Example (DOE:Ref 1)
Landfill	High	Liable to prolonged settlement	Often aerobic	Rapid vertical movement	Evenly from base of wastes	Hammerwich	Low	Minimal subsequent settlement	Commonly anaerobic	Slow vertical movement. Sub horizonal movement above lenticular low permeability layers	Significant horizontal discharge from low permeability layers	Ingham (in part)
Tip	As above	As above	As above	As above	As above	Not examined. Colliery waste tips	As above	As above	As above	As above	As above	Rainham

fissure systems. The interstitial water in the Chalk matrix acts as a reservoir, the rate of diffusion, and degree of equilibriation achieved determining the importance of the pore-water in the dynamics of solute movement.

Horizontal flows in response to hydrodynamic-head differences developed in the aquifer dominate movement in the groundwater zone. Except in the close vicinity of pumping boreholes and certain natural discharges, flow rates remain below the critical value for the onset of turbulent flow. Vertical mixing is slight and leachates with densities close to that of the host groundwater are swept away as an elongate ribbon in the upper layers of the saturated zone in the direction of groundwater flow. Attenuation of the leachate plume may still result from a combination of a number of factors including rock/leachate reactions, dilution by hydrodynamic dispersion and molecular diffusion and dilution by direct recharge of uncontaminated water along the leachate flow-path. Greater density contrasts between leachate and groundwater may impose a vertical component of flow on the plume of contamination.

Kimmel and Braids (15) have demonstrated that in an homogeneous aquifer, with uniform groundwater gradient, a simple, elongate, mainly parallel-sided plume develops, attenuating both along and transverse to the flow direction. By contrast, Childs _et al_. (16) have demonstrated that multi-component leachates may be partitioned into separate sub-plumes by virtue of different sorption/exchange relationships with minerals in both the unsaturated and saturated zones. Similar bifurcations, to produce multi-lobate plumes, could arise as a result of hydrogeological factors such as long-term changes in the recharge rate at the landfill, changes in the ratio of leachate: groundwater density brought about by alterations in the types of disposals, or by the entrapment of different levels of a single plume between alternating zones of low and high permeability in the aquifer.

Many of the factors discussed above have been encountered during the research programme sponsored by the Department (1), from which two examples are drawn.

Chromite ore processing sludge has been deposited in an abandoned quarry, excavated in an igneous dyke to a depth of 15-20 m below ground level, at Coatham Stob, near Stockton-on-Tees (Figure 2). The dyke is of doleritic composite and is intruded into red, terrestrial sandstones of Triassic age. Baking and fracturing of the sandstone has taken place along the margins of the dyke. Undisturbed groundwater gradients are at a low angle towards the east, passing some 5 - 6 m below the base of the quarry. Groundwater flows close to the line of the dyke are unconfined, but confined conditions prevail at distances greater than about 100 m. Excavation of the quarry removed the surface layer of low permeability glacial clay and led to diversion of surface flows from an area approximately equal in size to the quarry. This additional recharge, added to the water content of the sludge disposals, maintains a recharge mound 4-5 m high under the active tipping area. Hydrodynamic dispersion of the leachate laterally and upgradient in the groundwater zone has occurred, the mound being elongated in the direction of the dyke, which in itself acts as a partial groundwater 'dam'. Groundwater flows within the essentially flat-lying sandstones are dominantly intergranular, except near the dyke margin, where extensive baking and fracturing has created a zone of high secondary permeability. A density contrast between the fresh leachate and native groundwater has encouraged vertical flows along the dyke margin to depths of 80-100 m below surface level. Away from the zone of fractured sandstone, horizontal flows prevail, and the plume has split into a multi-lobate form, confined between lenticular low-permeability layers recognized from examination of cores, geophysical borehole logging and laboratory permeability determinations. Decreasing concentrations of chromium away from the landfill indicate that attenuation has occurred to a slight extent, through adsorption on clay minerals and precipitation in the sandstone matrix.

By comparison, a small landfill at Ingham, Suffolk provided an example of the 'conveyor belt' type of pollution plume. Mixed industrial, agricultural and chemical wastes were deposited for a 4-year period in a worked-out pit in glacial gravels overlying the Upper Chalk (Figure 3). The groundwater is unconfined with a low local gradient towards the south-west. An unsaturated zone about 20 m deep underlies the base of the landfill. Organic contaminants, measured as total organic carbon (TOC) attenuate rapidly from beneath the base of the landfill to the water-table, the maximum levels of groundwater contamination being confined to the upper 5 m of the saturated zone in the direction of groundwater movement. Marked attenuation of TOC, phenols and chlorinated solvents was noted in a distance of about 100 m in the direction of groundwater flows away from the landfill. At the time of the investigation, no recharge mound was detected, but increased TOC values in a borehole drilled close to the upgradient edge of the landfill suggest that a transient mound may have been developed during a period in the life of the landfill in which liquid disposals took place through lagoons excavated in the solid wastes.

ACKNOWLEDGEMENT

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At the end of the present research programme in March 1977, a final report will be published by the Department of the Environment in which the factors which affect the transport of pollutants will be more fully discussed and illustrated by the results obtained during the investigations carried out by the Water Research Centre, the Institute of Geological Sciences and the UK Atomic Energy Research Establishment.

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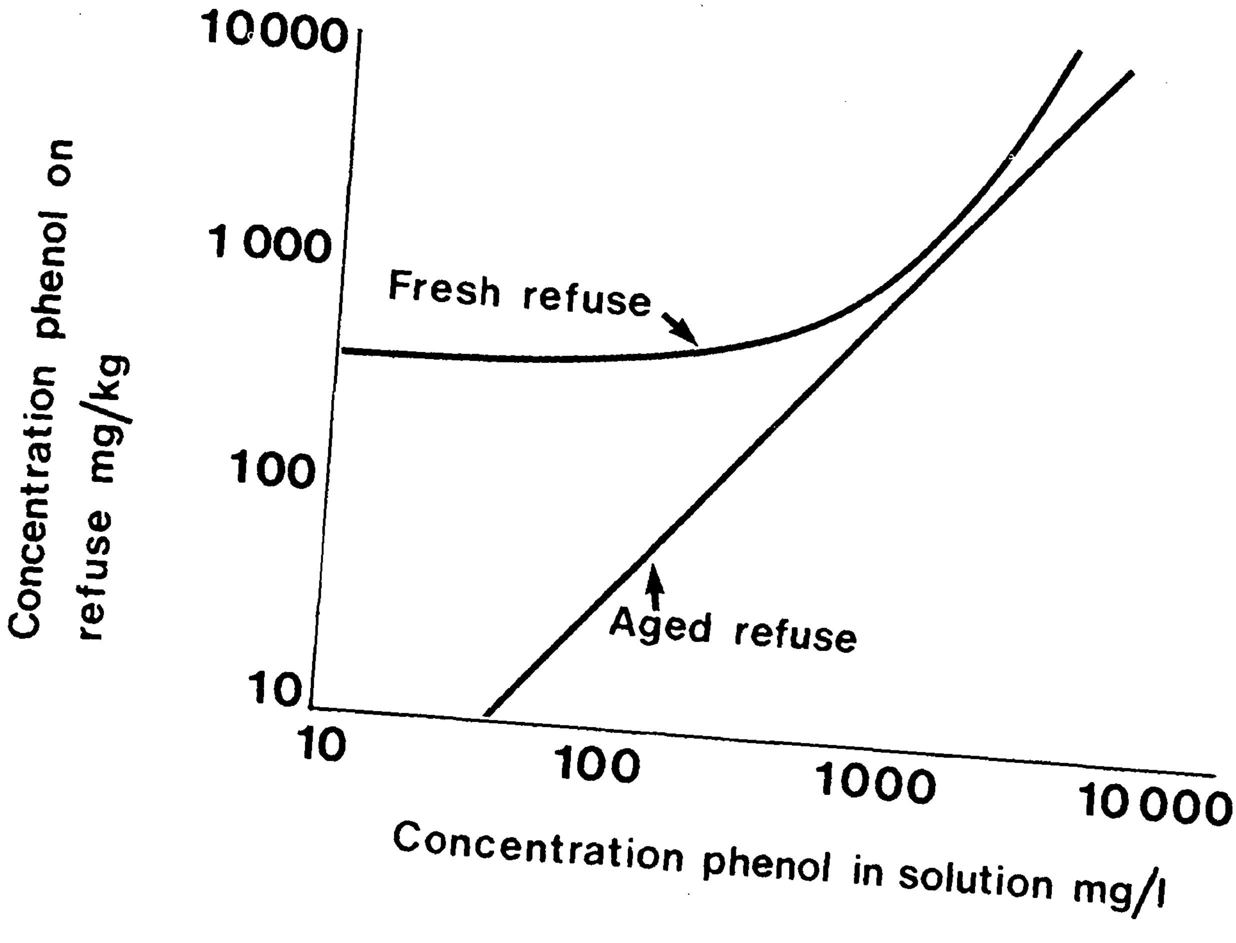

Figure 1. Adsorption of phenol on domestic refuse (Knox and Newton 1975)

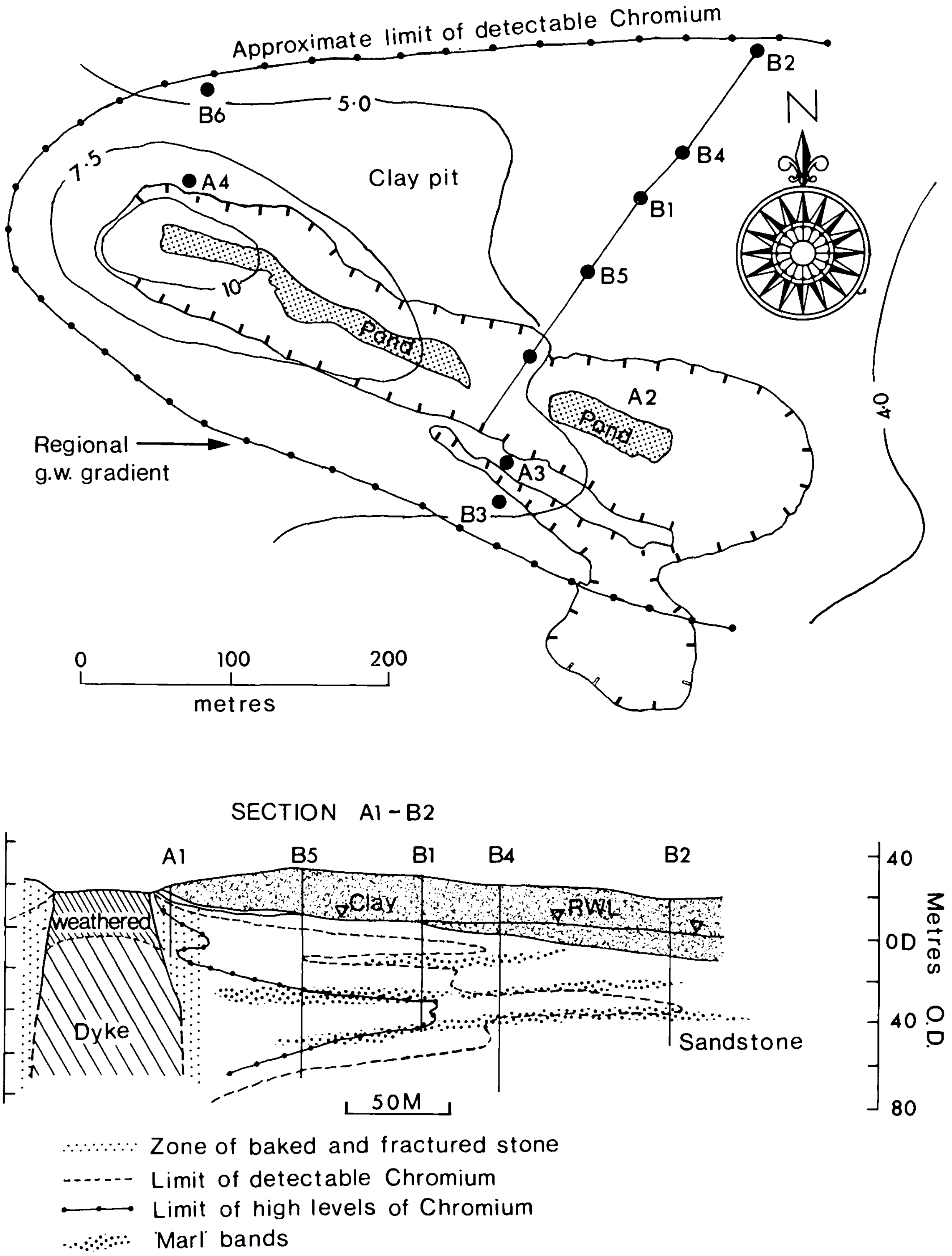

Figure 2. Coatham Stob site plan and section (Groundwater contours in metres O.D.)

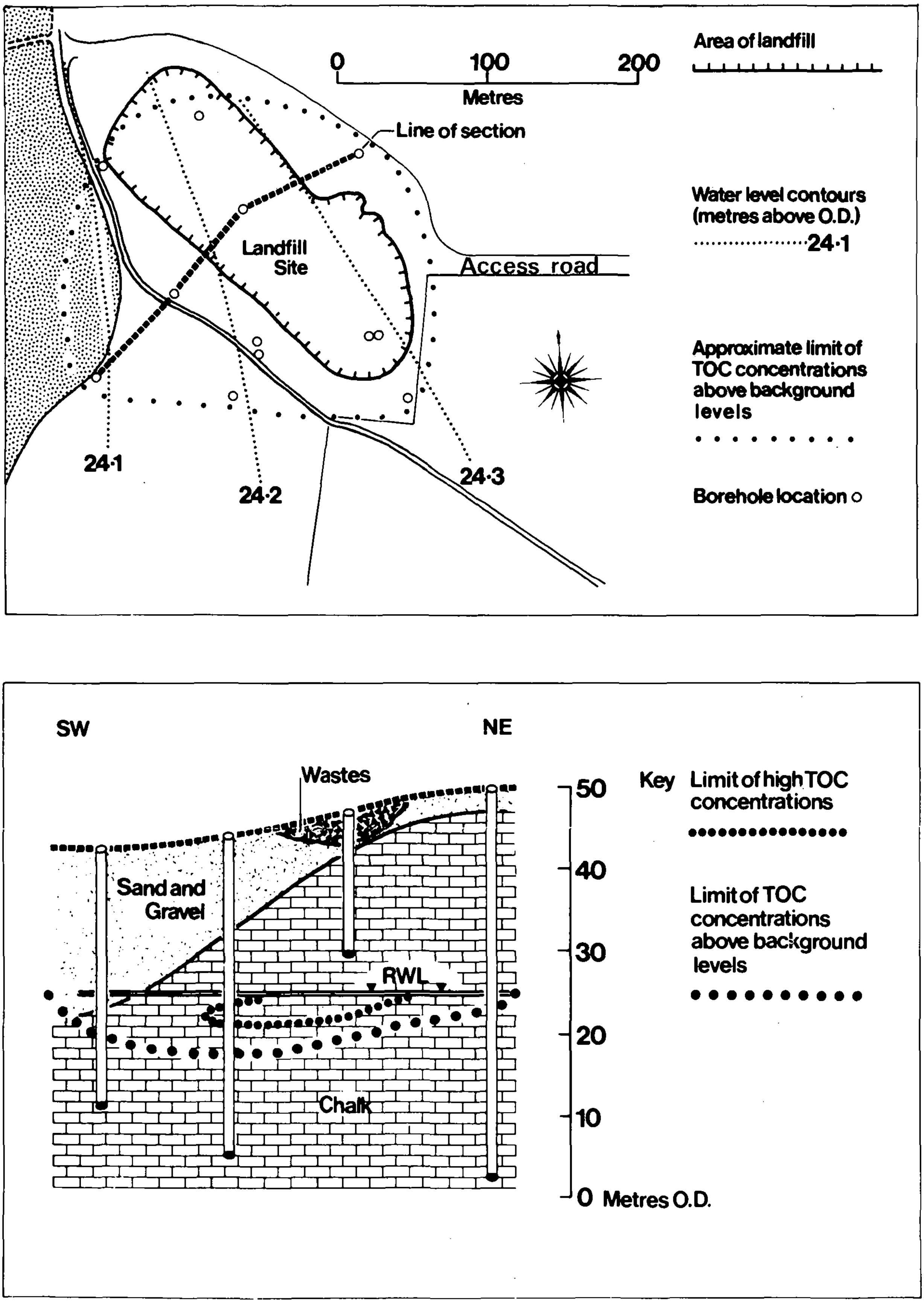

Figure 3. Ingham site plan and section

PAPER 14

INVESTIGATIONS INTO FACTORS AFFECTING THE NITRATE CONTENT OF GROUNDWATER

C. P. Young and E. S. Hall

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1. INTRODUCTION

A relationship between the consumption of nitrate rich water by young children and the condition known as methaemoglobinaemia or infantile cyanosis has been recognised since 1945 (1). Early studies by Walton (2) lead to the United States Public Health Service (3) and, later, the World Health Organisation setting maximum recommended limits for nitrate in water for public supply. The second edition of the World Health Organisation's European standards set a recommended limit of 11.3 mg/l NO_3-N for drinking purposes but suggested that waters with up to 22.6 mg/l NO_3-N would be acceptable if local public health officials were informed so that action could be taken to protect infants at risk. The public health aspects of nitrate in water supplies have been recently reviewed by Shuval and Gruener (4) whilst the situation in the United Kingdom has been summarised by Norval Taylor (5).

Nitrate concentrations at, or in excess of, the recommended limit of 11.3 mg/l NO_3-N have been reported from the two main United Kingdom aquifers, the Chalk (Cretaceous) in East Yorkshire (6), Lincolnshire (7), Sussex (8), and the Isle of Thanet (9), and from the Bunter Sandstone (Triassic) in Nottinghamshire (10), Yorkshire (11), and Shropshire (12). Recent surveys have recorded increases in the nitrate content of groundwater from several areas over the last decade and about 100 major public supply sources now consistently or intermittently abstract water above the recommended limit.

2. OBJECTIVES OF THE INVESTIGATION

During late 1974, the Water Research Centre initiated a research programme with the following objectives:

(i) an assessment of the extent of nitrate contamination of groundwaters in the main United Kingdom aquifers and in the interstitial water in their unsaturated zones;

(ii) the determination of relationships between hydrogeological, meteorological and land use factors and the rates of accumulation and movement of nitrate within the unsaturated zones;

(iii) the consideration of hydrogeological factors affecting the rates of accumulation and lateral dispersion within the saturated zone.

These objectives were set so that:

(i) estimates could be made, using mathematical simulation techniques, of potential future trends of the nitrate content of groundwater, initially on a detailed, local scale but proceeding to integrated quality/quantity groundwater catchment studies;

(ii) assessment of possible methods to control the rate of nitrate leaching could be undertaken;

(iii) future requirements could be estimated for the treatment of contaminated water, with particular reference to the ion exchange methods being developed at the Water Research Centre, and the need assessed for the planning of alternative sources to replace highly contaminated sources.

Because of the wide ranging nature of the programme the Centre has liaised with many other research bodies to ensure nonduplication of effort, consultation being maintained through joint discussions with the Institute of Geological Science, the Regional Water Authorities, the Institute of Hydrology and the Ministry of Agriculture, Fisheries and Food held under the auspices of the Central Water Planning Unit (Department of the Environment).

3. SELECTION OF RESEARCH SITES AND METHODOLOGY

An extensive drilling programme is being carried out on the Chalk and the Bunter Sandstone with the object of obtaining rock samples from which the interstitial water may be extracted by high speed centrifugation, and determinations made of the concentrations of nitrate, nitrite and environmental tritium. The criteria set for site selection and the experimental methods adopted have been reviewed by Gray et al (13), but may be summarised, for site selection, as

(i) location on an outcrop area of the aquifer, free from superficial deposits other than soil, in order to ensure comparability between sites on the same aquifer;

(ii) the presence of an unsaturated zone of at least 20 metres depth, so that effective determination of the apparent rate of downward movement of interstitial solutions could be made, and

(iii) the availability of detailed, long term land use and meteorological data.

The factor chiefly influencing the choice of drilling technique has been the need to obtain samples uncontaminated by extraneous fluids. This requirement mitigates against techniques employing a fluid medium to flush rock particles from the drilling bit. For that reason, augering and drive coring were generally adopted for sampling in the Chalk and the Bunter Sandstone. Under certain adverse drilling conditions in the Bunter Sandstone air flush rotary drilling was permitted (Gray et al (13)).

Site investigations have normally been carried out in two stages. A preliminary phase, in which disturbed rock samples were obtained by augering, has been followed by the recovery of continuous, undisturbed rock cores by drive coring or rotary drilling. Geophysical borehole logging, particularly gamma and caliper logs, has been completed at several sites, to amplify information gained from visual examination of cores and laboratory determinations of hydraulic properties. At certain sites, shallow auger drilling has been employed to supplement data gained from coring methods, whilst at three sites the preliminary sampling phase was omitted.

In addition to the criteria for site selection outlined above, a simple land use classification comprising

(a) arable rotation, including temporary grass leys,
(b) long term grassland, fertilized and
(c) long term grassland, unfertilized,

has influenced the choice and distribution of sites. Sampling has been carried out to date at 22 sites (Table 1), their locations being shown on Figure 1.

Table 1. Summary of site details

Site Name	National Grid Reference	Geological Formation	No. of auger holes	No. of cored boreholes (d = drive core r = rotary core)	Maximum depth of sampling (metres below surface)	Land use a = arable b = fertilized grass c = unfertilized grass
Bridgets Farm, Hampshire	SU 524 344	Upper Chalk	4	5d	60	a and b
Churn Farm, Oxfordshire	SU 523 848	Middle Chalk	2	2d	30	a
Epsom Downs, Surrey	TQ 223 588	Upper Chalk	2	1d	30	c
Westbury Common, Wiltshire	ST 900 511	Upper Chalk	1	-	20	c
Deep Dean, Sussex	TQ 535 022	Middle Chalk	1	-	20	c
Cornish Farm, Sussex	TV 572 968	Upper Chalk	2	-	30	a and c
Netherhales, Isle of Thanet	TR 280 669	Upper Chalk	1	-	23	a
Sprattling Court " " "	TR 350 652	Upper Chalk	1	1d	42	a
Cheesemans Farm " "	TR 324 670	Upper Chalk	-	1d	35	b
Sparrow Castle, " "	TR 319 676	Upper Chalk	2	-	20	a
Alland Grange, " "	TR 318 672	Upper Chalk	1	-	10	a
Heydon, Cambridgeshire	TL 420 430	Middle Chalk	6	-	30	a
Hurley, Berkshire	SU 815 827	Upper Chalk	-	3d	11.5	a and b
Heath House, Shropshire	SJ 603 246	Bunter Sandstone	1	-	4	c
Warran Farm, Shropshire	SJ 651 310	Bunter Sandstone	1	-	11	c
Lea Hall, Shropshire	SJ 497 216	Bunter Sandstone	3	1r	30	a
Gleadthorpe, Nottinghamshire	SK 589 707	Bunter Sandstone	2	-	28	a
Hungerhill, Shropshire	SJ 765 125	Bunter Sandstone	1	-	14	b
Atwell Park Farm, Shropshire	SJ 761 131	Bunter Sandstone	1	-	12	a
Ashwood, Staffordshire	SO 859 858	Bunter Sandstone	-	1r	150	c
Prestwood, Staffordshire	SO 865 878	Bunter Sandstone	-	1r	200	c
Bicton, Devonshire	SY 074 869	Bunter Sandstone	1	-	21	a

4. RESULTS OF FIELD INVESTIGATIONS

4.1. INTRODUCTION

An extensive literature exists dealing with rates of loss of nitrogen by leaching from soils under a variety of experimental and field conditions. Measurements of the nitrate concentrations in vertical sections have previously been restricted to the soil and upper subsoil zone in Britain (14, 6) or to depths of up to 30 metres in unconsolidated, granular aquifers in Israel (15) and the United States (16, 17, 18, 19 and 20). Young et al (21) reported the first detailed vertical profiles of distributions of nitrate, nitrite, and chloride in the interstitial water of the unsaturated zone of the Chalk, a consolidated aquifer with an important fissure flow and storage component. The present paper records and compares profiles measured in both the Chalk and the Bunter Sandstone aquifers.

4.2. NITRATE/NITRITE AND CHLORIDE PROFILES

Profiles measured beneath inorganically and organically fertilized arable land, on both the Chalk and the Bunter Sandstone have been found characteristically to exhibit high concentrations of nitrate often irregularly interspersed with zones of relatively low concentrations (Figures 2a-d). By comparison, profiles beneath permanent, unfertilized grassland show consistently low levels of nitrate in the interstitial solutions. (Figures 3a and b). Determination of the profiles under fertilized grasslands have generally provided examples intermediate between the arable and unfertilized grassland cases. Figure 3c illustrates an example from the Chalk containing a minor peak at 5 metres depth which has been interpreted by Young et al (21) as recording an increase in nitrate leaching associated with a short period of cereal growing which interrupted the grass crop some five years before measurement of the profile. A chloride profile has been determined at one site only (Figure 3c) but the form of the profile was used by Young et al (21) to substantiate the downward rate of solute transport deduced from the accompanying nitrate curve.

4.3. TRITIUM PROFILES

Measurements of the environmental tritium content of interstitial water has been completed at four sites in the Chalk (Figure 3d). The profiles are of similar form, with a sharp maxima in the range 250 to 300 TU at depths of between 8 and 10 metres and are comparable in shape to the earlier profile reported from the Chalk of the Lambourn catchment by Smith et al (22). Sufficient data are not yet available to allow comparison between tritium profiles in the unsaturated zone of the Bunter Sandstone, but initial results from the sites at Lea Hall, Shropshire and Gleadthorpe, Nottinghamshire (Table 1) suggest the presence of a broad, irregular maxima at about 22 metres below surface.

5. DISCUSSION OF RESULTS

5.1. INTRODUCTION

Following a detailed consideration of the solute profiles from a number of boreholes in the Chalk at the Bridgets Farm site (Table 1) Young et al (21) postulated a qualitative relationship between high nitrate leaching losses from arable soils and low losses from grassland. A simple mathematical model of solute migration through the unsaturated zone of the Chalk, using empirical control rules governing the rates of nitrate leaching under a variety of crop types, fertilizer application rate and infiltration conditions, produced satisfactory simulations of the observed nitrate, chloride and tritium profiles at some sites.

It was assumed in the earlier paper (21) that general relationships may exist between the rate of leaching of nitrate from a soil and antecedent events (changes in soil management, crop type, fertilizer applications, variations in the annual distribution of infiltration etc.). The findings of Stanford and Smith (23) that the nitrogen mineralisation potentials of a wide range of differing American soil types are closely comparable provide support for certain of the assumptions. The following discussion considers the biological factors which control the nitrogen budget of a soil and the interaction of biological and hydrogeological factors in determining the mechanisms of solute movement through the unsaturated zone.

5.2. BIOLOGICAL EFFECTS

Except where nitrogen has been added to soil in the form of ammonium salts and remains in this form for brief periods or during drought conditions, consideration of the progress and fate of nitrogen in soil includes the extent of its involvement in biological systems (24, 25). Three principal pathways of nitrogen to groundwater may be distinguished.

1. Uptake and fixation by growing plants and subsequent release of N with the decay of plant residues and dependent micro-organisms in soil.

2. Direct uptake by soil micro-organisms using organic residues already present in the soil or substances evolved from the roots of growing plants; as energy sources followed by their decay.

3. The direct leaching of unused N, particularly after periods of drought.

The chemical form of nitrogen in soil can be systematically described with reference to a scale of oxidation-reduction where the controlling influences are the fixation of carbon originating from plant growth and the input of oxygen facilitating plant decay. Figure 4 illustrates the existence of nitrogen in its various oxidation states as governed by the extent to which these vectors affect soil conditions. Conditions most favourable for the formation of nitrate in soil are the absence of growing plants and the institution of a high degree of aeration which facilitates the decay of organic nitrogenous matter, and the oxidation of ammonia. Retention of nitrogen in soil is promoted by the absence of aeration, which not only makes for a slow turnover of biological N, but also favours the retention of inorganic N through its absorption as ammonia by soil minerals. The latter condition, which is not agriculturally productive, occurs typically in poorly-drained soils and particularly in permanent grassland without nitrogen fertilization. The most pronounced release of nitrogen from soil occurs with the cultivation of permanent grassland or improvement in the drainage of wet soils (14, 15, 26, 27).

An interesting aspect of the condition of unfertilized grassland is the bio-chemical consequence of carbon-fixation occurring while nitrate-deficiency prevails. The overall effect of the generation of organic matter, without the nitrogen required for cell synthesis, is the production of extracellular carbohydrates, both by the growing plant and by soil micro-organisms (28, 29). This surplus product of photosynthesis provides the food source for nitrogen-fixing micro-organisms living both inside the plant and associated with the roots. Symbiotic bacteria around the roots avail themselves of food substances secreted from plants during their growth and include not only nitrogen fixers, but other organisms that can grow when nitrogen is not limiting.

Extracellular carbohydrates are produced also by micro-organisms in the form of capsular slimes which are composed predominantly of polyuronic acids (29). These substances appear to be waste products of the organism because this carbon source cannot be used by the originating organism in times of nitrogen availability (30). Furthermore, they are not generally useful as food sources because not all micro-organisms possess the necessary 'lyase' enzyme for depolymerisation (31). However, some soil bacteria are able to use polyuronides and these substances may therefore contribute to the capacity of soil in assimilating nitrogen or effecting denitrification.

Denitrification occurs in soils where a limitation on the access of atmospheric oxygen has given preference to the occurrence of organisms that are adapted to the use of oxygen content of nitrate for respiration. These appear to be confined to bacteria, particularly Pseudomonas, Achromobacter and Bacillus (32). The result of denitrification is the conversion of nitrate to the gaseous products, nitrous oxide and nitrogen gas. Representing as it does the loss of nitrogen from soil, denitrification is disadvantageous to agricultural productivity.

Denitrification involves, as a first stage, the reduction of nitrate to nitrite and the presence of the latter in small concentrations may therefore indicate that denitrification is, or has been, occurring. However, nitrite is also formed as an intermediate in the oxidation of ammonia and nitrogenous organic matter to nitrate. The presence of nitrite may, therefore, be used only as a general indication that a nitrogen transformation has occurred, but cannot be taken to identify either reduction or oxidation.

In the extrapolation of biological processes affecting nitrate in soil to those in the sub-soil zone, relevant considerations are the availability of carbon sources for nitrogen transformation, the extent to which microbial colonisation has extended from the soil layer and accessibility to oxygen. In well-drained unconsolidated formations, uniform biological activity occurring under aerated conditions may constitute the dominant regime. Nitrate formed or introduced into such a system would be rapidly transmitted with little or no attenuation. Poorly drained, unconsolidated deposits may contain essentially anoxic pockets of local accumulations of organic matter within which denitrification diminishes the nitrogen input from the surface. Increased denitrification losses associated with layers of impeded drainage in alluvial soils in California have been recorded (33).

Nitrate is also notably absent from formations associated with the presence of iron in groundwater, and from soils with a high iron content (34). Here there is an incompatibility between the high oxidation condition required for the persistence of nitrate and that represented by the presence of the Fe^{2+} ion. These are also conditions where iron sulphide if likely to occur and represent very strong chemical reduction.

In consolidated formations there is inherently greater difficulty in both measuring and assessing the effect of biological activity because of the non-uniformity of flow regime. With an extensive development of fissures there is a strong possibility that these carry a significant proportion of the recharge through the unsaturated zone. Biological colonisation from the soil would be expected to have occurred predominantly along the fissure walls, representing a system which cannot be sampled satisfactorily for examination or analysis.

However, even where groundwater flow occurs mainly through fissures, it is possible for diffusional interchange to occur between moving and static water (21, 35). It should be envisaged, therefore, that any part of an aquifer may potentially be involved in the biological interaction between events at the surface and final groundwater composition. Where there is the possibility of an aquifer containing even trace concentrations of organic matter and suitable micro-organisms, static water may be in a state of low oxygenation, providing conditions suitable for denitrification to occur.

Whether or not microbial activity occurs in an aquifer is governed by the availability of trace factors in addition to nitrogen and food source. This consideration may be of particular relevance to the availability of phosphorus, and perhaps iron, in the Chalk. The equilibrium solubility of phosphorus as phosphate is extremely low in the presence of the range of calcium concentrations and pH values common in Chalk groundwater and the conditions of aeration and pH that probably occur in Chalk fissures are not conducive to the transport of soluble iron. For these reasons, it is probable that microbial colonisation of the Chalk could develop only slowly through major fissures following a change in the historical development of the surface which results in a release or introduction of microbial nutrients to the aquifer.

An appreciation of the extent to which microbiological nitrogen transformations have occurred or could take place in both the soil and underlying aquifer in the field, and in representative samples obtained as a result of the drilling programme is clearly of considerable importance in the interpretation of the experimental data. Investigation of this problem forms a constituent part of the continuing research programme and it has previously been reported (21) that prolonged storage of a Chalk core from a shallow depth (1.2 metres) resulted in an increase in the nitrate content of the interstitial water from 1.5 to 29 mg/l NO_3-N. It is suggested that the high nitrate concentrations measured in samples taken within the upper 1.5 metres of most profiles (Figures 2 and 3) are the results of mineralisation of organically bound nitrogen, due to involuntary incubation of the samples between the time of recovery in the field and extraction and analysis in the laboratory.

Examination of Chalk cores from the site at Heydon (Table 1) has provided evidence of the activity of nitrifying bacteria to depths not greater than 2 metres (36) and work is being carried out on Chalk samples from Hurley (Table 1) to determine the extent of microbiological activity and the effects on the interstitial nitrate solutions of prolonged storage under various conditions. If microbial activity leading to nitrogen mineralisation occurs within the unsaturated zones of aquifers it may be necessary to induce mineralisation of samples by incubation, in order to assess the full potential for nitrate contamination. However, a study of nitrate leaching from Chalk-derived soils and subsoils in southern England (14) provided evidence of a constant N:Cl ratio below the soil base, suggesting that microbial transformations are generally restricted to the soil zone.

Similar observations of the depths to which bacterial colonisation may penetrate the Bunter Sandstone aquifer have yet to be made, but it is noted that determinations of the N:Cl ratio in interstitial water from granular, alluvial aquifers in the United States (17) and Israel (37) provide no evidence of denitrifying reactions below about 3 metres depth.

Other phenomena, such as

(a) the production of carbon dioxide accompanying the generation of nitrate by biological decay,

(b) the presence of carbohydrates as a potential food source for nitrate assimilation or denitrification and

(c) variations in the nitrate:nitrite ratio within the interstitial water,

may act as indications of biological activity in the unsaturated zone and have been examined.

Estimation of carbon dioxide evolved from Chalk heated to 200°C by gas chromatography (21), has indicated erratic concentrations, between 4 and 10 times the amount of free CO_2 + bicarbonate typical of Chalk groundwaters. These concentrations were calculated to be out of equilibrium with the calcium concentrations in the extracted pore water but were nevertheless consistent with the high carbon dioxide concentrations that sometimes occur in Chalk atmospheres. The highest concentrations of evolved carbon dioxide were obtained from samples with high nitrate levels. It was considered unlikely that the volatile carbon dioxide remained in phase with the nitrate solution during infiltration to depths of up to 40 metres. It was postulated that certain horizons in the profile were either enriched by carbon dioxide transmitted via fissures, or accessible to the effects of microbial colonisation of fissures. However, no direct bacteriological evidence has so far been obtained for such activity. At present, the identification of carbohydrates has not been extended beyond their characterisation by gas chromatography as totally insoluble substances which on hydrolysis and reduction yield principally mannose and glucose and/or gulose (38). The most probable form of this substance is an insoluble calcium salt of polyuronic acids. A monosaccharide composition similar to that found has been reported for the extracellular secretions from nitrogen-fixing soil bacteria (30). It is possible that these substances are formed as free polyuronic acids in nitrogen-deficient soils and become precipitated by calcium in Chalk. Determinations of the total carbohydrate in Chalk samples taken from the borehole referred to in Figure 2a were carried out by a colorimetric method (39). The carbohydrate content diminished from 1 g/kg at 1 m depth to 0.1 g/kg below 6 m and was considered to be an extension of the much higher concentration of carbohydrate present in the soil. Because the latter includes a substantial proportion of carbohydrate that is an integral component of soil micro-organisms, the high concentrations of carbohydrate measured in the upper horizons of the Chalk at this site may have included a contribution from microbial colonisation. An indication that carbohydrate may be involved in the nitrogen cycle in the unsaturated zone of an aquifer was that the carbohydrate content of nitrate-deficient Chalk under permanent grassland was approximately three times that under arable soil.

Analyses for nitrate and nitrite were completed on all samples. Nitrite may be easily oxidised under aerobic conditions and its presence may indicate either recent or continuing nitrification of ammonia or organic matter, or remnant denitrification. The occurrence of nitrite in unusually high concentrations has been noted at various depths in the Chalk both the Bridgets Farm and Isle of Thanet sites (see Figure 2b), possibly resulting from microbial activity in fissures intersected by the boreholes from which samples were taken. A general relationship between nitrate and nitrite concentrations has not been observed. Examples where nitrite and nitrate peak concentrations have been observed to coincide may be symptomatic of advanced contamination from the soil via a free draining fissure system. By contrast, a generally inverse relationship was found in samples from two boreholes at the Bridgets Farm site, possibly indicative of retarded drainage and denitrification.

5.3. MECHANISMS OF SOLUTE TRANSPORT

The hydrogeological characteristics of the Chalk and the Bunter Sandstone are dissimilar and the possible mechanisms of flow through the unsaturated zones of the two aquifers are considered separately.

The Chalk is a very fine grained, pure limestone traversed by frequent horizontal and near vertical joints and fissures. Joint spacing observed at surface outcrops varies between a few centimetres to several metres. The width of joints within the body of the rock is difficult to estimate because of the effects of surface weathering, but horizontal fissures up to 10 mm in width have been reported from the Norfolk Chalk (40) with tightly closed joints at shallow depths (41). Foster (35) has surmised that at least one high angle joint with an effective width of 0.1 mm intersects every metre of in situ Chalk. Close to the water table the joints may be enlarged by solution, giving rise to the high transmissivity often associated with the aquifer, but, in contrast to other, more consolidated limestone aquifers in the United Kingdom, macroscopic solution enlarged cavities in the unsaturated zone are extremely rare. This lack of weathering in the unsaturated zone and the anomalous calcium concentrations in pore water referred to above have lead to the suggestion (21) that an insoluble gel of a calcium polyuronide may provide protection to the fissure walls from solution. The rock matrix is composed of fossil fragments between 1 μm and 100 μm diameter, with pore dimensions commonly less than 3 μm, giving rise to intergranular permeabilities of the order of 1×10^{-3} m/day and porosities in the range of 0.35 to 0.50. This combination of characteristics has lead to speculation regarding the mechanism of recharge. Smith et al (22) considered intergranular seepage with piston displacement to be the dominant mode of movement.

Foster (35) has suggested that recharge occurs mainly via the fissures, but that diffusion of tritium ions between the mobile water in the fissures and the relatively static interstitial water accounts for the apparently slow rate of downward movement of tritium (0.88 m/yr) proposed by Smith et al (22). This concept has been extended by Young et al (21) who have shown that diffusion from fissure flows may give rise to a slow downward migration of nitrate, chloride and tritium ions in interstitial water, comparable to that which would be predicted for intergranular seepage and piston displacement.

The Bunter Sandstone is typically a fine or medium grained, often cross bedded, red sandstone. Abrupt vertical changes in grain size are frequent and in some areas the formation consists of alternating sandstones and argillaceous siltstones.

Vertical intergranular permeability of the sandstones characteristically lie in the range 0.2 to 2 m/day and contrasts of up to 20 to 1 between horizontal and vertical permeabilities are common. Widely spaced, high angle jointing is widespread. Fissure flow has been shown to be an important factor in groundwater movement in the saturated zone (42), but weathering of the rock to depths of between 10 and 20 metres has been observed at the experimental sites (Table 1) and it is suggested that the dominant recharge mechanism in those areas is by intergranular seepage. Vertical changes in lithology in the unsaturated zone may produce temporary and localised perched levels of saturation during recharge, with lateral movement of solutions migrating downwards from the surface. The dissimilar profiles obtained from adjacent boreholes at the Gleadthorpe site (Figures 2c and d) may be attributable to this mechanism.

5.4. MATHEMATICAL SIMULATION AND ESTIMATION OF SOLUTE TRANSPORT RATES

Having shown that similar downward migration rates of ions in interstitial water would result from both fissure recharge and intergranular seepage through the Chalk, Young et al (21) used a mathematical model based on the uniform downward migration hypothesis to simulate the nitrate, chloride and tritium profiles measured at the Bridgets Farm site. In each simulation, the solute migration rate was adjusted to give the best match between the computed and measured profiles (Figures 5a and b). Computed migration rates ranged from 0.80 to 1.05 m/year, comparable with the rate of 0.88 m/year for tritium migration in Chalk suggested by Smith et al (22). It was recognised (21) that the simple control rules used by the model would not necessarily be applicable to all localities. Identification and quantification of all potential nitrate sources at the other sites is in hand. Preliminary attempts to simulate the profile measured at Sprattling Court Farm (Figure 2b), using a solute transport rate of 1.0 m/year, have indicated that the model provides satisfactory predictions of the depth to nitrate peaks at that site also.

A general test of the model hypothesis that solute inputs from the surface layers retain their identity during uniform downward migration has been made by comparing the depths of peak nitrate concentrations with the period of time before the date of sampling at which increased nitrate leaching losses would be expected, either from the ploughing up of permanent or temporary grassland or from above average fertilizer applications (Figure 6). A clear linear correlation is seen to exist, suggesting that solute migration rates in the interstitial water of the unsaturated zone of the Chalk are essentially uniform at locations spread across a wide area of southern and south-eastern England, and including both the middle and upper stratigraphic divisions of the Chalk.

Simulation of profiles measured in the Bunter Sandstone has not yet been undertaken. The tritium measurements recorded in Section 4.3 suggest a vertical movement rate of the order of 2 m/year, comparable to the nitrate migration velocities of between 1.5 and 2.6 m/year measured in sandy alluvial aquifers in the United States (33, 43).

6. CONCLUSIONS

(a) High concentrations of nitrate in interstitial water from the unsaturated zones of the Chalk and the Bunter Sandstone have been measured beneath arable farmland. In contrast, low nitrate levels have been found beneath grassland, but it has been recognised that the ploughing up of grassland releases large quantities of organically bound nitrogen for mineralisation and leaching. It is suggested that the recently noted increases in nitrate content of groundwater may have been caused, in part, by the large expansion in arable acreage, at the expense of permanent grassland, that occurred in England during the period 1939-46 (21).

(b) Alternative possible mechanisms of solute movement through the Chalk have been examined - an intergranular seepage model and a model of fissure flow with ionic diffusion into interstitial water. The rate of diffusion of salts into and out of intergranular storage in the Chalk is the subject of current laboratory experiments. However, it has been shown (21) that a single, simple model of uniform downward solute migration may be used to describe both alternatives. The model has produced satisfactory simulations of nitrate, chloride and tritium profiles at one site. Simulation of profiles at other sites is being undertaken. Results from experimental sites spread widely across the southern English Chalk outcrop indicate a general downward migration rate of nitrate and tritium ions of about 1 metre/year. Insufficient data have been accumulated for a similar estimate to be made for the Bunter Sandstone.

(c) Following validation of the mathematical model on data from a number of sites, predictions may be made of future nitrate concentrations in the unsaturated and groundwater zones. Expansion of the model to embrace complete groundwater catchments is being undertaken.

(d) Evidence of microbial nitrogen transformations has been recorded at shallow depths within the unsaturated zone of the Chalk. The identification of carbohydrates and non-equilibrium concentrations of carbon dioxide at greater depths within the unsaturated Chalk have suggested the possibility of microbial activity at depth and work is in hand to define the limits to which biological activity extends.

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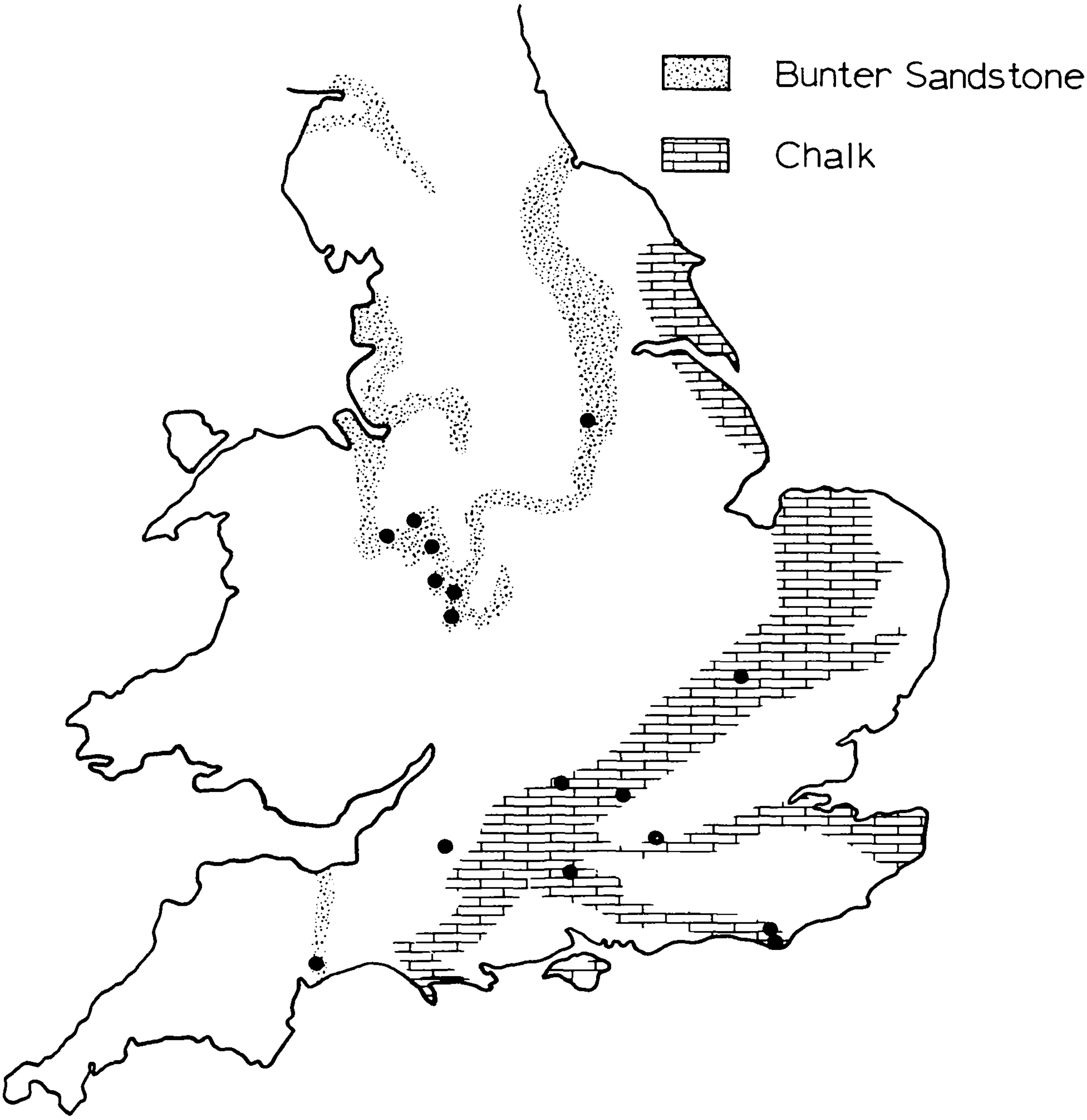
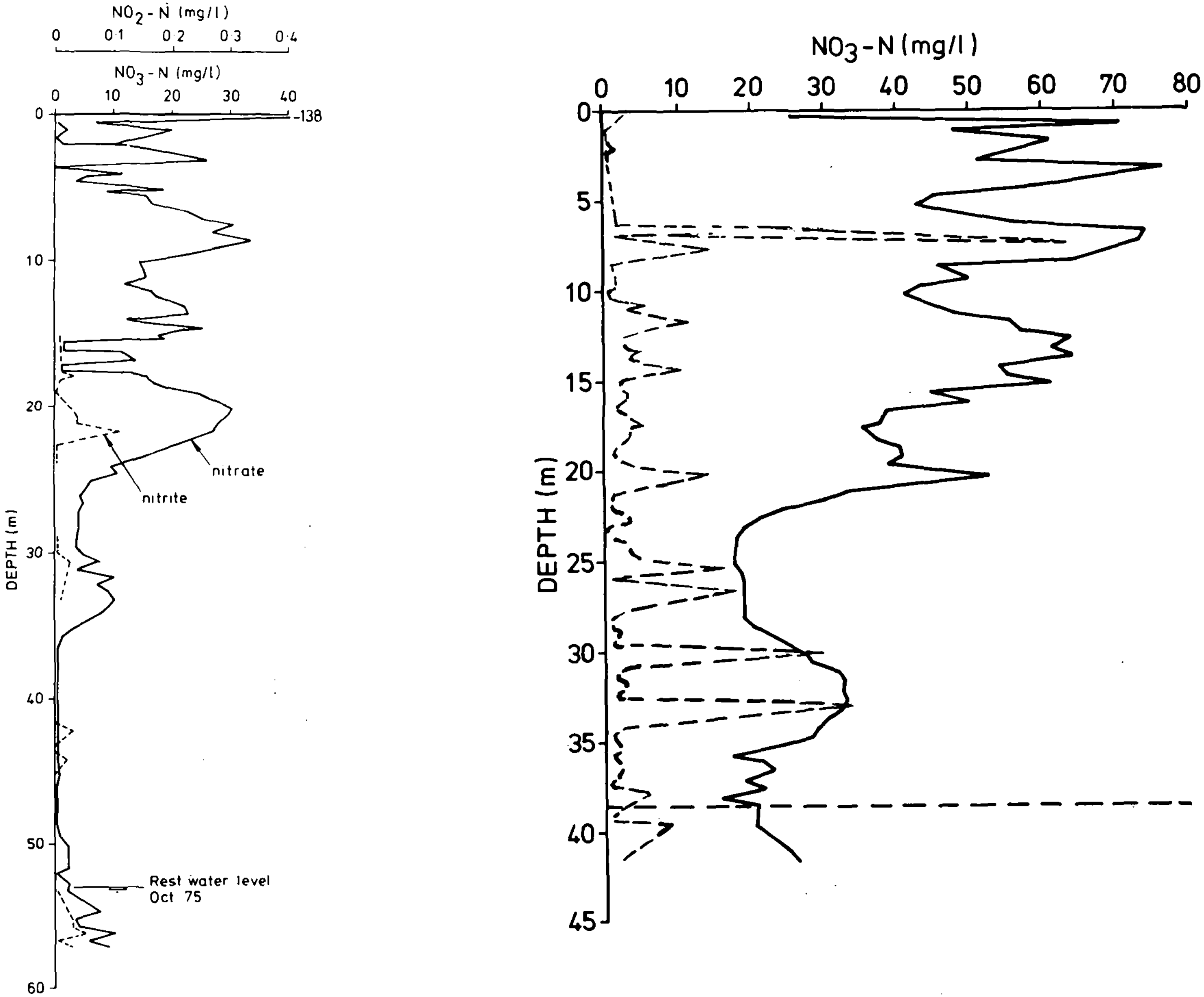


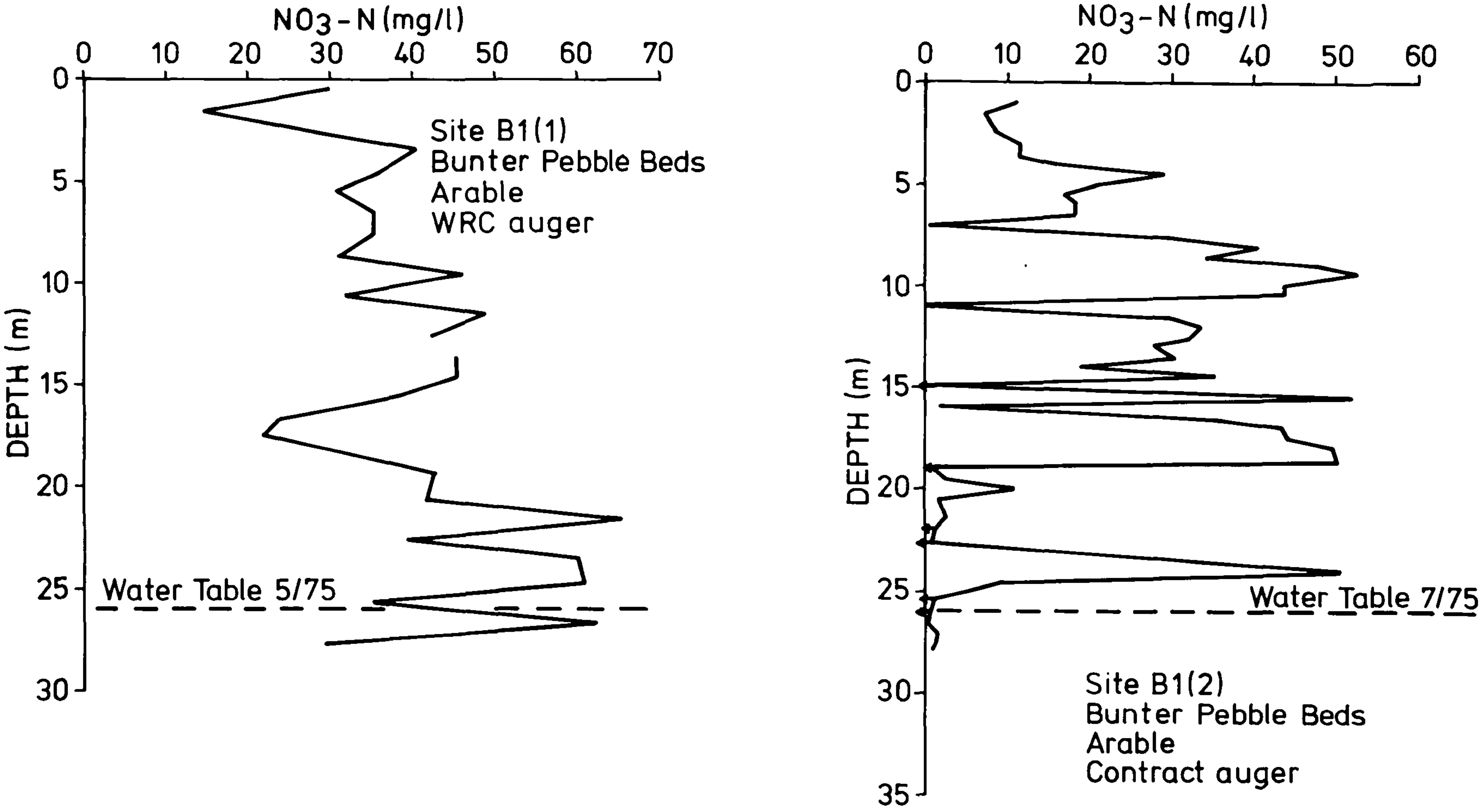
Figure 1. Locations of experimental sites.



(a) Bridget's Farm, borehole E - Chalk

(b) Sprattling Court Farm - Chalk

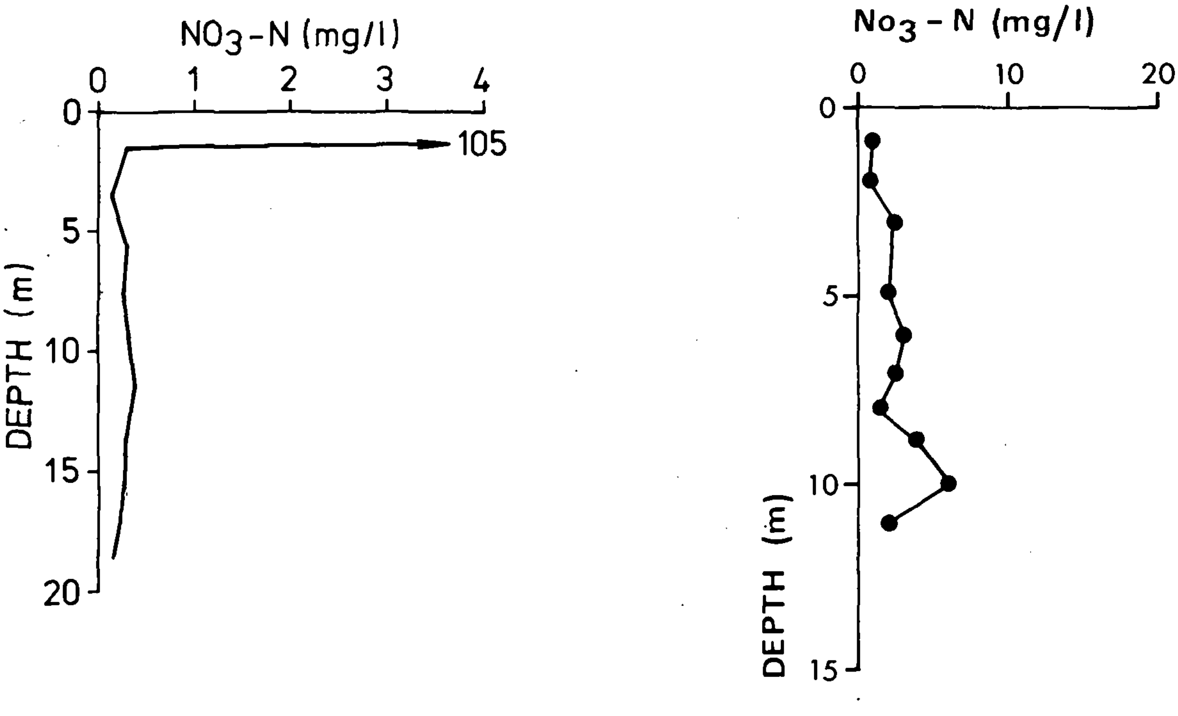
Figure 2. Nitrate profiles - arable land



(c) Gleadthorpe borehole No 1 - Bunter Sandstone

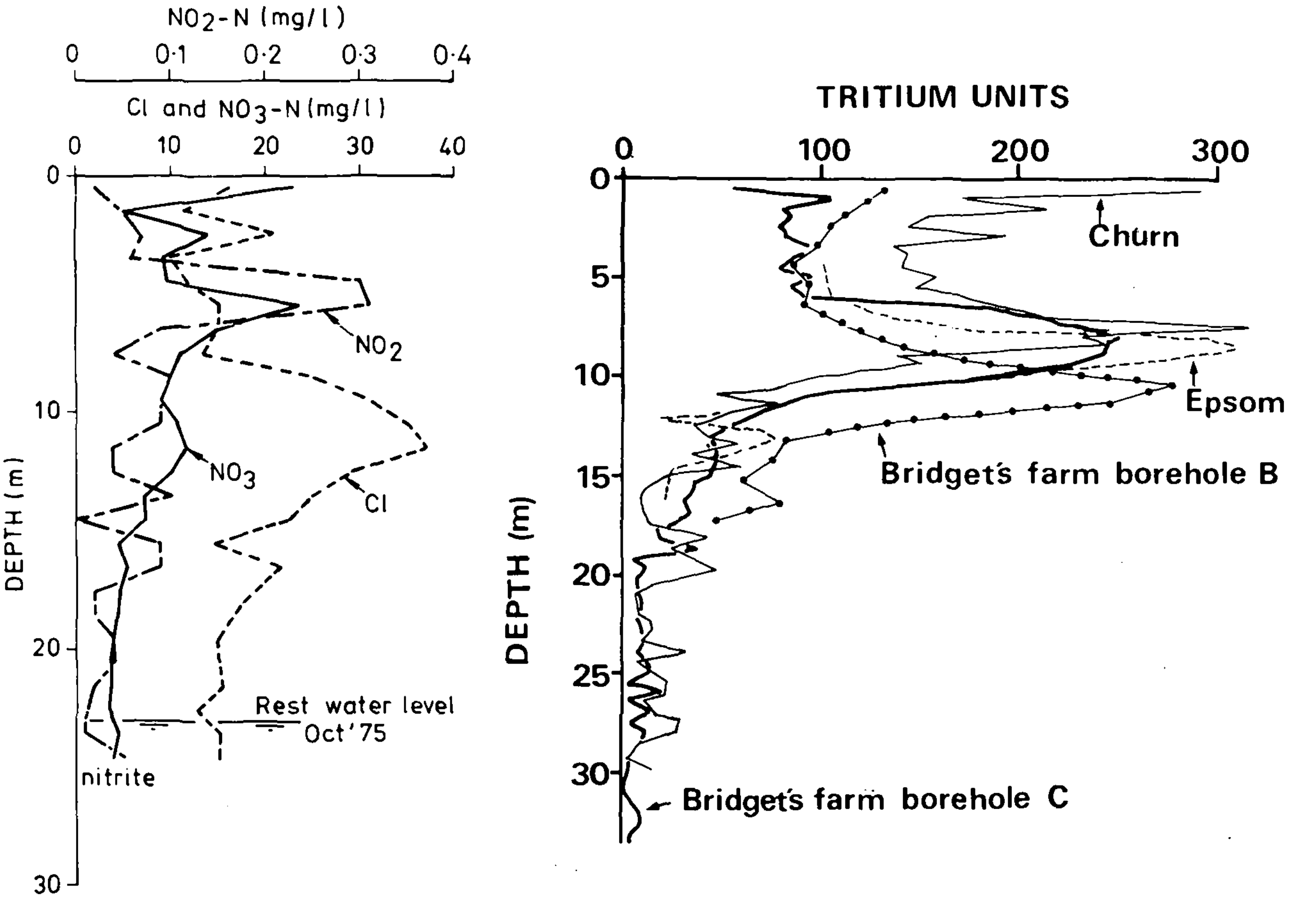
(d) Gleadthorpe borehole No 2 - Bunter Sandstone

Figure 2. Nitrate profiles - arable land



(a) Westbury - Chalk. Unfertilized grass

(b) Warran Farm - Bunter Sandstone. Unfertilized grass



(c) Bridget's Farm, borehole G - Chalk. Fertilized grass

(d) Comparison of tritium profiles for Chalk sites

Figure 3. Nitrate profiles - grassland sites, and comparison of tritium profiles

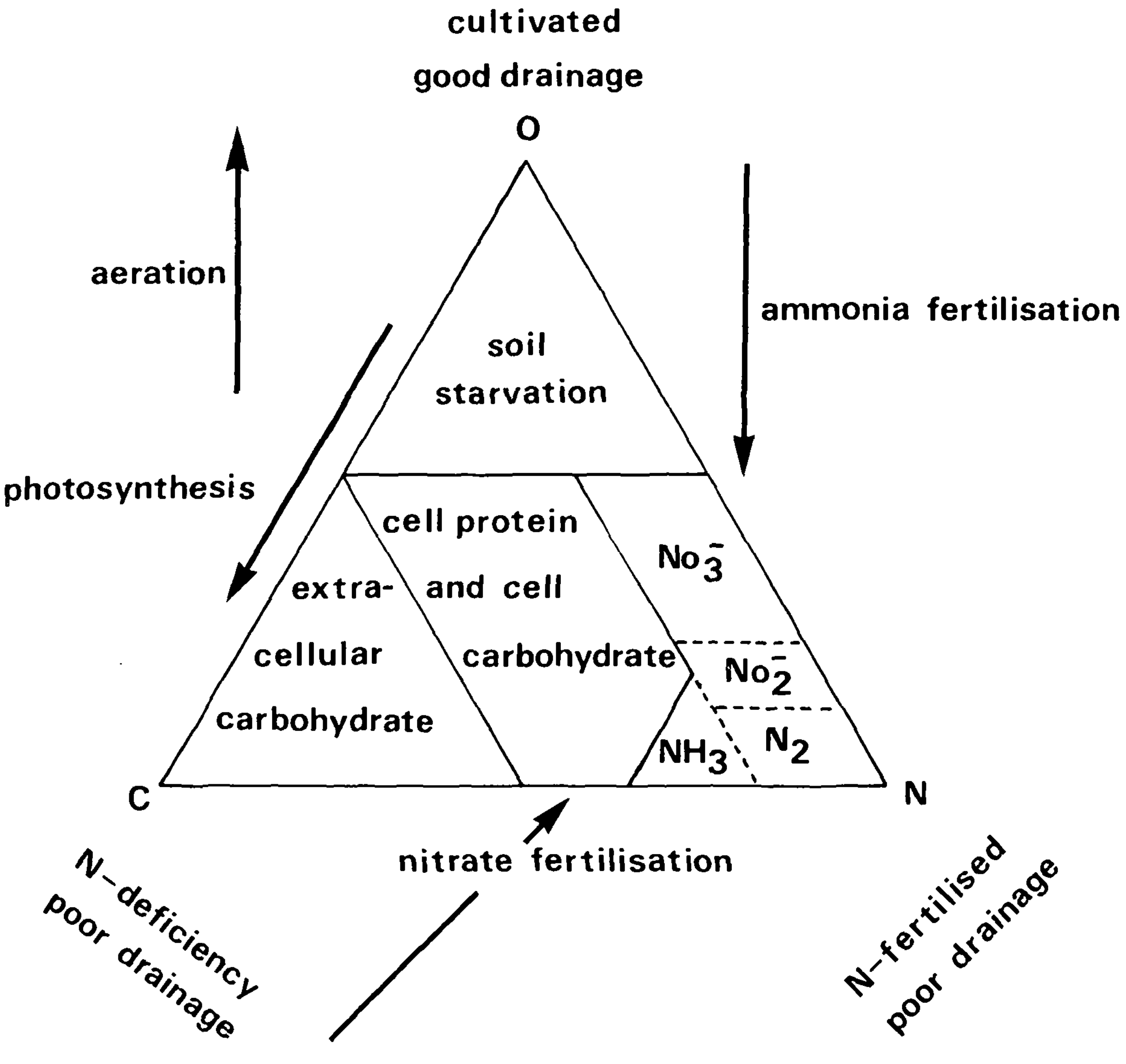
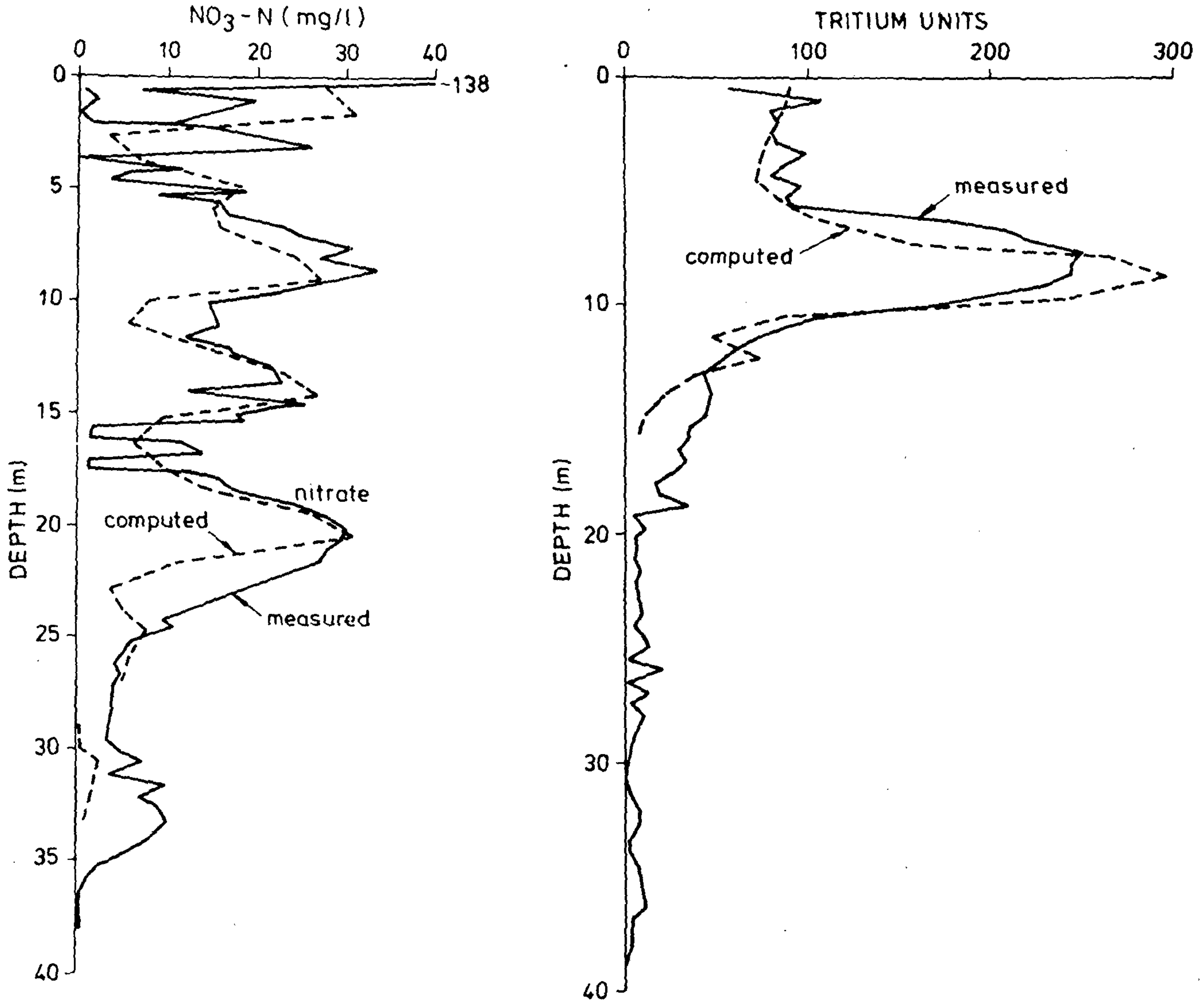


Figure 4. Carbon, nitrogen and oxygen composition diagram of nitrogen transformations



(a) Nitrate profile in borehole E, Bridget's Farm

(b) Tritium profile in borehole C, Bridget's Farm

Figure 5. Comparison of measured and computed profiles at a Chalk site (after Young et al, 1976)

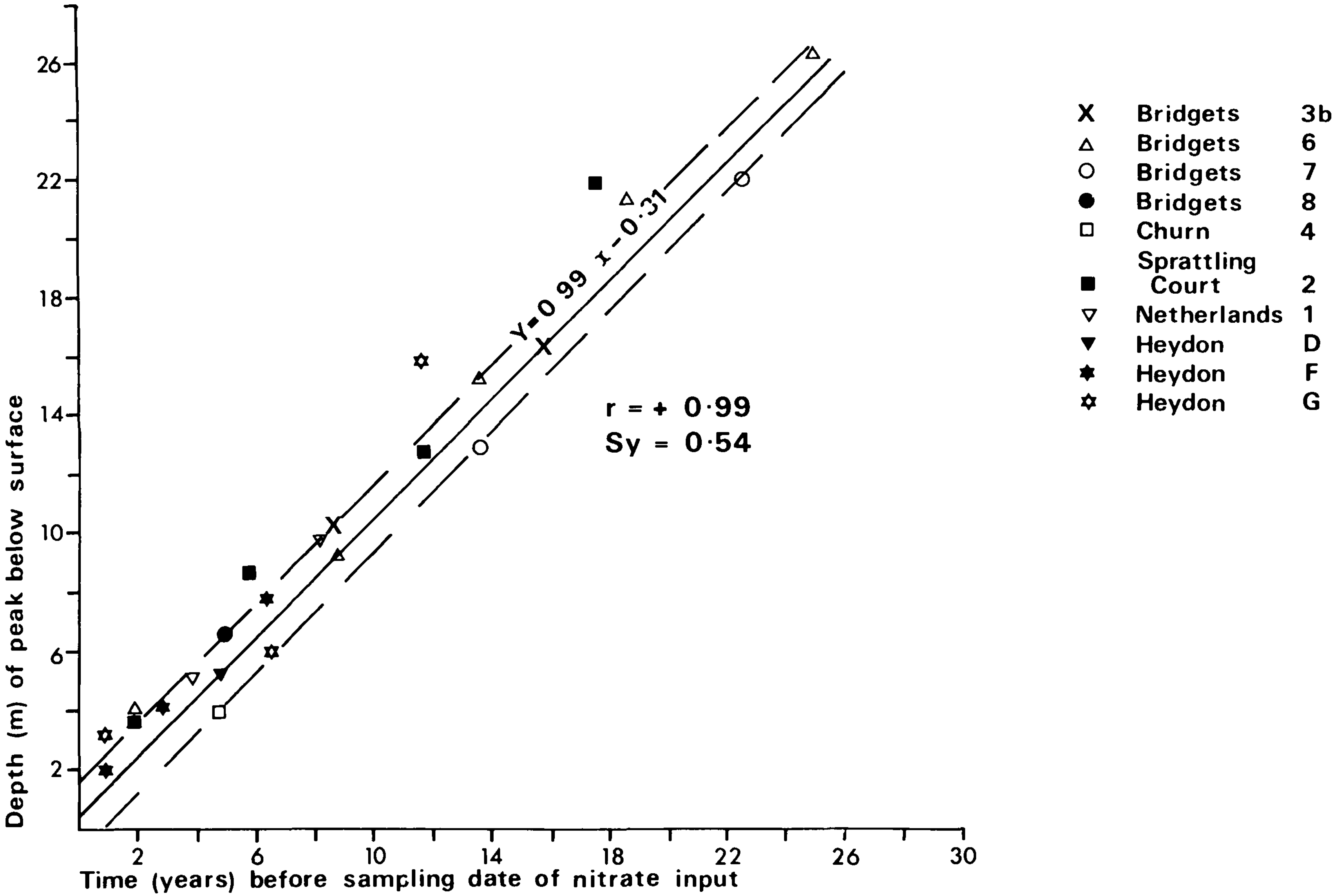


Figure 6. Correlation of depth to peak nitrate concentrations with time elapsed since major input - Chalk sites

SUPPORT PAPER K

GROUNDWATER QUALITY AND CORROSION - THE AUSTRALIAN SCENE

G. J. Kelly

ABSTRACT

Groundwater resources are widely dispersed in Australia and are used extensively for town water supplies, stock watering and irrigation. Recovery is by a variety of pumping techniques ranging from low volume, high head, wind-driven reciprocating pumps, to much more sophisticated vertical turbine pumps.

Over recent years there has been an increasing concern by pump owners about unsatisfactory and unpredictable performance due to corrosion. Examination of these problems has highlighted the need for more accurate characterization of water quality, which, in turn, has been found to be dependent on procedures used for sample collection and storage. So-called 'unstable' quality variables which are primarily dependent on the partial pressure of oxygen and carbon dioxide are often of paramount significance in so far as they influence the kinetics of corrosion processes, yet are given only cursory attention in analytical reports.

In this paper, the problems associated with sample collection will be elucidated, and the need for improved sample collection procedures will be developed by examining corrosion failures that could have been avoided. Some reference will also be made to design deficiencies in vertical turbine pumps which limit their versatility for operation in aggressive groundwaters.

1. INTRODUCTION

The continent of Australia is characterized by the fact that it is the driest land mass in the world. More than half is arid, and half the continent has an altitude of less than 300 metres. Permanent rivers and streams run in only a small part, and groundwater is a more important source than surface water in about 60 per cent of the country. Furthermore, the ratio of water held in storage beneath the ground to that stored in streams and lakes is considered to be considerably higher than the value of 30 which is the average for all continents (1).

Accordingly, there is considerable development of groundwater resources for domestic, agricultural and stock requirements. The total number of operational sub-artesian 'bores'* is in excess of 200 000 delivering some 1.7 million Ml of water annually. The majority of these are small wind-driven reciprocating pump units, but there is an increasing development in the area of vertical turbine pumps, and during the past 10 to 15 years many unconsolidated sediment formations have been exploited using these types of units. Depending on the quantity of water available, pump units range in size from 20 to 40 l/s capacity with average pressure heads being in the range of 25 to 50 m.

In recent years, the performance of the vertical turbine pump has shown wide variation from the corrosion viewpoint and this has been the subject of an extensive investigation throughout Australia (2). That groundwaters may be corrosive has been recognized for many years (e.g. Alexander (3), Larson (4), (5)) and manufacturers and suppliers are well aware that pump components are susceptible to premature failure under certain operating conditions. Much work has been done to identify water quality characteristics which play a significant role in corrosion processes, yet the ability to predict performance of common materials of construction in contact with a groundwater of specified quality remains rather limited.

2. CORROSION PROCESSES IN NATURAL WATERS

Corrosion, as an electrochemical phenomenon, occurs under conditions which favour the spontaneous oxidation of metals and alloys. Such conditions

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* 'bore' - synonymous with the term 'deep well'. Dimensions vary from 10 to 100 cm in diameter and 10 to 1000 m in depth. Sub-artesian bores are classified as non-flowing under natural conditions and must be equipped with pumps in order to recover the water. Artesian bores, on the other hand, flow of their own accord.

are those which either prevent the formation of stable and protective oxide films on metal surfaces or do not allow similar protection by the deposition of scale-forming calcium carbonate. As in other electrochemical cells, oxidation reactions (at anode sites) must also be accompanied by reduction reactions (at cathode sites), and so for the corrosion of a metal surface it is necessary to have cathodic reactants which may include oxygen (O_2), hydrogen ions (H^+), or heavy metal ions.

In natural water, then the corrosion resistance of metallic components is governed, not only by the presence of conditions favouring spontaneous oxidation, but also by the dissolved oxygen content and/or the pH of the water concerned and/or the presence of heavy metals. Thus, the quality characteristics of a water could be classified according to their influence on each electrode process. Since some properties influence both processes, it is more convenient to classify according to general action. Thus water components which facilitate corrosion include hydrogen ions (H^+), chloride (Cl^-), sulphate (SO_4^{2-}), nitrate (NO_3^-), oxygen (O_2), carbon dioxide (CO_2) and hydrogen sulphide (H_2S), whereas those which facilitate the formation of passivating or protective films include calcium (Ca^{2+}), magnesium (Mg^{2+}), the three alkalinity forms, carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and hydroxyl (OH^-) ions and silica. It could be argued that oxygen comes into both groups since its presence is necessary to develop oxide films. Thus the above classification should not be considered completely rigid, but should be taken as a guide only.

The influence of each species cannot be considered separately since natural waters invariably contain a number of them at significant levels. Indeed the problem of predicting corrosion performance for a specified quality is compounded by the multiplicity of interactions between one variable and another. Perhaps of greatest importance in the corrosion of steel is the role played by dissolved oxygen, particularly under flow conditions, where oxygen transport to cathode sites is considered to be rate controlling (6). Another significant influence is that of calcium carbonate depositions, and the Langelier Saturation Index (LSI) has been widely used as a measure of potential hazards in water handling equipment(7). The influence of other species, particularly dissolved salts, is generally considered to be indirect in that they modify either the protectiveness of precipitated $CaCO_3$, or the corrosion reaction-product films which otherwise form. Of particular note is the influence of chloride ions which are well known to facilitate the processes of iron dissolution.

Groundwaters, as a particular class of natural water, are characterized by the fact that their quality is governed by both the geological strata through which they percolate and the fact that they are in contact with subterranean gases and not the atmosphere. These factors have a pronounced influence on quality in two major ways. Firstly, variation in quality can be very substantial from place to place; secondly, some properties change when water is removed from the underground environment and brought into contact with air - these are often classified as 'unstable' properties and include pH, HCO_3^-, CO_3^{2-}, Fe^{2+}, CO_2 and O_2.

It can be seen that the 'unstable' properties are also the ones which influence corrosion. Clearly, then any exercise to ascertain the likely reactivity of a metallic structure in groundwater is dependent, first of all, on accurate and representative quality characterization of the water in question.

3. GROUNDWATER CORROSION IN AUSTRALIA

Since the cost of installing and operating a vertical turbine pump greatly exceeds costs associated with other forms of groundwater pumping, premature failure of turbine pumps has distinct economic overtones, and so it is this class of equipment which has been given greatest attention. In Australia, both lineshaft and submersible types of pumps are used and their construction is generally according to the American National Standards Institute (ANSI) specification(8). The materials which are used for individual components vary from one manufacturer to another, with standard construction materials being given in Table 1.

Table 1. Materials Specifications for 'Standard' Construction Pumps

Component	Standard material
Bowl	Cast iron (usually vitreous enamel coated)
Impeller	Bronze (generally leaded gunmetal, 85Cu, 5Pb, 5Sn, 5Zn)
Pump shaft	Stainless steel (type 304 or 316)
Line shaft	Mild steel or stainless steel (type 416 or 431)
Delivery column	Mild steel
Bearing retainer	Bronze (as above)

Bowls and impellers made from other materials for operation under 'corrosive' conditions are offered by manufacturers and include a range of bronzes as well as 316 stainless steel. However, it is not always a practical proposition to specify alternatives because of unrealistic delivery times and the lack of any guarantee that there will be long-term cost advantages.

The major corrosion problems are found to be:

(a) rapid deterioration of cast-iron pump elements
(b) failure of column pipe at screw-coupled joints
(c) premature failure of alternative materials used for pump bowls and impellers, particularly leaded gunmetal and austenitic cast iron
(d) failure of first length of column when directly coupled to a non-ferrous pump
(e) water-line attack due to alternating periods of wet and dry conditions.

Most of these effects are identical to action reported in the literature (for example, Alexander(3), Larson(4), (5), Fabrin(9), (10), Adair and Newton(11)). The intensity of corrosion under (a) and (b) above can be so severe that complete collapse of pumps occurs in 12 to 18 months of intermittent operation equivalent to some 1000 to 1500 hours of pumping.

Often such action is found to be associated with unbuffered acidic waters of pH less than 5, where standard construction materials should not be considered in the first place. Other failures are a direct consequence of the basic design, and the following design features, as they influence corrosion, are worthy of note.

(a) Delivery column. Column pipe is invariably used as it is received as black steel. There are some moves in the industry to apply coatings but the conditions of installation are such that gross defects develop at coupling ends.

(b) Column coupling and bearings. Each section of column is screw-coupled, and each joint incorporates a non-ferrous bearing retainer in the case of lineshaft pumps. Such a design is brought about by the need for low cost (first cost), and easy installations of a water-tight nature. Flange-coupled joints are time-consuming to install, apart from the fact that the bore is invariably too small to accommodate them.

(c) Non-standard bowls. When non-standard materials such as bronze or gunmetal are chosen for bowl assemblies they are usually screw-coupled directly onto black steel column pipe.

(d) Flow conditions. The pumps are mechanically designed for operation at nominal speeds of 1500 and 3000 rpm with the latter predominating, to achieve high head pressures. For common size pumps, this corresponds to impeller peripheral velocities of 15 to 20 m/s. In the delivery column, typical linear velocities are of the order of 2 m/s giving typical values for Reynold's Number of 3×10^5, and these increase by 20% at the couplings due to reduced flow area.

From mechanical considerations, a vertical turbine pump is a well-engineered device as can be seen by close examination of the ANSI standard.

Tolerances are very fine and allowances for friction loss and other mechanical limitations are well catered for. Indeed the performance of such equipment has been quite acceptable in many situations in this country and it is likewise used very extensively throughout the world under various conditions of operation.

4. THE QUALITY OF GROUNDWATER IN AUSTRALIA

Although many premature pump failures are due to a lack of an appreciation of metal/water interaction, it has become clear from a study of the Australian scene that many apparently satisfactory groundwaters are quite aggressive. Three major reasons come to light.

(a) Basic quality differences. Australian groundwaters are generally dominated by sodium and chloride, or sodium and bicarbonate, so that for the same conductivity and pH, they are more corrosive than the calcium bicarbonate type waters which are found extensively throughout Europe and North America. Accordingly, the general 'rules-of-thumb' which have been imported to Australia do not apply.

Thus it would be the exception rather than the rule to find waters supersaturated with respect to $CaC0_3$, i.e. with a positive Langelier Index. From a survey of 300 municipal groundwater supplies, two thirds of the waters had a negative index and 90% were below +0.5. The highest value was +1.9 and many were below -3.0. Furthermore, the frequent dominance of chloride, which is in contrast with the low levels normally accepted (e.g. Butler and Ison data for the United Kingdom(12)) can interfere with $CaC0_3$ deposition for supersaturated waters and so influence corrosion in a pronounced manner. Butler and Ison refer to a rule-of-thumb to determine the effect of chloride in saturated waters, suggesting that if chloride (and sulphate) contents are low, the Langelier Index is a good corrosion guide; however, at higher concentrations a ratio of hardness to chloride in excess of two is desirable for meaningful assessments.

(b) Effects of sampling acid, unbuffered waters. Some Australian waters are strongly acidic and very weakly buffered, particularly those from shallow unconsolidated aquifer formations. They are characterized by high levels of dissolved CO_2 and they are consequently difficult to sample and analyse. Carbon dioxide has been recognized as an important variable in metallic corrosion processes particularly under conditions of high flow where both localized high levels of acidity and erosive action by discrete bubbles of CO_2 are said to occur (e.g. Alexander (3), Larson (4)). If this is so, then it would appear important to have accurate CO_2 data. This necessitates taking representative samples after pumping for at least one hour, and then analysing samples for pH on the spot, or else taking sealed samples (in glass bottles and completely full) and avoiding lengthy storage. In the case of new bores or wells, there is a distinct practical difficulty in taking such samples unless special procedures are followed. In areas where corrosion is known to occur, or in new localities, the use of bailer samples must be discouraged, and samples taken at the end of the normal 24-hour pump test (which is carried out to ascertain capacity of the well).

The question of CO_2 effects is not well quantified, and it would be difficult to predict materials performance at specified levels of CO_2. This is considered to be due to the confusion that exists over the mechanism of CO_2 action.

Of particular note is the relative action of oxygen and hydrogen ions (from carbonic acid dissociation) as cathodic depolarizers. It is generally agreed that oxygen reduction plays a dominant role in natural water corrosion except at low pH, when hydrogen evolution also becomes important(6). At pH levels below 5 or 6, for carbonic acid waters (as distinct from dilute mineral acid of equivalent pH), oxide films are unstable, and, although hydrogen evolution occurs, oxygen reduction is still of greater importance provided oxygen concentration exceeds hydrogen ion concentration by one or two orders of magnitude. Thus for acidic groundwaters containing dissolved oxygen, the role of CO_2 may well be an indirect one as suggested by Evans(13), so that the 'aggressive' component of total CO_2 - the CO_2 in excess of that required to maintain the $CaCO_3$ saturation equilibrium - is not a direct measure of the propensity to cause corrosion (14) as usually reported in a water analysis report (14). 'Aggressive CO_2' effects are synonymous with the effects associated with waters of negative Langelier Index, i.e. they correspond to conditions where protective $CaCO_3$ films do not form. Under such circumstances, anode and cathode processes are able to occur quite readily, the latter now dependent on both the absolute level of oxygen and the conditions of flow. Thus it could be argued that high aggressive CO_2 would be significant in so far as a corrosion process is concerned when it was associated with a significant oxygen concentration.

Another role attributable to CO_2 is that associated with the passage of water through a pump where local variations in pressure are considered to develop discrete bubbles of CO_2. The bubble envelope would be of an acidic nature so enabling corrosion to proceed via hydrogen ion reduction. To the author's knowledge this explanation of the CO_2 mechanism has not been quantitatively validated, although it would appear to be quite plausible, particularly for water with a pH value less than 5.

Table 2. Selected Chemical Analyses of Australian Groundwaters

No.	Location	Na^+ $+K^+$	Ca^{2+}	Mg^{2+}	Fe^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Cond.	Hardness ($CaCO_3$)	SiO_2	pH	CO_2	O_2	Temp (°C)
1	Nullagine (W.A.) No. 1	10	11	5	0.6	71	10	-	2	15.7	48	-	7.1	9	-	-
2	Nelson Bay (NSW) No. 3	35	3	2	0.3	9	51	9	-	16.0	16	14	5.2	100	-	15
3	Ayr (Qld) No. 5	19	20	8	-	46	19	23	-	25.3	82	20	6.6	17	7.6	-
4	Exmouth (W.A.) No. E/70	69	57	35	-	280	106	-	-	61.4	286	-	7.6	10	-	-
5	Bundaberg (Q) D.M. No. 2	115	2	7	0.3	2.5	180	9	0.3	62.6	34	9	4.5	120	3.3	23.2
6	Jarvisfield (Q)	85	40	19	22	164	64	180	3	72.8	178	77	6.5	75	1.3	25
7	Warren (NSW) No. 1	261	4	1.7	0.2	619	47	-	0.1	96.5	17	-	8.3	5	2.4	-
8	Anglesea (Vic) AWB 5	193	9	19	24	31	300	64	-	118	99	12	5.0	420	7.8	28
9	Yunderup (W.A.) No. 1	199	106	22	1.4	268	307	132	-	123	355	-	7.2	24	-	-
10	Bargara (Q)	106	42	120	n.d.	159	370	90	45	166	600	-	6.4	93	2.7	24
11	Longreach (Q) No. 1	468	5	7	-	1045	121	12	-	187	12	-	7.7	18	-	74
12	Lincoln (SA)	642	144	78	0.1	382	1130	134	3	415	680	19	7.5	18	4.8	17.8

Concentrations expressed as g m^{-3}, conductivity as mS m^{-1} at 20°C. (1 mS m^{-1} corresponds to 10μΩ^{-1} cm^{-1})

n.d. - not detectable

\- - not determined

CO_2 - by calculation, except for No. 8 which was by measurement.

Hardness - by calculation, based on reported Ca and Mg.

(c) Variable oxygen concentrations. Dissolved oxygen concentrations are highly variable, ranging from practically zero up to near saturation with respect to atmospheric oxygen levels. Measurements at the discharge head for some 60 municipal supplies yielded an average concentration of 3.2 parts per million with almost half being above 4. The often-held assumption that groundwaters are deficient in oxygen is in distinct contrast with the high concentrations that have been found. An attempt was made to relate the above oxygen information with performance of the equipment involved; however, no clear correlation emerged, suggesting that factors other than oxygen must be accounted for if corrosion hazard is to be assessed.

The matters discussed above are illustrated with some selected quality data in Table 2. These results are from samples which were taken after at least one hour of pumping, and special precautions (mainly field measurements) were taken to obtain reliable values for the unstable quality parameters.

In order to highlight basic quality differences for the waters reported in Table 2, a geometric method of expression has been used, and is presented in Figure 1. Here a rosette form of diagrammatic representation graphically illustrates the differences. In particular it should be noted that, from a general quality viewpoint, Australian groundwaters are more closely related to diluted seawater than to what is generally accepted to be world average fresh water. It must be noted that the comparison is not strictly accurate since world average fresh water refers to river water rather than groundwater; however, the point must be made that general statements on quality of freshwater can be quite misleading.

5. WAYS TO ACHIEVE IMPROVED PERFORMANCE

In order to recover groundwater at minimum cost it is necessary to keep the cost of equipment maintenance and replacement, as well as running costs, to a minimum. Corrosion, then, is a factor that must be accounted for, since it usually determines the useful lifetime of equipment, and it has a substantial effect on efficiency of performance. Unfortunately, these effects are difficult to quantify and often they are not recognized until it is too late.

Vertical turbine pumps as specified by the ANSI standard are well-engineered units in terms of mechanical considerations. However, for operation in many groundwaters, steel and cast-iron components give very poor performance from the point of view of corrosion. In order to arrive at a decision on alternative materials, some measure of anticipated lifetime under typical operating conditions is required to ensure that benefits which might come from alternatives exceed the cost. For turbine pumps, a desirable lifetime of 12 to 16 years with possible extension to 20 years would be a reasonable objective.

Apart from material costs, the labour costs associated with pump installation amount to significant values. Thus direct comparisons of material costs are misleading and substantially higher materials costs could be justified if labour costs were also considered.

The results of some field tests on alternative materials for cast components have indicated that austenitic stainless steel is one of the most promising materials despite its high initial cost. Conjecture about the performance of stainless steel under low oxygen or anaerobic conditions is valid since the resistance to pitting and crevice corrosion is dependent on the presence of oxygen. It would appear, however, that corrosion processes of these types are unlikely since low oxygen conditions preclude the development of differential oxygen cells which are a necessary prerequisite for pitting and crevice action. Although of a limited nature, tests have been carried out using stainless steel turbine pumps under conditions where cast iron and steel have failed within one and a half to two years. After six years' operation, the performance can only be described as excellent, with not the slightest sign of surface deterioration.

Although alternative metallic materials should resolve the pump element problem, the other major area of failure in vertical turbines, namely the failure of screw-coupled steel column pipe, could be resolved by other means as well. The pump column problem is as much a design problem as anything else. The use of coatings, though necessary under almost all operating conditions, cannot be properly exploited at screw-coupled joints; however, the supplementary application of cathodic protection could be advantageous. Development of bearing retainers from base alloys to give natural cathodic protection is worthy of consideration. Periodic replacement of such components would prove cheaper than column replacement. Other forms of coupling need to be studied, as does the use of reinforced plastics designed to take the loads imposed by vertical modes of operation.

6. CONCLUSIONS

The widely variable performance of groundwater pumping equipment in Australia is attributable to the variable quality characteristics of the water being pumped. There is a need to place greater emphasis on more precise and reliable water quality characterization particularly in regard to 'unstable' properties such as pH and dissolved oxygen content. Once this has been achieved, the anomalies in materials performance should become apparent, and assessment exercises on alternative materials and designs should be more fruitful.

ACKNOWLEDGEMENTS

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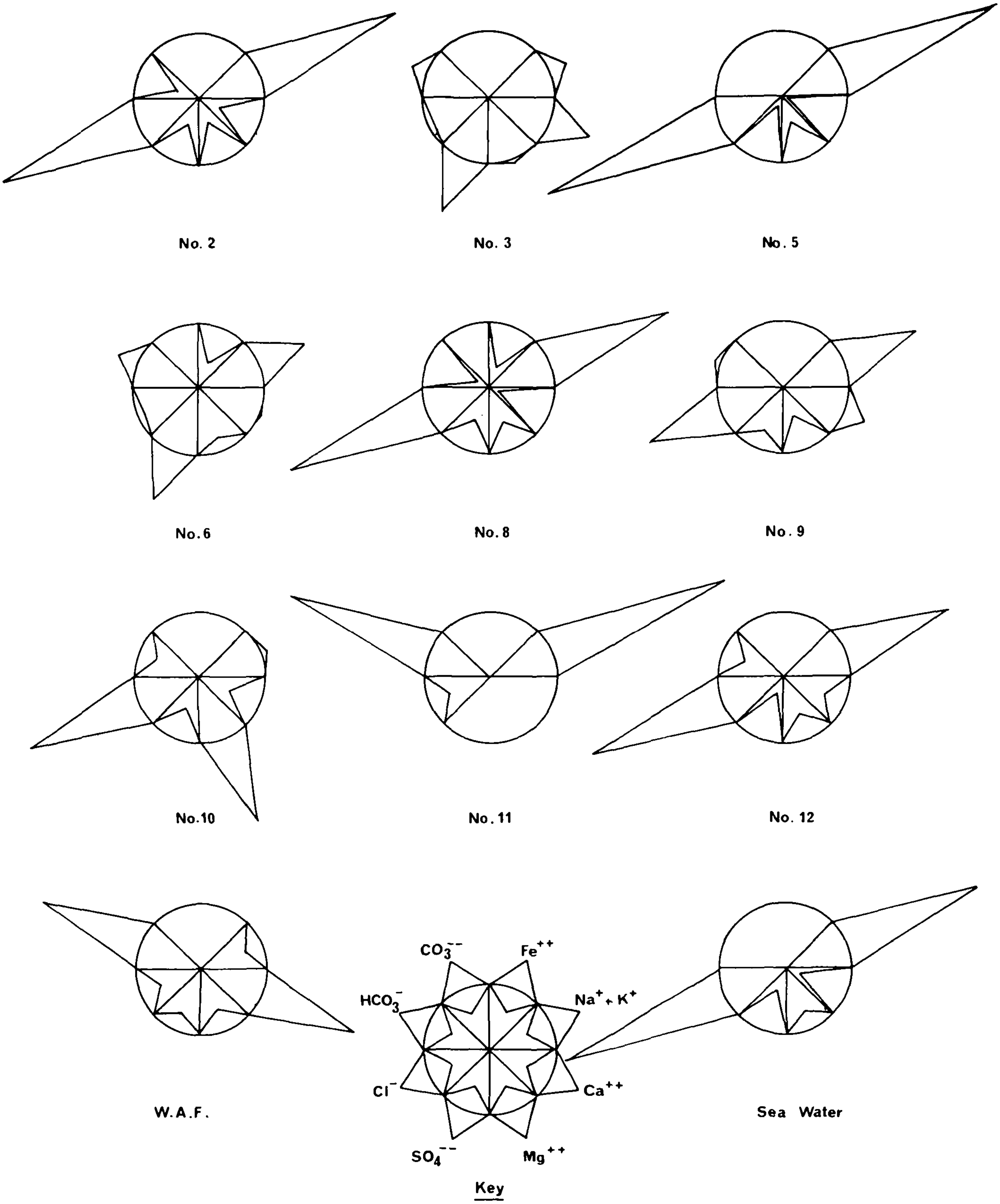

No. 2 No. 3 No. 5

No. 6 No. 8 No. 9

No. 10 No. 11 No. 12

W.A.F. Key Sea Water

FIGURE 1: WATER QUALITY DIAGRAMS FOR SELECTED AUSTRALIAN WATERS - See table II.
W.A.F. - World Average Fresh water.

SUPPORT PAPER L

THE HYDROGEOCHEMISTRY OF PERMO-TRIASSIC AND QUATERNARY DEPOSITS OF SOUTH YORKSHIRE

D. S. Chadha

SUMMARY

This paper describes the results of an investigation into the chemistry of groundwaters of Permo-Triassic and Quaternary deposits around Doncaster, South Yorkshire (National Grid 446 to 470E and 400 to 423N).

A detailed study of the major and minor inorganic and physical variables in the groundwaters shows that seven major categories may be distinguished according to their areal distribution patterns, total dissolved ionic concentrations, lithology and movement of groundwater. Four categories are associated with the Bunter Sandstone aquifer, two with the Permian Limestone aquifers and one with the Drift aquifer.

The first category is the 'normal' uncontaminated Bunter Sandstone water. The second category shows Bunter Sandstone water contaminated by the recharge from the Magnesian Limestone and also passage through the Drift deposits. The third category comprises water from multi-aquifer wells and the fourth category represents Bunter Sandstone water which has been locally polluted by recirculation of industrial effluents.

The waters in the fifth and sixth categories are derived entirely from the Permian Limestones and the Permian Limestone and Marls respectively.

Finally, the Drift aquifer reveals very high mineral content and is grouped into a seventh category.

1. HYDROGEOLOGY OF THE AREA

The main area covered in this investigation lies in the lower reaches of the Rivers Don and Went. The geological succession in the area is shown in

Figure 1. There are five major aquifers of which three, the Basal Permian Sand and Breccia, the Lower Magnesian Limestone and the Upper Magnesian Limestone, dip gently eastwards and are confined downdip. The Bunter Sandstone and the Quaternary deposits (the Drift) overlie these and effectively consitute a single unconfined aquifer.

The Basal Permian Sand consists of incoherent, poorly cemented yellow sands and typical desert piedmont breccias. The Upper and Lower Magnesian Limestones are variable rocks with compositions ranging from limestone to dolomite. They are confined by marl beds and rich in soluble salts of anhydrite, gypsum and halite.

The Bunter Sandstone is fine to medium grained in the south and fine grained in the north of the area. Usually the rock is red or buff coloured containing nodules of red marl which vary in size from a few millimetres to a few centimetres; the sandstone is intercalated with bands of marl of variable thickness which thin out vertically and laterally. The Drift shows great variation in lithology. The older deposits contain Boulder Clay, glacial sands and gravels, whilst the recent deposits consist of gravels, sands, valley deposits, peat and alluvium.

Post-Permian and Post-Triassic earth movements have affected the Permian rocks with the result that, in places, the Lower Magnesian Limestone has been brought into hydraulic continuity with the Upper Magnesian Limestone at the outcrop. The Bunter Sandstone has also been affected by post-Triassic earth movements. There is lack of evidence to suggest that the movements of strata further away from the faulted Permo-Triassic boundary have been enough to bring about hydraulic continuity between the Upper Magnesian Limestone and the Bunter Sandstone.

Detailed investigation into the fluctuation of the groundwater levels suggests that there has been no appreciable lowering of water levels in the area over the last few years. Topography controls the movement of groundwater in the outcrop area of the limestones and the sandstone. The groundwater divide in the sandstone runs north-south, east of the River Don. Heavy pumping in the south-east by the public supply boreholes of the Doncaster District Joint Water Board has altered the groundwater regime. Low hydraulic gradients with an almost static water table prevail in the north-east. The Bunter aquifer is effluent to the River Don except at two localities where the hydraulic gradients are reversed due to heavy pumping,at Thorpe Marsh Power Station (GR 607097) and Prosper du Mulder (GR 572045).

2. CHEMISTRY OF GROUNDWATERS

A detailed study of the major and minor inorganic and physical variables in the Permo-Triassic and the Quaternary groundwaters was undertaken in the summer of 1970. Forty-two chemical analyses on various types of groundwaters included thirty samples from the sandstone, eight from the limestone and four from the Drift deposits. Temperature, pH, conductivity, total dissolved solids, total hardness, alkalinity and concentrations of calcium, magnesium, sodium, potassium, silica, chlorides, sulphates and bicarbonates were measured as major variables. A comprehensive graphical representation and interpretation of hydrogeochemical data is given by Chadha, 1972.

Characteristics of seven major categories of groundwaters may be distinguished in South Yorkshire according to their areal distribution, total dissolved ionic concentrations, lithology and movement of groundwater. Four categories are associated with the Bunter Sandstone and two with the Magnesian Limestones and one with the Drift.

The first category is the 'normal' uncontaminated calcium bicarbonate Bunter Sandstone water with a low mineral content (Table 1); mean Total Dissolved Solids (TDS) ($\bar{x}$) 310 mg/l, standard deviation (σ) 80 and range (R) 248 to 438 mg/l. This type of water is found in the south-east part of the area. The Bunter Sandstone is free from the Drift cover and most of the public water supply boreholes penetrate the full thickness of the aquifer. Groundwater abstraction is very high (135 million litres per day) with a result that there is relatively fast movement of groundwater. The duration of mineral - water equilibria is short.

The boreholes grouped in the second category have water with higher ionic concentration than the 'normal' Bunter Sandstone water (TDS $\bar{x}$ 619 mg/l, σ 5251, R 212-1072 mg/l). These wells are located near the eastern side of the faulted Permo-Triassic rock boundary and a few of them are located in the north-east of the area. Higher concentrations of Mg^{2+} and SO_4^{2-} are due to recharge from the Permian Limestones. In the north-eastern part increased concentration is due to the presence of a thick Drift cover, low hydraulic gradients with almost static water table and absence of large-scale abstraction.

The third category comprises water from multi-aquifer wells with fairly high mineral content which can be attributed to the presence of anhydrite in the Permian Upper and Middle Marls. There is blending of limestone and sandstone waters and it can be termed as calcium-sulphate water (TDS $\bar{x}$ 1116 mg/l, σ 6905, R 1130-2219 mg/l).

The fourth category represents localized pollution of the Bunter Sandstone water around Armthorpe Colliery due to disposal and recirculation of industrial effluents on to the Drift-free sandstone (TDS $\bar{x}$ 4544 mg/l, σ 6620, R 3924-5164 mg/l).

The fifth category comprises water from wells which are entirely in the Permian Limestones (TDS $\bar{x}$ 657 mg/l, σ 166, R 484-1318 mg/l). These are calcium bicarbonate waters with high mineral content.

The sixth category water samples are from wells which have penetrated both limestones and marls (TDS $\bar{x}$ 830 mg/l, σ 230, R 600-1060 mg/l). These waters have a high concentration of Ca^{2+} and SO_4^{2-} which can be attributed to the solution of anhydrite and gypsum within the Marls.

Finally, the Drift aquifer (TDS $\bar{x}$ 928 mg/l, σ 171, R 666-1145 mg/l) which is in hydraulic continuity with the sandstone reveals waters of high mineral content. It is grouped into a seventh category.

3. STATISTICAL ANALYSIS

Analysis of variance proves that there is a significant difference between the four categories of water in the Bunter Sandstone aquifer (Chadha, 1972). Similar statistical analysis on the two categories from the limestone shows that they belong to the same population. The statistical significance in the sixth category seems doubtful as there is only one degree of freedom. However, the lithological and hydrochemical evidence indicates that waters in the fifth and sixth categories should be treated separately.

4. CONCLUSION

Groundwaters in the Permo-Triassic and Quaternary deposits of South Yorkshire have been primarily classified according to aquifers. Within the aquifers lithology and duration of mineral - water equilibria exerts strong influence on the total dissolved ionic concentrations.

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Table 1. Summary of chemical data - 42 groundwater samples

Category	I			II			III			IV		
No. of Samples	9			16			3			2		
Ion	$\bar{x}$	σ	R	$\bar{x}$	σ	R	$\bar{x}$	σ	R	$\bar{x}$	σ	R
Ca^{2+}	42	10	22-63	88	32	27-140	280	180	128-532	370	54	317-424
Mg^{2+}	17	3	11-21	47	23	12-90	65	4	60-68	138	14	124-152
Na^{+}	21	14	10-53	28	15	5-64	127	89	19-237	99	6	93-105
K^{+}	-	-	-	8	8	2-17	5	5	4-11	12	2	10-14
HCO_3^{-}	165	68	112-205	319	181	93-610	200	142	283-317	126	20	107-146
Cl^{-}	26	6	26-40	57	22	29-116	67	90	8-194	1981	216	1765-2195
SO_4^{2-}	37	26	16-54	141	90	23-301	561	571	339-1345	483	152	331-636
TDS	310	80	248-438	619	251	212-1072	1116	905	1130-2219	4544	620	3924-5164

Table 1 continued.

Category	V			VI			VII		
No. of samples	6			2			4		
Ion	$\bar{x}$	σ	R	$\bar{x}$	σ	R	$\bar{x}$	σ	R
Ca^{2+}	106	34	48-268	153	39	114-192	125	23	96-160
Mg^{2+}	52	12	35-73	58	12	46-70	62	19	40-90
Na^{+}	18	5	14-31	15	1	14-16	40	10	34-50
K^{+}	5	2	3-9	4	1	3-5	22	12	6-41
HCO_3^{-}	310	253	134-463	329	2	327-331	352	180	282-507
Cl^{-}	51	21	28-120	25	17	8-43	99	26	54-124
SO_4^{2-}	135	47	79-438	298	162	136-460	298	93	137-370
TDS	657	166	484-1318	830	230	600-1060	928	171	666-1145

$\bar{x}$ = Mean

σ = Standard Deviation

R = Range

All concentrations expressed in milligrams per litre.

The Bunter Sandstone

I - Low concentration of ions S.E. of area.
II - High concentration of ions - Rest of the Bunter Sandstone.
III - Drift + Sandstone + Marl + Limestone.
IV - Industrial pollution of the Bunter aquifer around Armthorpe.

The Permian Limestone

V - Limestone strata alone.
VI - Limestone and Marl.
VII - The Drift.

Analysts:

Category 1 - Doncaster District Joint Water Board.

Rest - D. S. Chadha.

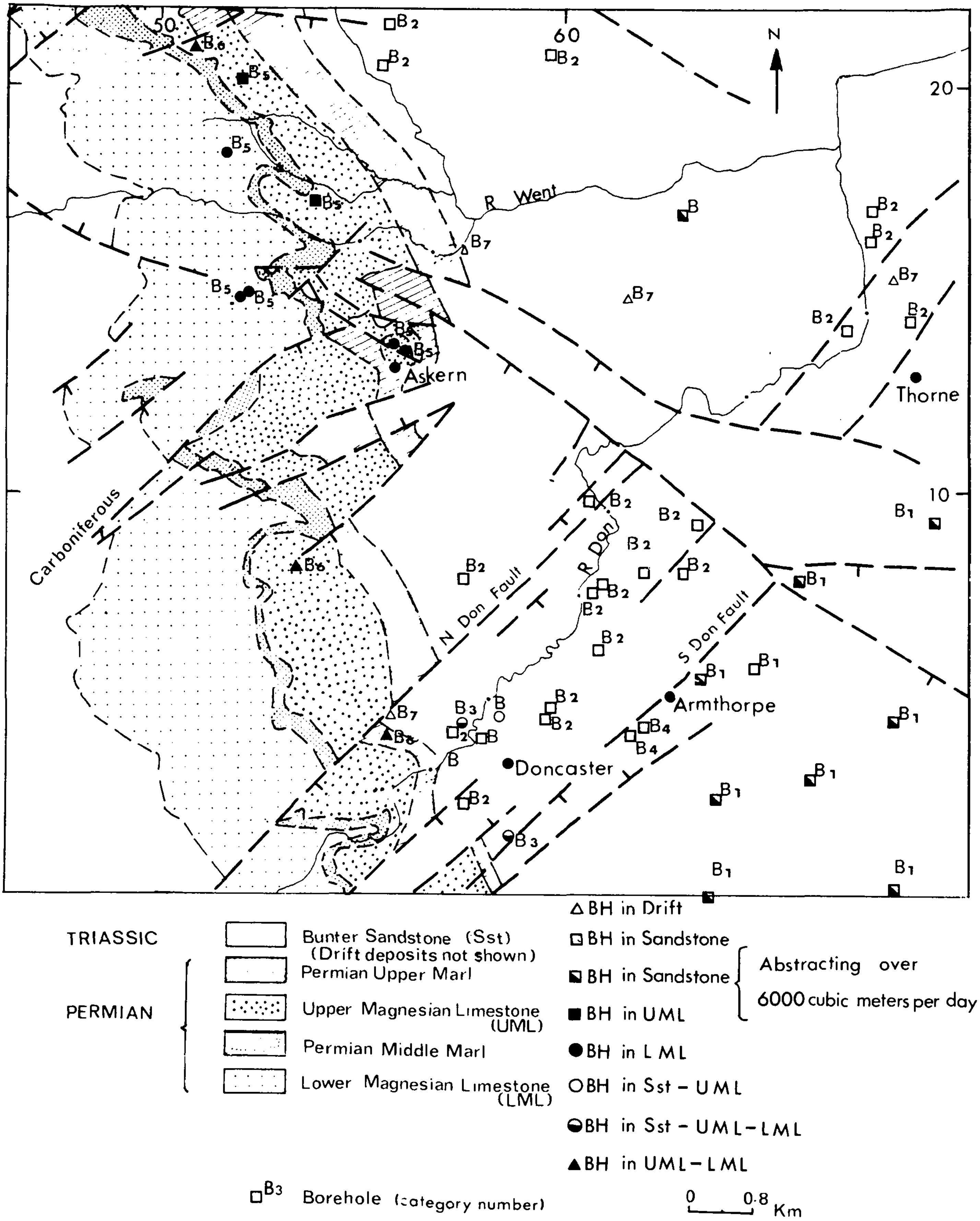

Figure 1. Geology and well sites in the Permo-Triassic and Quaternary Deposits of South Yorkshire

SUPPORT PAPER M

GROUNDWATER DEVELOPMENT IN THE LEE VALLEY, LONDON, AND ITS EFFECTS ON GROUNDWATER QUALITY

K. J. Edworthy and K. M. Baxter

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1. INTRODUCTION

Since the eighteenth century, but more particularly during the last 130 years, groundwater in the London Basin has been abstracted in large quantities. Immediately before the Second World War in excess of 80 M m^3/a were abstracted, more than half for public supply, and a large proportion of that was drawn from the Lee Valley area shown in Figure 1. Since that time there has been a decline in use and present abstraction is only about 75% of the above figure.

The Metropolitan Water Board started high-rate abstraction at the turn of the century, in the Lee Valley in particular, and the greater part of the storage now available has developed since that time. An estimated 175 M m^3 of storage is calculated to exist in the aquifers within the area shown in Figure 1, which was defined initially by the Water Resources Board as particularly suitable for artificial recharge. Proposals for recharge in the Lee Valley were made by the Water Resources Board (WRB) to obtain further detailed information which would augment the valuable experimental recharge work which had already been carried out by Boniface (1) using existing pumping stations.

Geologically the London Basin is a relatively simple area. The Chalk and Tertiary rocks have been folded about a south-east to north-west axis which plunges gently toward the east. The Upper Chalk aquifer is overlain by the Lower London Tertiary deposits including the London Clay so that it is completely confined, geologically, over virtually the whole of the Greater London area, except for small 'windows' of little extent.

The Tertiaries contain a basal arenaceous interval which constitutes a hydrogeological unit, the Basal Sands (2). The unit incorporates the Thanet Beds, and varying proportions of the overlying Woolwich and Reading Beds, Blackheath Beds and London Clay (Figure 2). In the Lee Valley area the Basal Sands reaches 25 m in thickness.

Following the Water Resources Board recommendation set out comprehensively in a special report (3), a series of pilot-scale recharge experiments were carried out at two sites, one specially constructed, the other an existing large diameter well specially adapted. Experiments at the two pilot sites have been completed (2). Results confirm that recharge of the Chalk aquifer is readily performed through small diameter wells or boreholes, but is only possible at low rates directly into the Basal Sands. Important questions were also raised by this work over the interconnection of the Chalk with the overlying Basal Sands and the effect on water quality of storing treated potable water in them. In particular, high sulphate concentrations were encountered in abstracted water after recharge and temporary storage, and they are outlined in this paper.

To obtain more information about the aquifer systems and their particular features a series of 15 exploratory/observation boreholes has been drilled and cored and the detailed results of this work have been reported by Edworthy et al (4). To help provide more information on the general mechanisms in action, historical records of variation in abstracted groundwater quality with progressive dewatering in the Lee Valley have been examined.

First the results of artificial recharge are outlined, followed by a summary of the detailed studies of the Basal Sands aquifer. The natural changes in abstracted groundwater quality are then considered in this context.

Some of the work reported in this paper was done as part of projects undertaken jointly with the Central Water Planning Unit. Their agreement to the use of this information is greatly appreciated.

2. ARTIFICIAL RECHARGE EXPERIMENTS

The full details of the pilot experiments are given in Volume IV of the London Basin Artificial Recharge Series (5). For the purposes of the present paper, It is important to record that the Chalk and the Basal Sands aquifers were apparently not connected at one of the two sites studied. At the other site, at Ponders End, there was free interconnection, but there was some uptake of sulphate as a result of water storage in the Basal Sands aquifer.

The Ponders End well was constructed in 1902 to 63.0 m depth and 3.96 m diameter, as one of a series in the Lee Valley, by the Metropolitan Water Board. The well is completely lined through the Lower London Tertiaries and the Chalk and is served by more than 1.8 km of adits. At the start of experiments, the groundwater level was slightly above the top of the Chalk, so that nearly 6 m of the 10.0 m thick Basal Sands was available for storage.

Three recharge/abstraction experiments were carried out, saturating and draining approximately the same volume of aquifer. The rates and quantities in the first and third experiments were closely similar, and the quality of the recharged water was similar for each. Dissolved oxygen saturation was in excess of 80% in each case, average sulphate content less than 80 mg/l and nitrate less than 8.0 mg N/l.

Shortly after the start of recharge, the quality of the groundwater in the Basal Sands deteriorated and eventually very high concentrations of sulphate and total hardness were found to occur in observation borehole samples. No detectable changes except for mixing and replacement were seen to occur in the Chalk aquifer. The concentration of sulphate in the abstracted water following these two recharge periods is compared in Figure 3. It should also be noted that nitrate in the abstracted water was about 0.5 mg N/l, a similar concentration to that in the Chalk groundwater locally, and dissolved oxygen between 0.5 and 2.0 mg/l. The abstracted water was believed to be mainly derived from the Chalk but modified by admixture of Basal Sands water draining vertically in the Chalk. This kind of flow pattern could explain the level of sulphate concentration by straightforward mixing, but it is not possible to explain the very low NO_3-N and dissolved oxygen in the same way.

In order to account for the high sulphate concentrations found, it was concluded that oxidation of iron sulphide in the Basal Sands aquifer was taking place and that there was probably direct uptake of sulphate already present in the aquifer. It was therefore important to determine the source of the sulphate. Was there a pattern of local concentration of soluble sulphate in the Basal Sands, or might this effect be found at all sites in this area? Furthermore it was necessary to decide, if possible, whether the sulphate was solely from the Basal Sands or produced by drainage from the even younger overlying strata as a result of the long-term regional dewatering.

3. RECENT GEOLOGICAL STUDIES

Continuous core through the arenaceous strata of the Lower London Tertiaries was taken from 14 new sites during 1974-75. A number of chemical or petrological studies have been followed as well as detailed and basic geological work on the definition of the Basal Sands (Figure 2), and valuable information on the variability of the aquifer has been obtained. It has been established that the strata which make up the Basal Sands are petrologically and texturally relatively uniform as indicated by the study of some of the more directly useful grain-size parameters, shown in Figure 4. This similarity is reflected by a petrographical uniformity, most of the rock types being subarkoses, arkoses or feldspathic graywackes (6).

Chemical extraction of selected core samples by bromine/acid has been carried out to determine the amount of iron present. The distribution shows there to be no particular areas of high concentration in the Basal Sands, though there is a marked tendency for the upper part of the Woolwich and Reading Beds and the basal London Clay to be more ferruginous than the Basal Sands.

Data are shown plotted with some geological detail in Figure 5. Some thermogravimetric work has also been done on core samples, which shows a similar lack of overall trend in variability. This work has also given useful indications of presence and abundance of gypsum, carbonates, sulphides and organic matter and more work is in progress to evaluate the technique.

Some groundwater samples from the Lower London Tertiary succession and some pore water samples, uncontaminated by drilling, have been analysed to try to determine whether there is any indication of very high sulphate concentrations under natural conditions, and if so, whether there is significant vertical variation. The results to date are given in Table 1 and show that there are some relatively high concentrations, and also that there is considerable variability in any one borehole. There has been no artificial recharge at any one of the locations listed.

Work done by Bessey and Lea (7) on the analysis of groundwater and sub-soil samples from the London Clay shows sulphate concentrations in shallow groundwater to be fairly uniform locally but to vary widely with seasonal rainfall. Gypsum was identified in core at a number of sites but not at others, partly supporting the chemical evidence that the sulphate in the sub-soil varies considerably with depth and from place to place. Typical values in groundwater from Benfleet, Essex, vary from 2671 to 3768 ppm SO_4 for December and from 308 to 2144 ppm SO_4 for March values. Sub-soil values range from 613 to 3798 ppm (1 m below surface) to 735 to 34550 ppm (3 m below surface).

4. THE EFFECTS OF LONG-TERM ABSTRACTION

To assess this, all the available analytical records since 1906 have been examined (8) and a considerable amount of additional information on groundwater levels and total annual abstraction provided by the Metropolitan Water Division of the Thames WA. From even a superficial knowledge of the Chalk groundwater produced in the London area, it is clear that the Lee Valley wells have always differed from those in the Kent area in containing significant amounts of ammonia-N, frequently turbidity due to ferric hydroxide, and in many cases noticeable hydrogen sulphide evolution at the well-head.

Comparison of the quality changes observed in the Basal Sands observation boreholes during recharge at Ponders End (5)(9) shows them to be clearly very similar in nature, and indicative in both cases of the same anaerobic, slightly acidic conditions, giving rise to the above features. To test this assertion, the concentrations of some of the constituents in selected Lee Valley wells is shown in Figures 6a - c against time; also shown is groundwater level with respect to the top of the Chalk and average annual abstraction. At all three wells, but especially at Wanstead and Chingford Mill, there has been an increase in both carbonate hardness and chloride concentration. At Hadley Road well, where levels have remained within the Chalk since the start of development, there has nevertheless been an increase in total hardness, and a decline in non-carbonate hardness. At both the other sites, where water levels have remained within the Basal Sands (Thanet Beds) there has been a large increase in concentration of all constitutents, except for the non-carbonate hardness at Chingford Mill, as the Basal Sands have drained.

It is likely, however, that some of the abstracted water quality changes are due to short-term variations in pumping schedule not distinguishable in the form plotted in Figures 6a - c. It is expected that a clearer picture will emerge as more complete historical data become available from the Thames Water Authority.

5. DISCUSSION AND CONCLUSIONS

Pilot-scale recharge experiments pointed to the existence of a significant chemical quality problem in recharging the Chalk/Basal Sands aquifer system. It was not known whether the particular problems encountered were of purely local relevance or if they might occur elsewhere in the Lee Valley. The subsequent exploratory/observation borehole drilling and coring programme and the various studies arising from it have shown clearly that the Basal Sands aquifer varies to some degree in its stratigraphical make-up even within the relatively confined Lee Valley area. The Thanet Beds, which are always part of the unit, and the Woolwich and Reading Beds sands, present in most cases, have attracted most attention in the recent studies (4).

Median grain-size, graphic standard deviation and skewness as defined by Inman (10) have been used to characterize the grain-size distribution and enable comprehensive comparisons to be made within the succession at each borehole site and across the area. The data shown in Figure 4 illustrate the overall uniformity across the area. The Woolwich and Reading Beds sands are not distinguished from the Thanet Beds in the data shown, since the distributions are the same as far as can be determined. The information also shows that there is a proportion of ill-sorted coarse-sand and pebble intervals, but that the 'average' sand is very fine-grained and moderately well-sorted and tends to be fine-skewed. The calculation of permeability from grain-size distribution gives unrealistically high results compared with some laboratory determinations (5)(11). The chemical and petrographic data support the general contention that no major trends exist, but it is recognized that the observations made so far, particularly on chemistry, are very much at the reconnaissance level. The results of porewater analysis of samples taken in recent Thames Water Authority drilling show that, at two of the three sites included, there are both low and high sulphate concentrations at some levels in both Woolwich and Reading Beds, and Thanet Beds. These are all shown in Table 1 and the third site listed illustrates well the compartmentalization that can occur in this aquifer.

The main problem of sulphate uptake during recharge does not appear to be a result simply of oxidation of pyrite by dissolved oxygen and nitrate. Only approximately one-third of the sulphate increase at Ponders End can be accounted for in this way. The presence of directly soluble sulphate, probably as gypsum, is therefore the most probable explanation. The origin of this, assuming that it represents a concentrate from a larger source, is difficult to determine. One possible source is the London Clay, which may have released sulphate as a result of the regional reduction in groundwater levels which has had the effect of reversing the direction of groundwater flow upward through the London Clay, so that drainage will have taken place. If this were the case then downward movement of sulphate-rich water might continue to depths into the underlying Tertiary deposits which would depend on the presence of intervening aquicludes. While the flow reversal concept is a reasonable one it would not account for any concentration of sulphate except as perched water bodies within the Tertiaries. There is indication also that relatively high existing sulphate concentrations in groundwater might be linked geographically to the vicinity of the 'windows' in the London Clay, on the basis of information collected by the Thames Water Authority, Lee Division. Natural recharge of groundwater in these areas may be significant and higher than elsewhere in the Lee Valley so that leaching of part of the Lower Tertiary succession could be taking place.

The historical changes in water quality in the Lee Valley constitute what must be an important dimension to our eventual understanding of the processes at work. As explained above, the Lee Valley Chalk groundwater has always differed from the N. Kent Chalk groundwater in its content of NH_3-N and frequent turbidity due to ferric hydroxide. Geologically the areas differ widely in that the Kent Chalk is unconfined and the Lee Valley Chalk is geologically confined throughout, the southernmost wells being some 16 km from outcrop (excluding the structural windows in the London Clay). The general chemical evolution of groundwater across the London Basin, in terms mainly of solution and ion-exchange, was set out by Ineson and Downing (12) though this interpretation does not appear to take into account the possibility of drainage from the tertiaries or the specific influences of anaerobic conditions. The distribution of sulphate in the Lee Valley area is certainly far more complex than the scheme put forward by the above authors implies, probably because the hydrogeological conditions are much more complex than along the main section described. The disturbance of the natural groundwater gradient will also necessarily cause a redistribution of any zones established, to some extent even without the complication of a composite aquifer, and a long-term change in water level, which we are dealing with in the Lee Valley. At Hadley Road well (Figure 6b) the water level has been below the Chalk since construction and has remained at least 30 m below this level since pumping started in 1902. If there has been any drainage of the Basal Sands it will have taken place at some distance from this site so that chemical effects might be expected to be small. An initial slight increase in non-carbonate hardness becomes a large reduction in the long term up to the early 60's; this may be the result of 'low sulphate' water to the south, following the scheme of Ineson and Downing (12), being attracted as a result of pumping. This would not explain the continued fall in non-carbonate hardness in spite of reducing abstraction during the 50's however. The Wanstead Pumping Station records plotted in Figure 6c show a marked rise, over the long term in both total hardness and non-carbonate hardness as well as in chloride. While the reversal of the established natural trends might also be an explanation for some of this variation, it is believed that drainage from the Tertiary deposits may provide an important contribution here where a small part of the Basal Sands has been dewatered. At Chingford Mill (Figure 6a), the Basal Sands have been more extensively dewatered since the late 40's and there was also an increase in non-carbonate hardness which reversed in 1950. Total hardness increased by about 50% to a maximum of 310 ppm between 1910 and 1972. At all sites, but especially Chingford Mill, there has been an increase in groundwater chloride concentration.

The details of the inter-relation of groundwater composition, water level and rate of abstraction are hidden in the generalized information presented in the above graphs and more detailed analysis is desirable. It is clear, however, that pumping of groundwater over a long period has had a significant effect on groundwater composition.

Important changes in groundwater quality are believed to arise largely through drainage from the Tertiaries, but there are obviously other factors and these are not clear at the moment. It is probable that there are also some changes in water quality in the Chalk with increasing depth in this area so that progressive changes in quality with water level and pumping rate would be expected. The slight changes in chloride concentration tend to support this.

While the various mechanisms at work have not yet been defined properly, therefore, our basic understanding of the aquifer system has improved considerably. By paying special attention to the groundwater level data in new recharge and abstraction operations, the relative importance of the various factors will be resolved further and future changes due to the planned intensive development might be predicted.

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Table 1. Sulphate concentrations in pore waters and borehole waters in the Lee Valley

Site	Depth (m) below surface (a)	Sulphate (mg/l) Pore water	Standing water
1	13.95*		154
	16.73	165	
	19.23	234	
	21.27	181	
2	21.03*		465
	25.30*		210
	25.47*		211
	28.79		405
	29.23	371	
	31.23	183	
	32.54	170	
	35.23	117	
3	18.95*		118
	28.23*	976	
	34.23	1050	
	39.23	78	

(1) Lee Bridge Pumping Station (TQ36088655)

(2) Chingford South Pumping Station (TQ37369491)

(3) Greaves Pumping Station (TQ36229179)

(a) Samples taken from Thanet Beds unless (*) which signifies Woolwich and Reading Beds.

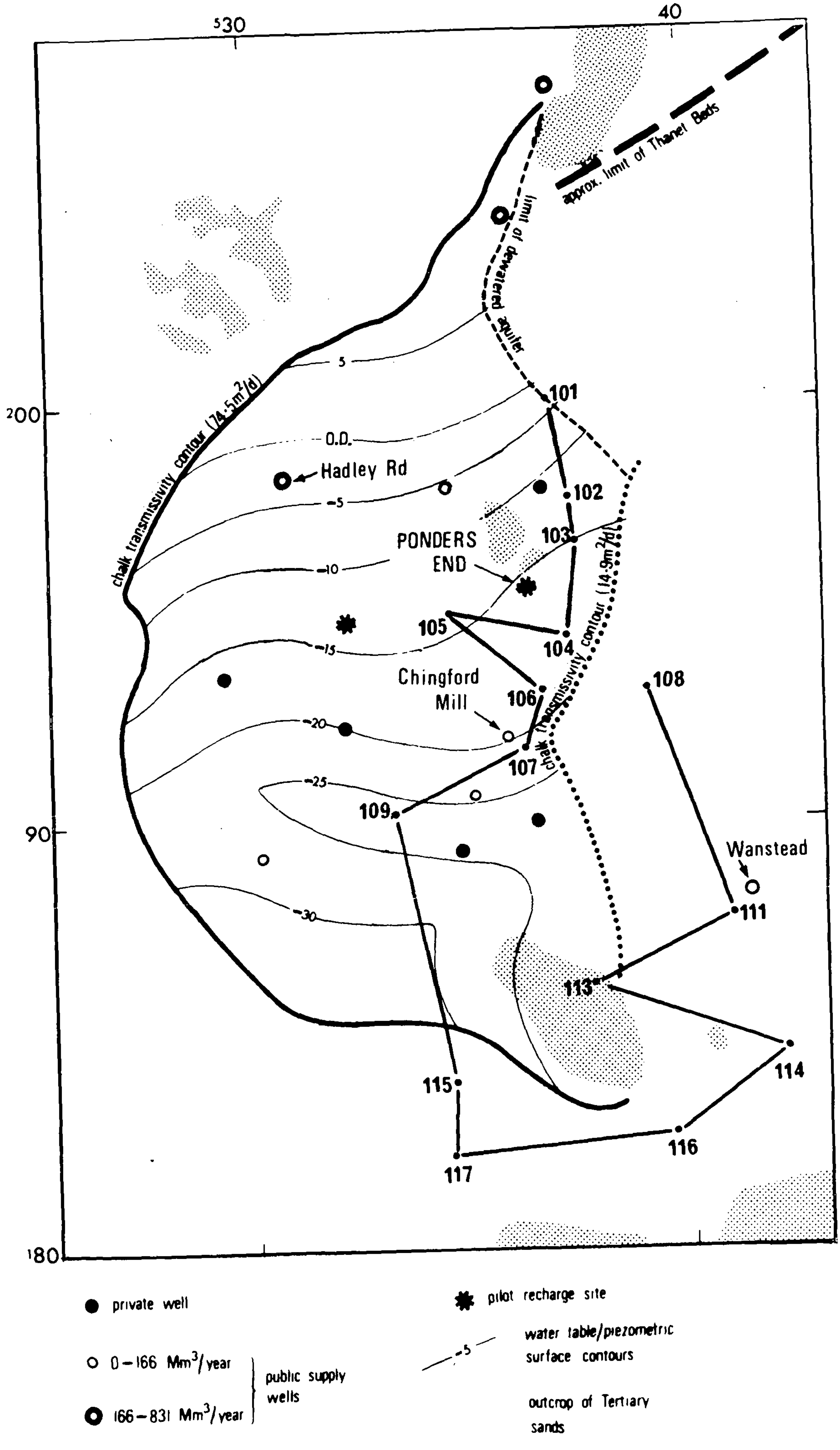

Figure 1. Location plan and line of section.

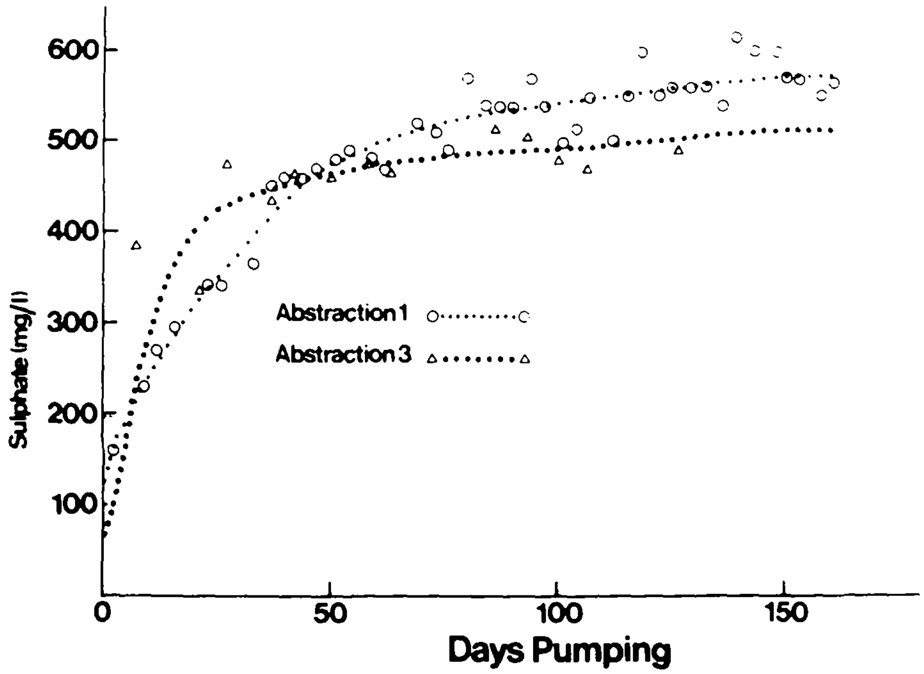

Figure 2a. Changes in water quality during pumping at Ponders End - sulphate

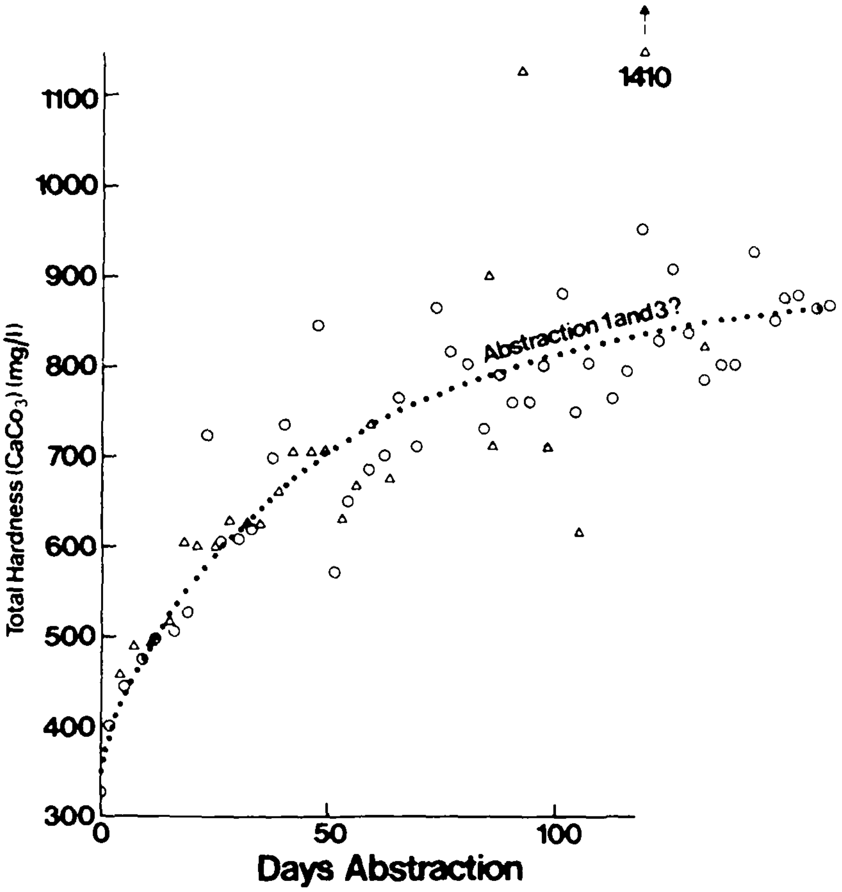

Figure 2b. Changes in water quality during pumping at Ponders End - total hardness

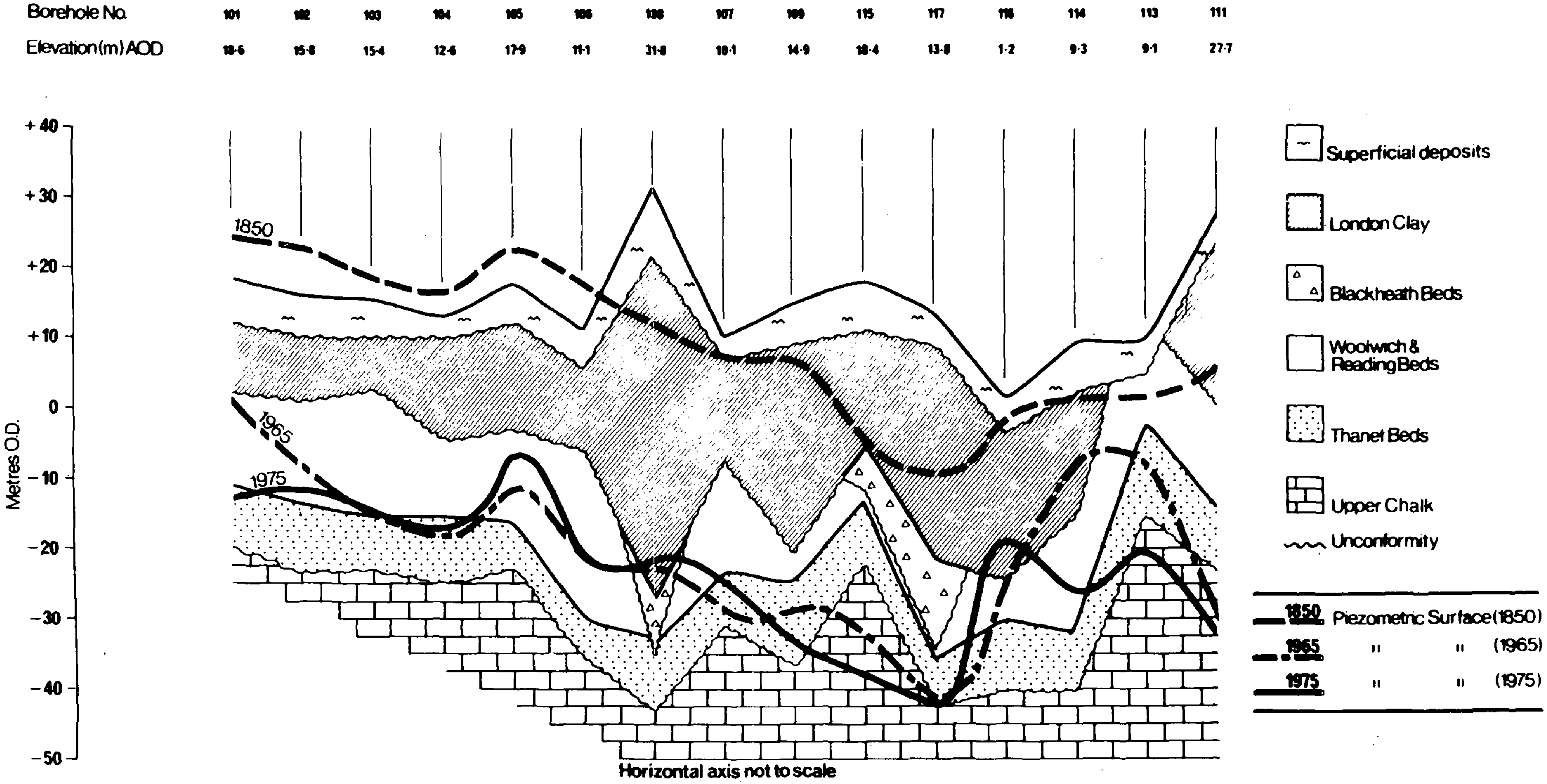

Figure 3. Diagrammatic geological section (plan shown in Figure 1)

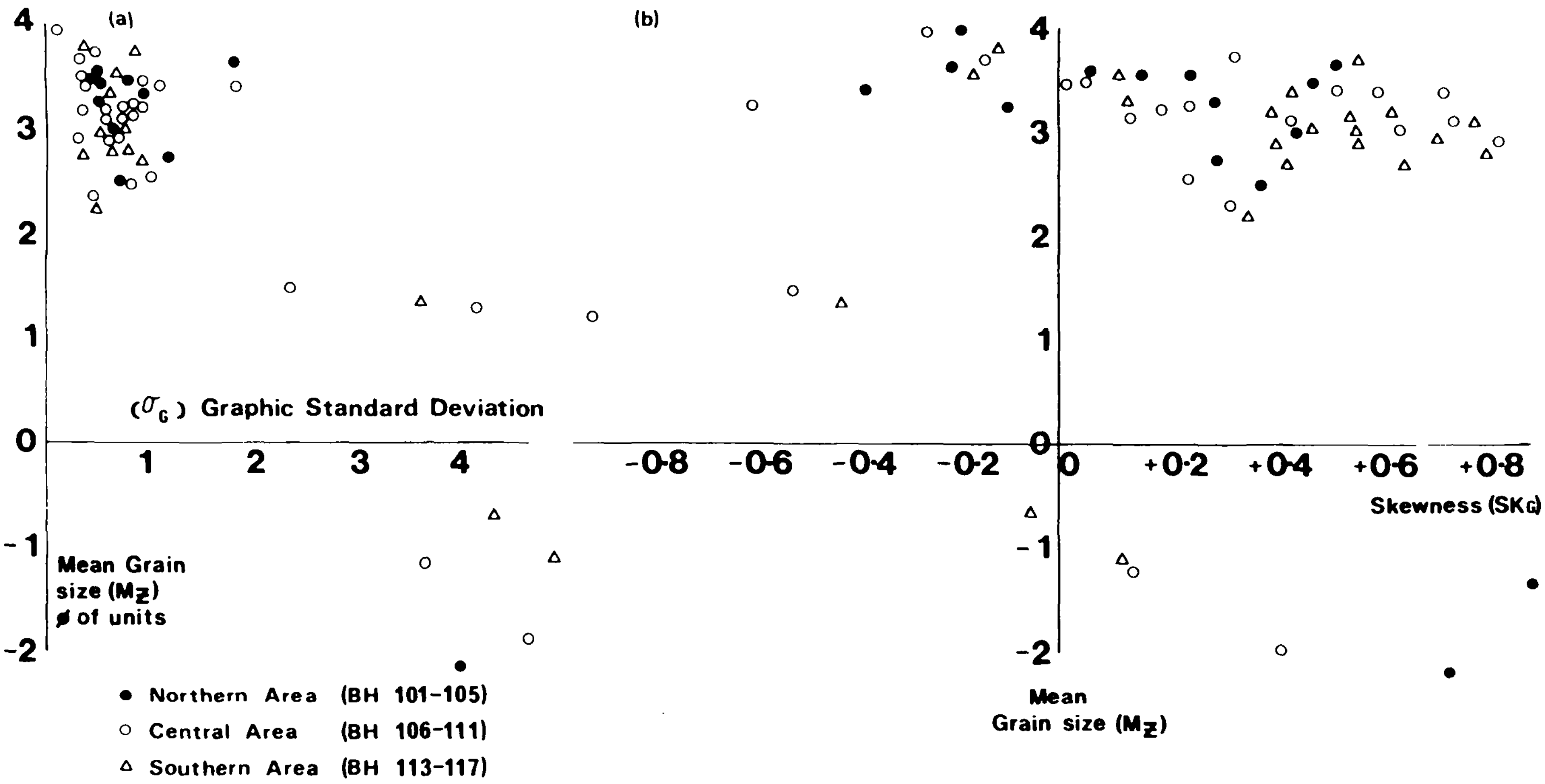

Figure 4. Relationships of selected grain-size distribution parameters.

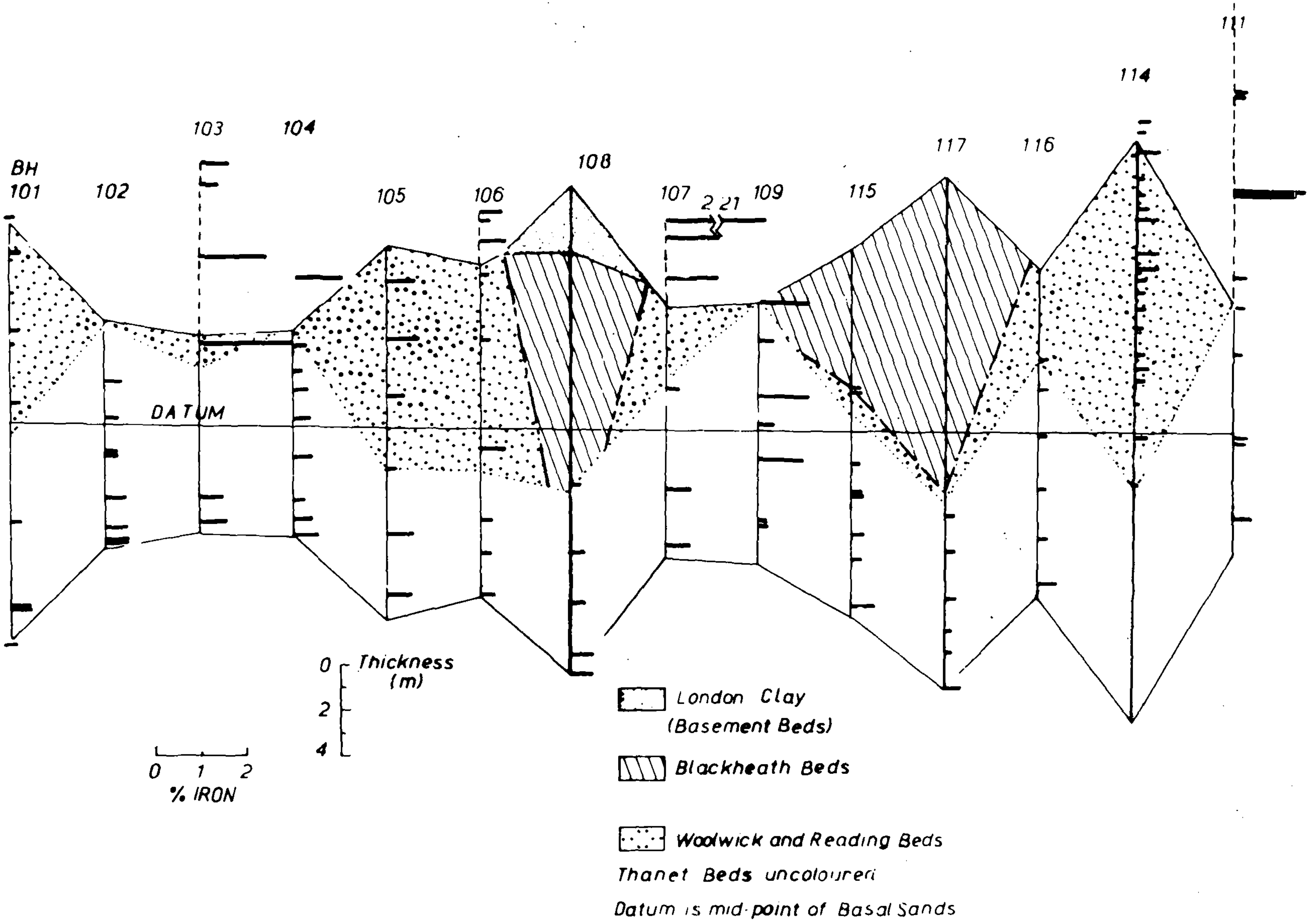

Figure 5. Lee Valley Basal Sands - per cent extractable iron.

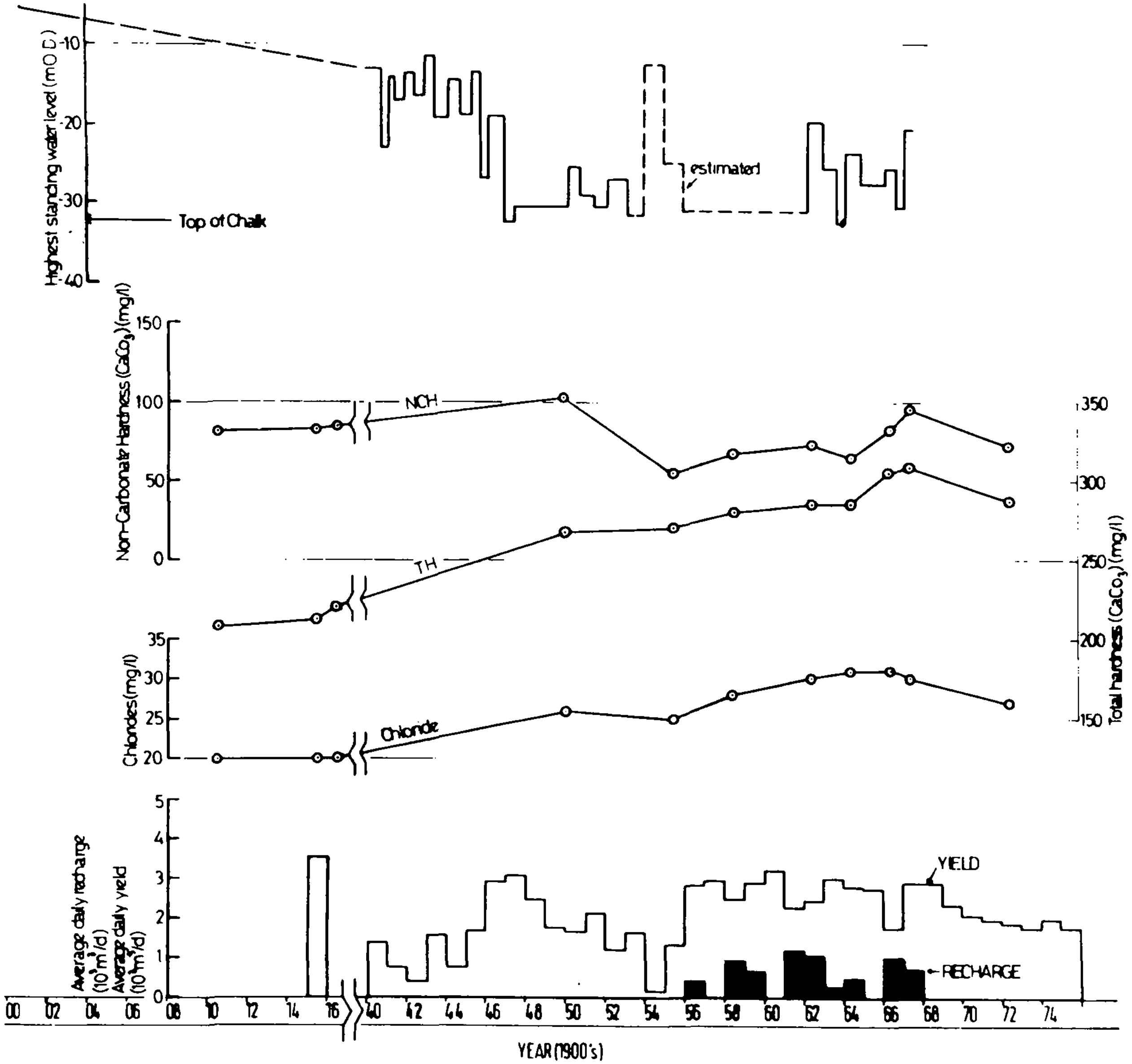

Figure 6a. Historical quality and pumping data - Chingford Mill.

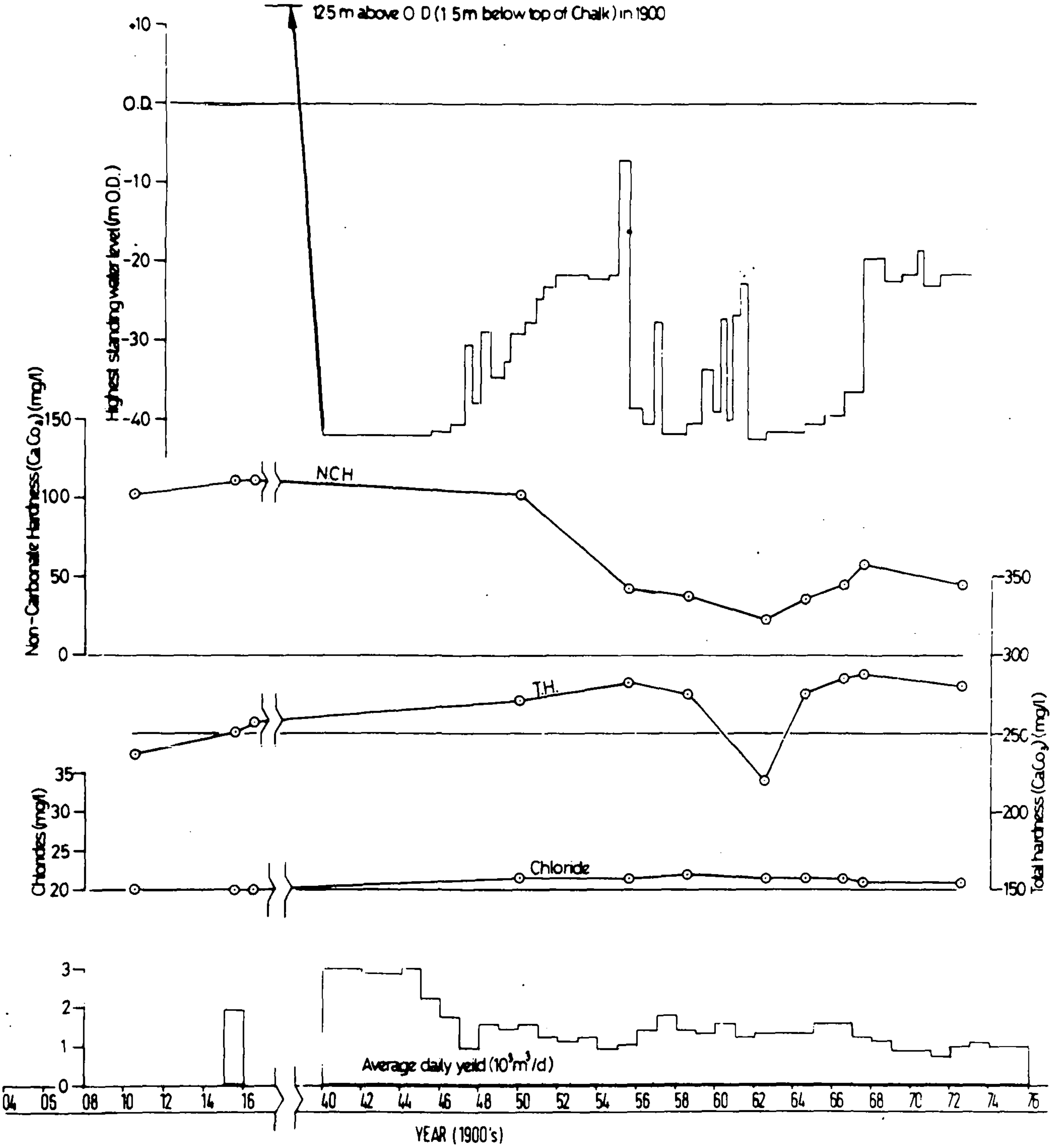

Figure 6b. Historical quality and pumping data - Hadley Road.

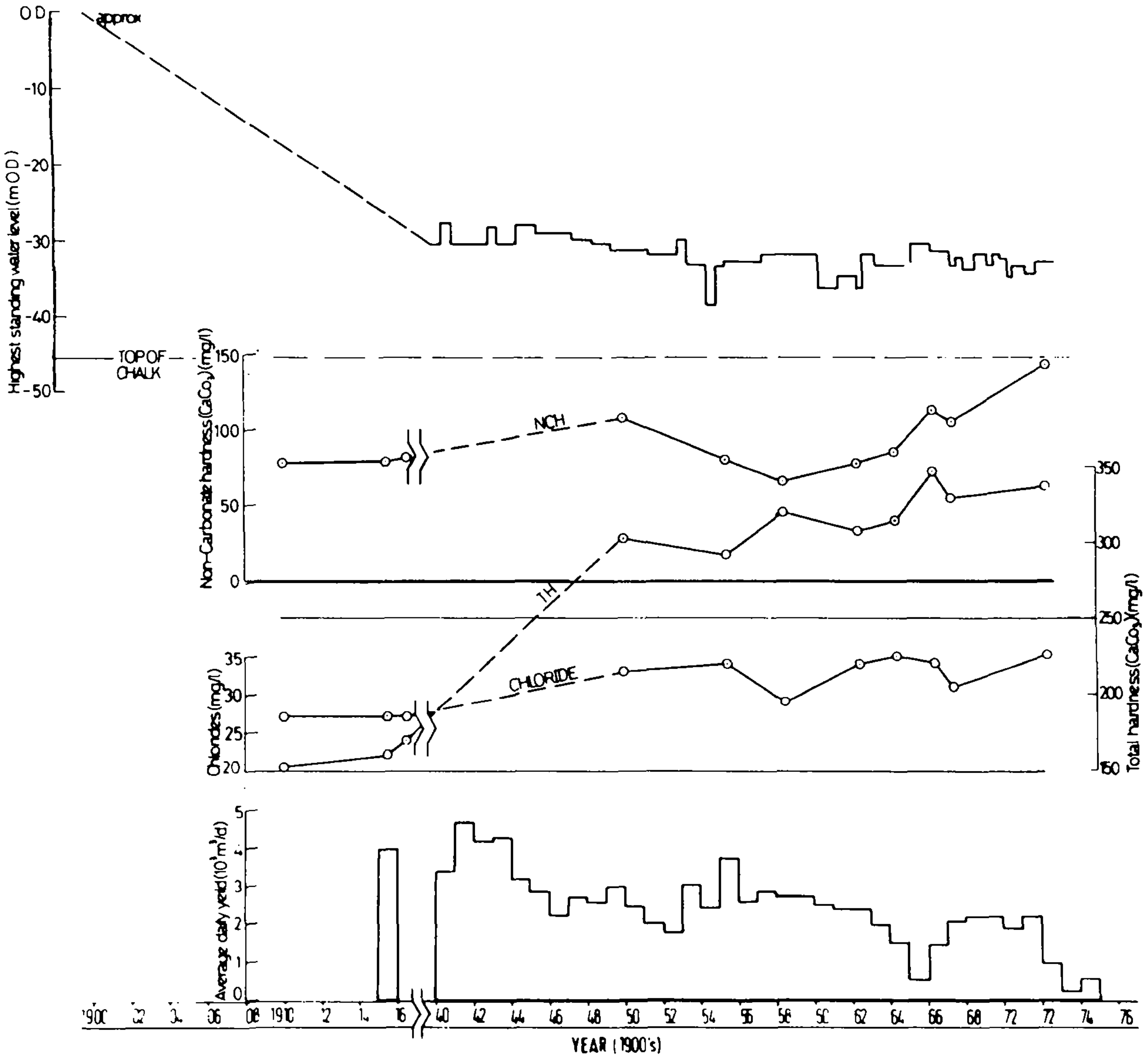

Figure 6c. Historical quality and pumping data - Wanstead pumping station.

SUPPORT PAPER N

SOME GROUNDWATER SUPPLIES OF QUEENSLAND

M. A. Simmonds.

In this short support paper it is not proposed to provide a highly technical dissertation but rather to describe a few unusual problems encountered in some of the underground waters of Queensland. It is hoped they will prove interesting and the younger generation may find it well worth while to remember some of them.

Experience in Queensland indicates that it is impossible to guarantee either the volume or the quality of an underground water. One can usually predict the general type of underground water in an area and a knowledge of the geological formations will also assist predictions. However, geological maps rarely delineate boundaries to within 20 metres and this is frequently all that separates two bores supplying entirely different types of water.

1. BRIBIE ISLAND WATER SUPPLY

Bribie Island is a small island near Brisbane. It consists entirely of sand and is well covered by trees and other vegetation. It is now rapidly developing as a weekend and holiday resort.

The only fresh water available is groundwater stored in the sand. In the wet season the groundwater table may rise above the surface forming marshy swamps.

The Council developed a water supply by drawing water from bores 10 to 20 metres deep.

The first groundwater pumped was soft. Differences in chemical composition were not sufficient, at that stage, to cause any significant problems. However all bores were characterized by a very high colour (200 to 300 standard Pt. Co. units) and a high concentration of iron.

The clarification of this water required very close control of the chemical coagulants. The colour colloid could only be 'cracked' at a pH value of 5.8 to 6.0.

With the growth of the town the Council required more water and an area of about 250 hectares was investigated. A total of 30 Test Bores were drilled over this area in grid formation about 230 metres apart. The bores were test pumped and samples collected for analysis.

The chemical composition of the groundwater in this area varied between the two extremes shown on the attached analysis report sheet No. 1. Changes in composition were more or less uniform in one direction.

Some of the major variations were as follows:

Colour	from 175 units to 500 units
Total ionized salts	from 65 mg/l to 950 mg/l
Alkalinity as $CaCO_3$	from 2.5 " to 280 "
Total hardness as $CaCO_3$	from 12.5 " to 310 "
Chloride as Cl	from 40 " to 300 "
pH value	from 5.2 to 7.1

They were all characterized by a very high colour and varying concentrations of iron.

The output from 3 or 4 bores would generally be required to supply the system. Imagine the problem of adjusting the chemical doses to suit the new water composition every time a different bore was placed 'on line'.

It was mentioned that this was an island of sand and the problem was solved by excavating a large lagoon about 4 m deep. This rapidly filled to the standing water level of the whole area and provided a water of uniform composition for treatment.

2. BUNDABERG WATER SUPPLY

Bundaberg is a coastal city in the centre of a large sugar growing area. In an area of 14 000 hectares (35 000 acres) there are over 500 pumped irrigation bores. Modern automatic irrigation systems may extract from 300 to 450 m^3/h from one bore.

The water in this whole area is characterized by two common factors. All waters have a low pH value and very high concentrations of carbon dioxide, most of which is aggressive carbon dioxide.

Most bores supply water containing 80 to 100 mg/l of aggressive carbon dioxide but many have concentrations in the 100 to 150 mg/l range with a few higher still. A typical analysis is shown on the analysis sheet No. 1.

Long before irrigation of sugar cane became so essential the City Council was using this underground water for its reticulated supply.

The pH value was too low for copper service pipe, and plastic pipe had not yet been invented, so the only suitable alternative was galvanized iron. Zinc was removed very rapidly. Consumers were advised always to flush their pipes before using the water in the morning. About 20 years ago the Council considered treatment to remove the aggressive carbon dioxide.

At that time there were two or three bores placed at strategic locations around the town and more were required. This meant that a number of small treatment plants would have to be serviced. A simple, automatic method for removing the carbon dioxide was desirable.

Because of the high concentrations, spray aeration was more economical than chemical treatment for removing carbon dioxide. However, even a 95 per cent removal would only raise the pH value to about 6. 0. To avoid the maintenance of chemical treatment plants the use of limestone beds as final treatment was investigated. Pilot plant studies indicated that this treatment would be effective so plants were designed and built. A total of seven plants have now been operating on this same principle for many years with final pH values of the order of 7. 0 to 7. 5. The only maintenance is a 'topping up' of the limestone bed once or twice a year. The peculiar features of these installations which have made them so successful are considered to be as follows:

(a) The raw waters contain less than 5.0 mg/l of calcium and and alkalinity and therefore have an affinity for calcium. This system does not work with hard water.

(b) A very pure limestone containing negligible silica was used to avoid sealing the stone with colloidal silica.

(c) The limestone bed is not flooded but operates as a trickling filter providing film contact with the limestone and additional loss by aeration.

(d) Pumping is intermittent, which ensures periodic drying of the surface stone, thus preventing the growth of algae.

3. SUPERSATURATED WATERS

Many of the underground waters of Queensland are supersaturated in respect to calcium carbonate. In these bores trouble is experienced with the deposition of calcium carbonate within the pump and rising pipe.

Pumps are generally bronze impellers in cast-iron bowls and galvanic action is severe. It is considered that this galvanic action increases the rate of precipitation of calcium carbonate from supersaturated waters.

The Claredale water analysis shown on analysis sheet No. 2 shows how supersaturated these waters can become.

There have been several instances where the bore has had to be abandoned because the rapid build-up of calcium carbonate has caused the pump to seize. In high alkalinity, hot, artesian waters this can occur at low calcium concentrations.

3.1. KARUMBA BORE

An interesting case of this occurred at Karumba where the problem was complicated by a variable water composition. The chemical composition of artesian bores is generally extremely stable. The artesian bore at Karumba operated for several years under 'free flow' conditions without trouble.

As the demand increased a pump was installed but no trouble was experienced while the pumping time was limited to 8 to 10 hours per day.

Several months after pumping increased to 16 to 20 hours per day the pump seized.

The pump was found to be blocked by brown deposits of magnetic iron oxide with some calcium carbonate. Thereafter the pump blocked at 4 to 6 month intervals but, on all subsequent occasions, the blockage was caused by white deposits of pure calcium carbonate.

Flow measurements were made and samples analysed over many months but there appeared to be no correlation between flow and composition.

The pump was generally stopped about 9.00 p.m. and restarted about 8.00 a.m. the following morning but the bore continued to discharge under free flow conditions during the night.

It was eventually realized that a 200 mm diameter bore more than 10,000 metres long can hold a lot of water and a calculation showed that water discharged under free flow at 8.00 a.m. probably entered the bottom of the bore before 9.00 p.m. the night before during pumping conditions and therefore the sample actually represented the pumped water supply.

When allowance was made for this fact one could accurately predict the composition for any pumping rate. The maximum pumping rate which would not cause deposition could then be determined. This rate was not sufficient to supply the demand.

A second bore was drilled close to the first but proved to be dry and no water was obtained. This emphasizes the unpredictability of underground water supplies.

A surface supply is now being developed from the Norman River. This supply is also peculiar to Queensland conditions. Fresh water is available for only 6 to 8 weeks in the wet season and during this time sufficient water must be pumped to an off-stream storage to supply the town for the remainder of the year.

4. JULIA CREEK WATER SUPPLY

The analysis of an artesian bore at Julia Creek is shown on the analysis sheet No. 3. This is much more typical of our artesian waters than that at Karumba. Most artesian waters consist almost entirely of sodium salts. Those in the Northern portion of the artesian basin tend to have higher alkalinities while those in the South generally have high concentrations of chloride.

Because of the absence of calcium most artesian waters have significant concentrations of fluorine up to about 4.0 mg/l.

It was often stated that one could identify a man from Julia Creek by his black mottled teeth. This is quite true because the Julia Creek water is the only domestic supply with a high fluoride content but which is also sufficiently low in dissolved salts to be used for human consumption. All other artesian domestic supplies with high fluoride are also too saline for domestic consumption.

It is interesting to note that, before 1920, the State Dental Service reported on the black teeth of the children of Julia Creek. However they also reported that they rarely had to fill any cavities while in this town.

Note that the Karumba water contained 16 mg/l of fluoride.

5. RICHMOND WATER SUPPLY

Complaints of 'red water' and/or staining caused by iron and maganese occasionally occur. These are often reported irregularly from different parts of the reticulation. One of these came from the town of Richmond.

The water being pumped from these sub-artesian bores often shows no trace of either iron or manganese and the reticulation contains no uncoated iron pipes. However, the bore water usually contains very high concentrations of aggressive carbon dioxide.

It has been suggested that the following conditions give rise to these complaints.

While pumping, the detention time of the water within the bore casing is short and does not permit any detectable corrosion of the bore casing. However consumption during the night is very low and generally drawn from storage. Therefore, the pump may be stopped for five to six hours.

These are not artesian bores and during this period of no flow the aggressive carbon dioxide, assisted by a high conductivity and dissimilar metals, rapidly corrodes the bore casing and provides a 'slug' of 'red water' which, when the pump starts, is delivered directly into the reticulation. This red water is probably pumped for less than one minute but could travel through the pipes without much mixing. There is usually a small percentage of manganese in the bore casing steel which could explain the presence of manganese in the corrosion product.

An automatic by-pass which would automatically reject the water to waste for the first few minutes after start-up would probably reduce the incidence of complaints.

Several bore waters were analysed for a client who was looking for a 'soda' water bore so that he could establish a health spa where tourists could 'take the waters' and become rejuvenated. Two interesting facts emerged from this investigation. The first was that a bore was actually found which bore some resemblance to a 'spa' water. The second was that a local soft drink manufacturer stated that modern 'soda' water = town water supply + carbon dioxide.

The analysis of this 'soda' water is shown on analysis sheet No. 3.

WATER ANALYSIS REPORT

Sheet No. 1 of 3

WATER SUPPLY		BRIBIE ISLAND		BUNDABERG
		Low TDS	High TDS	Typical
GENERAL ANALYSIS	mg/l			
Colour (apparent) Std. Pt. Co. Units		175	500	
Total ionized salts (calculated)		65	950	140
Conductivity at 20°C	µS/cm	125	1350 ±	250
pH value		5.2	7.1	4.6
Carbonate alkalinity	as $CaCO_3$	nil	nil	nil
Bicarbonate alkalinity	as $CaCO_3$	2.5	280	2.0
Total alkalinity	as $CaCO_3$	2.5	280	2.0
Free carbon dioxide	as CO_2	30	35	90
pH_s (at $CaCO_3$ equilibrium)		10 +	7.05	10 +
Free carbon dioxide (at equilibm.)		nil	37.5	nil
Aggressive carbon dioxide as CO_2		30	nil	90
Calcium hardness	as $CaCO_3$	5.0	250	2.0
Magnesium hardness	as $CaCO_3$	7.5	60	18
Total hardness	as $CaCO_3$	12.5	310	20
Sulphate	as SO_4	Trace	5	Trace
Chloride	as Cl	40	300	85
Nitrate	as N	nil	nil	1.0
Total Iron	as Fe	1.0	5.0	Trace
DETAILED ANALYSIS	m-equiv/l			
Calcium	as Ca	0.1	5.0	0.04
Magnesium	as Mg	0.15	1.2	0.36
Sodium	as Na	0.9	8.0	2.04
Carbonate	as CO_3	-	-	-
Bicarbonate	as HCO_3	0.05	5.6	0.04
Sulphate	as SO_4	-	0.1	-
Chloride	as Cl	1.1	8.5	2.4
Nitrate	as NO_3	-	-	Trace

WATER ANALYSIS REPORT

Sheet No. 2 of 3

WATER SUPPLY		CLAREDALE	KARUMBA	
		As Pumped	Free Flow	Pumped Flow
GENERAL ANALYSIS	mg/l			
Colour (apparent) Std. Pt. Co. Units		Very low	Very low	Very low
Total ionized salts (calculated)		530	2150	2835
Conductivity at 20°C	µS/cm	625	2950 ±	4075 ±
pH value		8.8	8.4	8.2
Carbonate alkalinity	as $CaCO_3$	22.5	25	15
Bicarbonate alkalinity	as $CaCO_3$	262.5	575	435
Total alkalinity	as $CaCO_3$	285	600	450
Free carbon dioxide	as CO_2	nil	3.5	4.0
pH_s (at $CaCO_3$ equilibrium) at 25°C		7.3	8.0	7.4
Free carbon dioxide (at equilibm.)		25	8.5	22.5
Aggressive carbon dioxide as CO_2		nil	nil	nil
Calcium hardness	as $CaCO_3$	140	15	85
Magnesium hardness	as $CaCO_3$	120	1	40
Total hardness	as $CaCO_3$	260	16	125
Sulphate	as SO_4	Trace	2.5	5
Chloride	as Cl	60	700	1250
Fluoride	as F	nil	16	16
Total iron	as Fe			
DETAILED ANALYSIS	m-equiv/l			
Calcium	as Ca	2.8	0.3	1.7
Magnesium	as Mg	2.4	0.02	0.8
Sodium	as Na	2.2	32.28	42.65
Carbonate	as CO_3	0.45	0.5	0.3
Bicarbonate	as HCO_3	5.25	11.5	8.7
Sulphate	as SO_4	Trace	0.05	0.1
Chloride	as Cl	1.7	19.7	35.2
Fluoride	as F	nil	0.85	0.85

WATER ANALYSIS REPORT

Sheet No. 3 of 3

WATER SUPPLY		JULIA CREEK Artesian Supply	RICHMOND As Pumped	'SPA' WATER As Pumped
GENERAL ANALYSIS	mg/l			
Colour (apparent) Std. Pt. Co. Units		nil	Low	Low
Total ionized salts (calculated)		465	290	1475
Conductivity at 20°C	µS/cm	500	380	1510
pH value		7.6	6.8	6.2
Carbonate alkalinity	as $CaCO_3$	nil	nil	nil
Bicarbonate alkalinity	as $CaCO_3$	225	130	675
Total alkalinity	as $CaCO_3$	225	130	675
Free carbon dioxide	as CO_2	9.5	35	650
pH_s (at CaCO equilibrium)		8.8	8.0	7.1
Free carbon dioxide (at equilibm.)		nil	2.0	80
Aggressive carbon dioxide as CO_2		9.5	33	570
Calcium hardness	as $CaCO_3$	5.0	50	100
Magnesium hardness	as $CaCO_3$	2.5	55	20
Total hardness	as $CaCO_3$	7.5	105	120
Sulphate	as SO_4	5.0	15	70
Chloride	as Cl	47.5	42.5	150
Fluoride	as F	3.0	Trace	nil
Total Iron (as pumped)	as Fe		0.2	
(in reticulation)	as Fe		1.5 - 2.0	
DETAILED ANALYSIS	m-equiv/l			
Calcium	as Ca	0.1	1.0	2.0
Magnesium	as Mg	0.05	1.1	0.4
Sodium	as Na	5.95	2.0	16.75
Carbonate	as CO_3	nil	nil	nil
Bicarbonate	as HCO_3	4.5	2.6	13.5
Sulphate	as SO_4	0.1	0.3	1.45
Chloride	as Cl	1.35	1.2	4.2
Fluoride	as F	0.15	Trace	nil

SUPPORT PAPER O

THE EFFECTS OF RECHARGING PRIMARY SEWAGE EFFLUENT INTO A GRAVEL AQUIFER

J.B. Joseph and W. Liddell

ABSTRACT

A mixed industrial and domestic sewage effluent has been recharged into a Quaternary gravel aquifer at Cilfynydd, in the Taff Valley, for more than eighty years. Recharge is effected through irrigation ditches. It is believed that the alternating periods of recharge and rest resulting from the frequent moving of the ditches has been a major factor in the proven ability of the aquifer to remove pollutants over a long period of time. The acidity and high iron content of the soil may contribute to the removal of phosphates. The quality of the water issuing as seepages and small springs at the end of the recharge field is appreciably higher than that of the recharged effluent, substantial reductions having been made in the concentrations of ammoniacal nitrogen, total oxidized nitrogen, total organic carbon, ortho-phosphate, phenols, anionic detergents and most of the heavy metals. A huge increase in the concentration of iron is ascribed to the leaching of iron from the soil, perhaps by a process similar to podsolization.

1. INTRODUCTION

Since the end of the nineteenth century a proportion of the sewage from Merthyr Tydfil, an industrial centre in the Taff Valley in South Wales, has been brought fourteen kilometres south along the valley to Parc Newydd. Here it is passed through settling tanks and the resulting primary effluent is spread over a series of fields on the river terraces at Cilfynydd.

Merthyr Tydfil has been an industrial centre for more than 200 years; the first blast-furnace was commissioned there in 1759. Although individual firms have come and gone, the overall mix of industry has changed little since the turn of the century. In the very short term the quality of the town's sewage shows considerable variation, comprising as it does not only domestic and industrial wastes but also the output of the storm drainage system. For the same reasons, however, the long term quality has not changed significantly this century. Because of the storm drainage content, and the entry of groundwater along the length of the sewer, the liquors spread over the field at Cilfynydd are more dilute than most primary effluents.

During 1975 and the early part of 1976 an investigation was carried out to determine the efficacy of the local aquifer in removing pollutants from the recharged effluent at Cilfynydd. A series of five boreholes were drilled in the recharged zone in one of the fields to provide groundwater sampling points and to determine the superficial geology in more detail than was previously available. The quality of the input and output of the system was monitored by taking samples from a collector on the distribution pipe and from a spring, one of a series of seeps and springs issuing from the river bank at the edge of the recharge zone. (Figure 1 carries a location map and diagram of the investigation area.) The overall changes in quality between input and output will be covered in this paper, rather than the more detailed changes taking place within the aquifer.

2. GEOLOGY AND HYDROGEOLOGY OF THE AREA

In general the geology at the Cilfynydd site is relatively simple; up to 12 metres of undifferentiated river terrace deposits overlie Upper Carboniferous Pennant Sandstones. In detail the superficial deposits are complex, comprising lenses of silt, sand and gravel commonly up to about two metres thick, and occasionally reaching a thickness of five metres. The strata immediately below the soil contain a slightly greater proportion of gravel than those lower in the sequence. The gravels are estimated to form more than 50% of the terrace deposits in the area under investigation. There is some evidence that the river terrace deposits are separated from the sandstones by glacial boulder clay on the northern edge of the area investigated, but the lateral extent of this boulder clay is not known with any certainty.

The geology and topography of the site indicated that the water table was likely to be close to the surface and to fall towards the west (in the direction of the river). Water level measurements taken when the boreholes were drilled, and on sampling visits thereafter, confirm this picture and show that the water table is between 2.5 and 4 metres below ground level. The superficial deposits are in hydraulic continuity with the underlying sandstones and with the River Taff.

The western edge of the field, which is bounded by a small tributary of the River Taff, is marked by a very steep scarp three to five metres high. At the base of this scarp are a number of small springs and seeps, and it is from the largest of these that the 'output' samples were collected. Because of the extended period of high volume recharge, the anisotropic nature of the aquifer, and certain chemical factors, it is a reasonable assumption that natural groundwaters do not form any significant part of the waters issuing from the scarp base. Figure 2 is a diagrammatic cross-section of the recharge area and shows the assumed hydrogeology.

3. RECHARGE, RAINFALL, ETC.

The effluent is spread across the field in which the investigation was carried out by means of a series of irrigation ditches, the liquors infiltrating through the beds of the ditches. Three primary channels are in continuous use while disposition of the several secondary channels is varied frequently so that a fairly even coverage of the irrigation area is achieved in the long term. As far as the unsaturated zone of the aquifer is concerned the effect is one of alternating periods of recharge and rest. (New secondary infiltration channels are cut when it appears that the existing channels are about to overflow, a condition which is related to the composition of the effluent and the saturation of the soil.)

The maximum rate of discharge through the distribution pipe from the Parc Newydd settling tanks is almost 10 Ml/d, of which around 2.25 Ml/d are recharged through the field investigated. (The discharge pipe almost invariably runs full from the tanks, and any excess flow is discharged direct to the River Taff.)

The nearest rain gauge is at the Cilfynydd CEGB sub-station some two thousand metres to the north east, and one hundred and twenty metres higher in altitude. The average annual rainfall at the sub-station represents a gross volume of recharge through the field of 0.11 Ml/d, whilst the lower than average rainfall during the ten months of the investigation represents a gross volume of 0.072 Ml/d. The nearest points to Cilfynydd for which evaporation figures are available are at Rhoose Airport, Bridgend and Port Talbot, all more than twenty kilometres away. However, on the basis of the evaporation figures provided from these stations the nett volume of recharge from the rainfall during the investigation was 0.045 Ml/d. It can be seen that the average daily volume of natural recharge to the field is negligible when compared to the daily volume of effluent recharged.

4. SAMPLE COLLECTION AND ANALYSIS

Flowing water of a reasonable depth is found at both the spring and the collector on the distribution pipe used for sampling. Because of this it was possible to take representative samples from these points by bailing. Unfortunately it was not possible to carry out bacteriological or virological analyses.

The chemical analyses were carried out in the Welsh National Water Development Authority - Glamorgan River Division's laboratory at Bridgend. Ammoniacal nitrogen, total oxidized nitrogen, nitrite nitrogen, chloride and ortho-phosphate were determined on the Technicon Auto Analyzer (II) System. Alkalinities were determined in accordance with the standard procedure for 'total alkalinity'.

Calcium, magnesium, sodium and potassium were determined by means of a Perkin-Elmer Model 306 Atomic Absorption Spectrometer. Standard additions of lanthanum chloride were made to the samples prior to analysis.

The metals iron, copper and zinc were determined as their soluble forms. After filtration the samples were acidified with nitric acid and concentrated tenfold by evaporation. The metals were determined in the concentrate by Atomic Absorption Spectrometry.

Phenols were determined as total monohydric phenols by the 4-aminophenazone method. The determinations of anionic detergents were carried out by the method described by Slack (1, 2).

Very full analyses were carried out during the first 154 days (6 months) of the experiment, but the number of determinands was reduced considerably for the remaining 103 days (3½ months). Balances have been carried out for all determinands for the 154-day period and for the major determinands for the full 257-day period.

5. EXPERIMENTAL RESULTS AND DISCUSSION

A special survey carried out on the sewage at Parc Newydd at the end of January 1976 showed that the sewage quality varied substantially, even on an hourly basis (3). Because of this there is a very wide range in quality in the samples collected from the distribution pipe; the variation in quality of the spring samples is rather less marked. The number of samples analysed was insufficient for a proper statistical analysis, and some reductions in the sampling schedule have meant that the mean and median concentrations of the determinands do not necessarily give a true picture of the overall quality. Instead, the bulk input and output of the system have been determined (by measuring the area under the concentration vs. time curves) and used in the drawing of conclusions.

Evidence taken from a comparison of rainfall figures with the trace of an autographic water level recorder shows that the recharge waters pass through the unsaturated zone in between two and five days. An attempt to trace the passage of a number of sharp temperature changes and inversions of the magnesium/potassium ion concentration ratio from input to output appears to show that the average retention time of the recharged waters is between one and two months. This time is not particularly long compared to the ten months during which samples were taken, and the bulk figures, although by no means accurate, should give a reasonable representation of the situation.

5.1. NITROGEN, DISSOLVED OXYGEN AND ORGANIC CARBON

Details of the bulk material losses will be found in the appendix; in percentage terms losses were as follows:

	154-day period	257-day period
Ammoniacal nitrogen	61.1%	56.5%
Total oxidized nitrogen	83.1%	79.4%
Nitrogen (total inorganic	63.9%	60.4%
Dissolved oxygen	51.8%	63.3%
Total organic carbon	48.1%	48.5%

Ammonia is lost to the system by oxidation to nitrate. (Any ammonia that is lost by adsorption onto clay or other particles is likely to be part of a conservative cycle, and to replace previously adsorbed ammonia which has since been oxidized and released.) Although the dissolved oxygen content of the recharged effluent only once dropped below 30% saturation, it was never adequate to account for more than 20% of the ammonia oxidized. The rest periods for the aquifer, between recharge, are thus very important as they allow oxidation of the ammonia in the unsaturated zone by atmospheric oxygen (4, 5), and also the replenishment of the atmospheric oxygen in the pores which can oxidize some of the ammonia during the next period of recharge.

As a result of this process the recharge waters entering the saturated zone of the aquifer are rich in nitrates and virtually anaerobic. If sufficient organic carbon is available denitrification can occur, the organic carbon effectively providing the energy for the biological reduction of the oxidized nitrogen. The ultimate products of the denitrification process include nitrogen, nitrous oxide and water under field conditions. The nitrogen and nitrous oxide are released eventually to the atmosphere.

The stoichiometric equation for denitrification shows that at least 0.7 milligrammes of organic carbon are required for the reduction of one milligramme of nitrate nitrogen (4). This condition is more than fulfilled at Cilfynydd, the ratio of organic carbon to nitrogen losses often being in the range between 1.5 and 2.1.

5.2. PHENOLS, ANIONIC DETERGENTS AND ORTHO-PHOSPHATE

The concentrations of phenols, anionic detergents and ortho-phosphates are all markedly reduced during the passage of the recharged effluent through the aquifer. The loss of anionic detergents, between 85 and 95% of input, can almost certainly be ascribed to biodegradation following adsorption in the soil layer (6). Since around 5% of anionic detergents cannot be degraded biologically (7) the efficiency of removal is even higher than it appears. Phenols may also be degraded biologically, although some 15 to 20% passes through the system.

Phosphate removal is generally attributed to the affinity of phosphates for soil particles (8) and the presence of iron may be important because of the formation of insoluble iron salts (9). Removal of phosphate is often found to occur within the first thirty centimetres of the soil sequence, and may be due to the replacement of hydroxyl ions in the clay lattices. It is thought that phosphorus retention is at a minimum when the pH of the soil is between 6 and 7 (8). The pH of the soil at Cilfynydd is between 4.9 and 5.9 (3), and between 80 and 90% of the ortho-phosphate input is removed by the system.

5.3. HEAVY METALS

Determinations were made on a number of heavy metals and, of those which could be detected in the recharged water, most were reduced substantially in concentration before the water reached the spring; for example, copper and zinc removal over the 154-day period was 66 and 77% respectively.

The concentrations of copper and zinc in the soil at Cilfynydd (3) are, in each case, sufficient to account for more than twice the amount of material lost from the liquors, if the calculated losses during the investigation are assumed to be representative of the losses during the entire eighty-year recharge period.

Iron was somewhat unusual in showing an overall fourteen-fold gain between input and output - concentrations averaged over the 154-day period. The concentration of iron, as Fe, runs as high as 2.9% in some parts of the field, and was not below 1.7% in any of the samples collected (3). It is likely that leaching of iron from the soil, by a process similar to podsolization, has led to the overall gain in iron. The amount of iron gained represents about 1% of the average iron content existing at present in the top ten centimetres of soil in the field.

5.4. CHLORIDE ION AND ALKALINITY

The results of the chloride analyses show a nett gain in the system of 22% for the 154-day period and 7% for the 257-day period. The most probable explanation of this phenomenon is that salt spread on the roads of Merthyr Tydfil during cold spells, and entering the sewer through the street drains, appeared in the spring samples although sampling started too late for it to be found in the settled liquor. There was a prolonged cold spell three weeks before the start of the sampling schedule, but there was little cold weather during the period of the investigation. It must be said, however, that part of the apparent gain almost certainly results from the inherently large approximations made in the calculations.

The small reductions in alkalinity, less than 4%, tend to confirm that the spring waters are derived almost solely from recharged sewage effluent (10).

6. CONCLUSIONS

The analytical results show that the quality of the sewage effluent from Merthyr Tydfil is considerably improved by artificial recharge through the superficial deposits at Cilfynydd. Phosphates and heavy metals, except for iron, seem to be removed by adsorption in the top layers of the soil. Iron appears to be leached from these same horizons. Phenols and anionic detergents are removed by biodegradation, as is around 50% of the incoming organic carbon. A large proportion of the ammoniacal and oxidized nitrogen recharged is removed, the ammonia being oxidized to nitrate and then denitrified together with the existing oxidized nitrogen. The chloride figures confirm the general finding that there is no loss of chloride from percolating waters (8, 10).

The system whereby the infiltration ditches are moved at regular intervals, thus giving the aquifer alternating periods of rest and recharge, appears to be an important factor in the ability of the aquifer to remove pollutants over a very long period.

ACKNOWLEDGEMENTS

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Department of the Environment, through the Central Water Planning Unit, and the Water Research Centre. The work was carried out under the overall guidance of Mr K. J. Edworthy.

A full report on the investigation has been prepared for the Central Water Planning Unit.

APPENDIX

BULK CHEMICAL BALANCE SHEET

	154-day period			257-day period		
	in	out	loss	in	out	loss
Organic carbon	13.1	6.8	6.3	17.1	8.8	8.3
Ammoniacal nitrogen	4.63	1.8	2.83	6.42	2.79	3.63
Total oxidized nitrogen	0.71	0.12	0.59	1.31	0.27	1.04
Nitrogen (total inorganic)	5.34	1.93	3.41	7.73	3.06	4.67
Dissolved oxygen	1.7	0.82	0.88	3.62	1.33	2.29
Phenols (as C_6H_5OH)	0.016	0.003	0.013			
Anionic detergents (as Manoxol OT)	1.31	0.1	1.21	1.97	0.2	1.77
Ortho-phosphate	0.64	0.07	0.57	0.84	0.12	0.72
Copper (x 10^{-3})	8.9	3.0	5.9			
Zinc	0.047	0.011	0.036			
Iron	0.17	2.57	-2.4			
Chloride ion	13.2	16.1	-2.9	25.5	27.3	-1.8
Alkalinity (as $CaCO_3$)	53.0	52.9	0.1	86.1	82.6	3.5

Notes

1) All measurements are in tonnes. Values in the 'loss' columns preceded by a minus (-) sign represent nett gains to the system.

2) The values against 'Nitrogen (total inorganic)' are the sums of the values for ammoniacal and total oxidized nitrogen in the same column.

3) Determination, on a regular basis, of Phenols, Copper, Zinc and Iron was discontinued after 154 days.

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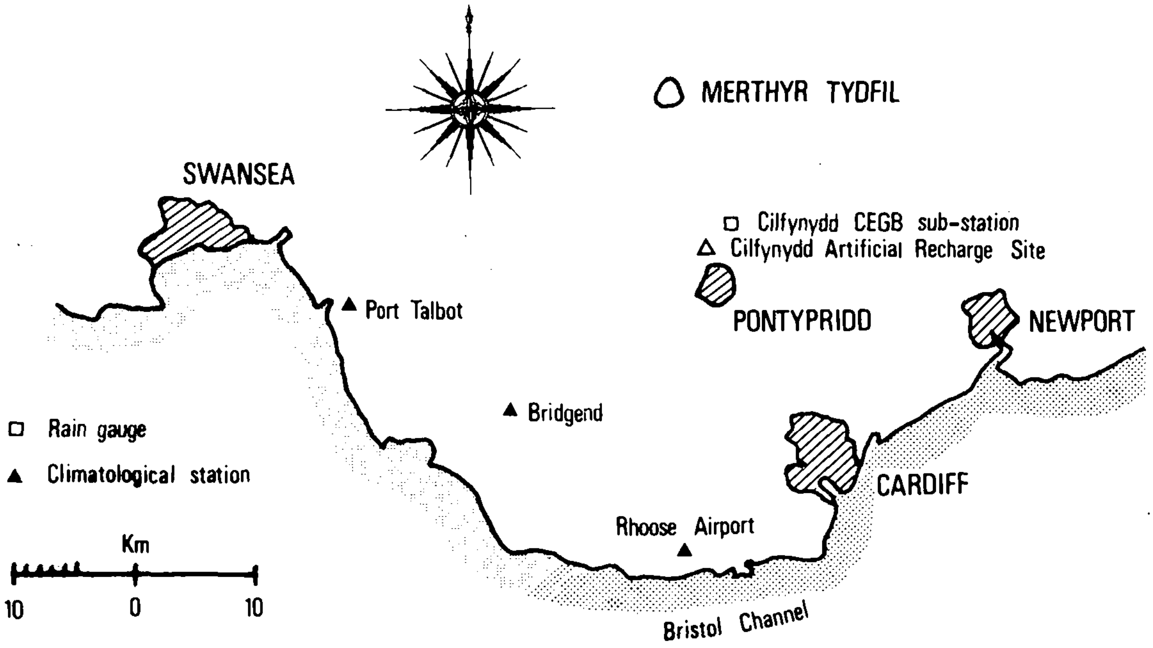
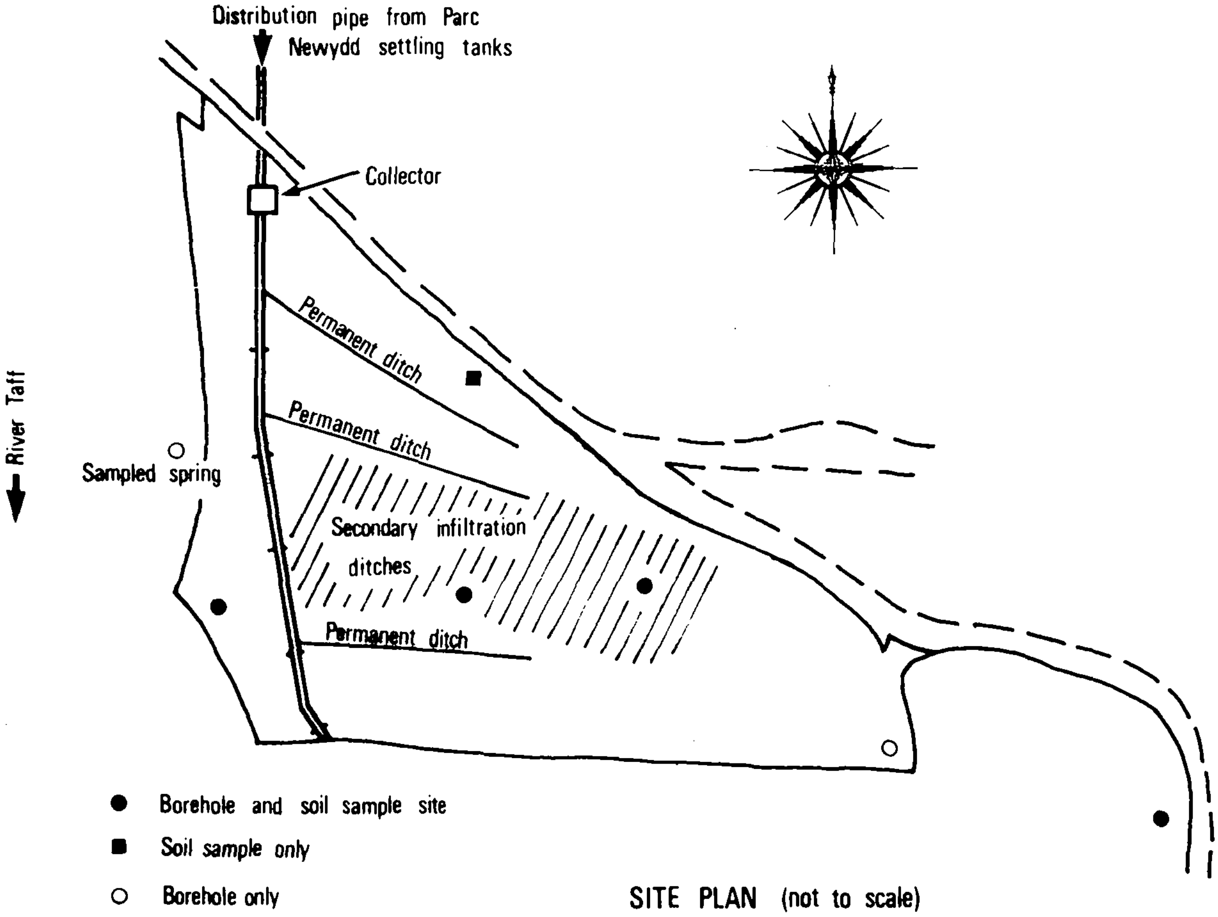


LOCATION MAP



SITE PLAN (not to scale)

Figure 1. Location map and diagram of the field investigated at Cilfynydd

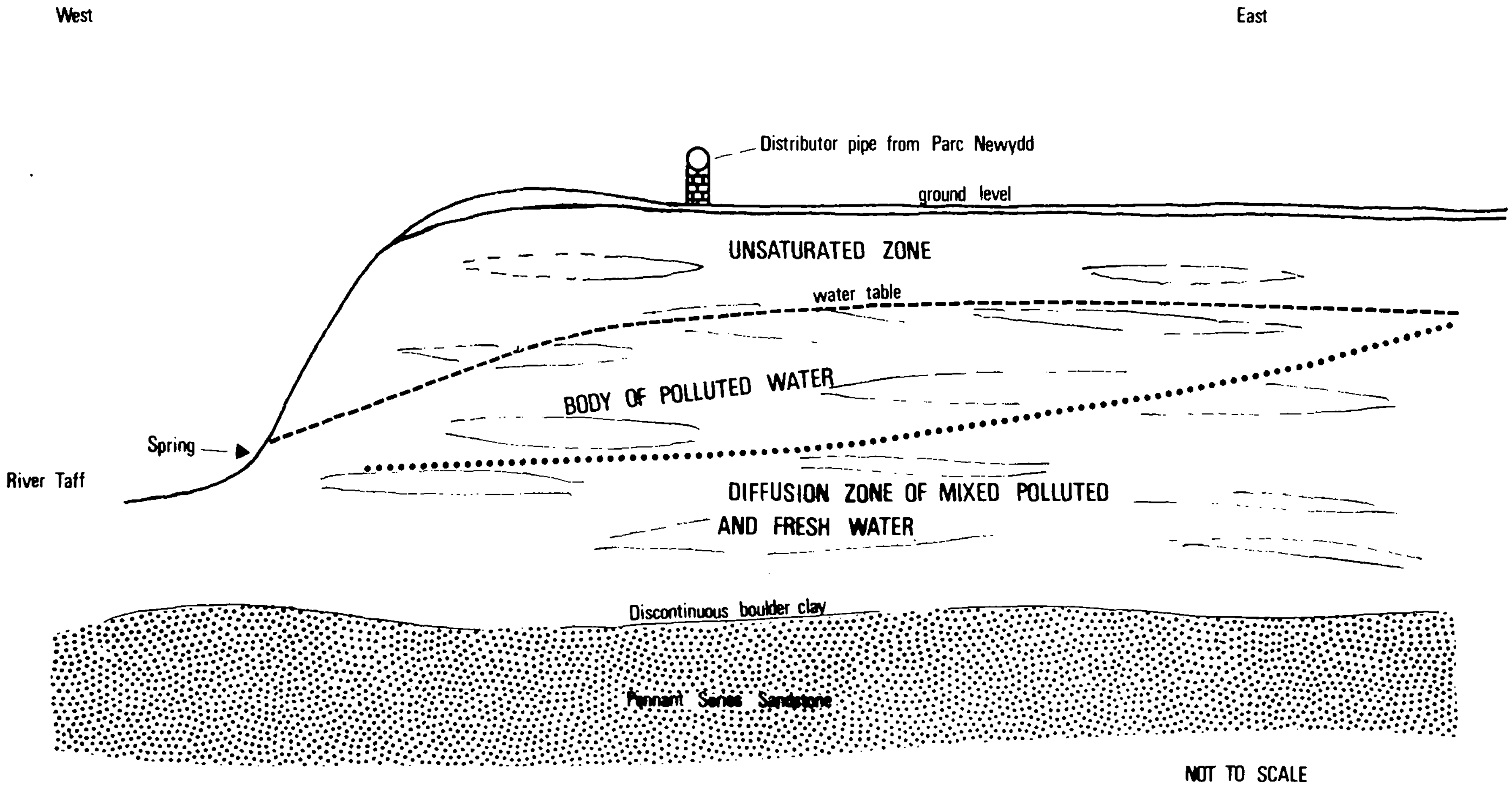


Figure 2. Diagrammatic section of the recharge site at Cilfynydd

SUPPORT PAPER P

SEWAGE WATER INFILTRATION AND THE SUBSEQUENT CHANGES IN GROUNDWATER QUALITY REGISTERED IN HET GOOI (THE NETHERLANDS)

W.R. Groenendijk, L.J. Hendriks, J. van der Laan and A.J. Roebert.

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1. INTRODUCTION

The northwestern part of the ice-push ridge formed during the Riss Glaciation - at least that part of it which is still visible at the surface - is called Het Gooi (Figure 1). At its highest points the ridge comes up to 25 m + O.D. In the area now under discussion the surface level is between 5 m and 10 m + O.D. The areas immediately to the east and west of the ridge are approximately at O.D. level. The recharge of sewage water has been going on since 1875 in the so-called 'Wasmeren', east of the town of Hilversum. Originally the sewage water was not treated before infiltration; later, partial pre-purification was introduced.

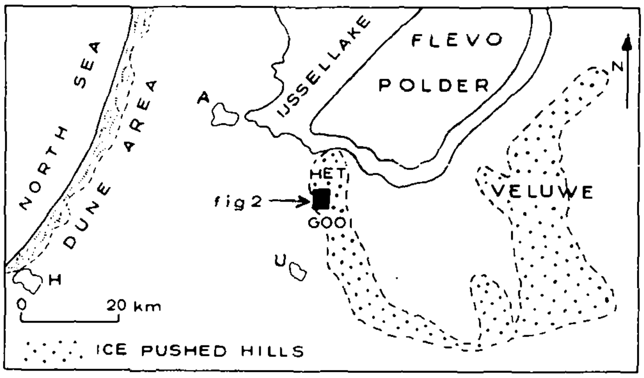

Figure 1. Ice-push ridges in the Central Netherlands

In 1888 a groundwater pumping station (P.S. Hilversum) for Amsterdam was put into operation. Another pumping station (P.S. Laren), for Hilversum, started work in 1901. The two stations are located 1500 m to the north-west of the Wasmeren (Figure 2).

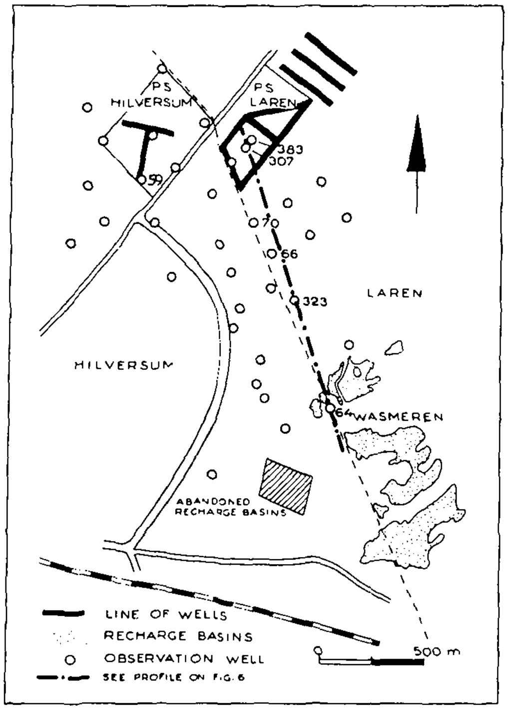

Figure 2. Layout of Wasmeren area and position of the observation wells.

We do not know exactly at what time the operators of this system awoke to its flaws. We do know, however, that in 1912 the town council of Hilversum rejected, on sanitary grounds, a proposal for a drastic extension of the recharge basins.

Since 1970 the town of Hilversum has developed and put into operation a system for the purification and disposal of sewage water. This no longer includes infiltration into the soil.

The present article discusses the infiltration of sewage water and the changes it undergoes in the soil. While preparing the material for this article the authors found that the data available so far are not sufficient as a basis for a more detailed study. The present article may serve as an introductory survey of observations carried out until now.

2. HYDROGEOLOGICAL SITUATION

To a depth of 160 m - O.D. the subsoil of Het Gooi is made up of alternating layers of medium coarse sands of good permeability and finer-grained sands. The sands are of Pleistocene origin and were pushed to 60 m - O.D. during the Riss Glaciation.

The whole complex functions as a single aquifer, with a transmissivity of about 5000 m^2/day, the sand itself having a permeability of about 30 m/day. Precipitation minus evaporation in Het Gooi is circa 350 mm. The water moves from the recharge area towards the pumping stations at a speed of about 30 m a year. The specific yield of the Pleistocene sands is generally put at between 0.35 and 0.40. Groundwater analyses show the presence of infiltrated sewage water at the very bottom of the aquifer, even straight under the recharge basins. This proves that the sandlayers have a good vertical as well as horizontal permeability. The aquifer rests on the clay layers of the Tegelen and Icenian formations. Figure 3 shows two isopieze maps of the area; one for 1914, the other for 1970.

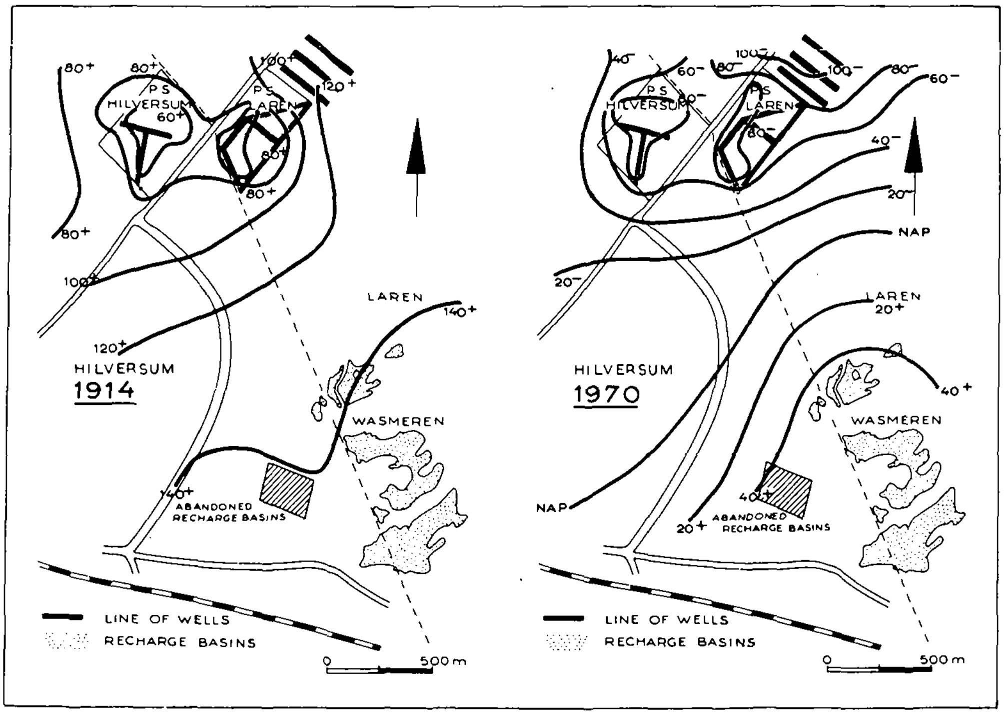

Figure 3. Isopieze maps of the groundwater in 1914 and 1970

3. A FALLING GROUNDWATER LEVEL

The isopieze maps show the groundwater level to have declined about one metre between 1914 and 1970. This is due to a variety of causes:

a. Groundwater extraction by water supply companies and industry.
b. The extension of the total hard-surface area (roads and buildings) and the operation of a central sewage system.
c. The increase of woodland in the catchment area.
d. The lowering of the controlled water level in the polders surrounding Het Gooi.
e. The possible effects of the big reclamation project just north of the catchment area.
f. The possible effects of sand excavation.

To complete the picture, we must add that perhaps a slight recovery of the groundwater level occurred after the closing in 1932 of the great dam which cuts off the Ijsselmeer from the direct influence of the North Sea. Also, the particular groundwater levels in 1914 and 1970 will to some extent correlate with the meteorological situations at those particular times. The natural fluctuation of the groundwater level in the area is between 0.5 and 1 metre.

4. GROUNDWATER EXTRACTION AND RECHARGE BY INFILTRATION

Over the years, the two pumping stations have increased their output as follows:

Extraction in	P.S. Laren	P.S. Hilversum
1905	0.5 million m^3	0.9 million m^3
1925	1.9 million m^3	1.1 million m^3
1950	5.0 million m^3	1.7 million m^3
1975	7.2 million m^3	1.9 million m^3

With respect to the extraction of groundwater by industry in the Hilversum area we have very little detailed information, but we estimate that this has by now increased to something like 1.5 million m^3 a year.

Water taken from wells in the Hilversum town area indicates pollution of the groundwater there. Finally we note that the annual quantity of sewage water infiltrated in the Wasmeren was about 1.5 million m^3.

5. TYPICAL WATER ANALYSES

The table below shows a number of recent groundwater analyses. At the end of this article we give some information on the differences registered.

			1	2	3	4	5	6
Conductivity	µmho	cm^{-1}(20°C)	860	600	690	160	380	280
pH			7.6	6.7	6.7	8.2	7.6	8.1
Organic matter (expressed as mg/l $KMnO_4$ consumed)			130	90	21	1	5	3
Oxygen	O_2	p.p.m.	1-2	<1	<1	6	2.3	3
Chloride	Cl^-	p.p.m.	92	110	120	15	39	23
Nitrate	NO_3^-	p.p.m.	0.4	1.0	<0.5	<0.5	2.0	14
Sulphate	SO_4^{--}	p.p.m.	62	83	4	9	16	20
Bicarbonate	HCO_3^-	p.p.m.	335	73	245	67	170	105
Free Carbon dioxide	CO_2	p.p.m.	18	43	83	1	12	1
Phosphate	PO_4^{---}	p.p.m.	35	0.2	0.40	0.07	0.02	0.19
Ammonium	NH_4^+	p.p.m.	36	28	14	<0.05	0.17	<0.05
Calcium	Ca^{++}	p.p.m.	57	6.0	38	28	62	39
Magnesium	Mg^{++}	p.p.m.	9.0	2.8	2.8	1.2	3.9	3.4
Sodium	Na^+	p.p.m.	89	90	98	8,5	23	19
Potassium	K^+	p.p.m.	16.5	13.5	3.6	0.6	1,3	1.4
Hardness		meq/l	3.60	0.55	2.15	1.50	3.40	2.21

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1. infiltrated sewage water
2. bore 64, filter 4 (14 m - O.D.)
3. bore 323, filter 3 (70 m - O.D.)
4. original groundwater (40 m - O.D.)
5. P.S. Laren (mixed raw water)
6. P.S. Hilversum (mixed raw water)

6. CHANGES IN WATER QUALITY AT THE PUMPING STATIONS

Figure 4 shows a striking change in quality of the water extracted by the two pumping stations. The P.S. Hilversum registers a steep rise in nitrate and also sulphate content and a moderate one in chloride content.

The rise in nitrate content occurs with the rapid spreading of residential areas since the 1930's. Leaking sewers and other sources pollute the groundwater in the upper part of the aquifer. In the aerobic zone the ammonium is oxidized to nitrate.

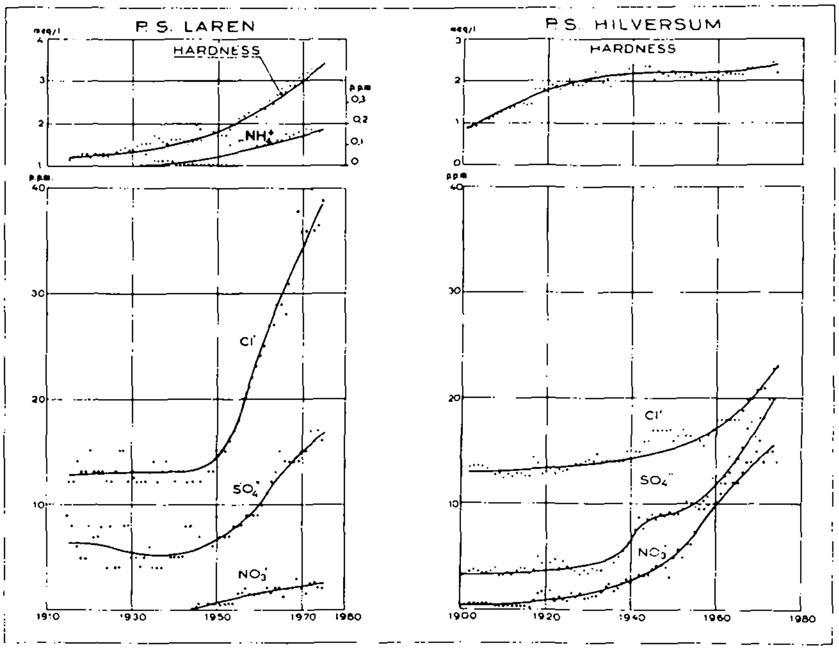

Figure 4. Evolution of the water quality in the pumping stations

The quality changes registered at the P.S. Laren are of a quite different nature. The years around 1950 show a marked rise in chloride content, with a less marked rise in hardness and sulphate content.

The slight rise in hardness before 1950 must be imputed to extraction of deeper groundwater while the chloride content remains more or less the same. In contrast with P.S. Hilversum the P.S. Laren registers only a slight increase in nitrate content. The high chloride content particularly indicates that the main pollution source of the water at Laren is the infiltrated sewage water, which used to contain more waste products than the water infiltrating under Hilversum.

7. THE SPREAD OF THE INFILTRATED WATER

In 1934 the Netherlands Government Institute for Drinking Water Supply published a report, warning that the recharged sewage water would inevitably reach the abstraction sites. According to the report, the infiltrated water would reach the pumping stations by the year 1970. Increased extraction at the station has, of course, accelerated the process. Figure 5 is based upon a combination of the available data; it shows the moving boundaries of both the high chloride content groundwater and high ammonium content groundwater.

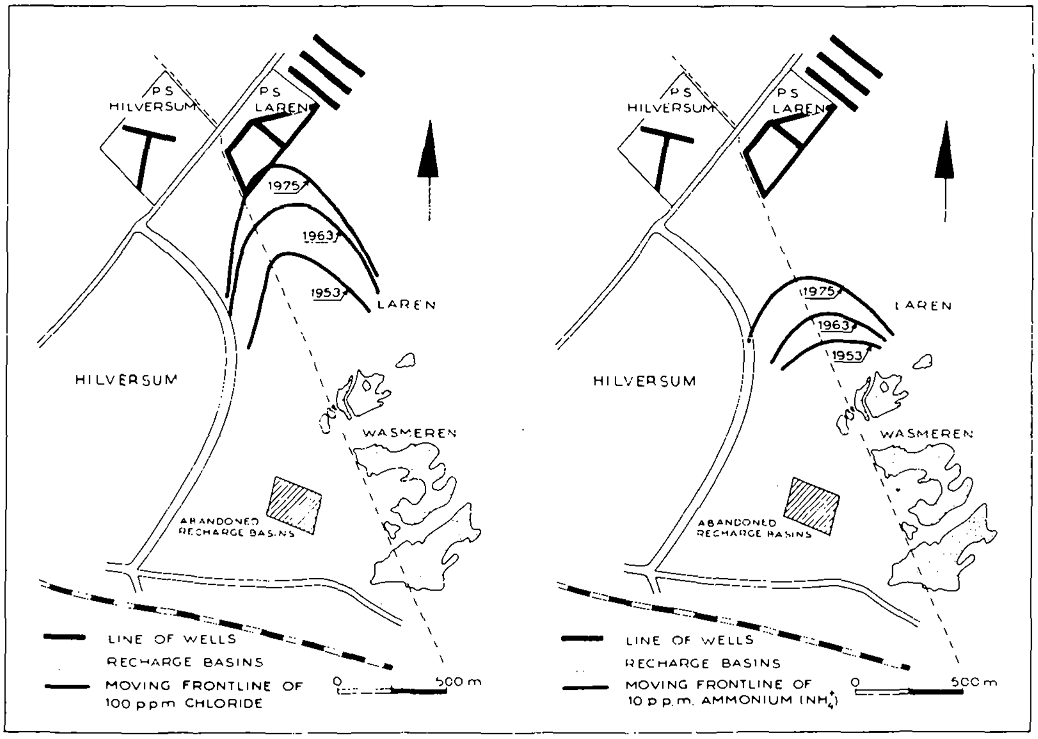

Figure 5. Moving boundaries of chloride and ammonium

As we pointed out before, the data - although obtained through intensive sampling - are still incomplete, so that some reservations have to be made as to the exact positions of the chloride and ammonium fronts. Even so, the following table is remarkable enough.

Progress of the fronts in 10 years halfway between the recharge area and the abstraction area

According to hydrological calculations:	300 m
Movement of the 100 p. p. m. chloride front:	250 m
Movement of the 10 p. p. m. ammonium front:	200 m

The chloride is not converted in the soil and is subject only to diffusion and dispersion. The latter processes have apparently caused the observed retardation in the movement of the front. They also slowed down the ammonium front, the progress of which was further restricted by oxidation, to 200 m in ten years.

Until about 1950 the chloride content of the water at the P.S. Laren ranged between 12 and 15 p.p.m.; the rather dramatic change at this point (see Figure 4) must be imputed to the arrival of the first infiltration water at that abstraction site. Most of the other observation wells are not deep enough to yield any information about the downward movement of the recharged sewage water. But water samples drawn from a new bore, No. 323, showed the influence of the water down to a depth of 160 m - O.D., halfway between the recharge area and the abstraction area. This is illustrated by Figure 6, which represents a vertical profile with isochloride lines for 30, 60 and 100 p.p.m. drawn in for the year 1975.

Figure 6 clearly shows how the infiltration water is forced down to deeper layers by precipitation and how it is drawn up to some extent by the rather shallow wells of the P.S. Laren. Most of the other substances in the groundwater are more or less subject to change. The behaviour of ammonium in groundwater is of special importance. High ammonium levels are found in the infiltration water and in some of the observation wells.

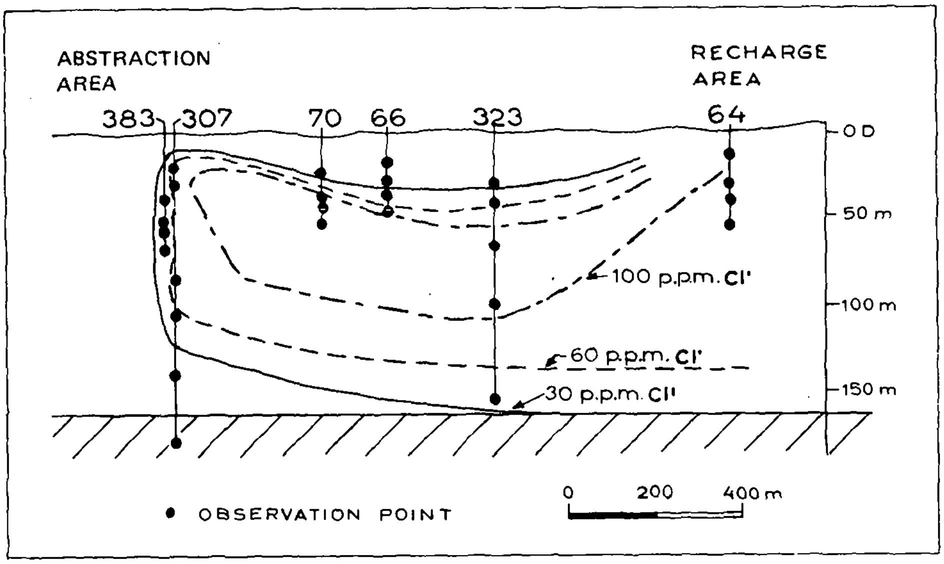

Figure 6. Vertical profile with isochloride lines

8. CHANGES IN WATER QUALITY

The present isopieze picture indicates the progress of the water from the recharge area to the abstraction area. As the quantity of water extracted exceeds largely that of the water recharged it is obvious that natural groundwater is attracted as well. A quantitative survey of the changes of the chemical parameters in the groundwater is not yet possible, the main obstacles being:

a. The major changes in quality of the sewage water.
b. The great and varying size of the recharge basins.
c. The complex hydrological structure of the area.
d. The relatively small number of observation wells and groundwater analyses, due to which it takes years before the water has moved from one observation point to the next, a time-lag which greatly complicates comparison of observation data.

With respect to the last point it must be noted that the analysis of the effluent of the sewage water treatment plant took account of chloride, ammonium and phosphate only. In the table on page 5* the typical analyses of a few relevant water varieties are given. The conclusions mentioned below are based on more data than just those shown in the table on page 5.*

*Now page 550

When it arrives at the filter (at O.D. - 14 m) of observation well 64, which is nearest the recharge area, the effluent, which has then travelled for anything from less than a year up to several years, appears to have changed considerably already. For one thing, virtually all of the phosphate has disappeared. It may have been deposited in the soil as ferrous phosphate or as calcium phosphate, or as apatite. Furthermore, most of the calcium appears to have precipitated (reducing the calcium content from 57 p.p.m. to only 6 p.p.m.).

If the water tends to deposit the calcium (in this case at a value of $pH > 7.7$) it may be deposited as calcium carbonate. With lower pH values deposition as calcium phosphate seems possible. If the soil contains loamy sands there may be an exchange of calcium for sodium. Most remarkable at this point, however, is the fact that circa 10 p.p.m. ammonium has been converted. If we assume that the ammonium is oxidized in the soil, the question arises where the huge quantities of oxygen needed to support such a reaction come from. Also, there is a decrease in bicarbonate content and an increase of free carbon dioxide. Both findings would be in agreement with the aforesaid reactions. At a distance of some 600 metres from the recharge site and a depth of 70 m the main changes from observation well 64 are:

- calcium, free carbon dioxide and bicarbonate increase again
- sulphate shows a slight decline (sulphate reduction)
- ammonium, chloride and the permanganate value remain virtually constant.

The travel time between recharge and observation well 64 is more than 20 years. Any nitrate formed on the way is reduced to nitrogen under anaerobic conditions (denitrification), which accounts for the very low nitrate content of the infiltrated groundwater.

9. CONCLUSION AND ACKNOWLEDGEMENT

During the travel time in the subsoil the quality of the partially purified sewage water is considerably improved in the original aerobic subsoil zone of Het Gooi. So far, we do not know how long the subsoil keeps its purifying character.

In view of the very slow movement of the underground water there is no question whatsoever of an immediate threat as far as the purification of drinking water is concerned.

It would not have been possible to write this article without the help of a great many former and present employees of both companies and of the town of Hilversum who spared no pains in doing a lot of sampling, taking observations and explaining the phenomena.

SUPPORT PAPER Q

AN INVESTIGATION INTO GROUNDWATER POLLUTION FROM A COW SLURRY LAGOON

C. Chumbley, Mrs E. Gray and M. Appleton

1. INTRODUCTION

There are many large dairy farms on the Chalk land of southern and eastern England. Organic wastes from the dairy herds include manure or slurry and various wash waters, and these accumulate daily. The approximate volumes of these wastes for a 100 cow herd are indicated in Table 1. In some dairying systems the manure or slurry is kept separate, leaving the relatively lightly polluted water to be spread on the land or possibly treated in a barrier ditch system. In other systems the wash waters and the manure slurries are mixed and the resulting large volumes of dilute slurry are spread on the land, either by irrigation equipment or by tanker spreading.

Storage is almost always needed as it is very rarely possible to spread every day, and on many farms several months of storage is required. Storage may be in above-ground tanks but this is rather expensive and more commonly an excavated earth banked pit, often called a lagoon, is used. The question arises as to whether the pit should be lined or not. Since these are often not lined, the possibility of groundwater pollution must be considered.

Table 1. Typical volumes of liquid wastes produced daily on a dairy farm with 100 cows

Source of liquid waste	Volumes (litres)
Manure slurry	4 000
Washings from milking parlour and milking plant	3 000
Washings from dirty concrete in collecting yard, including rain	2 500

Whenever cow slurry is stored, three layers form, a top layer of floating fibrous material, a middle layer with relatively low total solids content, and a layer of wet sludge on the bottom. There is some evidence from farming practice that this sludge layer will seal up pores and fissures in subsoils and rocks, so that it does not necessarily follow that an unlined lagoon in pervious rock represents a continuous contamination threat to groundwater.

2. SITE DESCRIPTION

The Ministry of Agriculture, Fisheries and Food maintains a number of experimental husbandry farms (EHFs) as part of its advisory service for farmers (The Agricultural Development and Advisory Service), and one of these is Bridgets EHF near Winchester, Hants. It is a large (420 ha) dairy and arable farm where the soils are developed on Upper Chalk strata. Dilute slurry from the farm's 300 cows was spread by irrigation equipment until recently but from the autumn of 1975 it has been put into a large unlined lagoon excavated into the Chalk by enlarging a derelict chalk quarry. The lagoon is at an elevation of 114 m above O.D., at the top of a slope which runs down to the River Itchen. The diameter of the roughly circular lagoon is approximately 35 m, and the depth when full is 3 m on one side and 1 m on the other. The floor was sloped to allow more complete emptying, and a ramp left to allow plant access, in case it were ever necessary.

The geology of the Bridgets Farm area is described in detail by Young et al (1) from which it will be seen that Bridgets Farm is situated on Upper Chalk on the north side of the Itchen valley syncline. The Marsupites testudinarius zone of the Upper Chalk, a soft, very fine, white chalk with many echinoderm fragments, and plentiful small sporadic flint nodules underlies the northern part of the farm. Underlying this zone is the Micraster coranguinum zone, which is also a soft white chalk with many, usually large, flint nodules. On inspection of the empty pit a few very small and fragmented flints were found and it is believed that the pit is therefore in the lower part of the Marsupites testudinarius zone. The dip was difficult to ascertain but from the few flints observed the strata appeared to be virtually horizontal.

3. GROUNDWATER CONDITIONS

In order to monitor groundwater pollution a permanent borehole was drilled to 15 m below the water table at a point approximately 100 m east-south-east of the lagoon at a position as near as possible to the line of groundwater flow (see Figure 1). The borehole was drilled in July 1975 and was lined with uPVC to 2 m below the water table. The lining was grouted in with cement grout to prevent vertical flow down the outside of the lining.

A second temporary borehole was auger drilled to 20 m at a point approximately 20 m south of the pit (see Figure 1) in September 1975 to obtain the background nitrate concentrations of the interstitial water (Table 2). Disturbed samples were taken every metre and the borehole was backfilled on completion.

Table 2. Nitrate concentrations of interstitial water in borehole near lagoon

Depth (m)	NO_3 - N mg/l
0 - 1	31.8
1 - 2	14.0
2 - 3	22.1
3 - 4	15.6
4 - 5	16.1
5 - 6	7.3
6 - 7	7.1
7 - 8	6.7
8 - 9	7.4
9 - 10	11.5
10 - 11	11.2
11 - 12	11.3
12 - 13	10.3
13 - 14	10.8
14 - 15	11.8
15 - 16	12.6
16 - 17	11.8
17 - 18	11.6
18 - 19	11.3
19 - 20	11.3

An autographic chart water level recorder has been installed on the observation borehole since November 1975. Groundwater levels in the area did not rise generally in the winter of 1975/76 and apart from slight recharge in December 1975 there has been a steady decline in water level in the borehole from 52.4 to 51.7 m A.O.D. (Table 3).

Table 3. Borehole water levels

Date	Water Levels	
	Metres below surface	Metres A.O.D.
27.8.75.	58.10	52.42
28.11.75.	58.31	52.21
17.12.75.	58.09	52.43
16.1.76.	58.20	52.32
24.2.76.	58.48	52.04
23.4.76.	58.69	51.83
12.5.76.	58.80	51.72

From groundwater level observations taken since 1963 by Southern Water Authority at a borehole 2 km to the north of the farm, the annual regional fluctuation is normally about 3 - 4 m per annum (2). However, there was only slight recharge in the winter of 1975/76 and the levels listed above are similar to those obtained elsewhere in the area.

The water table below the pit is estimated at about 52 m O.D., approximately 62 m below ground level. The bottom of the pit is about 3 m deep so that the water table will normally be between 55 and 63 m below the base of the pit.

4. EFFECTS OF SLURRY DISPOSAL

When starting to fill the lagoon in mid-August 1975 it was observed that a great deal of liquid was lost, but by the end of November the pit was full and it remained full, apparently without further loss. A floating layer of solids formed which gradually thickened. The volumes of slurry put into and taken out of the pit each month were recorded, but it must be emphasized that the volumes are approximate and conclusions drawn are tentative. A total volume of 2 240 m^3 of slurry was put into the pit from mid-August 1975 to the end of November 1975 and none was taken out. If rainfall and evaporation are ignored, and the volume of the pit when full is taken as 1380 m^3, the volume of liquid lost to the groundwater was 860 m^3. It is almost certain that a sludge layer of very low permeability had formed on the bottom by the end of November, impeding the movement of liquid into the Chalk.

The borehole water has been sampled about once a month and the samples analysed for phosphorus, potassium, sodium, chloride, sulphate-S, ammonium-N, and nitrate-N. The pH and specific conductivity were also recorded. The samples have been drawn from the bottom of the water column, and in all cases the samples have been clear and bright once the chalk sediment has settled. The nitrate-N was determined using an Orion nitrate electrode and a Pye 290 pH meter. Ammonium-N was determined by a distillation method and the sulphate-S determinations gravimetrically. The analytical results are shown in Table 4 and it is clear that no important changes in the composition of the water have occurred so far. Nitrate-N has remained steady at about 5 mg/l.

Table 4. Chemical analysis results

Date sampled	pH	P (mg/l)	K (mg/l)	Na (mg/l)	Cl (mg/l)	SO_4 (mg/l)	NH_4-N (mg/l)	NO_3-N (mg/l)	Cond (μmhos)
27.8.75.	7.4	0.003	1.38	8.4	13.0	8.2	0.44	5.5	351
6.11.75.	7.3	0.007	1.50	8.4	15.1	4.3	0.10	5.4	499
17.12.75.	7.7	0.016	2.57	9.2	17.8	-	0.10	3.8	474
16.1.76.	7.2	0.004	0.77	8.7	14.9	3.2	0.10	6.1	442
24.2.76.	7.2	0.011	0.62	7.6	14.0	3.8	0.28	3.9	449
24.3.76.	7.6	0.012	0.35	6.5	12.9	4.8	0.23	4.2	448
12.5.76.	7.2	0.005	0.72	6.8	13.1	3.7	0.30	4.4	442

The effect of any pollution of the groundwater is likely to be observed first in the conductivity and chloride, and if there is any sign of increase in these it is hoped also to monitor the Chemical Oxygen Demand of the water samples.

5. DISCUSSION

From the work done by the Water Research Centre in assessing the movement of liquid from the ground surface to the water table in this area (1), an estimated 10% of infiltration moves along the fissures, with 90% moving through intergranular flow. With a constant head pressure such as that developed at the pit before formation of a crust the percentage of fissure water movement may be greater. Fissure water movement has been estimated as 0.6 m/day (1), so that the water containing pollutants from the pit may be expected at the water table vertically below in about 100 days from the start of infiltration. The horizontal movement will be mainly in the direction of groundwater flow, and as noted before may not be towards the observation borehole (Figure 1). Taking the estimates of aquifer properties given by Young et al (1976) and assuming a local groundwater gradient of 8×10^{-3}, and an effective porosity of 0.02 for the Chalk, transit times from a point beneath the lagoon to a distance of 100 m along the line of groundwater flow would be 2 to 5 days. As the one observation borehole is not exactly in the direction of natural groundwater flow, it is not expected that pollutants will be observable for some time. It may therefore be necessary to pump from the borehole to change the groundwater flow and draw the pollutants to the sampling point.

The concentration of pollutants from an unlined slurry pit on Chalk will of course be greatly reduced by dispersion, and much of the liquid will be stored in the unsaturated zone. At Bridgets Farm the unsaturated zone of over 55 m is very thick, but at other sites the unsaturated zone may be thinner and pollution of the groundwater could be more rapid.

6. SUMMARY AND CONCLUSIONS

A large pit to store cow manure slurry has been dug in Upper Chalk strata at Bridgets Experimental Husbandry Farm near Winchester, Hants. The pit is unlined and at first lost liquid down fissures in the chalk, but after a few months its base became almost impermeable with slurry solids. A borehole constructed nearby has been lined to the water table and sampled monthly and has not yet shown evidence of groundwater pollution. Monitoring for several years and possibly a short pumping test will be needed before it is certain that no pollution of the groundwater has occurred.

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2.	HMSO	Groundwater Year Book 1967. HMSO, 1970, 176 pp.

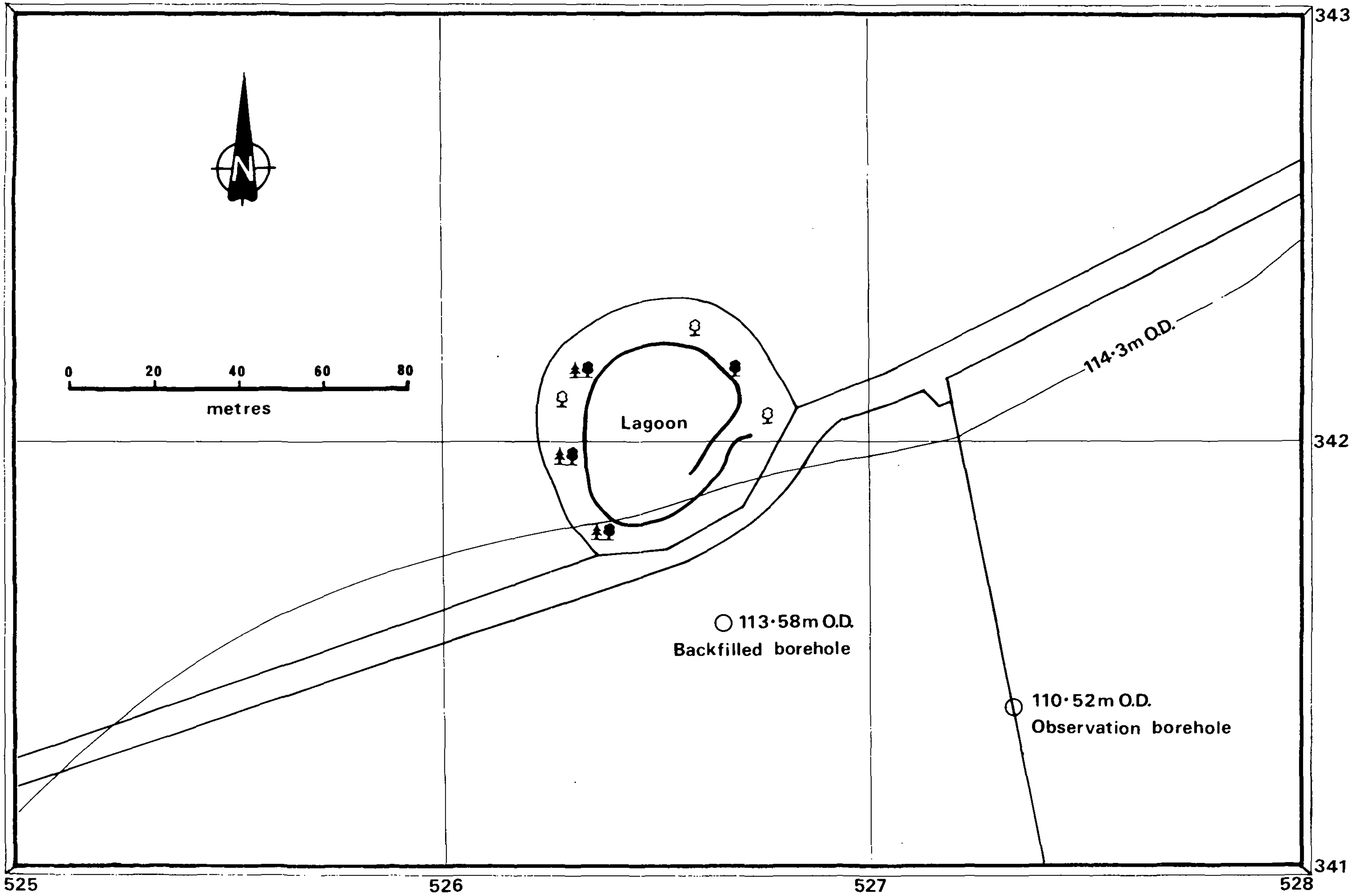

Figure 1. Positions of slurry lagoon and observation boreholes at Bridgets Farm.

SUPPORT PAPER R

GROUNDWATER CONTAMINATION BY HEAVY METALS LEACHED FROM WASTE DISPOSAL DEPOSITS

A. Golwer, G. Mathess and W. Schneider.

ABSTRACT

At three waste sites in the Frankfurt area (Federal Republic of Germany), the contents and behaviour of As, Pb, Cu, Zn, Cd, Cr, Ni, Hg and Ag within the contamination plumes are investigated together with other trace elements.

Under given hydrogeological conditions, a groundwater flow distance of 150 - 200 m yields unhazardous quantities.

1. INTRODUCTION

From 1967 - 1973 the influences of three waste deposits in the area surrounding Frankfurt were examined.

Site A: area: 24 000 m^2; volume: 240 000 m^3; contents: garbage and construction rubble.

Site B: area: 260 000 m^2; volume: 18 300 000 m^3; contents: garbage, construction rubble and - to a lesser extent - industrial waste.

Site C: area: 64 000 m^2; volume: 600 000 m^3; contents: garbage, industrial waste and sewage sludge.

The programme of analyses covered numerous determinations of not only the usual major constituents and other physico-chemical data, but also organic substances and the heavy metals As, Pb, Cu and Zn. At Site B determinations of Cd, Cr, Ni, Hg and Ag were made as well.

All waste sites are underlain by porous, non consolidated, unconfined aquifers (Quaternary sand and gravel). The average groundwater velocity being less than 1 m/day through the deposits, the contaminated groundwater plume is purified over a distance of some hundred metres by means of dilution and self-purification processes. These include geochemical and biological processes, under the influence of nearby surface-waters and air permeating into the aquifer strata above the groundwater table.

With concentrations of dissolved oxygen increasing with distance downstream of the source of contamination, respective zones may develop of anaerobic and aerobic organisms separated by a transition zone.

Cessation of dumping caused a decrease in organic pollution and a positive shift of redox-potential during the first three years. The observation period was too short for a general statement in respect of the longterm behaviour of the contaminated zone after cessation. Considering the observations at other waste sites, a decline of the inorganic contamination could be expected (for detailed information refer to Golwer et al. (1976)).

2. RESULTS

Although industrial wastes are present in high proportion at Site C, where groundwater is in permanent contact with the deposit, the heavy-metal contents (with the exception of As = 0.04 mg/l) are lower than downstream of Site B (Figure 1).

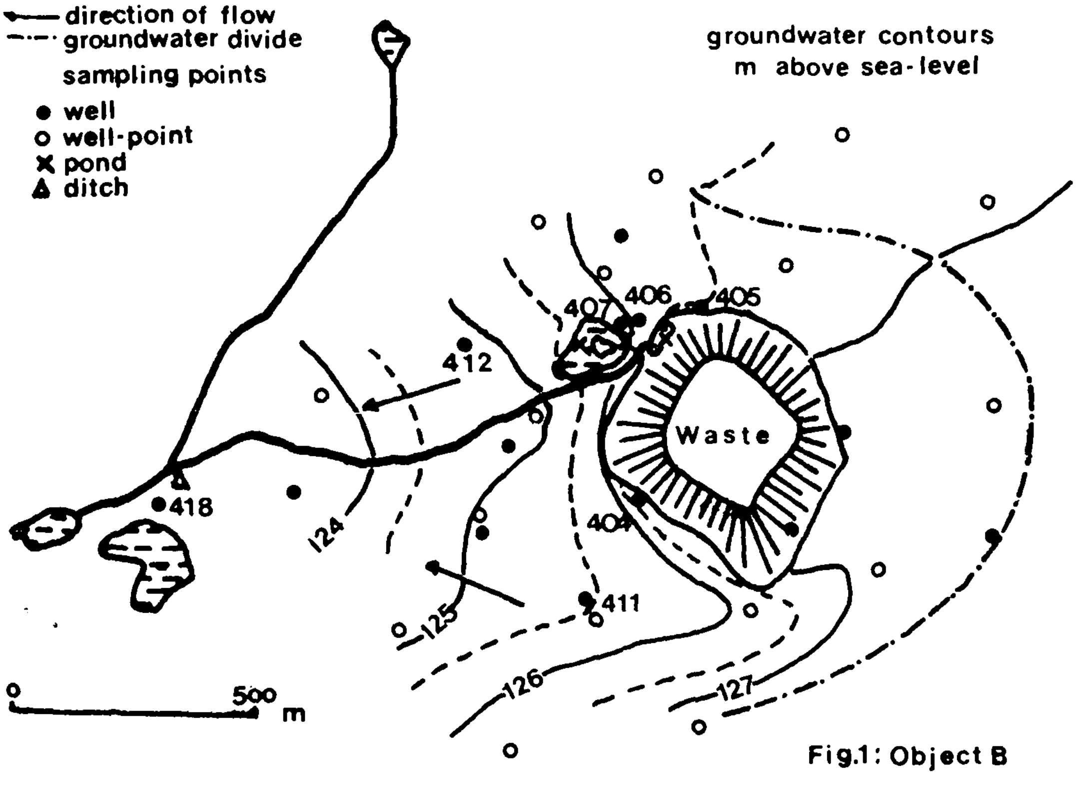

Fig.1: Object B

There the maxima detected are mainly at the deposit's margins and exceed the upper limits of the 'Trinkwasserverordnung' concerning Pb, Cd, Cr and Zn (Table 1).

Table 1. Max. heavy-metal contents of ground- and surface water at Site B compared with the prescribed limits of the Trinkwasserverordnung (31.1. 1975)

Element	Limit mg/l	Groundwater mg/l	Sampling-point	Surface water mg/l	Sampling point
As	0.04	0.032	405	0.033	
Pb	0.04	0.19	404	0.19	19
Cd	0.006	0.013	404	0.015	19
Cr	0.05	0.056	404	0.19	19
Cu	-	0.18	418	0.016	20
Ni	-	0.15	406	0.09	19
Hg	0.004	0.0008	405	0.0002	28
Ag	-	0.001	415	-	-
Zn	2.0	4.0	412	2.0	20

Data of Hg and Ag are close to detection limits and do not show any dependence on the distance from the dumping area.

Along a small ditch, draining site B to a pond, maximum heavy-metal contents are found in general in the upper section of the ditch, where Cr-values of the drainage water exceed those of the groundwater significantly.

Decreasing concentrations in waters from well 412 and 411 below WHO - limits (excluding Cu with 0.084 mg/l) indicate that under given hydrogeological conditions the contents of heavy-metals are reduced to safe levels quantities along a groundwater flow-distance of 150 - 200 m. Decline of concentrations off the waste sites is caused by precipitation of sulphides (within the zone of reduction) and by co-precipitation with Fe (III) - hydroxides (within the transition and oxidation zone).

Tab. 2: Heavy-metal and cyanide contents of sludges from wells and ponds at Object B

Sampling point	H_2O %	Annealing residue %	As mg/kg	Hg mg/kg	Cd mg/kg	Cu mg/kg	Zn mg/kg	Ni mg/kg	Fe mg/kg	Mn mg/kg	Cr mg/kg	Pb mg/kg	Total cyanide$^+$
Well													
405	3.21	11.23	31	0.45	3.4	69	2130	56	27624	2046	59	96	0.9
407	3.55	7.98	30	0.27	1.8	60	470	97	25880	361	115	141	0.1
410	1.71	2.51	5,4	0.09	1.1	79	205	153	25460	131	135	47	n.d.
413	2.79	8.15	24	2.0	8.3	343	680	102	50699	725	89	148	n.d.
Ponds													
23	2.73	10.65	22	3,1	0.2	28	480	49	24162	2614	6	112	n.d.
24	5.47	26.64	39	2.5	3.9	42	440	60	28727	152	8	129	n.d.
30	3.05	7.24	15	0.19	0.2	44	230	70	28925	96	56	50	n.d.
31	3.27	16.34	47	0.88	8.8	190	1170	53	40610	1709	73	216	1.5
33	3.07	19.79	47	0.59	1.7	59	630	39	40688	2254	72	179	1.0

$^+$ mg/kg

Statistical evaluation of the relations between the contents of total dissolved solids (as total of analysed cations and anions) and the concentrations of As, Pb, Cu, Zn and Hg does not demonstrate any significant correlations. Only values of Cd and Ni show a relationship. Since the formation of heavy metal As, simultaneously with a diminishing sulphide,occurs at strongly reducing redox potential, a negative correlation between the redox-potential and the heavy-metal in question was expected, but this generally did not occur. Exceptions were found only in surface water (ditches and ponds) where Pb and Cd correlated negatively with the redox-potential. Correlations between Cd and Zn are often found in natural systems - but could not be found in the groundwater data for the range of the contaminated plume, probably because of the two elements' diverse uses.

In November 1972 sludge samples were taken from four well sumps and from two ponds, being qualitatively analysed by spectroscopy and X-ray fluorescence. The results, published in Golwer et al (1976) indicate that among the elements common to those sludges (Si, Fe, Al, Ca, Mg), heavy metals were present.

Table 2 contains further information concerning concentrations of sludges. Data are for air-dried sludges, % water lost on heating to 105^{o} and the % residue from heating to 450^{o}. Besides the fairly high Fe- and Mn contents there were remarkable concentrations of Zn and Pb.

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SUPPORT PAPER S

THE ORIGIN OF RIVERS SALINITY GRADIENTS AND THEIR SIGNIFICANCE IN THE DEVELOPMENT OF GROUNDWATER RESOURCES IN CENTRAL SAUDI ARABIA

L. Clark Messrs Fahad Al Marshoud and Mohamed Abu Butain

SUMMARY

The salinity distribution in the Upper Minjur and Wasia aquifer systems is complex. In places, the salinity of the groundwater decreases with the distance from the outcrop; that is, there are reverse salinity gradients in the aquifers. The water quality patterns in the aquifers are explicable in terms of structural control and recharge potential. The reverse salinity gradients however are explicable only by the increasing aridity of the climate since the Pleistocene, and hence the increased salinity of the waters recharged to the aquifers. The areas of good quality water, isolated from the aquifer outcrop by reverse salinity gradients, have been important in directing groundwater development in central Saudi Arabia. Similar reverse salinity gradients should occur in other arid countries, and the Saudi quality patterns can act as a guide to groundwater exploitation in their regional aquifers.

1. INTRODUCTION

The geological succession in central Saudi Arabia is a series of sedimentary rocks dipping gently westwards off the metamorphic shield area of western Arabia. The sedimentary succession, summarized in Table 1, comprises mainly marine carbonate rocks, but the Triassic Jilh and Minjur Formations and the Cretaceous Biyadh and Wasia Formations are two thick, mainly continental sandstone-shale sequences. The arenaceous beds in these formations form the major central Saudi Arabian aquifer systems. The carbonates locally form good aquifers, but, on a regional basis, they have low porosity and are poor aquifers.

The Upper Minjur Formation is the main source of water at the moment for Riyadh, and it is tapped by numerous boreholes in the vicinity of the city. This formation is also used for the water supplies of several rural communities. The Wasia Formation is utilized on a large scale only in the Eastern Province of Saudi Arabia, where saline water from the formation is used for injection into the oil-bearing formations.

Table 1. Stratigraphic succession of central Saudi Arabia

Age	Formation	Lithology
Quaternary and Tertiary	Superficial deposits	Alluvium and aeolian sand
	Dammam	Limestone and dolomite
	Rus	
	Umm er Radhuma	
Cretaceous	Aruma	Sandstone and shale, minor dolomite and limestone
	Wasia	
	Shu'aiba	
	Biyadh	
	Buwaib	
	Yamama	Limestone
	Sulaiy	
Jurassic	Hith	Anhydrite
	Arab	Limestone and anhydrite
	Jubaila	Limestone
	Hanifa	
	Tuwayq	
	Dhruma	Limestone and shale
	Marrat	Red shale and limestone
Triassic	Minjur	Sandstone and shale
	Jilh	
	Sudair	Shale

The aquifers of the Upper Minjur Formation and the Wasia Formation have been studied in detail to assess their potential as future sources of water supplies for Riyadh (MacDonald, 1975). The salinity distribution in these aquifers is complex and, in places, the salinity of the groundwater decreases with the distance from the outcrop; that is, there are reverse salinity gradients within the aquifers. This paper discusses the causes of the complex salinity distribution, the origin of the reverse salinity gradients and the influence of the salinity pattern in planning groundwater development in central Saudi Arabia.

2. THE GEOLOGY AND HYDROGEOLOGY OF THE AQUIFER SYSTEMS

2.1. THE UPPER MINJUR FORMATION

The Minjur Formation is an alternation of sandstones and shales which has been subdivided into three hydrogeological units:

The Upper Minjur aquifer system
The Middle Minjur shales and mudstones
The Lower Minjur aquifer system

The Upper Minjur aquifer system is the predominantly arenaceous upper third of the Minjur Formation. Its top is well defined by the base of the Lower Marrat limestone but the definition of its base is much more subjective. Regional correlation of the three subdivisions of the Minjur Formation shows that the Upper Minjur thins from about 120 metres at Riyadh to 80 metres at outcrop, but maintains its thickness along the strike. In Sudair District, 150 kilometres north-west of Riyadh, it is about 130 metres thick. However, at the Petromin-Chiyoda well, 44 kilometres south-east of Riyadh, the arenaceous succession of the Upper Minjur has been replaced by shales and the extent of this lithofacies change is not known.

The sedimentary succession is part of the Saudi Arabian interior homocline in which the strata dip gently eastwards at about half a degree. This uniform structure is interrupted west of Riyadh by an arcuate line of en echelon graben structures (Map 1). These are very narrow and are probably expressions of tension fractures in the underlying basement complex. The downthrow in the grabens varies but reaches 350 metres in places. These structures cut and severely disrupt the Minjur Formation between its outcrop and Riyadh.

The Upper Minjur at Riyadh is a continental, multiple aquifer system, with an average composition of about 57 per cent sandstone and 43 per cent shale. The sandstones occur in beds of medium to coarse cemented sandstone, each with an average thickness of 6 metres, but with some beds over 20 metres thick. The average horizontal permeability of the Upper Minjur sandstones is about 6.9 m/day. The aquifers in the Upper Minjur aquifer system are separated by intervening confining shale beds and the aquifer system as a whole is confined beneath the Lower Marrat limestone and the thick Middle Marrat shales. The vertical permeability of these confining layers is extremely low and under Riyadh the confined head of the system is about 1200 metres, raising the water from the aquifer at 1300 metres depth to a present dynamic water level about 120 metres from the surface.

Prior to large scale pumping in Riyadh, the piezometric surface dipped northeastwards at about 1 in 3300. The main piezometric feature at the present day is the deep cone of the depression around the Riyadh wellfield (Map 1). The southern edge of this cone is severely disrupted by the graben.

The total salinities and iso-salinity contours of water in the Upper Minjur aquifers are shown on Map 1. The main feature of this salinity map is a long trough of good quality water extending northwards from Al Ha'ir to Riyadh, subparallel to the Minjur outcrop. This peculiar salinity distribution means that there is a reverse salinity gradient in the Upper Minjur downdip from outcrop to Riyadh.

Consideration of the aquifer piezometry and the age of the water shows that the water quality distribution pattern is the result of a complex groundwater flow regime governed mainly by the graben structures. The grabens act as impermeable barriers to groundwater flow across them. Their impermeability has been demonstrated by a pump test at Testwell M1 and is also shown by a 27 metre head differential across the graben at Al Muzahimiyah.

There is evidence however, that the permeability of the Upper Minjur aquifers may be much greater than normal close to the graben. The average rate of flow in the aquifer prior to the Riyadh pumping, calculated using Darcy's Law, would be about 0.8 m/year. The age of the water at Al Kharj, 125 kilometres from outcrop along the Nisah Graben, is 26 000 years, implying a flow velocity of 4.8 m/year. The ages of water south of Riyadh are less anomolous but still imply rates of flow parallel to the graben of about 3 m/year.

The impermeable graben have deflected the downdip flow pattern from Dhruma in the north-west, eastwards towards Ha'ir, along the zones of high permeability. At Dirab and Bu'ayja the Muzahimiyah and Awsat grabens die out and allow the deflected water to escape to the north and east. The water quality pattern and ages suggest that the waters, on leaving the confine of the graben system, have been deflected more sharply than expected. This deflection was possibly caused by a barrier boundary near Petromin-Chiyoda where the Upper Minjur aquifers have thinned out almost completely.

At Al Barrah, north of Dhruma, the continuity of the Muzahimiyah graben is broken, but the rate of flow across the graben must have been small. The age of the Huraymilah water (>35 000 years) shows the average rate of flow from outcrop to have been less than 0.2 m/year.

2.2. THE WASIA FORMATION

The Biyadh and Wasia Formations comprise a largely arenaceous sequence about 550 metres thick. The Wasia Formation is clearly defined from borehole records, particularly geophysical logs. The Wasia section from Testwell WB 1 is given in Table 2. The bipartite subdivision of the Wasia is maintained over the whole area.

Table 2. Wasia Lithology in Testwell WB 1

Formation	Unit	Lithology	Depth (metres)
Aruma	- -	Dolomitic limestone	33.6 - 208.7
Wasia	Upper Wasia shales	Blue-grey shales with fine sands	208.7 - 243.6
	Main Wasia sand	Medium to coarse sand. Well sorted	243.6 - 382.5
Shu'aiba		Yellow and blue-grey shales with sands	382.5 - 463.5
Biyadh	- -	Medium to coarse sand with shales	463.5 - Total depth

Thin aquifers occur in the Upper Wasia shales and in the Shu'aiba Formation, but the most important aquifer by far is the Main Wasia sand. This sand contains coarse sand and gravel lenses, and thin shales in places, but it is mainly a white, unconsolidated, uniform, medium to coarse grained, well-sorted, quartz sand almost 150 metres thick. The porosity of the sand is 30 to 35 per cent and the aquifer permeability is high, ranging from 6.9 m/day to 36.3 m/day, with an average value of 15.5 m/day (average from seven wells).

The regional dip is to the east-north-east at about half a degree, but this gentle homocline is interrupted at Khurais by a very gentle upwarp along a north-north-westerly axis. A parallel synclinal structure occursbetween Khurais and Testwell WB 6 to the west of the anticlinal axis at Khurais. The succession and thicknesses of the stratigraphic units are remarkably constant over the whole area shown in Map 2, except in this syncline. Here the thicknesses of each unit of the Wasia are increased considerably, the argillaceous units by a factor of three, and the Main Wasia sand by a factor of two.

The Wasia and Biyadh Formations in the south of the area are cut by the easterly extension of the graben system discussed earlier. The narrow Nisah Graben continues eastwards as a faulted synclinal structure, the Mugrah trough. The Wasia and Biyadh Formations have been let down into the Nisah and Sahaba depressions and these formations now underlie the alluvium along the length of Wadi Sahaba.

The static water level in the Wasia north of a line some 40 kilometres north of Wadi Sahaba is more than 200 metres deep. This means that the Wasia aquifer is unsaturated at outcrop and as far east as the Ad Dahna sand dunes (WB 8 to WB 3 line) is unconfined or just confined. The Wasia piezometry shows that the regional flow is towards the east-north-east except in the south along Wadi Sahaba where it is towards the east. Active recharge along the Wadi Sahaba produces a piezometric 'high'.

The total salinities and iso-salinity contours for the Wasia are shown in Map 2. The salinity pattern has the following major features:

i) A high salinity area, centred on WB 5, is surrounded by a low salinity area. There is a marked reverse salinity gradient downdip from WB 5 to Khurais.

ii) A very high salinity area in the north-east around Jaham 802 well.

iii) Very low salinity areas centred on wells WB 8 and Qirdi 801.

The increase in salinity to the north west at Jaham is part of the normal regional downdip salination of the Wasia groundwater.

The very low salinity at WB 8 is anomalous and carbon-14 age dating of this water shows that the water is modern and hence anomalous in age also. This lens of good quality water is believed to be caused by rapid recharge to the Wasia Formation through a karstic collapse structure in the overlying Aruma limestone. There is some geophysical evidence that vertical pipe-line collapse structures do penetrate these formations (MacDonald, 1975, Vol. 2).

The remaining broad salinity pattern is largely explicable in terms of regional variation of opportunity for recharge. The main recharge source is Wadi Sahaba where the aquifers are in contact with saturated wadi-fill deposits. This recharge is clearly shown by the steep piezometric gradient along the wadi and arcuate piezometric contours across the mouth of the wadi. Fresh water flows down the Sahaba trough as far as Bir Wasia where it begins to fan out into the regional aquifer and a stream of recharge water is directed north-eastwards towards Qirdi.

The northern part of the area near Khafs Banban also has some recharge potential where the Wasia crops out at the foot of a limestone escarpment alongside a large alluvial depression. This depression marks the confluence of the consequent rivers draining the cuesta of the Tuwayq escarpment to the west, and collects the floodwaters from a wide catchment. The water from part of the depression drains into the karstic collapse crater of Khafs Banban and flows eastwards towards Rumah.

There are, therefore, probably two streams of fresh water flowing around the north and south sides of a central area of slower moving, more saline water. The slow movement of water in the central area is confirmed by carbon-14 dating. The rate of movement of groundwater from outcrop to Jaham is about 3.9 m/year, from outcrop to Qirdi 801 about 3.0 m/year, but from outcrop to Testwell WB 9 it is less than 1.6 m/year.

The slow movement of this water between outcrop and WB 9 near Khurais is possibly the result of two factors: firstly the lack of recharge in this area producing a relatively stagnant backwater, and secondly, the thickening of the aquifer in the synform parallel to the Khurais anticline. The latter feature increases the cross-sectional area of the aquifer and will have the effect of slowing the flow of water. There is also a slight indication that aquifer permeability may be comparatively low in this area as the permeability at Testwell WB 5 is only 6.9 m/day compared with the average Wasia permeability of 15.5 m/day.

3. GROUNDWATER CHEMISTRY

The waters from wells tapping the Upper Minjur and Wasia aquifers have been sampled for chemical analysis. The analyses show the water to be mainly of one type with ionic ratios:

$SO_4^{--} > Cl^- > HCO_3^-$

$Na^+ + K^+ \geq Ca^{++} > Mg^{++}$

About fifty metres of screen are used in each well and all thick sandstones within the aquifer systems are screened. The water samples from the wells are therefore composite samples representative of the whole aquifer systems. While the salinity of the samples varied, their composition remained generally similar (Figure 2).

The water quality distribution in the Upper Minjur and Wasia aquifers can be explained by the flow regimes described above. The absolute salinities of the water, however, cannot. The quality of the water in the Wasia at WB 8 and Qirdi is actually better than the quality of modern recharge water. The deterioration of water quality from these areas of good quality aquifer outcrop must reflect a deterioration in climatic conditions since the Pleistocene.

The climate of periods within the Tertiary and Quaternary eras was much wetter than at present. Lakes stood in depressions and the consequent drainage lines cut great gorges in the headwaters of the Wadi Sahaba. In these periods of high rainfall, the last of which probably occurred in the late Pleistocene about 25 000 years ago, recharge of fresh water would be at a maximum. The progressively drier climate since the Pleistocene has resulted in a gradual decrease in the rate of recharge and hence in a more saline recharge water. The good quality water of late Pleistocene age is now left as lenses surrounded by more saline water.

4. GROUNDWATER DEVELOPMENT: THE EFFECT OF THE SALINITY DISTRIBUTION IN THE MINJUR AND WASIA AQUIFERS

The recharge to the Minjur and Wasia aquifers is so slow that any development must involve groundwater mining and the progressive depletion of the resource. It is therefore important that the groundwater development is planned to make optimum use of the resource and avoid unnecessary deterioration of the groundwater quality.

The Upper Minjur aquifer system is the major source of the Riyadh water supplies, but the Wasia is almost untouched except for water for injection wells in the Eastern Province oil fields. Water quality has been a major restraint on the development of the Minjur, for the quality of the present Riyadh supply is barely within the WHO limits of acceptability, and well outside the maximum desirable limits. Since groundwater quality deteriorates markedly westwards to outcrop and eastwards away from outcrop, and exceeds the acceptable quality limits, the development has been restricted to the zone of good quality water. Because this zone is surrounded by more saline water, it follows that the water quality must deteriorate in time, and that the rate of deterioration will be increased by heavy pumping regimes with excessive drawdowns.

The initial large scale development of the Minjur groundwater was sited fortuitously in the good quality zone beneath Riyadh. Mining by this development has produced a large cone of depression under the city, and the water levels in the Riyadh wells are falling rapidly. The Ministry of Agriculture and Water have, therefore, instigated studies to find alternative supplies for the city.

The second stage of development of the Minjur aquifers at Riyadh has been implemented by extending the present well field radially around the city to avoid excessive drawdowns. A planned third stage involves a second large well field about 35 kilometres northwest of Riyadh sited to take advantage of the water quality and again to spread the effects of the pumping. When this field is in production the Minjur aquifer in this area will be considered fully developed, that is, the projected drawdowns and rates of drawdown will be close to acceptable limits. Development could extend into the zones of low quality water if desalination was included in the treatment process, but it has been decided by the Ministry to concentrate on the Wasia aquifer for the development of further supplies for Riyadh.

There are two areas of good quality water in the Wasia, one is at Qirdi and the other is west of Khurais. The proposed initial development is in the west, as this is the area nearer Riyadh and thus offers considerable saving in pipeline costs. The well field is close to the high salinity area, but computer models of the well field have shown that salinity problems should not be expected to arise in the first twenty years of operations.

The areas of low salinity groundwater have been of the utmost importance in directing the development of the groundwater resources of central Saudi Arabia to date because they represent the only major water supplies that do not require desalination for domestic use. The Ministry of Agriculture and Water, however, has now put an upper limit of 700 mg/l total dissolved solids for water supplies. The Minjur and Wasia contain no water of this quality, therefore desalinized water will be an increasingly important part of the water supply. The proposed Wasia development, for example, now includes a desalination capacity. The good quality water will still be of importance in guiding the resource development in that it will be cheaper to purify than brackish water, but it will no longer be vital that the water mined is potable.

5. CONCLUSIONS

The groundwater in the Minjur and Wasia aquifer systems represents the major water resource of central Saudi Arabia. The water quality distribution in the aquifers is complex, but can be explained in terms of structural control, recharge opportunities and changes in the paleoclimate.

Areas of good quality water, isolated from the aquifer outcrop by reverse salinity gradients, have been very important in directing groundwater development to date. It will be of less importance in the future as the availability of large scale desalination plant eases the necessity for all groundwater developed to be of directly potable quality.

The occurrence of reverse salinity gradients and areas of good quality water isolated from the aquifer outcrop is a direct result of the deterioration of the climate to the present very arid one. This climatic deterioration since the Pleistocene was widespread, therefore one should expect similar salinity variations in regional aquifers of other arid countries. The Saudi experience can, therefore, be used to guide future exploration for groundwater in such locations.

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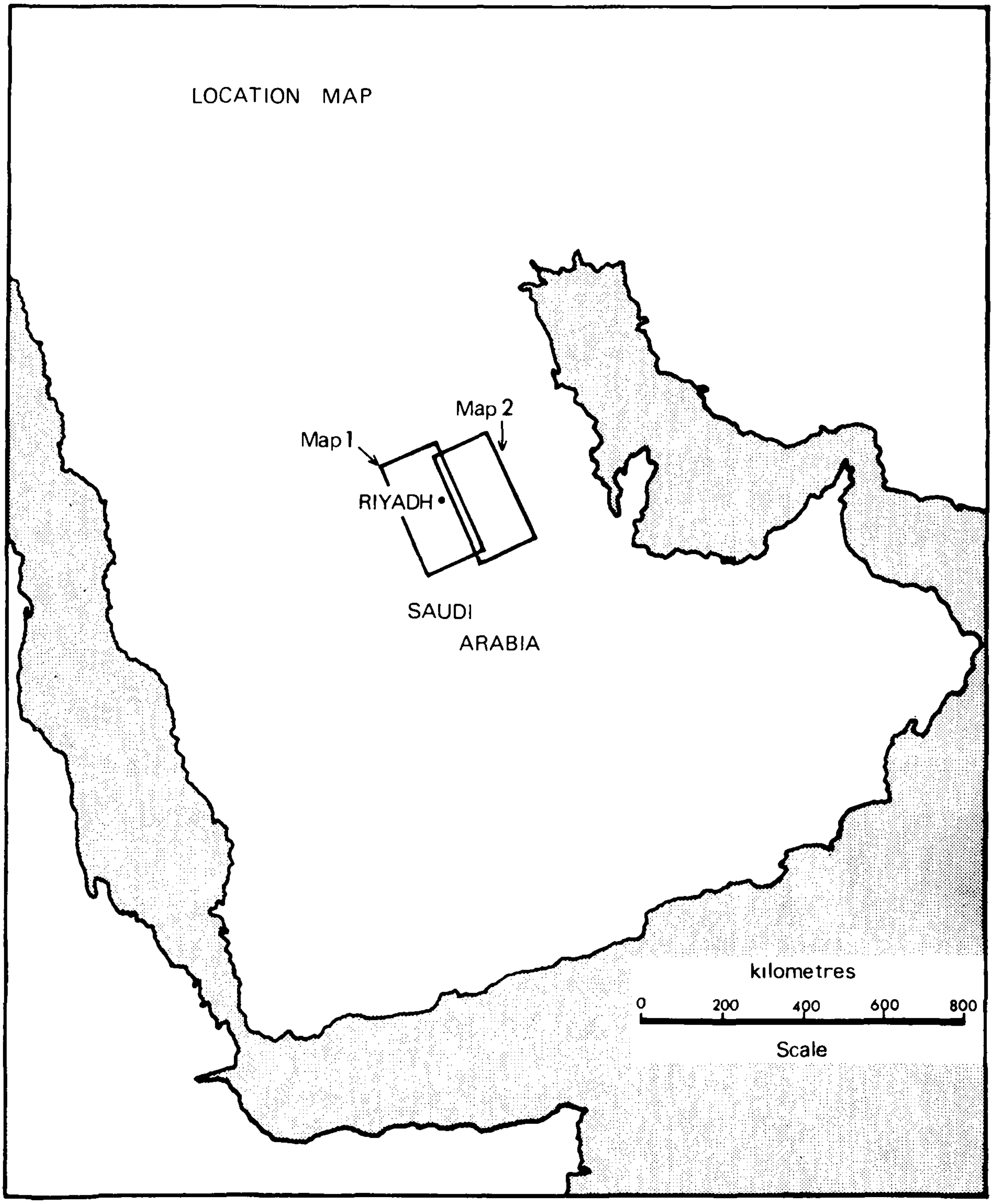


Figure 1. Location Map

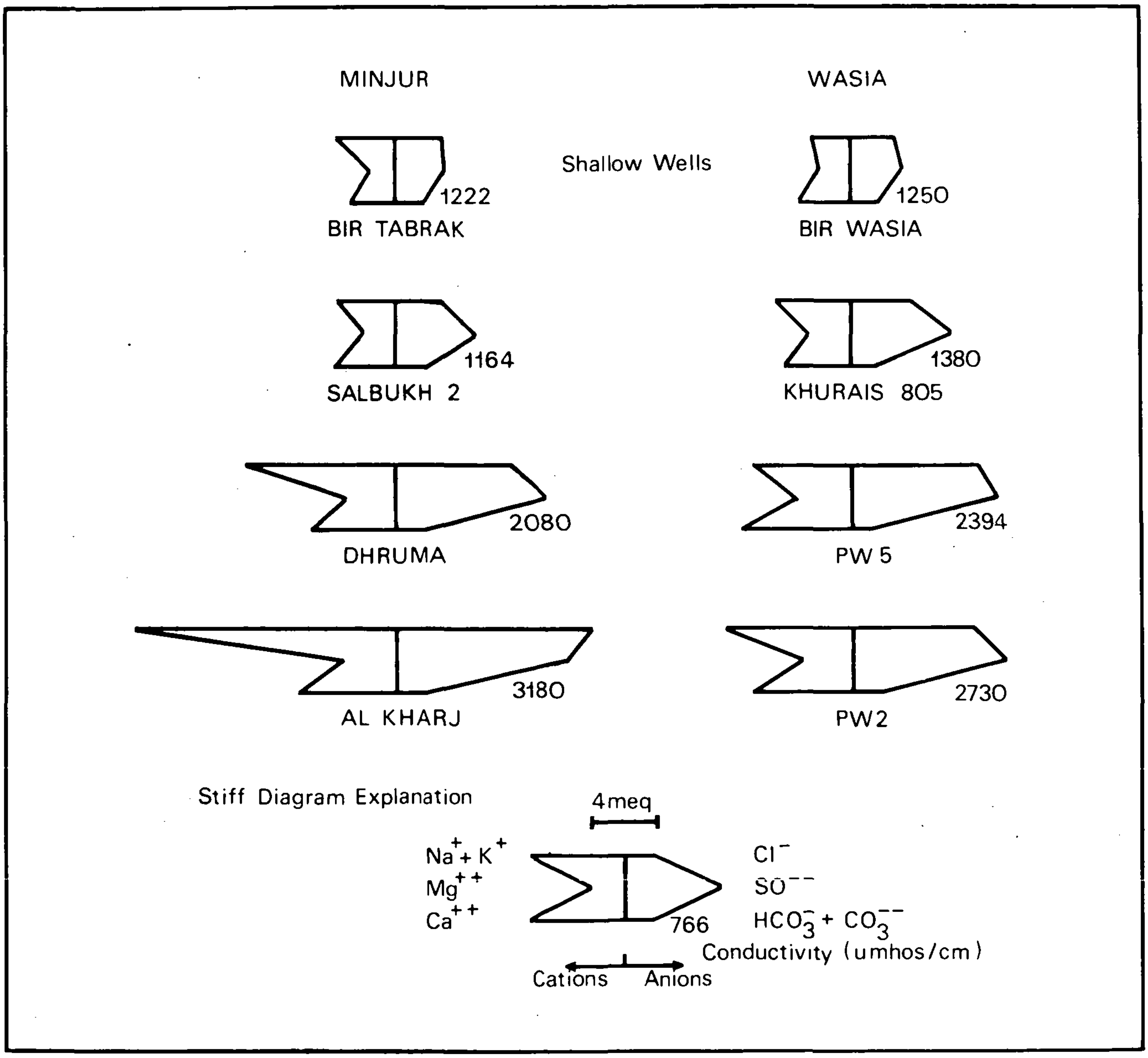
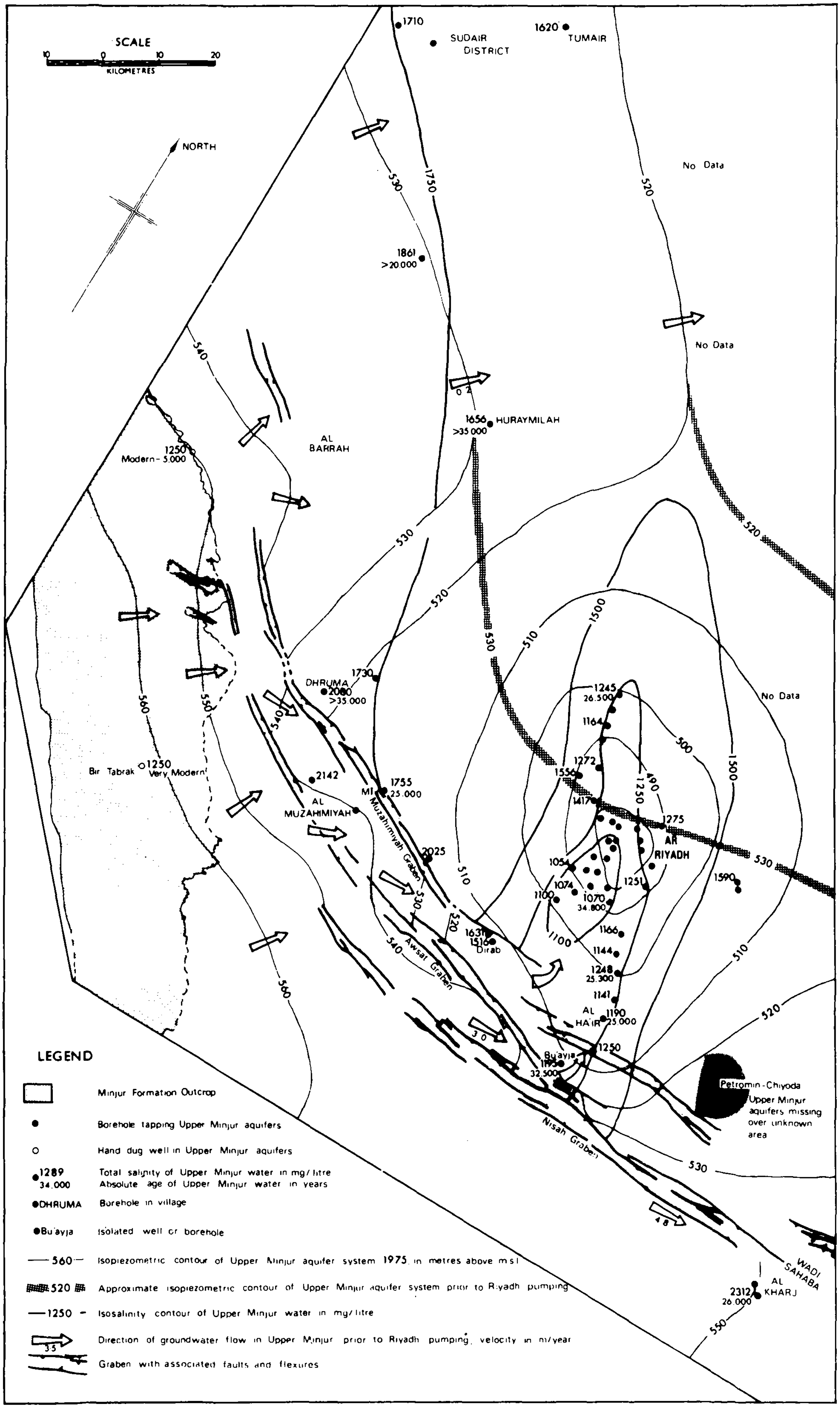
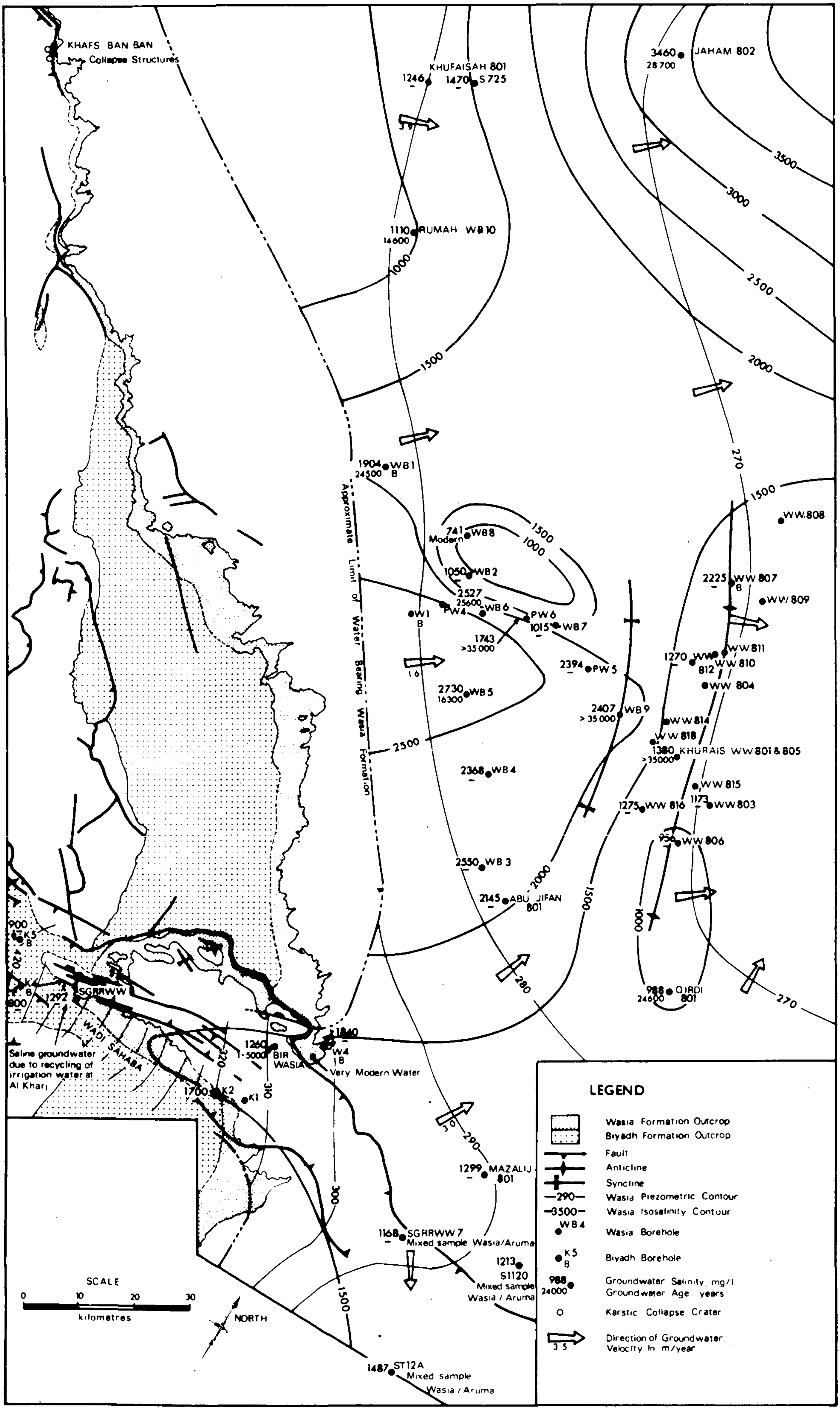


Figure 2. Water Quality Variation



Map 1. Water quality and piezometry of the Upper Minjur aquifer



Map 2. Water quality and piezometry of the Wasia aquifer

DISCUSSION - SESSION 4

Dr L. J. ANDERSEN, commenting on the paper by Messrs Young and Hall, said he would like once again to discuss unsaturated flow in a double-pored medium such as Chalk and sandstone. He thought that an understanding of the flow processes was very important to regional pollution. Two models for this flow have been mentioned by the authors to explain the hydrodynamical processes for unsaturated flow in fissured, porous rocks, namely:

(a) a simple, piston displacement model where infiltrated water displaces already stored water in the interstitial voids of the fissured rock over the total area.

With some dispersion this model seems to fit well with the tritium peak at 10 metres below surface in the Chalk, and even with the Bunter Sandstone, where the tritium peak has been measured at 22 metres below surface.

(b) a model of fissure flow with ionic diffusion into interstitial water.

From investigations on the tritium distribution in the unsaturated zones in porous sand and gravel (1), it was found that a displacement model with dispersion did simulate the tritium profile well. The model was combined with an evapotranspiration model for calculation of input concentration of tritium. The molecular diffusion from fissure water into interstitial water seemed insubstantial. Flow in the fissures will not take place at all if all pores smaller than the fissures are not saturated. The fissures will only transmit water if the intensity of precipitation and the infiltration rate are higher than the vertical hydraulic conductivity of the interstitial voids. It seems reasonable, therefore, to assume a downward flow in the saturated voids of the unsaturated zone, and this means the minor voids as they have the highest tension.

He went on to ask if profiles had been measured in the saturated zone. In Denmark three profiles in a water table aquifer (outwash sand and gravel) had shown that nitrate was only present in the upper 7 to 8 metres of the aquifer. In this zone the Fe^{2+} concentration was low. However, below the nitrate front the concentration of Fe^{2+} increased rapidly. He inferred from this that the Fe^{2+} had reduced the nitrate. No NH^{4-} ions were found, so he considered that the nitrate had been reduced to nitrogen.

In reply to Mr Andersen, Mr C. P. YOUNG referred to a report (2), in which the two possible mechanisms of water movement in the unsaturated zone of the Chalk were discussed more fully. He pointed out that the water content of samples of Chalk taken from the unsaturated zone were often found to be high close to saturation, the main exceptions being close to the land surface for samples taken during the summer months. Mr Young went on to postulate that the initial infiltration at the beginning of a recharge period would probably be absorbed into the intergranular voids in the upper part of the Chalk profile because of their high pore tensions, but once the intergranular voids had reached effective saturation, flow would take place down the fissures. The generally high level of saturation of the Chalk blocks in the unsaturated zone at greater depths would require relatively little additional water to reach saturation, and fissure flow at depth would not be greatly inhibited by imbibition of fissure water into the intergranular pores.

Mr Young confirmed that investigations on the Chalk had, so far, been to a maximum depth of 6 metres below the water table, but said that it was proposed to sample at greater depths in the saturated zone at future sites. However, boreholes in the Bunter Sandstone had been sunk to 180 metres below the water table, and variations in the nitrate concentrations appeared to correlate with broad changes in lithology of the sandstone. Mr Young also pointed out that the nitrate concentrations found below the water table in a borehole profile are not determined solely by the concentrations in the immediately overlying unsaturated zone, but may represent waters of mixed origin from upgradient sources in the groundwater catchment. Samples taken from spring discharges and boreholes would similarly be mixed.

Referring to the sites on unconsolidated sand and gravels in Denmark, as described by Mr Andersen, Mr Young replied that although localized lenses of iron-rich groundwater were known to be present in the Bunter Sandstone, these conditions had not yet been encountered during the Water Research Centre's investigation.

Mr E.S. HALL, in a written reply to Mr Andersen's discussion, added that since the first soil leachates of Autumn contained the highest concentrations of nitrate, the unsaturated intergranular capacity near to the land surface would imbibe concentrations that were higher than the average for all infiltration, whereas the subsequent infiltration that penetrated to lower fissures would be more dilute. Furthermore, even in a totally saturated system there was greater opportunity for light infiltration, with its attendant higher concentrations of nitrate, to attain more advanced equilibration with pore water. For these reasons the characteristic form of a typical nitrate profile, having an amplitude that diminishes with depth, could be interpreted as steady-state and not necessarily indicative of a threat for the future. From this viewpoint, it was perhaps not possible to draw a close analogy between the movements of tritium and nitrate, because tritium would have entered the system mostly by infiltration following the attainment of saturation and would, to this extent, differ from nitrate in its mechanism of movement.

With regard to the absence of nitrate in the presence of Fe^{2+}; this was of course predictable from its comparative oxidation-reduction properties. Nitrate was certainly absent from water drawn from the ironstone formations in Lincolnshire, and also from the iron-sulphide-rich Tertiary of the London Basin.

Dr J.D. MATHER asked Mr Stiff and Mr Young whether they were in a position to give guidelines on the ideal conditions which should be maintained at landfill sites to derive benefit from the various physical, chemical and biological processes they discussed. Should sites be lined with carbonates or montmorillonite, or situated on strata naturally rich in these materials? He asked whether sites with thick unsaturated zones merely delay the arrival of a pollutant, or cause attenuation, and whether wastes in a landfill site should be mixed, or should a policy of different sites for different wastes be adopted? Did the authors agree that the risks of groundwater pollution from domestic landfill sites under United Kingdom conditions have been over emphasized, particularly if a little hydrogeological common sense has been used in site selection?

Mr D. D. YOUNG, in a written discussion, strongly disagreed with Dr Mather's final comment. Far too many 'unknowns' exist about underground natural purification of domestic refuse leachates, to be complacent.

The main problem is one of foul tastes which may render water completely unacceptable to the consumer, rather than of direct hazard to human health. The Cowm incident, with the attendant political furore, illustrates the problem, even though it was not due to domestic refuse. Chlorination is as likely to enhance such taste problems as to reduce them. This, combined with the extraordinary sensitivity of the human palate, may cause water supplies to be rendered useless by contaminants at concentrations measured in microgrammes per litre, or less.

A considerable proportion of the organic content of these leachates is resistant to either aerobic or anaerobic degredation.

Earlier discussion in the Conference had stressed the relative permanence of contamination of groundwaters, and the paper by Headworth and Wilkinson shows that future trouble may be accumulating.

The asset value of a good groundwater source may be upwards of £150 000 Ml/d yield. It should also be noted that many essential groundwater sources lie in areas where available surface waters have already been exploited and replacement supplies may have to come from considerable distances at very great cost.

Given the above consideration, the Water industry must be very sure of its facts on purification. To do otherwise, is to adopt a 'Sorcerer's Apprentice' approach to the management of water and waste disposal.

Mr M. J. STIFF, in reply to Dr Mather, emphasized that certain steps, such as lining a site or situating a landfill on a thick unsaturated zone, would help in depressing the concentrations of contaminants, but that care should be taken not to exceed the field capacities of such measures.

Mr C. P. YOUNG agreed that comprehensive guide lines could not be set at this stage. However, field investigations had indicated that non-conservative contaminants often showed signs of attenuation within the unsaturated zone, and this preliminary conclusion had been incorporated in a recent Department of the Environment Report on licensing of waste disposal sites (3). He pointed out that more appeared to be known in the UK of the fate of leachates derived from hazardous waste landfills than of leachates from domestic refuse sites, and he agreed with Dr Mather that a modicum of hydrogeological sense applied to the siting of domestic landfills could probably result in pollution of groundwater supplies being avoided. He said his remarks were not designed to promote complacency, but rather to emphasize the need for hydrogeological considerations to be taken into account during site selection.

Mr M. J. STIFF said that the application of hydrogeological knowledge will not, in itself, reduce the risk of pollution, but will help in assessing the risk, so that better judgements may be made of the effects of a landfill on an aquifer. The distinction must be made between the components of the leachate which are normally found in leachate from domestic waste, and those which are solely derived from chemical wastes. It is more likely that amongst the latter would be found those which are resistant to biochemical treatment, and special consideration must obviously be given to them.

Mr J. J. FIELD submitted the following written comment on the paper by Messrs Stiff and Young.
In Devon there are a number of domestic refuse tips situated on strata having a low permeability. Generally, leachate from these tips appears as a point emission at the toe of the tip, together with a series of minor emissions at the tip face at levels which correspond with the horizons of the compacted covering-down material (soil or builders rubble). These surface emissions facilitate sampling and results of analyses carried out by the former Devon River Authority. The present South West Water Authority and the Devon County Council can provide a picture of the varying characteristics of leachate over a period of years.

The surface waste tips can be classified as follows:

(a) areal tips, which have a maximum depth of the order of 5 metres and a large surface to depth ratio;

(b) valley tips, which can have a depth up to, or even greater than, 30 metres and have a correspondingly smaller surface area to depth radio.

A review of the leachate analyses from these tip types shows that the strength of leachate falls off, with respect to time, more rapidly from the valley tips than the areal tips. Mr Field suggested that as the lower levels of refuse become stabilized by anaerobic digestion, these lower levels themselves provide a region where fresh leachate from new tipping layers can be effectively broken down, and the rate of transport of its various constituents retarded by physical, chemical, and bacteriological processes. This effect is obviously greater in the valley type tip.

Research in the United States by Pohland (4) has shown that recirculating leachate through a tip by irrigation can increase the rate of biological stabilization, with the result that the concentration of organic pollutants in the leachate is quickly reduced and the rate of increase in the density of the fill material is accelerated. This last factor increases the effective life of the tip.

Not being a chemist, Mr Field was unable to discuss the processes in any detail, but could point out some practical implications. He suggested that from a water quality point of view, valley type tips are to be preferred to areal tips if there is a real risk of affecting groundwater quality and, furthermore, that biological stabilization can be accelerated by an initial period of leachate recirculation.

Mr Field said he would like the comments of Messrs Stiff and Young on these points. He also suggested that a review of historical data from existing tipping sites may be as useful in the preparation of the eagerly awaited guidelines on the siting of waste tips, as the results of intensive site investigation of a small number of sites.

Mr C. P. YOUNG made the following reply to Mr Field.
Decisions on the siting of landfills should only be made after proper consideration of all available hydrogeological information. The deep, 'Valley type' landfills preferred by Mr Field present a minimal area over which direct infiltration could take place, thereby reducing the anticipated volume of leachate generated. At the same time, the greater thickness of wastes would provide an increased absorptive capacity for infiltration, possibly delaying the onset of leachate discharge from the base of the landfill. However, siting landfills in valley bottoms could encourage additional hydraulic loading of the wastes from run-off from the adjacent slopes, unless suitable cut-off drains were installed. Furtheremore in some areas, particularly on the Chalk, it was recognized that zones of high transmissivity are often associated with valleys and boreholes being concentrated in such areas. The siting of landfills in valley bottoms under such circumstances could lead to an increased risk of contamination of borehole supplies.

A review of historical data from a large number of existing landfill sites was carried out as a preamble to the current Department of the Environment sponsored investigations. In very few cases was the data found to be sufficiently comprehensive to allow even tentative conclusions to be drawn. This was particularly true in cases where groundwater was considered to be potentially at risk, and detailed investigations of sites are being carried out in order to rectify the lack of information.

Mr M. J. STIFF made the following reply to Mr Field. Recirculation of leachate should help in promoting stabilization of a landfill and that if it were practised, then some means of collecting leachate would have to be provided. The landfill itself would provide a means for breaking down organic matter to simpler substances and any leachate not recirculated could be disposed of in a suitable manner, perhaps after further treatment. Such steps would reduce the risk of groundwater pollution.

The leachate problem could be lessened by suitably engineering the site to limit the ingress of surface water, or of precipitation. However, it would be necessary to allow a finite input of water so that the biochemical processes could proceed if it were desired to bring about compaction, and thus increase the life of a landfill. Any recirculating leachate would have to be monitored to ensure that the concentrations of its constituents did not reach levels which could inhibit the desirable processes. If this were to happen, then a bleed-off would be necessary.

Mr K. B. ENGLISH, commenting on the paper by Young and Hall, said that by assuming the specific yield of a formation to be the limiting factor on gravity drainage in the unsaturated zone, and by taking average values of specific yields for Chalk formations of 1 to 2%, and values for the Bunter sandstone of 10%, and an annual rate of recharge of the order of 300 mm, these figures indicate that recharge must be taking place through the Chalk at a rate of 15 to 30 metres per annum and through the Bunter sandstones at 3 metres per annum.

If, however, infiltration rates are limited to 0.8 to 1.0 metres per annum for chalk and 1.5 to 2.0 metres per annum for Bunter sandstone, then again using the widely accepted figure of 300 mm infiltration for unconfined rock outcrop, this suggests that infiltration would be of the order of 95% through fissures for Chalk, and 50% through fissures for Bunter Sandstone. Thus, he concluded that the 0.8 to 1 metre per year rate of movement suggested for tritium and nitrate ions in the Chalk could only be accounted for by chemical diffusion. In view of the high proportion of recharge water which was either unaccounted for, or which appeared to be moving through fissures, he suggested that many contaminants may be transmitted rapidly to the water table with little opportunity for attenuation in the unsaturated zone.

Mr C. P. YOUNG, in reply to Mr English, said that the two models of transport through the unsaturated zone considered by WRC, displacement flow through intergranular pores and recharge via fissures with ionic diffusion of solutes, represented end members of what was recognized as being, in all probability, a gradational series. Mr English's specfic yields of 10 and 2% represented average values commonly applied to the Bunter Sandstone and Chalk aquifers respectively. However, specific yield is the ratio of water draining under gravity from a saturated block of aquifer to the total volume of the aquifer, and not a measure of the available storage in the rock. The latter is related to the effective porosity of the rock, which for Chalk may be in the range 30 to 45% and up to 30% for Bunter Sandstone. In coarsely grained rocks, such as some sandstones or gravels, the specific yield approaches the limiting value of the effective porosity, but in very fine grained materials, such as Chalk, pore tensions are so high that gravity drainage from intergranular voids is very limited, and low specific yields are measured. Indeed, the specific yield of Chalk determined by field tests probably relates primarily to the frequency of fissures. However, the high pore tension exerted by fine grained rocks may encourage imbibition of recharge into the intergranular storage in the unsaturated zone until such time as the aquifer blocks reach effective saturation, and fissure flow commences. This situation is most likely to arise under conditions of intense infiltration following heavy rainfall.

Referring to Mr English's remarks on the possibility of rapid and unattenuated transport of contaminants through the unsaturated zone, Mr Young commented that examples of rapid contamination of groundwater supplies from surface sources, particularly following periods of high infiltration rates, were well known, and that these occurrences were most common in areas of fissured aquifers. However, it was a matter of observation that attenuation of many contaminants, particularly the non-conservative varieties, had been recorded from the unsaturated zones of both the Chalk and Bunter Sandstone aquifers.

Mr A. W. DAVIES said that, whilst he was pleased at the extent of the development of the science of groundwater, he was concerned at the lack of application of the art of its interpretation. He deplored the 'take over' by mathematicians, and encouraged the use of field experience for a proper understanding of hydrology.

Mr Davies expressed concern that no costs had been applied to the research being undertaken, and reminded the researchers that they should forget neither the customers who are paying, nor the objectives of the research. Results should be simply and clearly presented and in such a way that the decision-maker knows what the chances are of his resultant actions succeeding.

On the subject of nitrate in the hydrologic cycle, Mr Davies asked whether any thought had been given to the 50% increase in the nitrate content of rainwater over the past ten years, and whether this could be due in some way to the combustion of fossil fuels. He also wished to know whether he was right to assume that the nitrate levels in groundwater were going to increase in the future.

Mr Davies went on to ask Mr Stiff and Mr Young whether surface waters in the vicinity of the landfill sites had been investigated by the research team, as he had found such surveys to be very useful in assessing groundwater contamination. Concluding, Mr Davies asked whether leachate infiltration should be accepted as a necessary part of the disposal of toxic and/or other wastes.

Mr C. P. YOUNG replied to Mr Davies by saying that the costs of research activities had not been included in either of the papers, but that approximate costings for various drilling and sampling methods in the Chalk and Bunter Sandstone were incorporated in the Support Paper by Gray et al.

The increased nitrate content of rainwater in certain areas had been noted, particularly in the vicinities of large conurbations, and it may be postulated that the increase is related to the burning of fossil fuels. However, rainfall nitrogen accounts for only about 10% of the total nitrogen budget, which is dominated in the majority of non urban situations by fixation of atmospheric nitrogen (between 30 and 60% of total input).

The WRC research programme showed that large quantities of nitrate are stored in the unsaturated zone of the Chalk and Bunter Sandstone aquifers, beneath arable farmland. Some circumstantial evidence suggested that the nitrate may be moving vertically, but it should be emphasized that investigations were not complete and the precise nature of the transport mechanism was not fully understood, nor were the possible effects of potential microbial activity in the unsaturated and saturated zones of the aquifers, in modifying the nitrate content of the water. However, predictions of future trends in groundwater nitrate levels had been made for one Chalk site, using two alternative solute migration models, Young et al, 1976.

Replying to the question on sampling surface water in the vicinity of landfill sites, Mr Young explained that many of the sites that had been examined were on aquifers remote from surface discharges, but that in cases where nearby springs on surface water flows existed, these were subject to monitoring and the information gained from these surveys was incorporated in the overall assessment of the site.

The problem of controlling leachate generated by a landfill could be examined in two ways. Firstly, direct infiltration to the wastes could, perhaps, be prevented by covering the landfill with an impermeable layer. In this case leachate generation would be minimized and possibly prevented, particularly if steps were taken to prevent laterial migration of liquid into the landfill from the surrounding rocks. Secondly, leachate generated within the landfill could be collected by lining the landfill area with an impermeable membrane and providing suitable sumps. The leachate would then be removed, or treated, perhaps including recirculating through the landfill to stabilize its composition.

Certain advantages and disadvantages could be recognized in either procedure. In the former case no leachate would be generated under normal circumstances, but the wastes would probably remain in an undecomposed form for a considerable period of time, with the potential to generate leachate should the impermeable cover be ruptured. In the second case, treatment of the leachate would seem to be essential but the wastes would be encouraged to decompose relatively rapidly and revert to a stable form.

Mr M. J. STIFF replied to the point that Mr Davies had raised about objectives, by stressing that it was most important that the objectives should be specified before research commenced, and that progress towards the achievement should be monitored carefully. It is important that customers are aware of their own requirements so that objectives can be adequately formulted.

In reply to Mr Davies, Dr W. B. WILKINSON said he believed that mathematical models played an important role in making groundwater quality predictions, but he would not advocate their use in every situation. He emphasized the importance of team work between the mathematician and the hydrogeologist from the start of a particular modelling project, and he agreed with Mr Davies that the decision-maker should be presented with a range of results and an indication of the levels of confidence that the project team had in particular solutions.

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Session 5

PREDICTION MODELS

Chairman:

H. J. Richards, BSc, PAIWES, FGS,
Head of Resources Division,
Central Water Planning Unit,
Department of the Environment

Presented Papers:

Support Papers:

PAPER 15

NUMERICAL AND PHYSICAL MODELLING OF GROUNDWATER FLOW IN COASTAL AQUIFERS

Prof. A. Verruijt

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1. INTRODUCTION

In this paper some of the most essential features of numerical and physical models of groundwater flow are discussed, with special emphasis on the flow in coastal aquifers.

The main characteristic of flow in coastal aquifers is the presence of two types of water in the ground: fresh and salt water. The fresh water body is floating on the heavier salt water. This fresh water can be used for water supply purposes, provided that there is a sufficient inflow of water, from natural or artificial sources (precipitation or artificial infiltration). In many cases the movement of the groundwater in the fresh water zone is so much faster than the movement in the salt water zone, that the variations in the groundwater head in the salt water zone can be neglected. The description of the flow in the fresh water zone then becomes somewhat simpler, but it still contains the essential difficulty that the extent of the fresh water body is a priori unknown. Thus, even when a sharp interface between fresh and salt water is assumed, the prediction of the flow regime may be a complicated problem, requiring sophisticated models. In this paper some examples are given of applications of physical and numerical models for problems that can be considered to be two-dimensional, the flow occurring either in a vertical or a horizontal plane.

2. THE HELE SHAW MODEL

The Hele Shaw model consists of two parallel plates, between which a viscous fluid is moving under the influence of pressures applied at the boundaries, and sinks or sources in the plane. For a detailed description of the model the reader is referred to Bear (1972). In this section the application of the model to flow in a coastal aquifer will be discussed.

The resistance to flow in a Hele Shaw model is generated by the friction between the fluid and the two plates. The flow is governed by a Darcy-type law,

$$v_x = -\frac{\kappa g}{\nu}\frac{\partial\phi}{\partial x}, \qquad v_y = -\frac{\kappa g}{\nu}\frac{\partial\phi}{\partial y}, \qquad \ldots\ldots 1$$

where v_x and v_y are the components of the specific discharge, g is the gravitational acceleration, ν is the kinematic viscosity of the fluid, κ is the permeability, and ϕ is the groundwater head. In the case of the model being used in a vertical position, the y-axis being directed upward, the head ϕ is related to the pressure p by the formula

$$\phi = y + \frac{p}{\rho g} \qquad \ldots\ldots 2$$

where ρ is the density of the fluid.

It can be shown (Lamb, 1932) that the permeability κ of a Hele Shaw model is proportional to the second power of the spacing d of the parallel plates.

$$\kappa = \frac{d^2}{12} \qquad \ldots\ldots 3$$

Because the discharge through a unit width in the prototype is represented in the model by the quantities $v_x d$ and $v_y d$, it follows that spatial variations in permeability can be simulated by varying the spacing, for instance through the insertion of filling plates. The permeability in the prototype is then proportional to the third power of the spacing.

The flow in a Hele Shaw model must also obey the equation of continuity, which can be written as

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \qquad \ldots\ldots 4$$

Here it is assumed that there is no storage in the interior of the model.

It appears that the flow in a Hele Shaw model obeys all the requirements for a simple potential flow. For this type of flow other powerful physical models exist, notably the electrical analogue, which also enables modelling of non-homogeneous anisotropic soils. The advantage of the Hele Shaw model, however, is that in this type of model the groundwater head, the fluid pressure and gravity are acting just as in the prototype. This means that in a Hele Shaw model a free surface and an interface between salt and fresh water can be simulated without any difficulty. Several applications of a Hele Shaw model to study the flow of a two-fluid system have been reported (De Josselin de Jong, 1965; Verruijt, 1969; Bear, 1972). In some of these applications the fluids used have been the prototype fluids: salt and fresh water. In other applications more viscous fluids have been used, such as oils and a mixture of glycerine and water.

When the boundary conditions vary with time, the position of the interface will depend upon time, with a delayed response due to storage. The Hele Shaw model is particularly suited for the study of such unsteady problems. An example of an application is shown in Figure 1, which refers to a homogeneous aquifer bounded at the upper side by an impermeable layer (Haitjema, 1976).

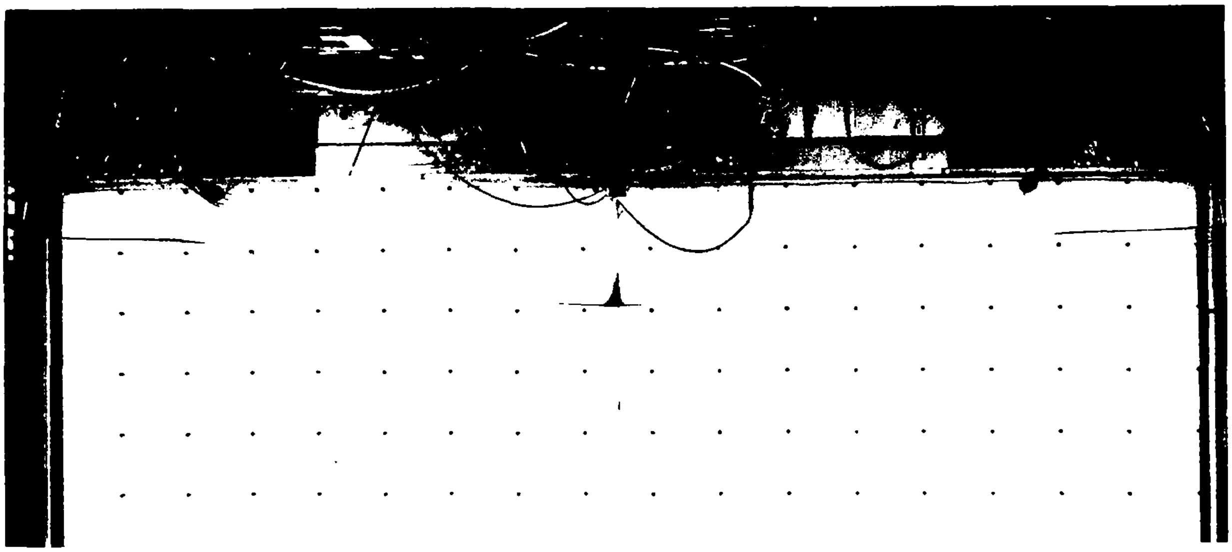

Figure 1. Hele Shaw model with central infiltration.

The aquifer is being used for storage of fresh water. In the case illustrated in Figure 1 infiltration takes place through a source in the middle of the model just below the impervious top, and the water is withdrawn through two sinks near the left and right end sides of the model, also located just below the impervious top. The fluids used were a mixture of glycerine and water for the heavy fluid (density $\rho = 1179\ \mathrm{kg/m^3}$), and a mixture of hexyleneglycol, glycerine and water for the lighter fluid (density $\rho = 1150\ \mathrm{kg/m^3}$). The kinematic viscosity of both mixtures was about $21 \times 10^{-6}\ \mathrm{m^2/s}$. The study concerned an investigation into the possibility of the effect of an interruption of the infiltration, in case the quality of the water available for infiltration (Rhine water) should be inadequate. It was investigated whether it would be possible to recover the water stored in the aquifer by pumping in the central well point originally used for infiltration. Figure 2 shows the situation after 6 months (in the prototype; in the model this situation occurs after 211 seconds). The salt water is seen to approach the well.

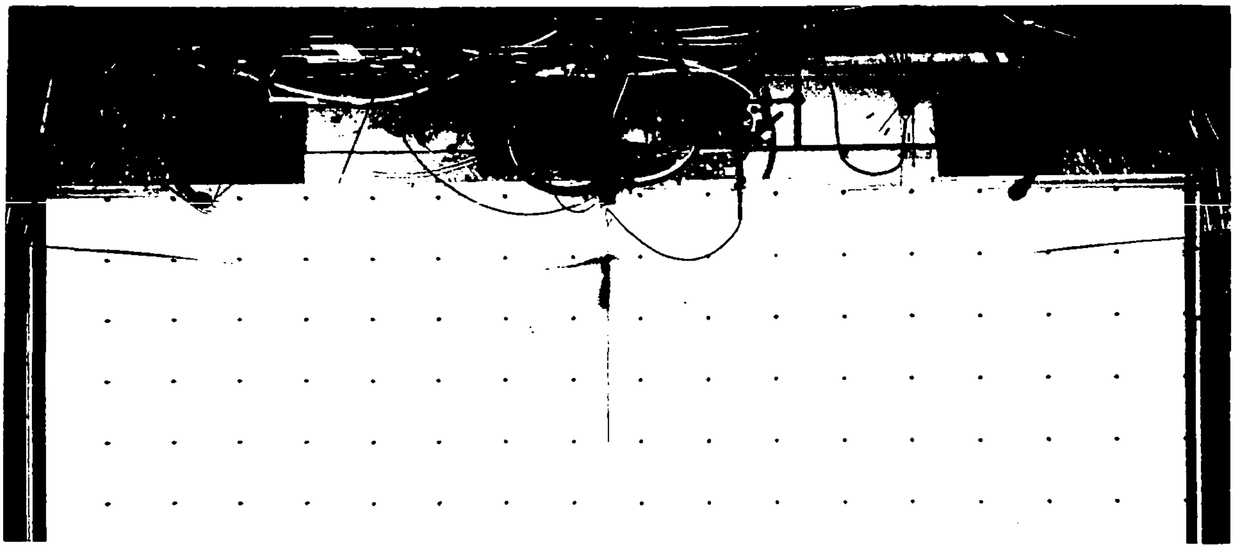

Figure 2. Hele Shaw model with central recovery.

In the experiments a brackish zone was laid upon the salt water. The brackish water consisted of a dark coloured fluid, slightly heavier than the fresh water. By doing so it was possible to study the behaviour of such a brackish zone as well. In Figure 1 the brackish water is seen to be concentrated below the point of infiltration. Along large parts of the interface the brackish water has been flushed away, to the left and right respectively, by the fresh water. In Figure 2 the brackish water is seen to approach the well somewhat before the salt water, but not yet in an alarming way.

In applications of a Hele Shaw model, the most simple device for measurements is a camera recording the position of an interface. Measurements of the head can be made by the installation of small standpipes at the rear side of the model. A difficulty arises in the measurement of the velocities, however (Haitjema, 1976). Because the velocity distribution in the model is parabolic over the thickness, it is to be expected that the velocity of a tracer particle will depend upon the particular position between the two parallel plates. When a relatively large mass of tracer particles is injected into the fluid, the fastest particle may travel 1.5 times as fast as the average velocity. In the experiments described above velocities were measured by following the fastest particle and then reducing the velocity by a factor 1.45, which was determined experimentally.

3. MATHEMATICAL MODELLING

The description of the movement of groundwater by means of Darcy's law and the principle of conservation of mass is usually very accurate. The limitations of such a description are that the flow must not be too fast (in order to avoid turbulence); that the soil mass in the aquifer must be rather stiff; that the soil must be completely, or almost completely, saturated with fluid. When the density of the fluid is continuously variable, Darcy's law should be formulated in terms of the pressure. In the general case of an anisotropic soil this formulation of Darcy's law is applied, using index notation

$$v_i = -\frac{\kappa_{ij}}{\mu}\left(\frac{\partial p}{\partial x_j} - \rho g_j\right) \qquad ......5$$

where μ is the dynamic viscosity, g_j is the gravitational acceleration vector, and κ_{ij} is the permeability tensor. Assuming the soil is completely saturated and that the spatial density variations are small, the principle of conservation of mass of the fluid leads, at least in the first approximation, to the following equation

$$\frac{\partial v_i}{\partial x_i} = - (\alpha + n\beta) \frac{\partial p}{\partial t} \qquad \ldots\ldots 6$$

where α is the compressibility of the soil, n is the porosity, and β is the compressibility of the fluid.

For the purpose of the present considerations the density of the fluid can be decomposed as follows

$$\rho = \rho_f + c \qquad \ldots\ldots 7$$

where ρ_f is the density of the pure fluid (fresh water), and c is the salt concentration. Conservation of mass of the salt leads to an equation of the following form

$$\frac{\partial c}{\partial t} = - \frac{\partial}{\partial x_i} (c v_i + D_{ij} \frac{\partial c}{\partial x_j}) \qquad \ldots\ldots 8$$

where D_{ij} is the dispersivity tensor.

Together with the appropriate initial and boundary conditions, the equations given above represent a complete mathematical description of the general groundwater flow problem. Because of the coupling of the two phenomena (movement of the fluid, and of the salt) through the density and through the dispersivity tensor (which depends upon the velocity, see Bear, 1972), the mathematical problem is rather complicated. Solutions are available only for simplified problems, the simplifications referring to a priori assumptions regarding the nature of the solution, and the geometry of the problem.

Analytical solutions for flow in coastal aquifers have been obtained for several special problems. A class of problems for which elegant analytical solutions have been obtained refers to flow in a vertical plane, with a sharp interface between fresh and salt water. These solutions are based upon application of complex variables and the so-called hodograph method (Strack, 1973). The main restrictions of this method are geometrical: the shape of the soil mass must be simple (for instance a single layer of constant thickness), and the soil must be homogeneous.

Another class of problem for which approximate analytical solutions have been obtained refers to aquifers of large extent in the horizontal plane. In such cases one may sometimes use the Ghyben-Dupuit approximation, which enables elimination of the variations of the head in a vertical direction. The mathematical problem then reduces, after linearization, to a two-dimensional diffusion-type equation. Again the solutions are restricted to aquifers of simple shape, and to homogeneous soils. More powerful mathematical methods are provided by numerical models, which are discussed in the next section.

4. NUMERICAL MODELLING

The major characteristics of all numerical models used for the analysis of groundwater flow is that the region considered is subdivided into a large number of smaller subregions of simple shape, for instance triangular or rectangular (see Figure 3). The analysis then consists of assigning values of the head to all nodal points, and of writing down an equation of motion (Darcy's law) and a conservation equation, involving local properties of the aquifer and the fluid. The result is a set of algebraic equations relating the values of the head in each nodal point to the values in the surrounding points. These algebraic equations are usually linear, at least in the first approximation, and therefore the set of equations can be solved fairly easily by means of a computer program.

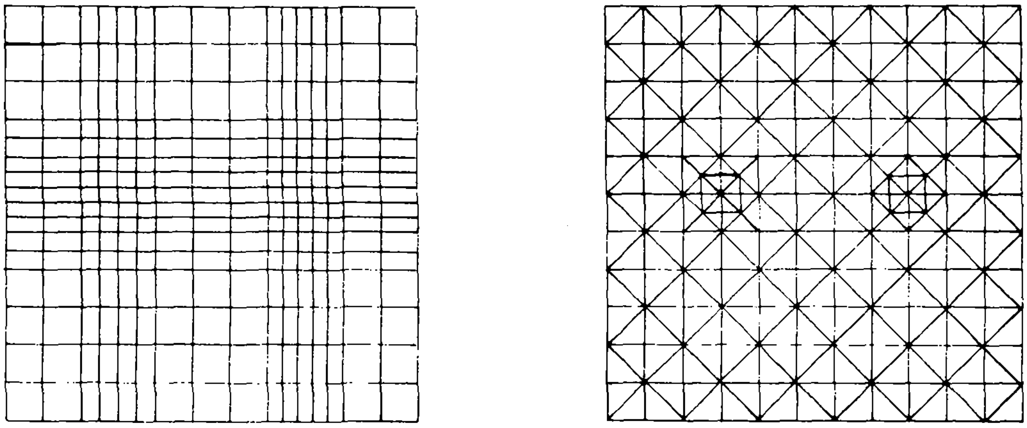

Figure 3. Typical networks for the finite difference method and the finite element method.

For the derivation of the system of equations two approaches can be distinguished; one based upon the finite difference method, and one based upon the finite element method. The main characteristics of both methods are outlined below. Restriction will be made to two-dimensional problems.

In the finite difference method (see for example Carnahan et al., 1969) the region considered is usually covered by a system on orthogonal straight lines, thus forming a network of rectangulars (see Figure 3). The algebraic equations are then derived by replacing all partial derivatives by finite difference approximations, of the following form

$$\frac{\partial f}{\partial x} \simeq \frac{f_{i+1} - f_i}{x_{i+1} - x_i} \qquad \ldots\ldots 9$$

where i indicates a numbering sequence in the x-direction. By repeated application of equation 9 it is also possible to derive approximations of higher order derivatives. As the denominator of these expressions is determined by the given size of the mesh, the derivation of the system of algebraic equations is straightforward. When these equations are linear they can be solved by a standard numerical inversion subroutine. In the case of the system being weakly non-linear, the solution can be found by an iterative procedure involving repeated application of such a standard inversion subroutine, with variable coefficients. In most cases the nature of the problem is such that the matrix of the system of equations is positive definite. The solution can then be obtained by the simple and efficient method of Gauss-Seidel-iteration (method of relaxation).

In the finite element method (see for example Zienkiewicz, 1971) a somewhat different approach is followed. Here the region considered is subdivided into a large number of small elements, for instance of triangular shape, see Figure 3. The properties of the aquifer and the pore fluid are either taken as constant throughout each element, or interpolated in a simple way (for example linearly) between the values in the nodal points. The system of algebraic equations is then obtained by some integral formulation, in which the equation of motion and the conservation equation are averaged over each element in a certain way. This system of equations is usually generated by a computer program on the basis of data describing the geometry of the elements and their properties.

In principle there is little difference between the two methods. The major differences are in the supply and handling of input data. The main advantage of the usual finite element method over the usual finite difference method is, in the author's opinion, the flexibility in the geometry. Because no restrictions are imposed on the dimensions and the arrangements of the elements, and because the handling of input data, including the setting up of the system of equations, is performed in the computer program, it is very easy to adjust the geometrical data before repeating the computations. This is particularly useful for transient problems involving a free surface or an interface. The network of elements changes with time, thus following the position of the interface (Verruijt, 1970).

An example of an application of the finite element method to an interface problem is given in Figure 4. In this Figure the change in position of an interface under the influence of infiltration in the fresh water is shown. The example refers to the axially symmetric case, which can be treated as a two-dimensional problem, with a radial and a vertical co-ordinate. The results shown in Figure 4 were obtained by Mr S. van Dongen for a thesis at the Delft University of Technology (1976).

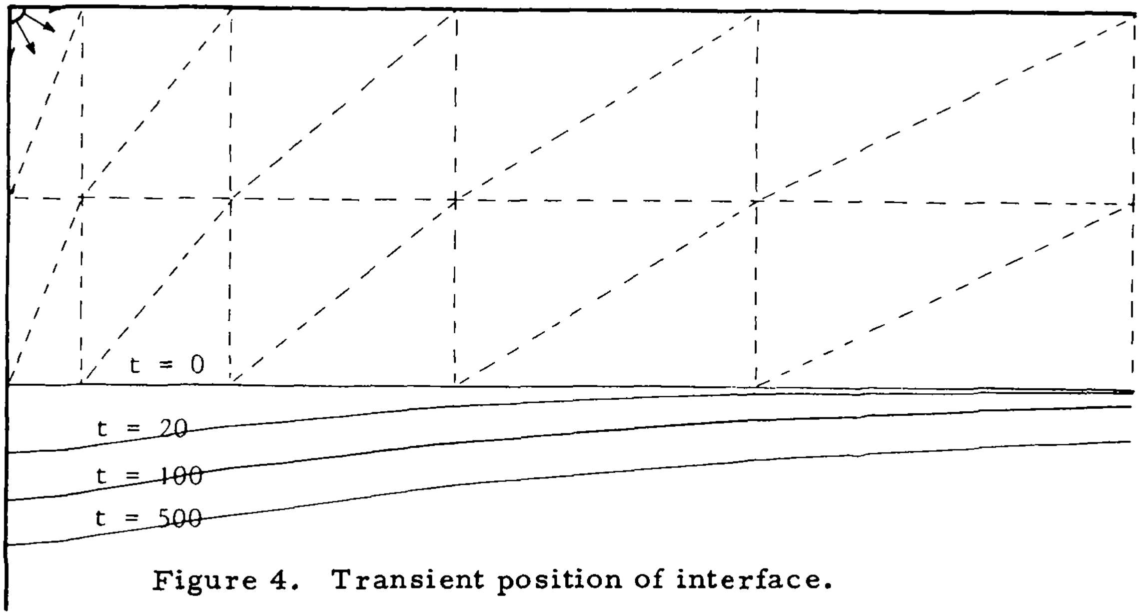

Figure 4. Transient position of interface.

Numerical methods can also be used for the analysis of flow in a horizontal plane. In order to make the problem two-dimensional it is then usually assumed that the head in the fresh water zone does not vary in the vertical direction (Dupuit's assumption), and that the head in the salt water is constant (this could be called the Ghyben-Herzberg approximation). This leads to the following relation between the level of the free surface h and the depth of the interface h' (see Figure 5),

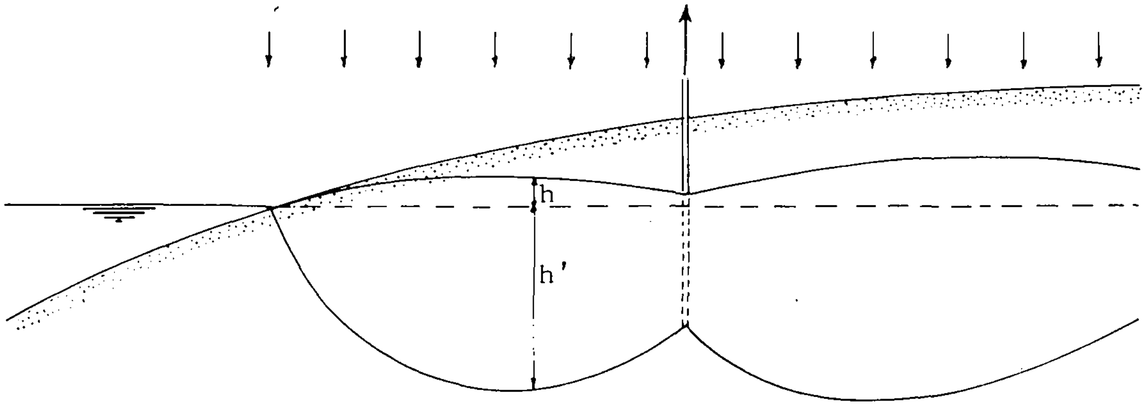

Figure 5. The Ghyben-Dupuit approximation.

$$h + h' = \frac{\rho_s}{\rho_s - \rho_f} h = \alpha h \qquad \ldots\ldots 10$$

where ρ_s and ρ_f are the densities of the salt and the fresh water, respectively. Because of Dupuit's assumption the level of the free surface can be identified with the head. For the case of a single isotropic aquifer with an infiltration rate p, and a phreatic storage coefficient ε, the basic differential equation becomes

$$\varepsilon \frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\left(kh \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(kh \frac{\partial h}{\partial y}\right) + \frac{p}{\alpha} \qquad \ldots\ldots 11$$

This equation lends itself readily to numerical modelling. Because the differential equation is non-linear it has to be linearized, and solved by an iterative procedure. In practice the variations of h during each time step are so small that a first order approximation is sufficiently accurate. In that case there is no longer any appreciable difference with the groundwater flow problem for a confined aquifer.

5. RESTRICTION OF NUMERICAL MODELLING

It is of interest to name some of the theoretical and practical restrictions of the application of numerical models.

Of course the first restriction concerns the limitation of the computer regarding storage and computing time. For two-dimensional problems these limitations are usually of little importance because of the capabilities of modern computers. For three-dimensional transient problems even modern computers are often not yet powerful enough.

Although computer programs are available for a relatively wide class of problems, such as transient flow in a layered system of non-homogeneous isotropic aquifer, the general problem for flow of a fluid with a variable salt content has not yet been solved satisfactorily. The main reason for this is the fact that the numerical approximation entails an averaging of the dependent variables over the elements, which is equivalent to a considerable spreading of the salt, often much more than is physically reasonable. This phenomenon of so-called numerical dispersion so far has been attacked with success only by semi-analytical methods (Pinder and Cooper, 1970).

A final limitation of the applicability of numerical modelling that has to be mentioned is the availability of sufficient data. In nature the physical properties of the soil may vary locally between fairly wide limits, and the numerical models in principle enable these variations to be taken into account. However, it is usually practically impossible to collect all the necessary information. Therefore the analysis has to be done with the insufficient data available. This also implies that the results obtained from the numerical model, which may appear as computer output with a great number of decimals, are to be used with caution, because of the uncertainties in the input data. It may be very useful to pay some attention to an analysis of the sensitivity of the solution to variations in the input data.

6. CONCLUSION

For the analysis of groundwater movement in coastal aquifers, physical and numerical models may be very useful. The Hele Shaw model is of great value for the analysis of two-dimensional interface problems in a homogeneous aquifer. For more general problems numerical models provide a powerful tool, but the applicability of such models in practice may be limited.

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PAPER 16

USE OF IDEALIZED MODELS IN PREDICTING THE POLLUTION OF WATER SUPPLIES DUE TO LEACHATE FROM LANDFILL SITES

D. B. Oakes

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1. INTRODUCTION

The Water Research Centre is currently involved in a programme of research on the behaviour of hazardous wastes in landfill sites, funded by DOE. The field investigations (1) have been supplemented by pilot scale and laboratory experiments, and by studies of groundwater flow regimes beneath landfills using mathematical models. This paper considers various aspects of the modelling studies and presents some solutions to idealized problems which give preliminary guidance on the suitability of various geologies for landfill location. It must be emphasized that the idealized solutions may only be valid when used within the limitations of the assumptions, and when all of the flow mechanisms in the aquifer are represented in the model. When an accurate description of contaminant flow in an aquifer is available from field measurements it is often possible to obtain sufficient data to construct a comprehensive model which reproduces the observed pollution pattern and which enables predictions of future pollutant movement to be made. The concepts and results contained in this paper are not related to this situation, but to the problem of selecting new landfill sites when data are scarce. In these circumstances the principal features of the study are:

- (i) geological environment: chalk, sandstone and gravel aquifers have been considered;
- (ii) depth to water table and properties of the unsaturated zone;
- (iii) magnitude and direction of groundwater flow;
- (iv) physical or chemical reactions and sorption phenomena in the unsaturated and saturated zones;

and

- (v) proximity of abstraction wells or streams in hydraulic connection with the groundwater system.

The nature of any chemical reactions or sorption effects will depend on the particular solute and mineralogy of the medium through which it percolates A number of model studies have assumed non-interacting solute and matrix (2)(3) while some have assumed a simplified representation such as a reversible linear isotherm for sorption (4). In any event, the result of sorption is to retard solute movement so that by omitting it from the present study we are omitting a retarding factor rather than a loss from the system.

Solution of the convective dispersion equation was effected by using the method of characteristics (5) which is particularly suited to simple flow regimes.

2. CONCEPTUAL MODEL

Figure 1 shows the principal features of the system. The landfill is separated from the water table by the unsaturated zone as will normally be the case. Flow through the unsaturated zone is assumed to be vertical, and through the saturated zone horizontal. In the absence of abstraction wells groundwater flow is assumed to be horizontal and uni-directional. The mechanism of fissure flow, which is known to be important in both the chalk and sandstone, is not considered explicitly in this study. In regional pollution investigations the effects of fissure flow will be evident from the extent of contamination and the rate of movement of the pollutant. These features will be reflected in field measurements of dispersivity providing the volume of aquifer sampled in the experiment is large enough.

Equilibrium conditions are assumed so that only long-term effects of leachate percolation are considered. In general, leachate percolation may be pulsed rather than continuous because of the temporal distribution of rainfall and because of the intermittent nature of waste disposal operations at a landfill. However, the unsaturated zone has a significant dispersive effect on discrete pulse inputs of solute as will be shown later, so that a continuous flux across the water table may be a reasonable approximation.

3. SOLUTE MOVEMENT THROUGH THE UNSATURATED ZONE

Indications of the rate of movement of conservative solutes through the unsaturated zone of the Chalk and Bunter Sandstone are provided by the natural tracers, such as tritium. Tritium has proved to be a particularly useful tracer during the past 10 years because of the significant increase above natural levels in rainfall arising from thermonuclear explosions (6). As part of the Centre's nitrate research programme, tritium profiles have been obtained from the interstitial water of chalk cores from near Winchester, Hants (7). The profiles indicate a downward movement rate of tritium of between 0.8 and 1.05 m/yr. Smith et al. (6) have reported a rate 0.9 m/yr for chalk in Berkshire. Similar movement rates have been deduced for nitrate and chloride ions (7). The solute flow mechanism giving rise to these show migration rates is illustrated in Figure 2. Recharge through the chalk to the water table occurs through the fissure system. The chalk blocks are fully saturated, even above the water table, with the water held static by high surface tension forces. Vertical flow rates down the fissures have been estimated to be, at most, 0.6 m/d (7). Rates of solute movement of about 1 m/yr may be obtained by assuming rapid diffusion of solutes between the fissure water and pore water. The same mechanism will be effective for all solutes and downward migration rates of about 1 m/yr may be assumed.

Tritium profiles from sandstone cores (8) indicate vertical movement rates of about 1.8 m/yr. Recharge through sandstone is probably partly by fissure flow and partly by intergrannular seepage, and it is probable that solute movement is retarded by diffusion of ions with static water. The static water content may be identified with the difference between the total and drainable porosities.

The solute migration rates measured in the unsaturated chalk near Winchester range between 0.8 m/yr and 1.1 m/yr. Two boreholes 10 m apart gave values of 0.8 and 1.05 m/yr reflecting the local heterogeneity of the chalk. It is anticipated that this is a characteristic feature of solute movement through the chalk. The variability of downward movement rates is equivalent to a large vertical dispersivity when solute input from a distributed source is considered. The unsaturated chalk will, therefore, tend to dissipate any fluctuations in the solute flux from the landfill to give a fairly steady input to the water table. It is expected that a similar mechanism will be effective in sandstone aquifers.

Movement of solutes through gravels will be more rapid than through chalk or sandstone and it is expected that little dispersion of solute pulses will occur unless clay or silt lenses are present above the water table.

4. SOLUTE MOVEMENT THROUGH THE SATURATED ZONE

4.1. DILUTION OF PERCOLATES BY GROUNDWATER

The percolate flux across the water table will be diluted with groundwater flowing beneath the landfill. The magnitude of dilution will depend on both groundwater flow rate and depth of mixing which will itself be determined by the local hydrogeology. For the present study the depth of mixing is taken to be the full depth of groundwater flow so that the percolate dilutions represent depth averaged values.

With the notation given in Figure 1, a mean percolation rate from the landfill of i m/yr, and a concentration of some pollutant in the percolate of c mg/l, the mass of pollutant transported to the water table each year will be iwlc gm under steady state conditions. If the groundwater flow rate is u m/yr, and the depth of flow is b m, then the concentration of pollutant in groundwater beneath the landfill is given as:

$$c(gw) = \frac{iwlc}{iwl + uwb} = \frac{ic}{i + ub/l} \qquad \text{mg/l}$$

If the dilution factor, d, is defined as the ratio of concentration in groundwater beneath the landfill to concentration in the leachate from the landfill, then:

$$d = \frac{i}{i + ub/l}$$

It is assumed in this mass balance that there is a continuous supply of leachate from the landfill, so that the dimensions w and l should relate to the active area.

The dilution factor has been used to relate geological environment to groundwater contamination vulnerability. Estimates of the product ub are required and this may be equated to the product of transmissivity and groundwater gradient. The gradient will depend upon transmissivity among other things and values of the product were estimated from field studies and groundwater model studies undertaken by WRC. Typical ranges for chalk, sandstone and gravel aquifers are given in Table 1. It must be emphasized that values outside the ranges given may not be uncommon, but the range for each geological type should encompass the majority of cases.

Table 1. Aquifer properties

Aquifer	ub (m^2/d)
chalk	3 to 10
sandstone	0.5 to 2
gravel	10 to 20

The calculated dilution factor depends also on the percolation rate which will be a function of rainfall intensity, local geology, the types of waste deposited and landfill management. For illustrative purposes i has been set equal to 0.3 m/yr which is a typical rainfall recharge rate for the exposed chalk and sandstone deposits in the UK. Calculated dilution factors are given in Table 2 for two different landfill sizes.

Table 2. Dilution in groundwater

Landfill length l (m)

Aquifer	50	300
chalk	$0.4\ 10^{-2}$ - $0.1\ 10^{-1}$	$0.2\ 10^{-1}$ - $0.7\ 10^{-1}$
sandstone	$0.2\ 10^{-1}$ - $0.7\ 10^{-1}$	0.1 - 0.3
gravel	$0.2\ 10^{-2}$ - $0.4\ 10^{-2}$	$0.1\ 10^{-1}$ - $0.2\ 10^{-1}$

If dilution is the main factor in landfill design then it is clearly better practice to site a rectangular landfill with its longer axis perpendicular to the direction of groundwater flow. The mass of pollutant reaching the water table would be the same as for any other orientation, but in this position it would be diluted with the greatest volume of groundwater flow. However, other factors such as the proximity of abstraction wells are of prime importance, and these aspects will be considered in a later section.

4.2. DISPERSION IN THE SATURATED ZONE

The development of a zone of pollution resulting from leachate percolation to the water table will be controlled by the processes of convection and hydrodynamic dispersion. Figure 3 shows the steady state pollution distribution in an homogeneous, isotropic aquifer for various values of longitudinal and transverse dispersivities. The source of pollution, in this case, is a landfill of dimension 50 m × 50 m.

A longitudinal dispersivity of 0.6 m has been estimated for sandstone by Oakes and Edworthy (9), and for a sandstone aquifer in Israel a value of 0.5 m has been reported (10). Cole (11) has reported a dispersivity of 12 m for chalk. Transverse dispersivity should be less than the corresponding longitudinal value in an isotropic medium, but they have been assumed equal in this analysis.

If the dispersivities given above for chalk and sandstone are representative of large-scale pollution movement, then the lateral spread of a pollution plume 1 km down gradient from a landfill will be at most 80 m in a sandstone aquifer, and at most about 120 m in a chalk aquifer.

Dispersion in a gravel aquifer is expected to be less than in sandstone.

5. CONCENTRATION OF LEACHATE IN WELL DISCHARGE

If a well is located directly down gradient from a landfill it is likely that all of the leachate will be induced to flow to the well. A dilution factor, defined now as the ratio of concentration in the well discharge to concentration in the landfill leachate, may be estimated from a mass balance. The dilution factors in this case are independent of aquifer type, but depend on the abstraction rate, the leachate percolation rate and the landfill area. Table 3 gives calculated dilution factors for various well discharge rates.

Table 3. Dilutions in well discharge

Well discharge rate (mgd)	Landfill dimensions (m)	
	50 x 50	300 x 300
0.5	0.9 10^{-3}	0.3 10^{-1}
1	0.5 10^{-3}	0.2 10^{-1}
2	0.2 10^{-3}	0.8 10^{-2}
5	0.9 10^{-4}	0.3 10^{-2}

If an abstraction well is located down gradient from a landfill, but displaced laterally from the down gradient direction, the proportion of leachate reaching the well will depend on the width of flow which contributes to the well discharge, and this in turn depends on the aquifer characteristics. The graphs of Figure 4 show the concentrations of pollutant in the well discharge relative to that concentration to be expected when the well is directly down gradient from the landfill as a function of lateral displacement. The aquifer properties used in the calculations were the minimum values from Table 1 for each geological type. The minimum values of ub results in each case in the most pessimistic forecast of well discharge contamination.

The concentration distributions were generated with a steady state model to simulate long-term behaviour. To augment these results the mean travel times of pollutants in the saturated zone have been determined within the framework of the idealized model. Estimates of the aquifer thickness, and porosity are required and the values selected are given below:

aquifer thickness = 20 m
porosity - chalk = 0.02
- sandstone = 0.20
- gravel = 0.20

Travel times were estimated by integrating fluid velocities along streamlines from the recharge zone beneath the landfill to the abstraction well which in this case is directly down gradient from the landfill. Using the aquifer properties given in Table 1 the following pollutant travel times were derived for a well discharge of 1 mgd.

Table 4. Pollutant travel times from beneath landfill to a well

Aquifer	Distance from landfill to well (km)	Range of expected travel times (days)
Chalk	1	30 - 80
	2	70 - 190
Sandstone	1	1000 - 1900
	2	2600 - 5800
Gravel	1	170 - 320
	2	370 - 700

The rapid transit time in chalk aquifers results from the low drainable porosity which is a feature of the fissure flow nature of this aquifer. While little water movement can occur in the chalk matrix it is apparent that there will be some diffusion of solutes between the fissures and pores as occurs in the unsaturated zone. Research is currently in progress at WRC to quantify this effect, but it will undoubtedly retard solute movement to some extent. In the extreme case of very rapid diffusion of solute ions between the pore water and fissure water the travel times will be larger by a factor of about 20. A similar mechanism may be effective in retarding solute movement through sandstone, though the retardation can not be as great as in the chalk.

6. LEACHATE MOVEMENT TO STREAMS

The time of travel of leachate to streams hydraulically connected to the aquifer may be estimated as before by integration of pore velocities along the streamlines. It is expected that if the stream is down gradient from the landfill most of the leachate will ultimately be discharged in baseflow. For the same assumptions as before the pollutant travel times are given in Table 5.

Table 5. Pollutant travel times from beneath landfill to a stream

Aquifer	Distance landfill to stream (km)	Range of expected travel times (days)
Chalk	1	40 - 130
	2	80 - 270
Sandstone	1	2000 - 8000
	2	4000 - 16000
Gravel	1	200 - 400
	2	400 - 800

Retardation of pollutants by diffusion may increase the travel times given in Table 5.

7. CONCLUSIONS

(i) Simple models of groundwater and pollutant movement have been used to provide information on the expected behaviour of landfill leachates in our major aquifers. The results have been expressed in terms of dilution factors relating concentration of some pollutant in groundwater or in well discharge to concentration in the leachate leaving the landfill base.

(ii) Dilution is dependent on the area of active landfill, and on the leachate percolation rate. With a landfill size of 50 m × 50 m and a percolation rate of 0.3 m/yr, it has been estimated that pollutants should be diluted at least 100-fold in chalk or gravel aquifers, and at least 15-fold in sandstone.

(iii) The dilution in well discharge is not related to aquifer type if the well is directly down gradient from the landfill. Leachate from a 50 m × 50 m landfill is expected to be diluted 2000-fold in a 1 mgd well discharge. To avoid pollution from a landfill reaching a pumping well the well must be displaced laterally from the down gradient direction. For a 1 mgd abstraction rate the necessary displacement varies between about 200 m for a gravel aquifer to 4.5 km for a sandstone aquifer.

(iv) Pollutant travel times through the saturated zone are rapid in comparison to travel times through the unsaturated zone though more research must be done to evaluate the role of solute diffusion processes in saturated flow. The value of porosity is of paramount importance to the calculation of travel times and accurate estimation of this parameter will be a necessary pre-requisite to a more detailed model study. Pollutant movement rates from the landfill to the water table are expected to be about 1 m/yr in chalk and about 1.8 m/yr in sandstone.

(v) The results presented show a wide range of variation even for a single aquifer, and must clearly be used with care. They can provide initial estimates of the relationship between geological environment and vulnerability of groundwater supplies. For detailed predictions of pollutant transport more sophisticated models are required. These are now readily available, but the difficulties of data collection may often preclude the use of such models.

ACKNOWLEDGEMENT

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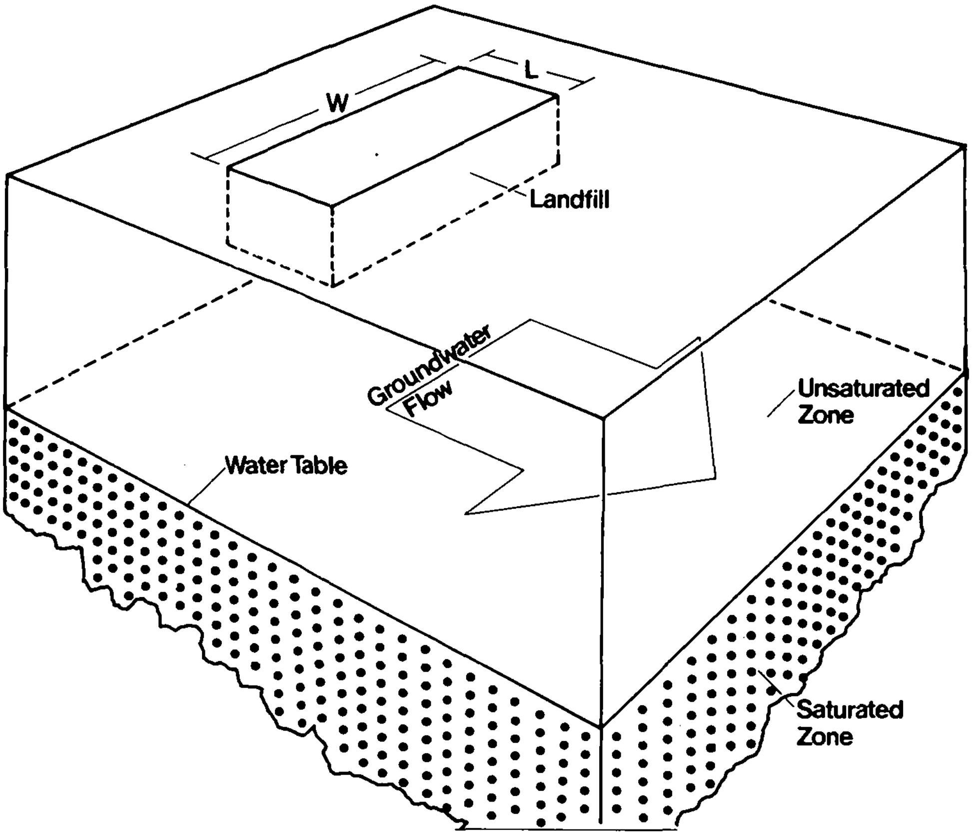

Figure 1. Idealized model of the landfill-aquifer systems.

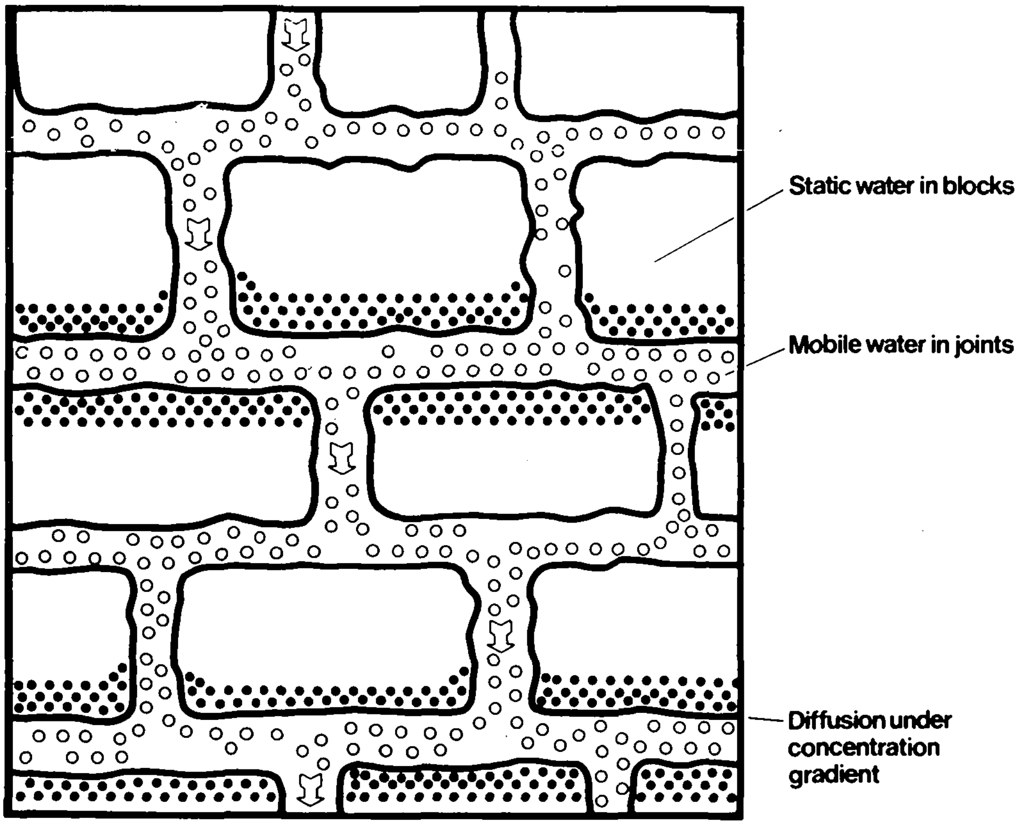

Figure 2. Solute movement in the chalk.

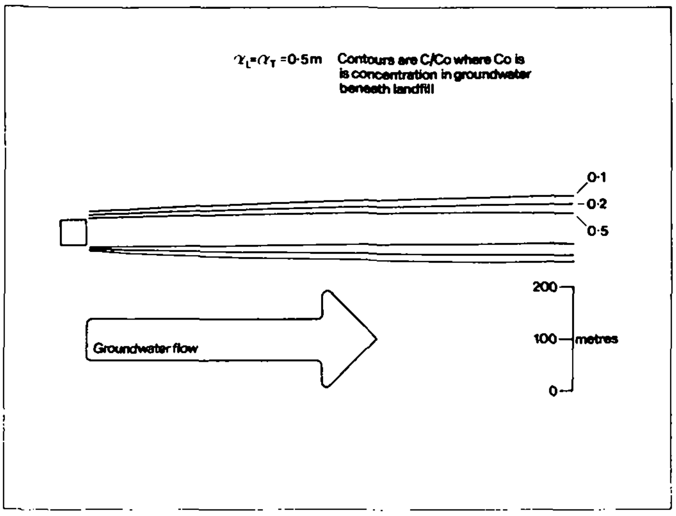

Figure 3 (a). Distribution of pollution in groundwater flow beneath a landfill.

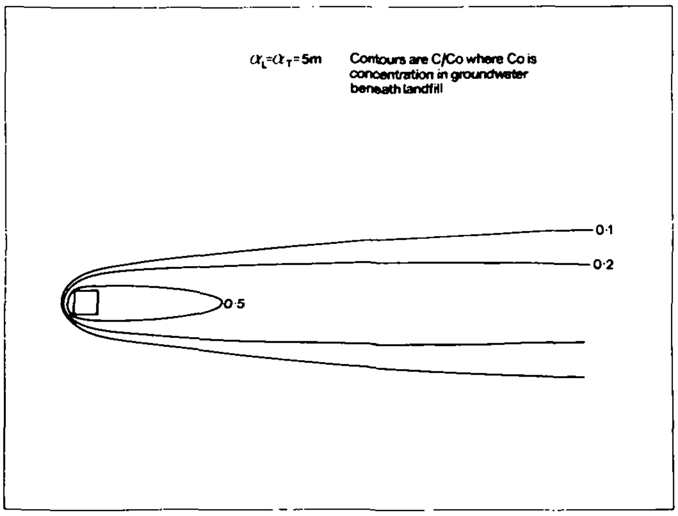

Figure 3 (b).

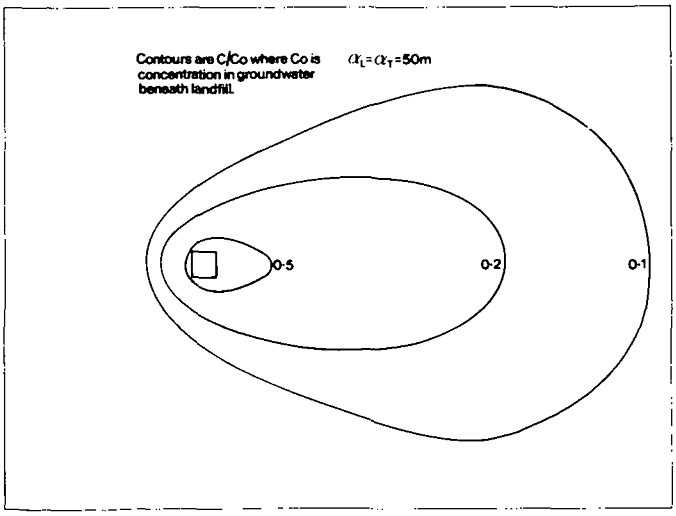

Figure 3 (c).

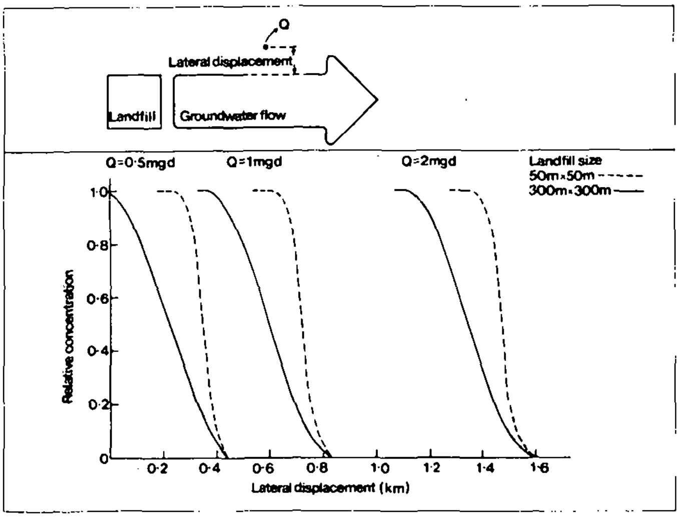

Figure 4 (a). Variation of relative concentration in well discharge with lateral displacement for a CHALK aquifer.

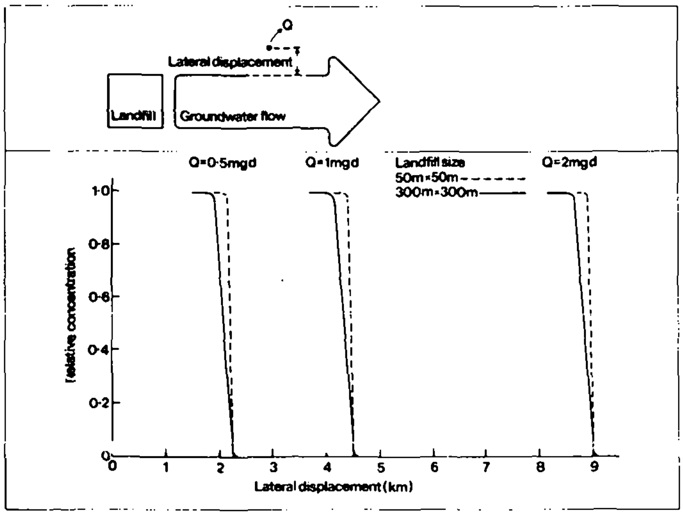

Figure 4 (b). Variation of relative concentration in well discharge with lateral displacement for a SANDSTONE aquifer.

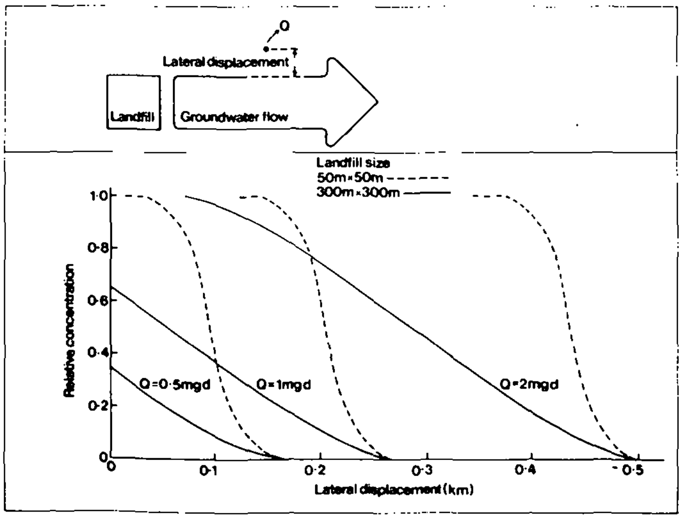

Figure 4 (c). Variation of relative concentration in well discharge with lateral displacement for a GRAVEL aquifer.

PAPER 17

APPLICATION OF SOLUTE-TRANSPORT MODELS TO GROUNDWATER QUALITY PROBLEMS

Leonard F. Konikow

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1. INTRODUCTION

Groundwater quality can be affected by a variety of man's activities. Because industrial, agricultural, and governmental activities will probably continue to develop and grow in the future, while groundwater supplies must simultaneously be protected from contamination, methods are needed to predict the effects of man's activities on the chemical quality of groundwater resources. Specifically, the capability to predict the movement of dissolved chemicals in flowing groundwater can be of help in (1) planning and designing projects to minimize groundwater contamination, (2) estimating spatial and temporal variations of chemical concentrations, (3) estimating the time of travel between a source of contamination and a groundwater sink (a discharge point such as a stream, spring, or well), (4) designing an effective and efficient monitoring system, and (5) evaluating the physical and economic feasibility of alternative reclamation plans for removing contaminants from an aquifer and/or preventing the contaminants from spreading.

Reliable predictions of contaminant movement can only be made if we understand the processes controlling the convective transport, hydrodynamic dispersion, and chemical reactions affecting the dissolved chemicals in groundwater, and if we can quantitatively represent them in a systematic model. A usable model for a variety of hydrogeologic situations must be accurate, functional, and transferable. Aquifers generally have heterogeneous properties and complex boundary conditions, therefore the solution of the mathematical equations that describe the transport processes generally requires the use of a deterministic, distributed parameter, digital simulation model.

2. GOVERNING EQUATIONS

2.1. BACKGROUND

The purpose of a model that simulates solute transport in groundwater is to compute the concentration of a dissolved chemical species in an aquifer at any specified place and time. Because convective transport and hydrodynamic dispersion depend on the velocity of groundwater flow, the mathematical simulation model must solve two simultaneous partial differential equations. One is the equation of flow, from which groundwater velocities are obtained, and the second is the solute-transport equation, describing the chemical concentration in the groundwater.

2.2. FLOW EQUATION

By following the derivation of Pinder and Bredehoeft (1968), the equation describing the transient two-dimensional flow of a homogeneous slightly compressible fluid through a nonhomogeneous anisotropic aquifer may be written in cartesian tensor notation as:

$$\frac{\partial}{\partial x_i}\left(T_{ij}\frac{\partial h}{\partial x_j}\right) = S\frac{\partial h}{\partial t} + W(x,y,t) \qquad i, j = 1,2 \qquad \ldots\ldots 1$$

where T_{ij} is the transmissivity tensor, L^2/T;

h is the hydraulic head in the aquifer, L;
S is the storage coefficient, L^0;
t is the time, T; and
W is the volume flux per unit area, L/T

If we only consider fluxes of: (1) direct withdrawal or recharge, such as pumping from a well, well injection, or evapotranspiration, and (2) steady vertical leakage into or out of the aquifer through a confining layer or stream bed, then W(x, y, t) may be expressed as:

$$W(x,y,t) = Q(x,y,t) - \frac{K_z}{m}(H_s - h) \qquad \ldots\ldots 2$$

where Q is the rate of withdrawal (positive sign) or recharge (negative sign), L/T;
K_z is the vertical hydraulic conductivity of the confining layer or stream bed, L/T;
m is the thickness of the confining layer or stream bed, L; and
H_s is the hydraulic head in the source bed or stream, L.

An expression for the average seepage velocity of groundwater can be derived from Darcy's Law and can be written in cartesian tensor notation as:

$$V_i = -\frac{K_{ij}}{n} \frac{\partial h}{\partial x_j} \qquad \ldots\ldots 3$$

where V_i is the seepage velocity in the i-direction, L/T;

K_{ij} is the hydraulic conductivity tensor, L/T; and
n is the effective porosity of the aquifer, L^0.

2.3. SOLUTE-TRANSPORT EQUATION

The equation used to describe the two-dimensional transport and dispersion of a given dissolved chemical species in flowing groundwater, was derived by Reddell and Sunada (1970), Bear (1972), and Bredehoeft and Pinder (1973), and may be written as:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(C\, V_i) - \frac{C'W}{nb} + \sum_{k=1}^{s} R_k \quad i,j = 1,2 \qquad \ldots\ldots 4$$

where C is the concentration of the dissolved chemical species, M/L^3;
D_{ij} is the dispersion tensor, L^2/T;
b is the saturated thickness of the aquifer, L;
C' is the concentration of the dissolved chemical in a source or sink fluid, M/L^3; and
R_k is the rate of production of the chemical species in reaction k of s different reactions, M/L^3T.

The first term on the right hand side of Equation 4 represents the change in concentration due to hydrodynamic dispersion and is assumed to be proportional to the concentration gradient. The second term describes the effects of convective transport, while the third term represents a fluid source or sink. The fourth term, which describes chemical reactions, must be written explicitly for all reactions affecting the chemical species of interest. This term may be eliminated from Equation 4 for the case of a conservative (nonreacting) species.

2.4. DISPERSION COEFFICIENT

The dispersion coefficient may be related to the velocity of groundwater flow and to the nature of the aquifer using Scheidegger's (1961) equation:

$$D_{ij} = \alpha_{ijmn} \frac{V_m V_n}{|V|} \qquad \ldots\ldots 5$$

where α_{ijmn} is the dispersivity of the aquifer, L;

V_m and V_n are components of velocity in the m and n directions, L/T; and

$|V|$ is the absolute magnitude of the velocity, L/T.

Scheidegger (1961) further shows that for an isotropic aquifer the dispersivity tensor can be defined in terms of two constants. These are the longitudinal and transverse dispersivities of the aquifer (α_1 and α_2, respectively). These are related to the longitudinal and transverse dispersion coefficients by:

$$D_L = \alpha_1 |V| \qquad \ldots\ldots 6$$

and

$$D_T = \alpha_2 |V| \qquad \ldots\ldots 7$$

After expanding Equation 5, substituting Scheidegger's identities, and eliminating terms with coefficients that equal zero, the components of the dispersion coefficient for two-dimensional flow in an isotropic aquifer may be stated explicitly as:

$$D_{xx} = D_L \frac{(V_x)^2}{|V|^2} + D_T \frac{(V_y)^2}{|V|^2} \qquad \ldots\ldots 8$$

$$D_{yy} = D_T \frac{(V_x)^2}{|V|^2} + D_L \frac{(V_y)^2}{|V|^2} \qquad \ldots\ldots 9$$

$$D_{xy} = D_{yx} = (D_L - D_T) \frac{V_x V_y}{|V|^2} \qquad \ldots\ldots 10$$

2.5. NUMERICAL METHODS

Three general classes of numerical methods have been used to solve the solute-transport equation: finite-difference methods, finite-element methods, and the method of characteristics. Each method has some advantages, disadvantages, and special limitations for applications to field problems. Each method also requires that the area of interest be subdivided by a grid into a number of smaller subareas.

The method of characteristics was originally developed to solve hyperbolic equations. If solute-transport is dominated by convective transport, as is common in many field problems, then Equation 4 may closely approximate a hyperbolic equation and be highly compatible with the method of characteristics. Although it is difficult to present a rigorous mathematical proof for this numerical scheme, it has been successfully applied to a variety of field problems. The method solves a system of ordinary differential equations that is equivalent to Equation 4. The development and application of this technique to problems of flow through porous media have been presented by Garder and others (1964), Pinder and Cooper (1970), Reddell and Sunada (1970), and Bredehoeft and Pinder (1973).

The numerical solution is achieved by introducing a set of moving points that are traced with reference to the stationary co-ordinates of a finite-difference grid. Each point has a concentration associated with it and is moved through the flow field in proportion to the flow velocity at its location. The moving points simulate convective transport because the concentration at each node of the grid changes as different points enter and leave its area of influence. The additional change in concentration due to dispersion, fluid sources, and chemical reactions is computed with an explicit finite-difference equation. This method has generally been coupled with finite-difference solutions to the flow equations. Because the movement of points is analogous to the flow of small volumes of water, it is relatively easy to visualize the relation of the model to the field problem.

Finite-difference methods solve an equation that is approximately equivalent to the partial differential equation. Although problems of numerical dispersion, overshoot, and undershoot may induce significant errors for some problems, these methods can provide accurate answers when dispersive transport is large compared to convective transport. In the latter case, the computation time required may be 2 to 5 times less than for the method of characteristics. In general, the finite-difference methods are the simplest mathematically, and the easiest to program for a digital computer. Lantz and others (1976) describe a three-dimensional, transient, finite-difference model that simultaneously solves the pressure, energy, and mass-transport equations.

Finite-element methods use assumed functions of the dependent variables and parameters to evaluate equivalent integral formulations of the partial differential equations. Recent articles by Pinder (1973), Segol and Pinder (1976), and Gupta and others (1975) have indicated that Galerkin's procedure is well suited to solve solute-transport problems. These methods generally require the use of more sophisticated mathematics than the previous two methods, but for many problems may be more accurate numerically and more efficient computationally than the other two methods. A major advantage of the finite-element methods is the flexibility of the finite-element grid, which allows a close spatial approximation of irregular boundaries of parameter zones. However, Gupta and others (1975, p. 69) report that in problems dominated by convection, the finite-element methods may also have difficulties.

The selection of a numerical method for a particular problem depends on several factors, such as accuracy, efficiency/cost, and usability. The first two factors are related primarily to the nature of the field problem, availability of data, and scope or intensity of the investigation. A trade-off between accuracy and cost is frequently required. The usability of a method may depend more on the availability of a documented program and on the mathematical background of the modeller. Greater efficiency is usually attainable if the modeller can modify a selected program to adapt it to the specific field problem of interest.

3. MODELLING FIELD PROBLEMS

3.1. DATA REQUIREMENTS

Many factors influence the flow of groundwater and the transport of dissolved chemicals through an aquifer. To compute changes in concentration, all aquifer properties and stresses incorporated in Equation 4 and associated equations must be defined at every node of the numerical grid. Solving Equation 4 also requires the specification of corresponding boundary conditions and initial conditions. Thus, many input data are required for the numerical model, and the accuracy of these data will affect the reliability of the computed results.

In most field problems there will be some inadequate data. Although the spatial variability of transmissivity (or hydraulic conductivity) and saturated thickness can often be defined, in many areas values of the storage coefficient and effective porosity must be estimated. Rarely are field measurements of longitudinal and transverse dispersivity available. All aquifer stresses (sources and sinks) must be defined, and the concentrations associated with all sources must be known. If leakage through a confining layer or stream bed is significant, additional parameters contained in Equation 2 must be defined. If chemical reactions are considered, then information describing the reactions must be known. Where contamination plumes are involved, it is likely that concentrations will vary on a smaller scale than will the hydraulic head. Hence, more control points may be needed to adequately define the concentration pattern than are needed to define the potentiometric surface.

Several different types of boundary conditions can be incorporated into a solute-transport model. These can be used to represent real boundaries of an aquifer as well as to minimize the data requirements and extent of the modelled part of an aquifer. For example, no-flow boundaries can be located to simulate natural limits or barriers to groundwater flow. A constant-flux boundary can represent aquifer underflow, well withdrawals, well injection, or recharge of some specified chemical concentration. A constant-head boundary in the model can represent partsof the aquifer where the head will not change over time, such as recharge boundaries or areas beyond the influence of hydraulic stresses. A constant-concentration condition may be specified where water within a part of the aquifer appears to be maintained at or near some equilibrium concentration, either due to zones of soluble minerals in the aquifer or to waste disposal activities.

In general, every field problem will be unique to some extent and will therefore require an individual evaluation of its data requirements for modelling. Because obtaining accurate data for a model will always be a major problem, some approximations will always have to be assumed to make a complex field problem tractable to a modelling solution. Gupta and others (1975, p. 6) point out that 'the methods available for determining the input parameters have not reached the level of sophistication to which.... mathematical models have reached'.

3.2. MODEL CALIBRATION

To demonstrate that a simulation model is realistic, field observations from the aquifer must be compared with corresponding computations of the model. The types of observed data that are most valuable for model calibration include head and concentration changes over space and time, and the quantity and quality of groundwater discharges from the aquifer.

The calibration procedure aims to minimize differences between the observed and computed data. In practice, the calibration is frequently accomplished through a trial and error adjustment of the model's input data (aquifer properties, stresses, and boundary and initial conditions) to modify the model's output. Because a large number of interrelated factors affect the output, this may become a highly subjective procedure. The degree of allowable adjustment of any parameter should generally be directly proportional to the uncertainty of its value or specification.

Because the groundwater seepage velocity is determined from the head distribution, and because both convective transport and hydrodynamic dispersion are functions of the seepage velocity, a model of groundwater flow must be calibrated before a reliable solute-transport model can be developed. Note that fewer parameters need to be defined to compute the head distribution than are required to compute concentration changes.

Mass balance calculations should be performed during the calibration procedure to check the numerical accuracy of the solution. As part of these calculations, the hydraulic and chemical fluxes contributed by each distinct hydrologic component of the model should be itemized to form hydrologic and chemical budgets for the aquifer in the modelled area. The budgets are valuable because they provide a measure of the relative importance of each component to the total budget.

Recent advances in parameter identification procedures, such as described by McLaughlin (1975) and Yih and Davidson (1975), will help to eliminate some of the subjectivity inherent in model calibration. However, the hydrogeologic experience and judgement of the modeller will always be an important factor in calibrating a model both accurately and efficiently. The modeller must also be familiar with the specific field area being studied to know that both the data base and the numerical model adequately represent existing field conditions.

3.3. PREDICTIVE CAPABILITY

A model that has been calibrated only to reproduce historical data, should not be considered a 'verified' model. Nevertheless, a calibrated model can be used to analyse or predict future aquifer responses. The accuracy of its predictions is the best measure of a model's reliability. A major limitation of predictive simulations is the uncertainty of future stresses. But if the range of future stresses can be estimated, then the range of future responses can be predicted.

Changes in water use or water management in an area can significantly affect both the flow and chemical quality of groundwater. Because a wide variety of alternative decisions or policies are possible regarding water planning, water management, and water-quality control, the alternatives should be optimized to minimize detrimental effects and maximize beneficial effects. The feasibility of any such plan would be strongly dependent on the hydraulic properties of the aquifer and on the type and source of contamination. Thus, an accurate solute-transport model can be a valuable planning tool because it can predict the impact of specific changes in water use or water management on the chemical quality of groundwater.

3.4. SENSITIVITY TESTS

Evaluating the sensitivity of the model to changes in values of input parameters is an important part of the calibration procedure, especially when data of only limited or uncertain reliability are available. The sensitivity tests can demonstrate the relative importance of all factors that affect solute transport. From this we may infer which data must be defined more accurately and which data are already adequate or require only minimal additional definition for the particular field problem under investigation. If additional data cannot be collected, then the sensitivity tests can help to assess the reliability of the model by demonstrating the effect of a given range of uncertainty or error in the input data on the output of the model.

To illustrate the value of a sensitivity analysis, a series of numerical experiments were designed to isolate and define the relative influence of several factors that affect solute transport in one hypothetical problem. The problem consists of one injection (or waste disposal) well and one pumping well located within a regional flow field. A finite-difference flow model was used to compute the heads and velocities for steady-state flow under a specified set of aquifer properties, stresses, and boundary conditions. The model was bounded by two constant-head lines located 5500 feet (1680 metres) apart and having a difference in head of 20 feet (6.1 metres). The model used a square grid with nodes located 500 feet (152 metres) apart. The method of characteristics was used to compute the concentrations after 1 year of pumping.

Several simulations were made to test the effect of increasing, by a factor of two, the value of selected parameters so that relative sensitivities could be compared. Figure 1 shows that doubling the longitudinal and transverse dispersivities decreases the area of high concentrations and increases the area of low concentrations. As expected, there was no effect on the line of mean concentration. Overall, there was only a minor change in the concentration pattern.

Parameters that affect the flow field have a greater affect on the concentrations. When the magnitudes of velocity are doubled by halving the effective porosity, as shown in Figure 2, both convective transport and dispersion are increased, although the head distribution in the aquifer was not affected. The velocities are also increased by doubling the hydraulic conductivity of the aquifer, (Figure 2). However, this also affects the flow field and decreases hydraulic gradients in the aquifer. Note that the same mass of chemicals were injected in the two cases shown in Figure 2 as was for the base conditions. But when porosity is 10 per cent, a given concentration per unit area reflects storage of only half the mass compared to a porosity of 20 per cent. Hence equivalent lines of equal concentration have advanced further from the injection well in the case of lower porosity than with higher porosity.

The effects of doubling the rate of injection (and mass of chemicals injected) are shown in Figure 3. Increased heads near the injection well result in higher velocities, consequently increasing both convective transport and hydrodynamic dispersion in that area. Although the solution is very sensitive to the rate of injection, this is often a difficult parameter to define in many field problems.

The relative sensitivities of the parameters that affect solute transport will vary from problem to problem. Thus the only generalization than can be stated with certainty is that a sensitivity analysis should be performed during the early stages of a model study of solute transport in an aquifer. Another example of the application of a sensitivity analysis with a solute-transport model is given by Schwartz (1975).

4. CASE HISTORIES

4.1. LITERATURE REVIEW

During the past 10 years there have been a number of reports that describe the application of solute-transport models to a variety of groundwater quality problems. Because the results of these previous investigations can be of value to future studies, brief summaries of the salient features of these model applications are presented in Table 1. Two of the modelling studies, the Arkansas River valley and the Rocky Mountain Arsenal, are discussed in detail later in this report.

These summaries indicate that all three types of models described previously can be applied successfully to complex field problems. In most field problems involving the movement of a contaminant, changes in concentration appeared to be controlled predominantly by the effects of convective transport, dilution with recharged water of a different quality, and reactions. The effects of dispersion appeared less significant in general. Very few previous studies have attempted to model the movement of organic chemicals or of non conservative (reactive) chemicals; the US Geological Survey is currently attempting to develop field tests and models for both.

4.2. ARKANSAS RIVER VALLEY

In the Arkansas River valley of south eastern Colorado, USA, salinity increases in groundwater and surface water are primarily related to irrigation practices. A solute-transport model was developed to predict changes in dissolved-solids concentration in response to spatially and temporally varying hydrologic stresses, such as well withdrawals, irrigation recharge, and changes in river stage. The model coupled an iterative alternating-direction implicit procedure, used to solve a finite-difference approximation to the groundwater flow equation, with the method-of-characteristics solution to the solute-transport equation.

Table 1. Summary of reported applications of solute-transport models to groundwater quality problems.

Reference	Description of field problem	Type of solute-transport model	Comments
Green and Cox (1966)	Storage of fresh water in salt-water aquifers	Two-dimensional, method of characteristics	Dispersion coefficient assumed constant
Pinder and Cooper (1970)	Transient position of interface between fresh water and salt water	Two-dimensional, method of characteristics	Model applied in cross-section. Flow is density dependent
Bredehoeft and Pinder (1973)	Movement of salt water in confined limestone aquifer	Two-dimensional, method of characteristics	Accounted for vertical leakage through confining beds, predicted future changes, and tested effects of protective pumping
Pinder (1973)	Hexavalent chromium seeped out of waste disposal pit and spread through underlying glacial outwash aquifer	Two-dimensional, Galerkin finite-element model using isoparametric quadrilateral elements	Assumed steady-state flow and predicted future concentrations
Konikow and Bredehoeft (1974a)	Salinity increases in alluvial stream-aquifer system were related to irrigation practices	Two-dimensional, method of characteristics	Assumed transient flow and computed water quality changes in both groundwater and surface water
Konikow and Bredehoeft (1974b)	Salinity increases in alluvial stream-aquifer system were related to irrigation practices	Two-dimensional, method of characteristics	Used calibrated model to evaluate effects of changes in water management and irrigation practices

Table 1. continued

Reference	Description of field problem	Type of solute-transport model	Comments
Lee and Cheng (1974)	Steady-state position of salt-water interface in unconfined coastal limestone aquifer	Two-dimensional, Rayleigh-Ritz finite-element model using triangular elements	Dispersion coefficient assumed constant
Robertson (1974)	Movement of industrial and low-level radioactive liquid wastes in interbedded basalt flows and unconsolidated sediments	Two-dimensional, method of characteristics	Model included effects of radioactive decay and adsorption
Robson (1974)	Contamination of shallow alluvial aquifer by seepage from sewage-treatment ponds	Two-dimensional, method of characteristics	Model was used to predict future concentrations and test alternative water-management plans
Gupta and others (1975)	Upward migration of salt water along fault zone in deep sedimentary basin	Three-dimensional, Galerkin finite-element model with mixed order isoparametric elements	Accurate geometric representation of stratigraphic boundaries and zones
Robertson (1975)	Movement of industrial and low-level radioactive liquid wastes in interbedded basalt flows and unconsolidated sediments	Three-segment model that combines one-dimensional analytic solution with one and two-dimensional finite-difference methods	Model of perched water body and unsaturated zones above and below it

Table 1. continued

Reference	Description of field problem	Type of solute-transport model	Comments
Grove (1976)	Movement of industrial and low-level radioactive liquid wastes in interbedded basalt flows and unconsolidated sediments	Two-dimensional, Galerkin finite-element model using rectangular elements	Model includes effects of radioactive decay and adsorption
Konikow (1976)	High chloride industrial wastes seeped out of unlined disposal ponds and spread through underlying alluvial aquifer	Two-dimensional, method of characteristics	Assumed steady-state flow. Model was calibrated with 30-year history of groundwater contamination
Segol and Pinder (1976)	Transient position of salt-water front in unconfined coastal limestone aquifer	Two-dimensional, Galerkin finite-element model using quadrilateral elements with linear sides	Flow is density dependent

Detailed field measurements of inflows, outflows, and changes in storage of both salt and water were made during a 1-year period in an 11-mile (17.7 kilometre) reach of the valley and were used to calibrate the model (Konikow and Bredehoeft, 1974a). The observed dissolved-solids concentrations averaged about 1000 mg/l in available surface water and about 2200 mg/l in groundwater. In general, the model accurately simulated monthly flow and water quality changes for both the stream and the aquifer. Calculated dissolved-solids concentrations were within 10 per cent of the observed values approximately 80 per cent of the time.

The calibrated model was then used to predict and evaluate the hydrologic and chemical effects on the stream-aquifer system of several possible changes in water-management practices. The model results, based on observed irrigation practices, were compared with those obtained after imposing different stresses on the model (Konikow and Bredehoeft, 1974b). Increased groundwater use produced significant groundwater salinity increases, water-table declines, and streamflow losses, while increased surface water use generally produced the opposite effects. Improving irrigation efficiency reduced the requirement for irrigation water, but induced a long-term build-up of salt in the aquifer. The model also indicated that if the major irrigation canal in the area would be lined to prevent seepage losses, then significant groundwater salinity increases and water-table declines would occur in the area between the canal and the river. In general, the model analyses demonstrated that initial and short-term responses to major changes in irrigation practices are strongly related to antecedent conditions in the aquifer, and do not necessarily reflect the long-term responses to these changes.

4.3. ROCKY MOUNTAIN ARSENAL

A 30-year history of groundwater contamination at the Rocky Mountain Arsenal, near Denver, Colorado, USA, is related to the disposal of liquid industrial wastes into unlined ponds (Walker, 1961; Konikow, 1976). From 1942-56 the high-chloride wastes were discharged to ponds a, b, c, d, and e, shown in Figure 4. Much of the area north of the Arsenal is irrigated, both with surface water diverted from one of the irrigation canals, which are also unlined, and with groundwater pumped from irrigation wells. Damage to crops irrigated with shallow groundwater was observed during 1951-54. The hydrogeologic characteristics of the alluvium in this area indicates that the aquifer is non uniform in thickness, sloping, discontinuous, and heterogeneous (Konikow, 1975).

Several investigations have been conducted since 1954 to determine both the cause of the problem and how to prevent further damages. Petri and Smith (1956) showed that an area of contaminated groundwater of several square miles existed north and north-west of the disposal ponds. These data indicated that the liquid wastes seeped out of the unlined disposal ponds, infiltrated into the underlying alluvial aquifer, and migrated downgradient towards the South Platte River. To prevent additional contaminants from entering the aquifer, a 100-acre evaporation pond (pond f) was constructed by the US Army in 1956 with an asphalt lining to hold all subsequent liquid wastes.

Data collected during 1955-56 indicated that one main plume of contaminated water extended beyond the north western boundary of the Arsenal, and that a smaller secondary plume extended beyond the northern boundary (see Figure 5). Areas, in which the alluvium is either absent or is unsaturated most of the time, form internal barriers that significantly affect the rates and directions of groundwater flow within the alluvial aquifer, and hence affect solute transport.

The method-of-characteristics model was used to compute a chloride concentration pattern after a 14-year simulation period (Figure 6); the computed pattern agrees closely with the observed pattern (Figure 5). The small difference in the directions of the axes of the main plumes between the observed and computed data is probably due mainly to errors in the computed flow field.

Since 1956 all disposal has been into the asphalt-lined pond f, thereby eliminating the major source of contamination. However, that alone could not eliminate the problem because such a large volume of contaminants was already present in the aquifer. As the contaminants continued to spread downgradient, the concentrations began to decrease near the former disposal ponds. The model was extended to simulate the period through 1972. The pattern of contamination computed for 1972 agrees closely with the pattern observed at that time. Both showed that by 1972 the areal extent of contamination, as indicated by chloride concentrations, had diminished significantly.

Other simulation runs were made with the calibrated model to predict the future effects on several alternative reclamation plans and of the option of no action. Among the plans tested were ones that proposed the construction of a line of wells or drainage trenches to intercept and remove the contaminated groundwater. The results of these analyses indicate that it would still take decades for this aquifer to recover naturally its original water-quality characteristics. But it was also found that carefully planned water management policies could reduce this restoration time to the order of years, rather than decades.

5. CONCLUSIONS

1. Although every groundwater contamination problem is in many ways unique, the general processes controlling solute transport remain the same. Several documented case histories show that where adequate hydrogeologic data are available, solute-transport models can predict the rates and directions of spreading of contaminants from known or projected sources.

2. Groundwater contamination problems can be successfully simulated with solute-transport models that use either finite-difference methods, finite-element methods, or the method of characteristics. But the selection of the 'best' numerical method depends largely on the nature of the specific field problem, and also depends to some extent on the mathematical background of the modeller. The majority of previously documented cases have used the method of characteristics.

3. Many input data are required for a deterministic solute-transport model. The accuracy of these data will affect the reliability of the computed results.

4. The required calibration of a solute-transport model is a somewhat subjective procedure. Thus the hydrogeologic experience and judgement of the modeller may strongly influence the success of a project.

5. Sensitivity tests are an important part of the calibration procedure and can provide measures of additional data requirements and of model reliability.

6. Concentration changes in many field problems were dominated by the effects of convective transport and dilution. Because convective transport and dispersion are both related to flow velocity, the development of an accurate flow model is a necessary prerequisite for the successful application of a solute-transport model to a complex field problem.

7. A calibrated model can be used to predict future trends and to evaluate the effects of alternative water-management plans.

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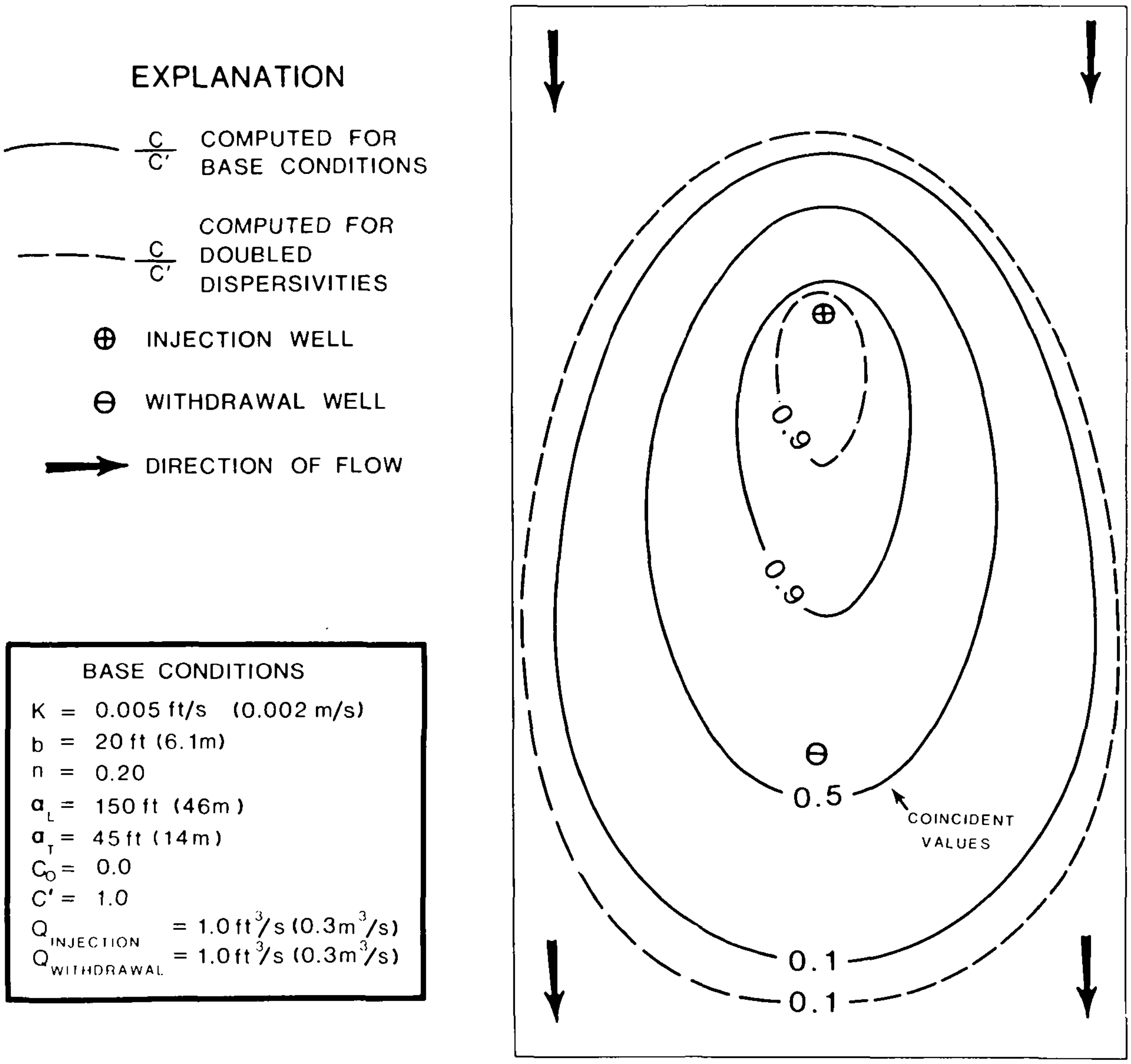

BASE CONDITIONS

$K = 0.005$ ft/s (0.002 m/s)
$b = 20$ ft (6.1m)
$n = 0.20$
$\alpha_L = 150$ ft (46m)
$\alpha_T = 45$ ft (14m)
$C_0 = 0.0$
$C' = 1.0$
$Q_{\text{INJECTION}} = 1.0\ \text{ft}^3/\text{s}\ (0.3\text{m}^3/\text{s})$
$Q_{\text{WITHDRAWAL}} = 1.0\ \text{ft}^3/\text{s}\ (0.3\text{m}^3/\text{s})$

Figure 1. Relative concentrations computed after 1 year for base conditions and for doubled dispersivities. Note that the 0.5-contours for both simulations are coincident

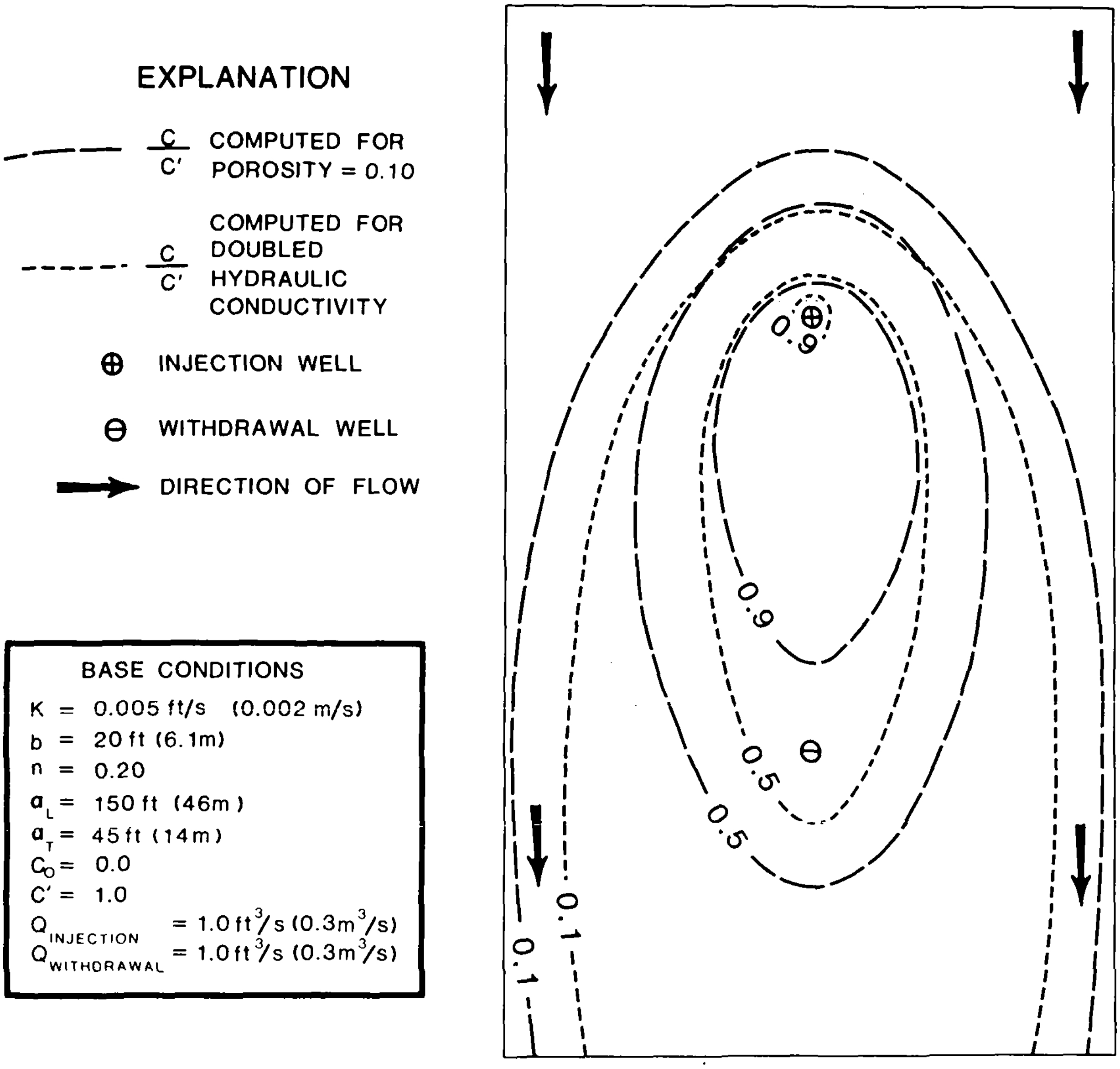

Figure 2. Relative concentrations computed after 1 year for porosity of 0.10 and for doubled hydraulic conductivity

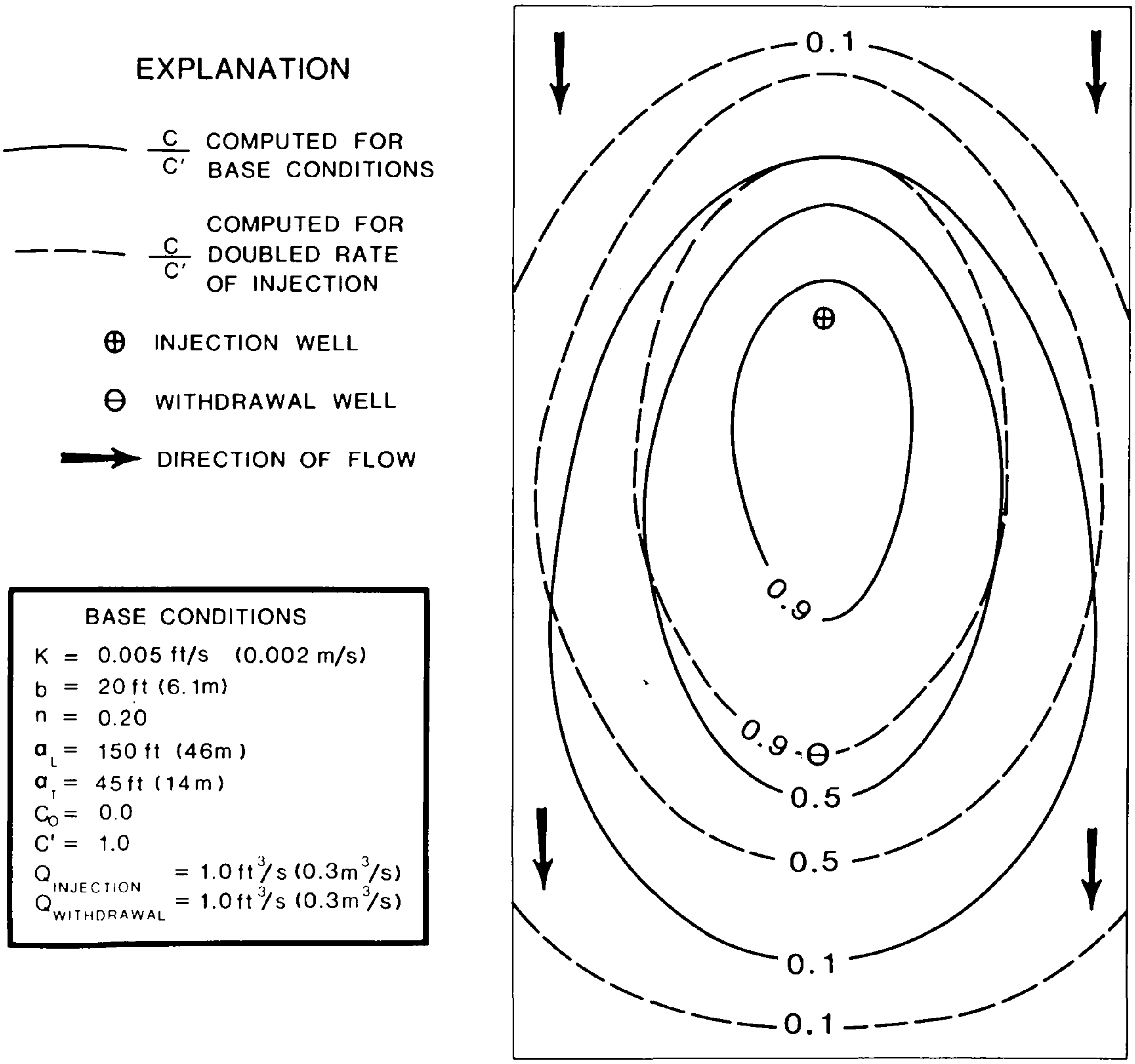

Figure 3. Relative concentrations computed after 1 year for base conditions and for doubled rate of injection

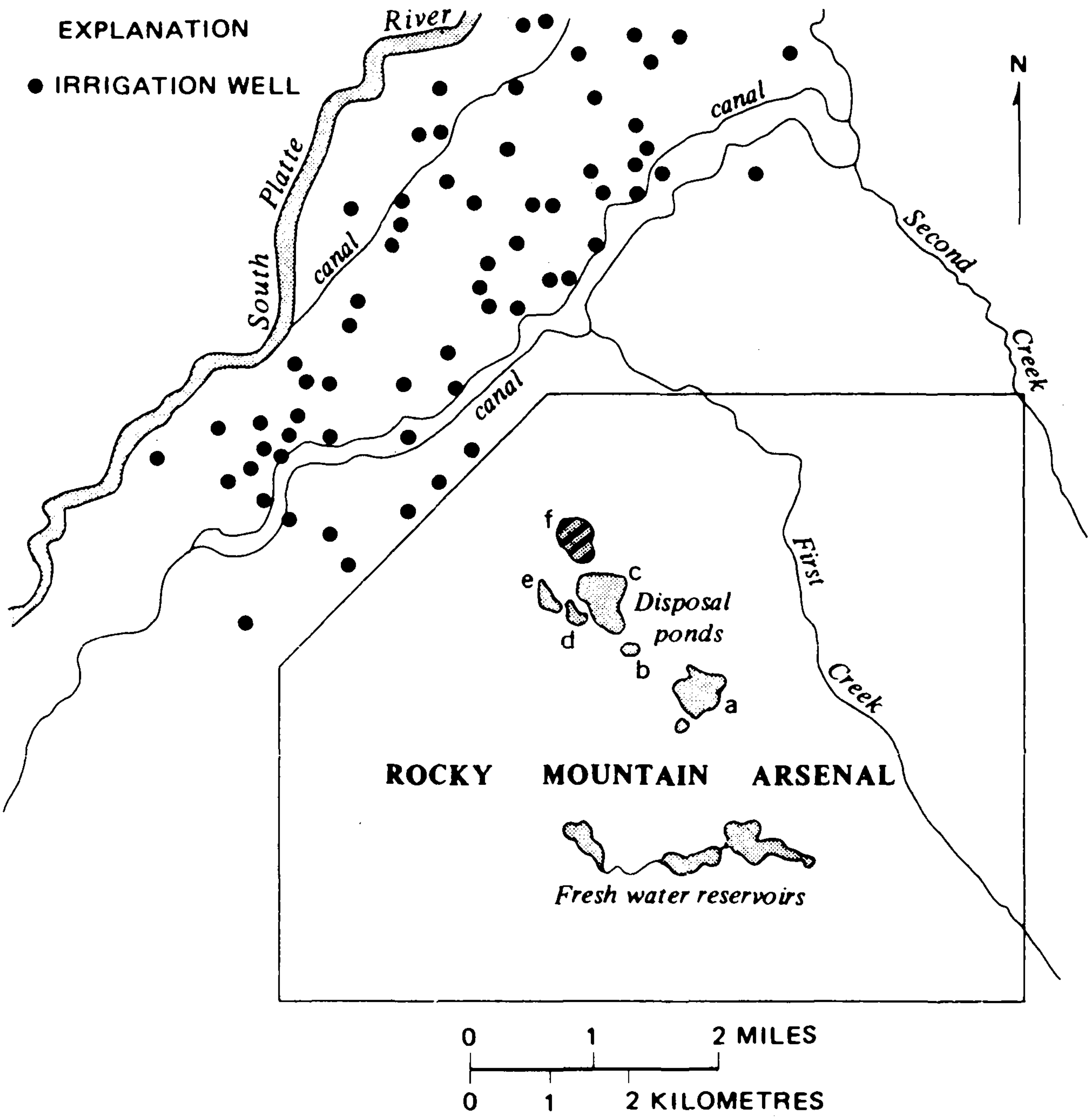

Figure 4. Major hydrologic features in and adjacent to the Rocky Mountain Arsenal, Colorado, USA

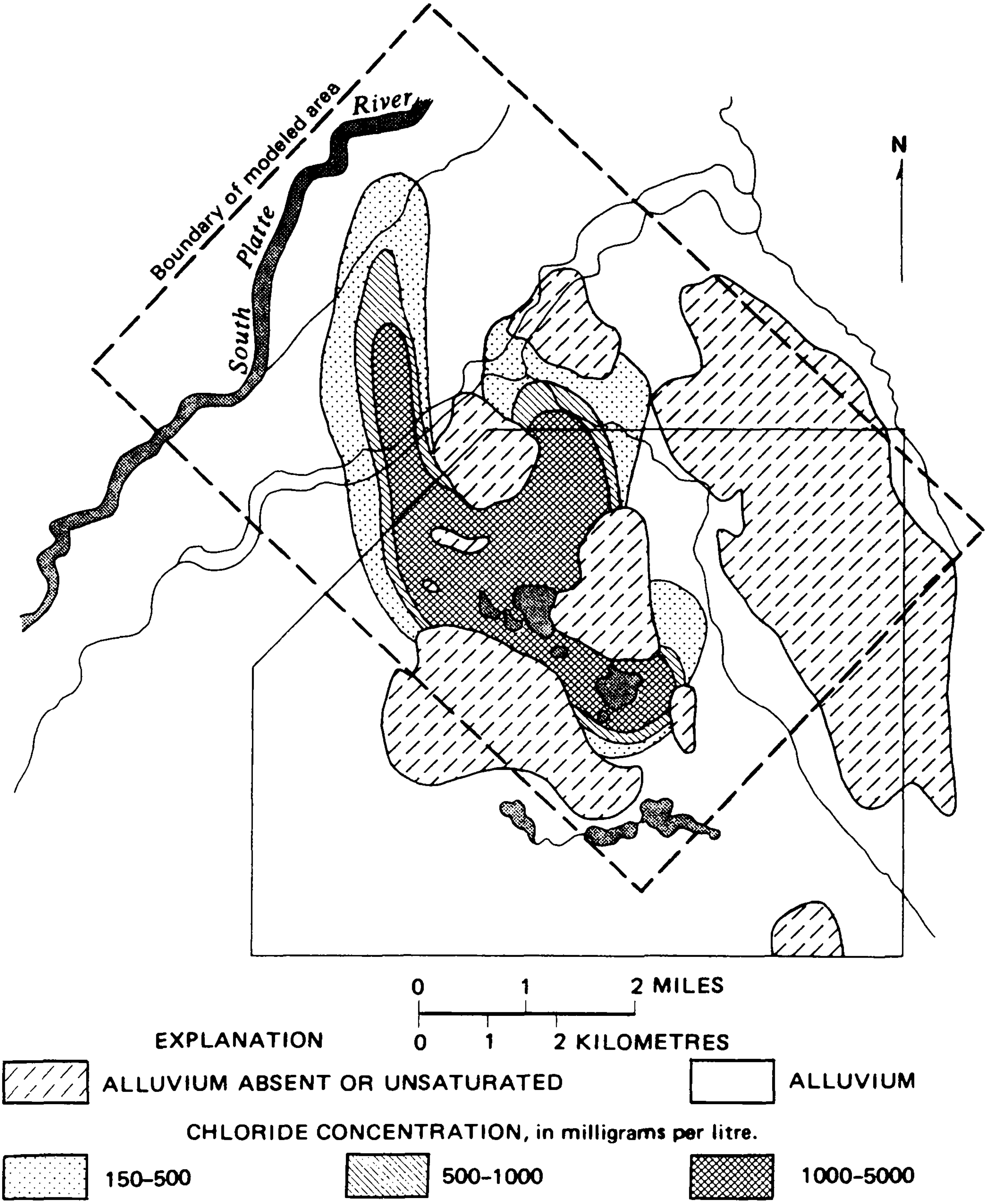

Figure 5. Observed chloride concentration, 1956, Rocky Mountain Arsenal, Colorado, USA

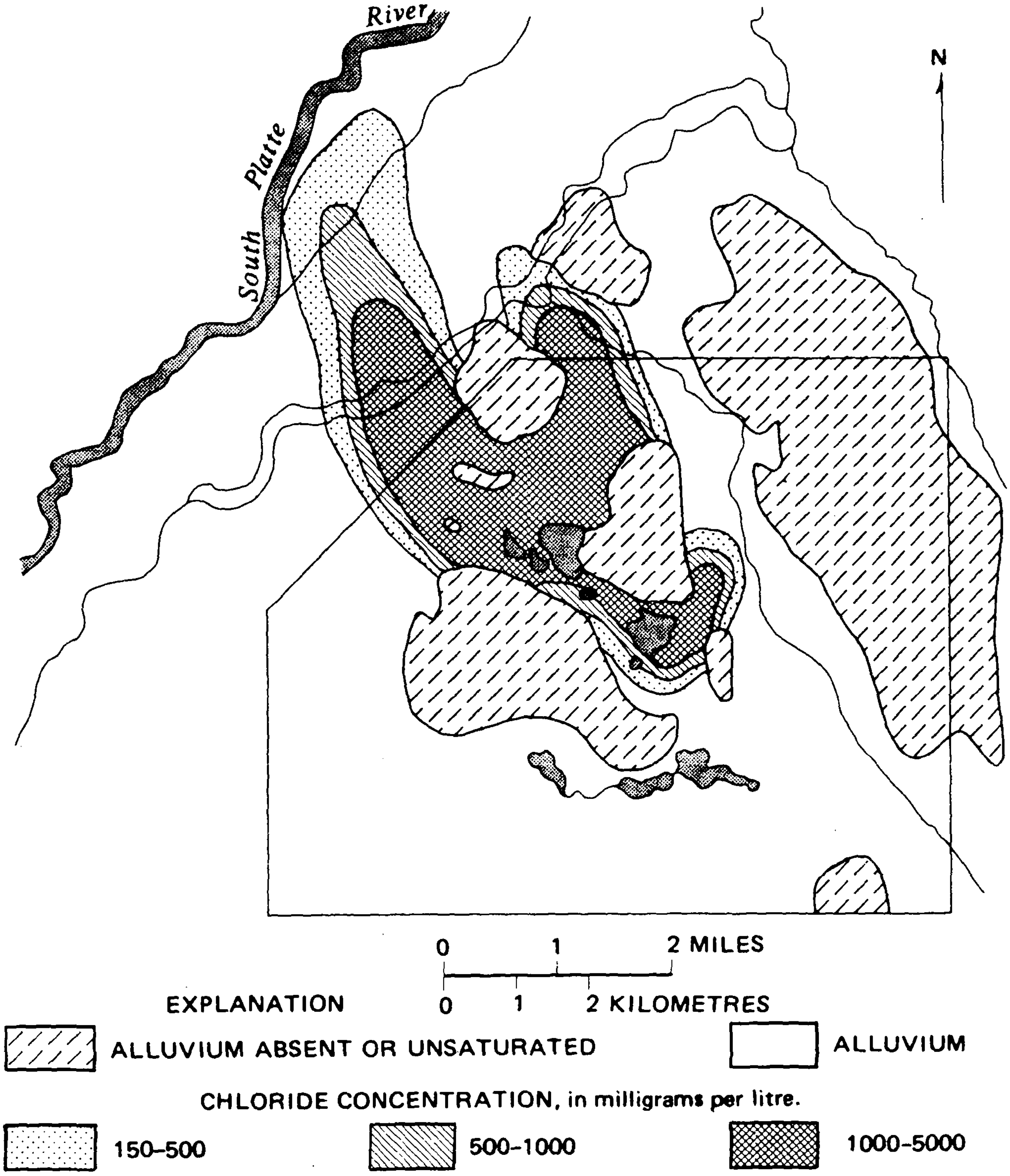

Figure 6. Computed chloride concentration, 1956, Rocky Mountain Arsenal, Colorado, USA

PAPER 18

THE USE OF MODELS IN GROUNDWATER QUALITY MANAGEMENT

A. Mercado

ABSTRACT

A powerful tool in planning the water quality control and management of a given aquifer system is its description by conceptual or semi-quantitative models, which expresses the fundamental properties of its components and the relationship among them. The use of models is essential in order to elucidate the cause and effect pathways in such complex systems, to 'guesstimate' possible pollution trends in the future, to screen proposed research projects, and to identify the most suitable means to meet acceptable water quality standards in the future.

It should be emphasized that models, and especially groundwater quality models, are always a simplification of reality and not merely its reproduction. The models presented here should be considered as semi-quantitative tools to be used at the decision level, rather than to be used for accurate predictions.

Groundwater quality systems are extremely complicated and only with the use of several working assumptions, based mostly on engineering judgement, some progress can be made. In this paper a practical approach is presented for studying pollution patterns in free-surface aquifers with the aid of digital models. They integrate pollution sources (both natural and man-made) on land surface, approximate representation of hydrological and physico-chemical parameters of the aquifer and the unsaturated zone, and variations of contaminant concentrations in pumping wells. Calibrated models were used to predict pollution patterns in the future and to examine alternative protection measures to conserve groundwater quality of the coastal aquifer of Israel. Uncertainty in defining physico-chemical and bio-chemical processes in the aquifer system, as well as scarcity of field data, were compensated in some cases with the aid of the Monte Carlo technique.

The application of such models for studying groundwater contamination by nitrates, and hazard evaluation of the possible contamination of groundwater sources by toxic substances in sewage effluents, are exemplified in the present communication.

1. INTRODUCTION

Development and evaluation of measures for environmental protection of groundwater sources, to ensure the quantity and quality of present and future water supply demands, requires a knowledge of the quantitative relationships among human activities, hydrogeological parameters of the aquifer system and aquatic chemistry. This knowledge is essential to elucidate some of the cause and effect pathways, to estimate pollution trends in the future, and to help in identifying the most suitable means of attacking major groundwater pollution problems.

Unfortunately, studies related to regional groundwater quality have not developed as rapidly as other fields of hydrology. Present hydrological models can predict, rather adequately, the effect of external stresses on hydrological systems relating to source, occurrence, quantity, movement and availability of water at sources. In comparison, till the middle 'sixties almost no similar quantitative predictions could be made with regard to the chemical character of groundwater. This gap is explained partly by the extreme complexity of physico-chemical processes occurring in natural aquifer systems, and the increasing number and quantities of miscible pollutants released to the aquifer environment. Another complementary explanation is the communication and co-operation gap between hydrologists, chemists, geochemists and sanitary engineers, towards the solution of groundwater quality problems.

In view of salinization and pollution trends observed in some of the major water sources in Israel, we believe that urgent protection measures should be taken in order to conserve groundwater quality. Appropriate engineering and economic decisions should be made now, although we still might lack conclusive descriptions of some of the physico-chemical phenomena in natural aquifer systems. The gap between the need for decisions and the lack of adequate physico-chemical knowledge can be filled partly with the introduction of systems approach.

The term 'system' is commonly associated with the collection of data describing the separate physical and chemical components of the system, studying the interrelationships among them, describing the function the system should fulfil, and defining the objectives which it has to achieve (Schwarz and Mercado, 1974). In case some information is not available, the process simulation structure provides a guide to the relative importance of the missing information, and the appropriate research activities that should be carried out.

2. THE GROUNDWATER QUALITY SYSTEM

Major paths of water and solutes in a given regional aquifer system can be described schematically in a flow chart (Figure 1) consisting, essentially, of three major sections:

(a) The land surface where most human activities associated with the release of contaminants, occur.

(b) The unsaturated zone (including the root zone of agricultural crops), which is considered to be the major 'chemical reactor' of the whole system; it is responsible also for the considerable time lag between the release of contaminants on the land surface and their arrival to the groundwater table.

(c) The aquifer which is responsible for the dilution of contaminants and their transport to pumping wells and springs.

This conceptual description of the groundwater quality system is especially suitable for the case of non-point sources. The selection of other groundwater quality models for different field problems is discussed by Schwarz and Mercado (1974).

State variables of this system are usually the water quality parameters included in water quality criteria and standards. Maximum acceptable levels of these state variables are dictated by their use (domestic, industrial or agricultural), subject to existing standards and criteria, by flow patterns in the aquifer, and by forecasted exploitation plans. Decision variables frequently encountered in groundwater quality studies are: location and timing of pumpage and artificial recharge, maximum tolerable load of various surface contaminants, concentration of toxic substances in sewage effluents, their control in pollution sources and the desired treatment level in plants, fertilizers, dosage to crops, etc.

Groundwater quality models are always conjuncted with flow models; the latter can be regarded as a subsystem of the hydrological cycle, and usually they can be used separately. In groundwater quality models the effects of surface activities and the processes occurring at the unsaturated zone should always be considered. This can be done by expanding existing groundwater models to include the relevant parameters of the land surface and the unsaturated zone, or by defining the boundary conditions (varying with time) between the groundwater subsystem and the overlying surface. In the latter case, the two models should be analysed separately, reaching a solution by a repetitive iteration on the boundaries between them.

The development of groundwater quality models usually takes the following steps:

(a) Implementation and development of flow models for both the aquifer and the unsaturated zone within the region of interest.

(b) Integration of flow models with existing models, describing the transport of chemically-inert solutes (for example, chlorides and tritium) in porous media.

(c) Expanding the above-mentioned models by superimposing chemical sources and sinks to describe major chemical reactions such as: dissolution-precipitation, adsorption, cation-exchange, oxydation-reduction, and biochemical degradation.

The laws of conservation of mass, for both water and aqueous species in the aquifer, provide a theoretical basis for developing a groundwater quality model of a given aquifer system. If the mass of aqueous species is to be conserved, the following relationship must be satisfied in any element of the system:

$$\left\{\begin{matrix}\text{Rate of mass}\\ \text{accumulation}\end{matrix}\right\} = \left\{\begin{matrix}\text{Net rate of}\\ \text{mass transfer}\end{matrix}\right\} + \left\{\begin{matrix}\text{Net rate of appearance}\\ \text{of mass by reaction}\end{matrix}\right\} + \left\{\begin{matrix}\text{Contribution rate of}\\ \text{mass by external sources}\end{matrix}\right\} \qquad \ldots\ldots \; 1$$

The mathematical statement of the above relationship, for both saturated and unsaturated zones of the aquifer system, are well known and will not be repeated here. The first term on the right-hand side of Equation 1 is described usually as a combination of hydrodynamic dispersion and convection. The latter is linked to the water balance. The form of the second term depends on the intrinsic characteristics and kinetics of the specific chemical reactions involved (Schwarz and Mercado, 1974; Mercado and Billings, 1975). The last term represents external inputs of contaminants to the specific section of the groundwater quality model. It should be remembered that the input function of the groundwater section is at the same time the output of the unsaturated zone model.

The combination of the separate differential equations which describe these relationships, and their solution according to a specified set of boundary and initial conditions, provides a model for studying groundwater pollution patterns in a given aquifer system. Examples for separate models of the unsaturated and saturated zones are numerous; however, only a few models describe simultaneously the overall system. The models used currently by our group were summarized by Schwarz and Blank (1972), Schwarz and Mercado (1974), Mercado and Avron (1975) and Avron and others (1976).

The use of such models for prediction purposes requires their calibration by fitting computed concentration variations to those measured in the field. In most instances, however, the scarcity of reliable field data, as compared to the complicated features of the terrestrial cycle of some contaminants, prevents the use of detailed models, and alternative approximate tools must be developed instead.

Lumped models, of the single-cell type, are considered to serve this purpose; they are built upon extensive simplification of the conditions prevailing in reality, and grouping of the pertinent characteristics and processes. Predefined parts of the aquifer are considered as fully mixed cells. Transport phenomena along the unsaturated column are expressed by the transit-time of chemically-inert solutes, corrected by the specific retardation factors due to adsorption and cation-exchange processes.

The use of such models is exemplified below for the preliminary assessment of the possible variations of some groundwater quality parameters in the coastal plain of Israel. They also provide the means for making economic and engineering decisions today, to be implemented immediately by planners.

3. NITRATE AND CHLORIDE CONTAMINATION OF THE COASTAL AQUIFER IN ISRAEL - REGIONAL STUDY WITH THE AID OF SINGLE-CELL MODEL

A continuous increase in nitrate content was observed (Figure 2) in the coastal aquifer of Israel. The average nitrate concentration has increased from about 0 to 10 ppm in the early 'thirties up to 51 ppm in 1972 (Harpaz, 1972; Kahanovitz and Blank, 1974; Ronen, 1974). The average annual increase in nitrate concentration is estimated at 1.1 ppm per year, as compared to 1.5 ppm per year with respect to chlorides.

It is a well-known fact that nitrates in large amounts can cause 'Blue Babies' (Methaemoglobinaemia) in infants; in addition, the possible formation of nitrosamine carcinogens in the stomach, enhanced by high nitrate concentration in drinking water, may cause stomach cancer in adults. Drinking water standards in most countries state that 45 ppm of nitrates is a limit which should not be exceeded. Following recent epidemiological research work carried out in Israel, the maximum permissible concentration of nitrates in water was raised to 90 ppm.

The observed trend of the continuous groundwater pollution by nitrates is, therefore, of particular concern to public health and water supply authorities in Israel, and calls for urgent measures to protect our groundwater sources. A prerequisite for taking such measures is to identify major pollution sources, estimate their relative weight in observed trends, and to develop approximate quantitative tools to assess future trends, as well as to estimate the response of the system to alternative protection measures.

For this purpose a single-cell model (Figure 3) was developed (Mercado, 1975) to study the regional chloride and nitrate pollution patterns in part of the coastal aquifer of Israel. The model integrates pollution sources on the land surface, hydrological parameters of the aquifer and the unsaturated zone, and variations of chloride and nitrate concentration distribution in pumping wells. Complicated hydrological and biochemical processes in the unsaturated zone were simplified and represented by two basic parameters - transit time of pollutants from land surface to the aquifer, and nitrogen losses in the soil column. A working hypothesis was used by Mercado (1975) to show that linear relationships exist between nitrogen quantities released on the surface and the quantities reaching the water table. Chloride and nitrate balances have been studied simultaneously. The effective volume of groundwater in the mixing zone of the aquifer was interpreted from the concentration variations of the chloride ion which is a conservative tracer. This value was used later for determining other parameters of the nitrogen terrestrial cycle.

The calibration of the model, by reconstructing present pollution levels, enabled its use for prediction purposes. In choosing model parameters for prediction purposes three alternative courses can be adopted: (a) the use of mean values based on the precalibrated range of model parameters; (b) the use of extreme values, obtained by calibration, that will maximize pollution forecasts; (c) random choice of parameters within the predetermined range. In view of the uncertainty in defining the pollution mechanism and difficulties in calibrating model parameters, the third alternative was applied here. The random choice of nine parameters, relevant to future nitrate concentration, was facilitated with the aid of one of the simplest versions of the Monte Carlo technique, described briefly below.

Each parameter is given minimum (X_{min}), maximum (X_{max}) and probable (X_{exp}) values, forming a triangle probability distribution for the values of a given parameter (Figure 4). By definition:

$$\frac{1}{2} f_{max} (X_{max} - X_{min}) = 1$$

where f_{max} is the frequency of X_{exp}. The cumulative probability function F_x ranges between 0 for X_{min} and 1 for X_{max}; its value for X_{exp} is given by:

$$F_{exp} = (X_{exp} - X_{min})/(X_{max} - X_{min})$$

A computer subroutine for generating random numbers between 0 and 1, representing F_x values, enables random draw of parameter values between X_{min} and X_{exp}. For $F > F_{exp}$:

$$X = X_{max} - [(1 - F) * (X_{max} - X_{min}) * (X_{max} - X_{exp})]^{\frac{1}{2}}$$

for $F < F_{exp}$:

$$X = X_{min} + [F * (X_{max} - X_{min}) * (X_{exp} - X_{min})]^{\frac{1}{2}}$$

A computer program SCMON performs both the random choice of parameters and the integration of the nitrate and chloride balance equations. This procedure is repeated until parameter distribution and the resultant concentration distribution converge to the normal Gaussian distribution. Convergence to normal distribution is checked with the aid of the t-Test for a given statistical confidence limit. The resulting distribution of average groundwater predicted concentrations is given in a probabilistic form (Figure 5); i.e. the probability of having concentration higher than indicated.

In order to estimate the disconnection of pumping wells from domestic water supply systems, some additional assumptions are required for the concentration distribution around average values, computed with the aid of the single cell model. Two working hypotheses related to the average concentration $\bar{C}$ may satisfy mathematically the conservation of aqueous species in the aquifer:

(a)

Concentrations C_i in individual wells vary with the same $\Delta\bar{C}$ values of average concentrations computed by the model, so that:

$$\bar{C}(t) = \bar{C}(0) + \Delta\bar{C}(t) = \frac{1}{n}\sum_{i=1}^{n}[C_i(0) + \Delta\bar{C}(t)]$$

where t is the time and the index '0' denotes initial concentrations measured at the reference date.

(b)

Concentration in individual wells varies proportionally to the computed variation of the average concentration, so that:

$$\bar{C}(t) = \varepsilon(t)\ \bar{C}(0) = \frac{1}{n}\sum_{i=1}^{n}[\varepsilon(t)\ C_i(0)]$$

where the ε coefficient is defined by:

$$\varepsilon(t) = \bar{C}(t)/\bar{C}(0)$$

According to the first working hypothesis, gradual homogenization of the nitrate concentration is expected, while according to the second hypothesis the relative spread ($\sigma_c/\bar{C}$) will remain constant. In order to be on the safe side, the first working hypothesis, which seems to be more critical, was chosen for prediction purposes.

The accumulation of nitrates in the aquifer will undoubtedly increase their concentration in pumped water. According to a prediction based on average parameter values (Figure 5) nitrate concentration will rise from 52.5 ppm in 1970 to 85, 115 and 145 ppm in the years 1985, 2000 and 2010 respectively. At these concentrations, 46%, 80% and 96% respectively of pumping wells will probably be disconnected from water supply systems (Figure 6) in order to meet the new drinking water standard of 90 ppm $N\text{-}NO_3^-$. The 1972 measured average of 57.8 ppm (Figure 5) is in fair agreement with the above estimates.

In view of the above forecasts, urgent protection measures should be taken in order to conserve water quality in the region studied. An aggravating factor is the time-lag of 5 to 15 years between the reduction of the pollutant load on the surface and the response of the aquifer system.

In this work 13 alternative protection measures have been considered and compared to the predictions made above (Figure 6). They can be divided into two major groups: (a) removal of nitrogen pollution sources from the surface, and (b) exchange of nitrate contaminated groundwater by recharging low-nitrate surface water and overpumping at similar rates.

In every alternative it was assumed that the proposed protective measures will be introduced gradually over a time-span of 5 years, starting from 1975.

3.1. REMOVAL OF NITROGEN SOURCES

The two major nitrogen sources in this region are sewage and fertilizers.

Sewage nitrogen can be removed by advanced treatment of sewage effluents, or by exporting sewage water for irrigating arid regions in Southern Israel. These two alternatives were considered as follows:

(a) Removal of 80% of the sewage nitrogen (Alternative 2 in Figure 6). This can be done by tertiary treatment of the effluents prior to their recharge into the aquifer or alternatively, by using secondary-treated sewage water for irrigation.

(b) Exporting 90% of the available sewage water to the south (Alternative 3). This will disturb the delicate hydrological balance by creating a deficiency of about 9 MCM (million cubic metres) per year. Roughly one-third of this deficit will be balanced by increased groundwater inflow from the east, and the remainder will require the recharge of low-nitrate surface waters.

The effects of these measures on groundwater nitrate concentrations are demonstrated in Figure 6a. Steady-state nitrate concentrations for these alternatives are 190 and 100 ppm respectively.

The quantities of fertilizers applied considerably exceed crop requirements. Furthermore, the amount of nitrogen in the irrigation water often surpasses nitrogen consumption by crops. Therefore, a reduction of fertilizer doses, in addition to denitrification of nitrates in return flow waters, may markedly improve groundwater quality in this region.

Figure 6b demonstrates the effect of reducing fertilizer quantities to one-half (Alternative 4) and one-tenth (Alternative 5) of existing doses. Note the considerable time-lag (about 10 years) of the aquifer response to fertilizer reduction.

3.2. GROUNDWATER EXCHANGE

Substituting nitrate-free surface water for contaminated groundwater is another alternative. Predicted concentrations for exchange rates of 10, 20, 30 MCM per year are shown in Figure 6c. Freezing the existing situation will require continuous recharge and pumpage at the rate of 30 to 40 MCM per year.

3.3. COMBINED ALTERNATIVES

The combination of fertilizer reduction and sewage treatment or removal, yields additional improvement. A practical combination is a 50% reduction in fertilizer quantities, tertiary treatment of sewage effluents which will remove 80% of the nitrogen, and a temporary groundwater exchange of 25 MCM between 1975 and 1985 (Alternative 14 in Figure 6d). By taking these measures, existing nitrate concentration can be practically frozen, keeping the percentage of disconnected wells as low as 10 to 20%.

Since groundwater pollution by nitrates can be decreased by any of three methods proposed above, it is of importance to examine exchange relationships among them. For the sake of brevity only the case of steady-state concentrations was considered. The following extreme situations can be evaluated from Figure 7b, which describes the exchange relationships between fertilizers decrease, sewage treatment and groundwater exchange:

(a) Rejection by farmers and municipalities of any attempt to decrease the nitrogen load would require a continuous groundwater exchange of 33.3 MCM per year.

(b) Considered as the only protective measure, fertilizer doses to crops would have to be reduced to about 15% of the present level.

(c) Even the most advanced sewage treatment ($\varepsilon_s = 0$) cannot, under any circumstances, serve as the only measure for freezing existing nitrate concentrations.

The sensitivity of the exchange relationships among sewage treatment and fertilizers decrease to changes of the desired ultimate nitrate concentration is demonstrated by Figure 7a.

The nitrate study is essentially an extrapolated evaluation of historical data. A similar study was done by Tahal (Mercado, Avron and Kahanovitz, 1975) with respect to future chloride salinity trends in the coastal aquifer. In cases where historical data are not available, decision formulation is based on probability estimates of the likelihood of particular pollution processes. The guiding principle in decision making under conditions of uncertainty is the 'safe side'. This means that even should it turn out that currently unknown characteristics have extreme values, the pollution will still be at a level beneath the permitted concentrations. The following case study demonstates the concepts of this approach.

4. POSSIBLE CONTAMINATION OF GROUNDWATER SOURCES BY TOXIC SUBSTANCES IN SEWAGE EFFLUENTS USED FOR IRRIGATION - RISK ASSESSMENT FOR THE COASTAL AQUIFER OF ISRAEL

Forecasts for the industrial and domestic demands indicate that they might be tripled by the years 2000 to 2050. Sewage reclamation will be introduced on a large scale to meet these requirements. Development programmes made according to these forecasts are based partly on the assumption that replacing up to 50% of existing fresh water agricultural consumption by sewage effluents is feasible. A question arises, however, of what will be the impact of this programme on groundwater quality of the coastal plain, and what precautions should be taken today in order to meet water quality criteria in the foreseeable future.

A current study being carried out by Tahal (Mercado and Schwarz, 1974), and sponsored by the Israeli Water Commission, might yield a preliminary answer to these problems. The objective of this study is to develop quantitative tools and decision criteria for accepting (or rejecting) proposed plans for irrigation by sewage effluents in a given region. It will also contribute to the design criteria of treatment plants, sewage reclamation projects, pollution source control programmes, and the implementation of dynamic regulations, to be issued by the Water Commissioner, for preventing groundwater pollution.

The assessment of potential pollution trends requires the development of semi-quantitative tools to simulate reality. These tools, essentially of the single-cell type, are based on the routes of water and contaminants, described briefly below.

The water supply in a typical cell (Figure 8) of the coastal plain aquifer consists of local pumpage (QP) and imported water through the National Water Carrier. A limited amount (QEXP) is exported to other regions. The total consumption (QSUP = QP - QEXP + QIMP) is divided between urban (QUR) and agricultural (QIR) sectors. The division or replacement coefficient (α = QUR/QSUP) is a decision variable, depending partially on water quality parameters. The desired replacement, on a nationwide basis, is in the order of magnitude of 50%. A part δ ($\simeq$65%) of urban consumption is reclaimed and used as a part of the water inventory. Urban losses are compensated by an equivalent amount of imported water.

Three alternative recycling schemes (Figure 8) of reclaimed effluents were conceptually defined in this study (Mercado and Avron, 1976) for the purpose of the risk assessment. These schemes emphasize different 'bottlenecks' of the groundwater quality system:

(i) Direct use of sewage effluents for irrigation (Scheme I) provided their quality will be suitable for irrigation purposes. This alternative will ensure maximum protection of groundwater quality.

(ii) Indirect use of sewage effluents for irrigation (Scheme III). This alternative will be employed whenever sewage effluents will not meet the requirements for irrigation water, or due to lack of sufficient surface storage to route winter effluents. The use of this alternative will obviously accelerate the deterioration of groundwater quality.

(iii) Partial replacement of imported water by sewage effluents (Scheme II), disconnecting urban consumption from the local aquifer system.

The present paper deals only with the first recycling scheme, shown in Figure 8. Following this scheme, the concentration of contaminants (CDR) in municipal water supply networks varies with time according to the rise of average concentration (CGW) in the aquifer. Imported water (QIMP) will probably remain free of contaminants. Municipal waters are contaminated by a constant addition (DC) to their original concentration (CDR). Part δ of the urban concentration returns to the sewage system at a concentration of CDR + DC and is then conveyed to treatment plants. Treatment plants are characterized by their specific removal efficiency (RMVL) for a given contaminant. Sewage effluents at a concentration of CEF [=(1-RMVL) * (CDR + DC)] are reclaimed for irrigation at a concentration of CIR, determined as a weighted average of the various components.

Contaminants in irrigation water percolate through the unsaturated soil column and reach the water table after a time of $\tau = t_w * RF$; t_w is the transit time of chemically-inert solutes and RF is the retardation factor of a specific pollutant due to cation-exchange and adsorption processes. The contaminants are then mixed with the effective groundwater volume V, causing a rise in the concentration of pumping wells tapping the aquifer.

The recycling scheme was simulated with the aid of a single-cell model (Mercado and Avron, 1976). The only 'sink' in the preliminary version of this model is the cell's treatment plant. Retarding processes in the unsaturated column, such as adsorption and cation-exchange on clay minerals, were neglected; they will be introduced in future versions of this model.

Possible concentration of problematical contaminants in groundwater were determined with the aid of the above-mentioned model. Computations were repeated for 242 model cells, representing most of the coastal plain area. The simulation of future pollution trends requires the employment of specific input data - both hydrological and chemical.

Hydrological parameters pertinent to the description of pollution processes are: natural replenishment, pumpage and artificial recharge distribution, water import and export data, effective aquifer thickness for dilution, and transit-time of chemically-inert solutes along the unsaturated column. The latter was estimated (Figure 9) by using the assumption that moisture content does not vary with time and that piston-flow convection is the major transport mode of solutes along the unsaturated profile. The above-mentioned parameters were determined by other studies. The estimated distribution of transit-times along the unsaturated column (Figure 9) may serve as an example.

Concentration estimates (Mercado, Kahanovitz and Avron, 1975) of toxic substances in raw sewage (C_{raw}) and treated effluents (C_{eff}) were based on field data of raw sewage composition within Metropolitan Tel Aviv and removal efficiencies (RMVL) of major treatment processes, i.e. biological (SEC), physico-chemical (TER) and advanced (ADV). The latter were based on recent literature. They are currently updated by the findings of a large-scale pilot plant in the vicinity of Tel Aviv.

The mean concentration of a given contaminant in effluents is predicted by:

$$\bar{C}_{eff}\,(SEC,\ TER,\ ADV) = \sum_{i=1}^{n} \delta_i\,(C_i)_{raw} \times [1 - RMVL\,(SEC, TER, ADV)]$$

where δ_i is the relative weight of section i of the metropolitan area, characterized by $(C_i)_{raw}$.

Due to scarcity of data, and the relative spread of existing data with respect to δ, C_{raw} and RMVL values, the above-mentioned Monte Carlo technique was employed again, and estimates with respect to 23 elements were given in a probabilistic form; the concentration distribution of Cobalt and Chromium (Figure 10) may serve as an illustration. Following this example it was 'guess-timated' that the concentration of chromium in secondary effluents will probably exceed the MPC (maximum permissible concentration) for both irrigation and drinking purposes, as compared to the low probability of exceeding the MPC in advanced treatment. It should be mentioned however, that recent data of our pilot plant suggests that our estimates were too pessimistic with respect to chromium, as tertiary treated effluents were below the MPC for chromium.

Following our estimates it was possible to grade toxic substances in sewage effluents according to their 'Relative Toxicity', defined simply by:

$$\text{Relative toxicity} = C_{eff}/(MPC)$$

Classification of contaminants according to this index (Figure 11), although trivial, is considered to be an important step in such studies, as it might draw maximum attention to those substances for which loads in raw sewage should be minimized, and removal efficiencies in treatment plants should be maximized. This classification also helps in assessing future trends of groundwater contamination, since only the critical contaminants must be considered in simulation runs.

Comparison of computed concentrations with standards for drinking water and recommendations for irrigation shows that treated effluents might not be used directly for either domestic or agricultural purposes. High concentrations of chrome, cadmium, lead and boron will limit the direct use of treated effluents for domestic purposes, even after advanced treatment. High concentrations of chrome, copper, cadmium, boron and nickel might limit the direct use of secondary effluents for irrigation. Preliminary results of a six months operation of the Dan Sewage pilot plant indicate that the above estimates might be too pessimistic. More field data are necessary to adjust estimated concentrations.

According to model computations, the northern part of the aquifer is most likely to be contaminated between the years 2000 and 2100 (Figure 12). On the other hand, the south-eastern part of the aquifer will remain intact probably for a period of more than 300 years. These computations are based on the assumptions that: (a) secondary effluents will predominate in the coastal plain. They are represented by chrome which has the highest relative-toxicity index (Figure 11); (b) recycling of one-half of the water consumption through urban consumers; (c) adsorption and cation-exchange will not play a significant role in determining the transit-time of pollutants due to possible chelation of heavy metals with soluble organic substances in sewage. Similar computations were carried out for tertiary effluents, showing that most of the aquifer will remain intact up to the year 2050, and only moderate pollution is expected by 2100. Tertiary effluents were represented by cadmium.

Besides determining possible concentrations in groundwater and other 'check points' of the system, the computer analysis also yields some design guidelines with respect to alternative protection measures, such as: maximum concentrations in raw sewage and treated effluents used for irrigation, recommended treatment levels (Figure,13), and necessary removal of contaminants at their source, possible recycling of sewage water in particular cells, etc. These recommendations are based on the dynamics of the groundwater system, and the requirement to meet acceptable water quality criteria up to a given 'target year'. Choosing the 'target year' is, so far, a subjective decision.

The recommended treatment levels, shown in Figure 13 are an example of translating simulation results to engineering alternatives, that can be evaluated directly by the decision makers. According to this example it seems that secondary treatment might not be sufficient to protect groundwater resources till the year of 2050, and the introduction of tertiary treatment will be necessary to reclaim sewage effluents in the northern and central parts of the coastal plain. On the other hand, treatment level will not play a significant role in decisions concerning the future groundwater quality of the south-eastern region.

In view of the uncertainties in defining pollution mechanisms and estimating physico-chemical parameters, it is important to analyse the sensitivity of pollution forecasts and proposed regulations to possible variations in model parameters and management constraints. Sensitivity analysis is a common procedure in decision models; it enables verification of decisions based on limited information, screening of proposed research projects and initiation of others, according to the missing information required for the decision process. Sensitivity analysis is also important to identify problematical pollutants, whose concentration and behaviour in the aquifer system might endanger groundwater quality, and they should therefore be studied in more detail.

Figure 14 is a typical example of such analysis. The sensitivity is measured in terms of increase (or decrease) in the number of polluted model cells at the year of 2050. The reference prediction is based on average values of model parameters, presuming that secondary treated effluents will dominate. Both parameter and pollution variations are expressed by dimensionless ratios.

Relevant parameters have been classified for this analysis into:

(a) Parameters related to the sewage and water supply systems; including: contaminant quantities released to sewage, removal efficiency of treatment plants, and water losses in urban water supply systems.

(b) Parameters related to development and management policy, such as: replacement of agriculture consumption by reclaimed sewage, 'target years' and water quality criteria.

(c) Physico-chemical parameters related to the transit-time of pollutants from land surface to the water table.

The relative low sensitivity of pollution forecasts to a possible decrease in the performance of various components of the system, indicates that there is a very limited risk in accepting our forecasts as a guideline for protecting the quality of groundwater sources in the coastal plain. On the other hand, the high sensitivity of pollution extent to performance improvement, suggests that slight modifications in treatment plants, source control measures and agricultural practices, might get a very high pay-off in terms of decreasing groundwater pollution hazards.

For example (Figure 14), a possible increase of chromium concentration in raw sewage by a factor of 50%, due to either expansion of industrial activities or inadequate analysis of field data, will increase the number of polluted cells by 15%. On the other hand an elimination of chrome contribution by 50% will decrease the polluted area to a significant one-half of the predicted one.

The selection of problematical contaminants that should be studied thoroughly depends mainly on the selected 'target year' and the dominant treatment level of municipal sewage. Choosing the year 2050 as the 'target year', and presuming secondary treatment to prevail, the following list of contaminants was proposed for further research: phenols, detergents, chrome, cyanide, cadmium, lead, mercury and boron.

Approximate computations of the retardation factors (RF) for problematical pollutants due to cation-exchange on clay minerals (Terkeltaub, 1976) indicate that cadmium, lead and copper might be retarded for long periods whereas the complexation of mercury with chlorides will prevent any significant retardation. Chrome will not be exchanged with clay mineral; it may be adsorbed, though, by the soil oxides. Due to the importance of these processes, a further research of the physico-chemical properties of these substances and their interaction with soil is highly recommendable.

The two case-studies presented above demonstrate the possible use of approximate models to groundwater quality management. These examples are considered, however, to be a very preliminary step towards the implementation of models for realistic decisions. Besides the economic analysis, which seems to be the obvious next step, we also believe that subjective factors, concerning mostly human behaviour, must be introduced to water quality models. Public opinion is very sensitive to pollution problems, and policy questions involving sewage reclamation and water resources management cannot be resolved solely by abstract models that optimize numerical coefficients. Otherwise model simulation, while being technically adequate, will be politely dismissed by the decision makers. Undoubtedly the integration of subjective variables with numerical data seems to be very difficult if not impossible. It seems however, that the methodology of simulating subjective factors at the decision level, as proposed by Kane and others (1973), might serve as a starting point.

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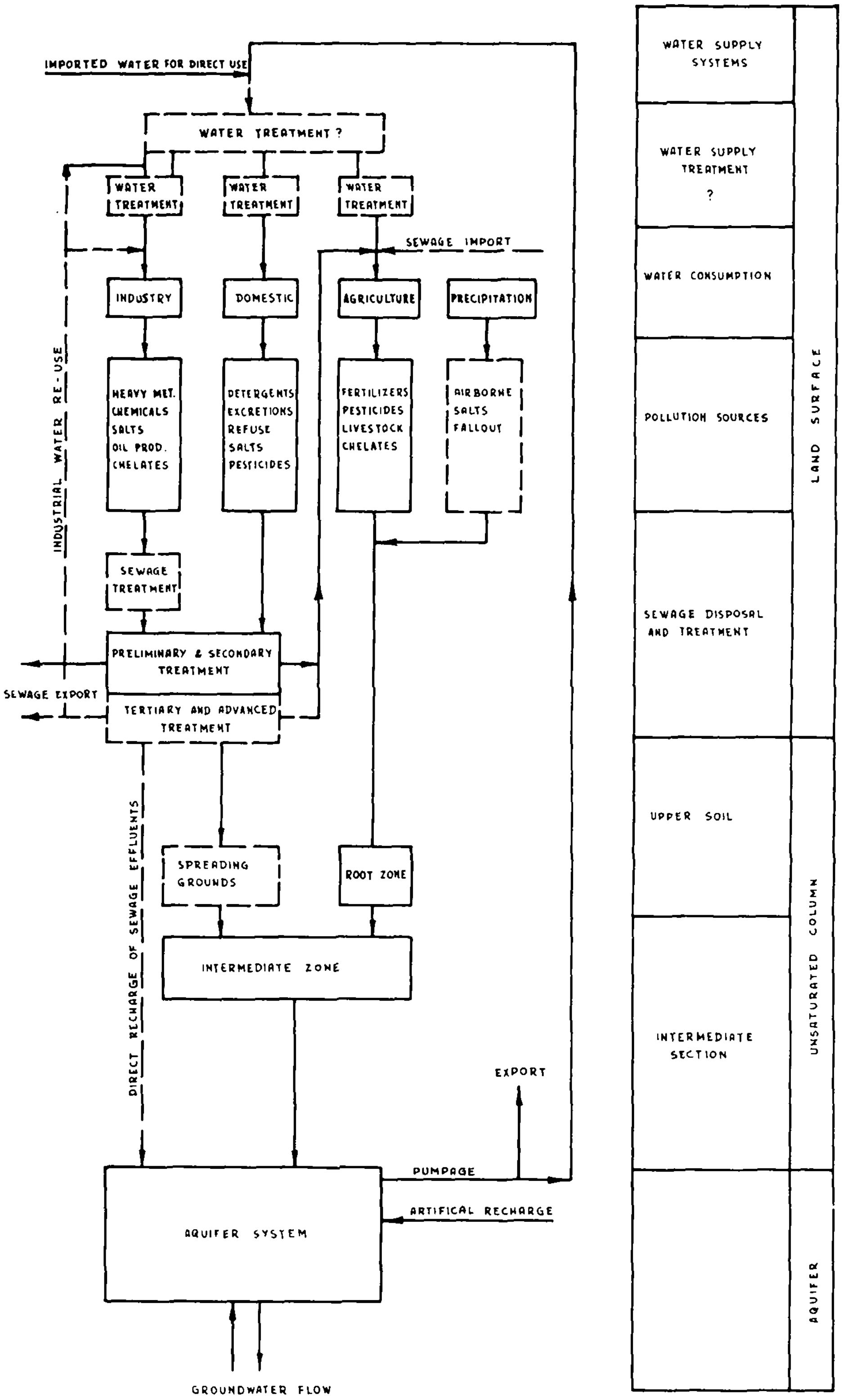
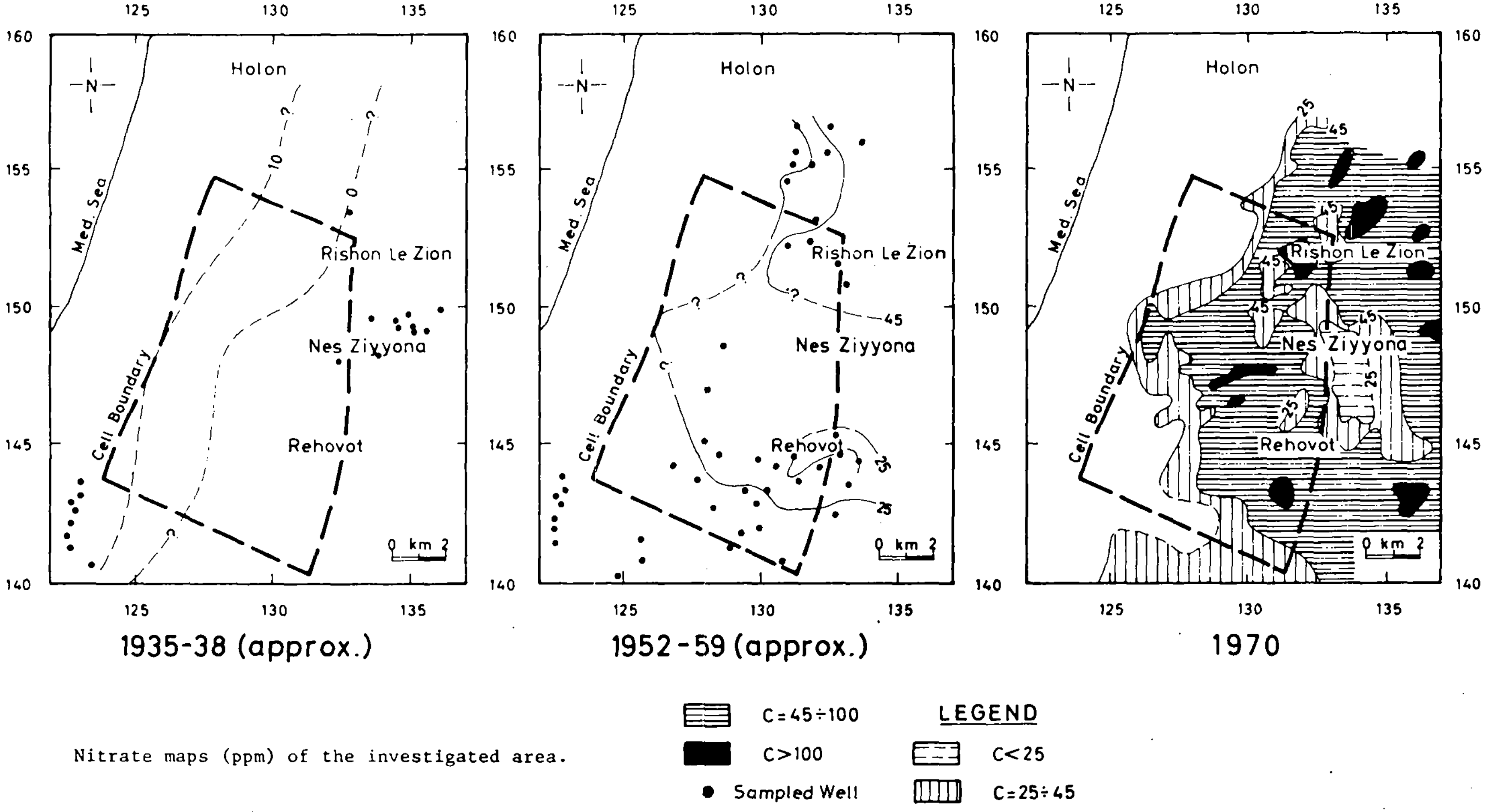
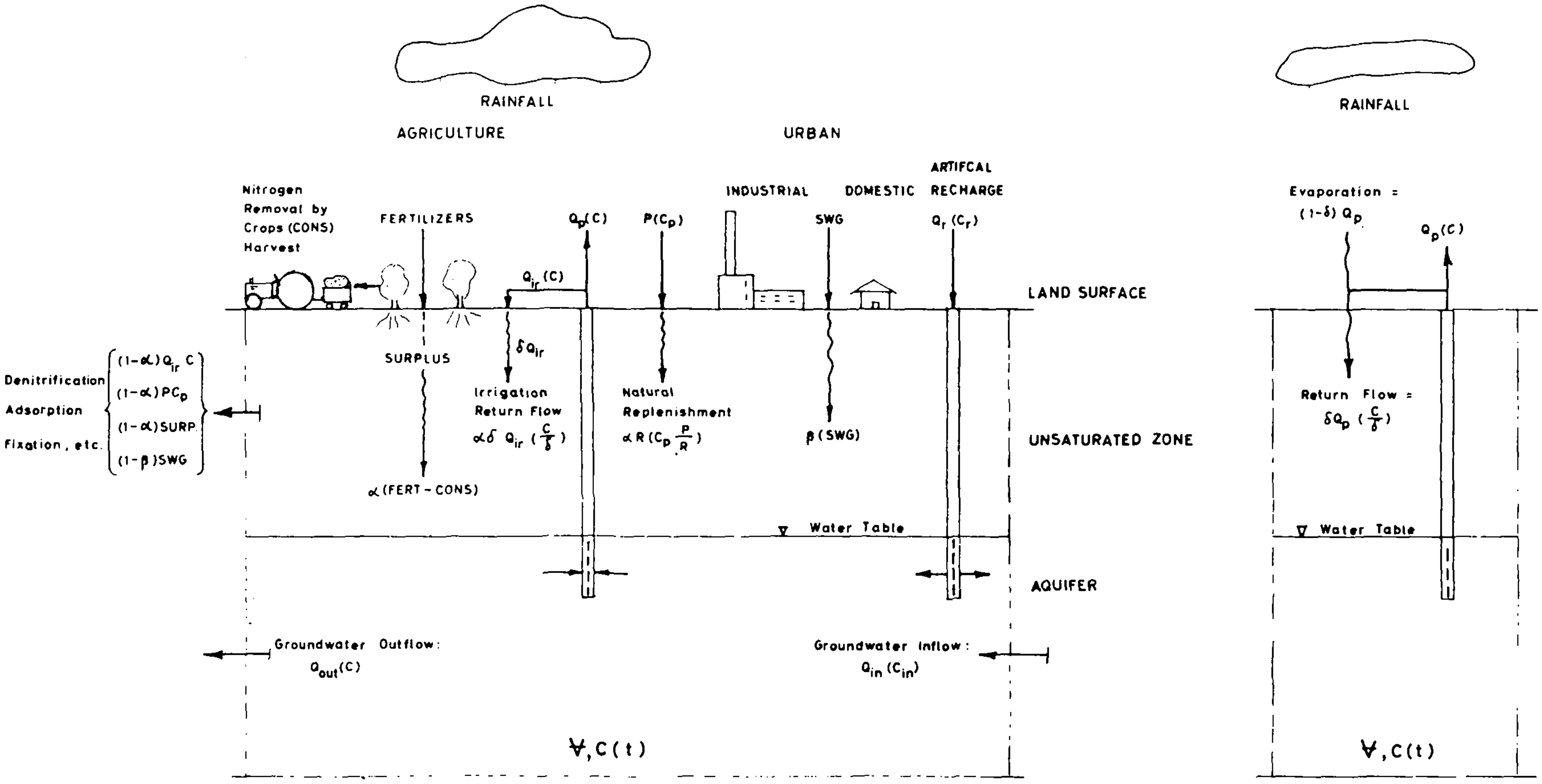


Figure 1. The groundwater quality system



Nitrate maps (ppm) of the investigated area.

Figure 2. Nitrate pollution in part of the coastal plain aquifer



a. Nitrates

b. Chlorides

Figure 3. Single-cell model for describing nitrate and chloride pollution

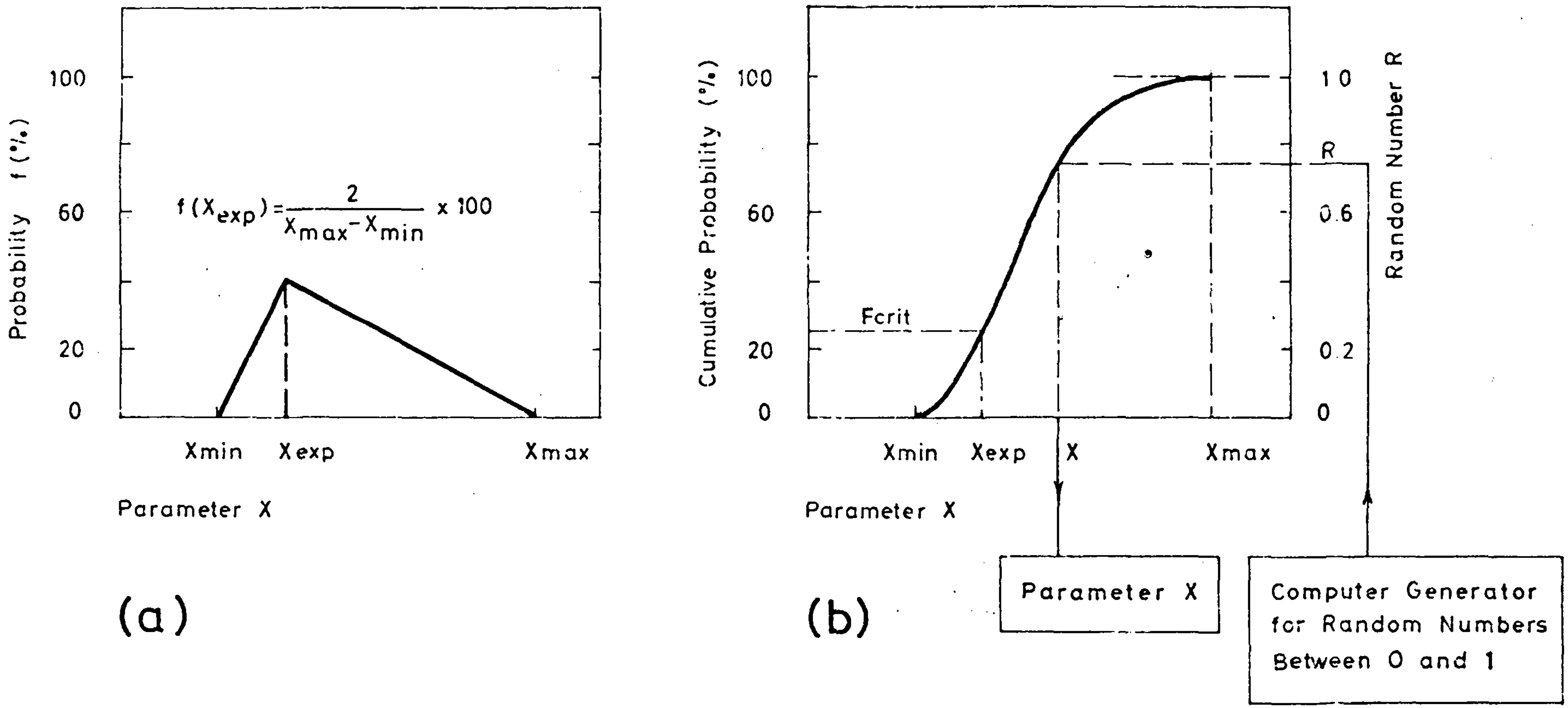


Figure 4. Random draw of parameter values with the aid of the Monte Carlo technique

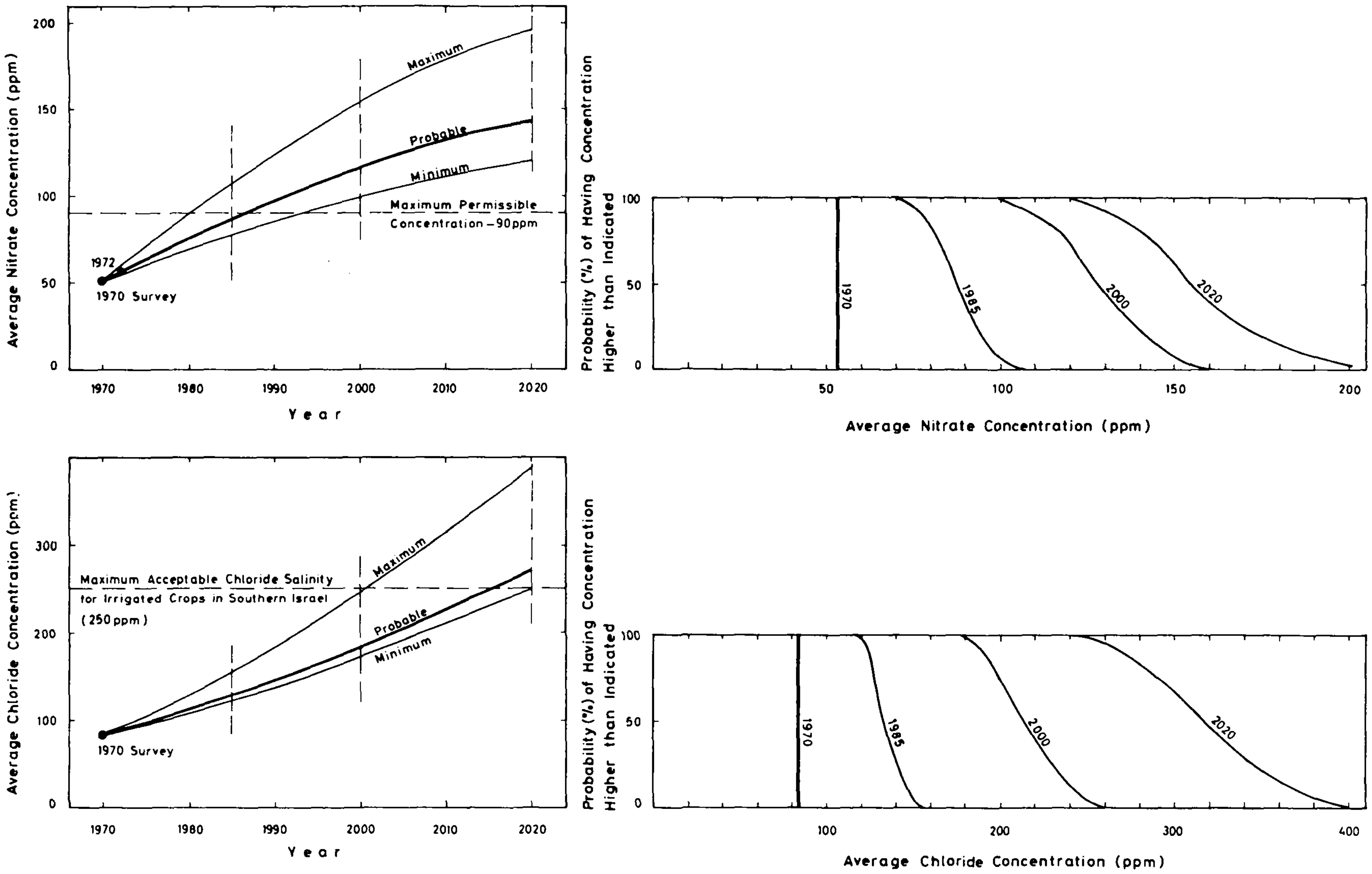


Figure 5. Predicted average nitrate and chloride concentrations as a function of time

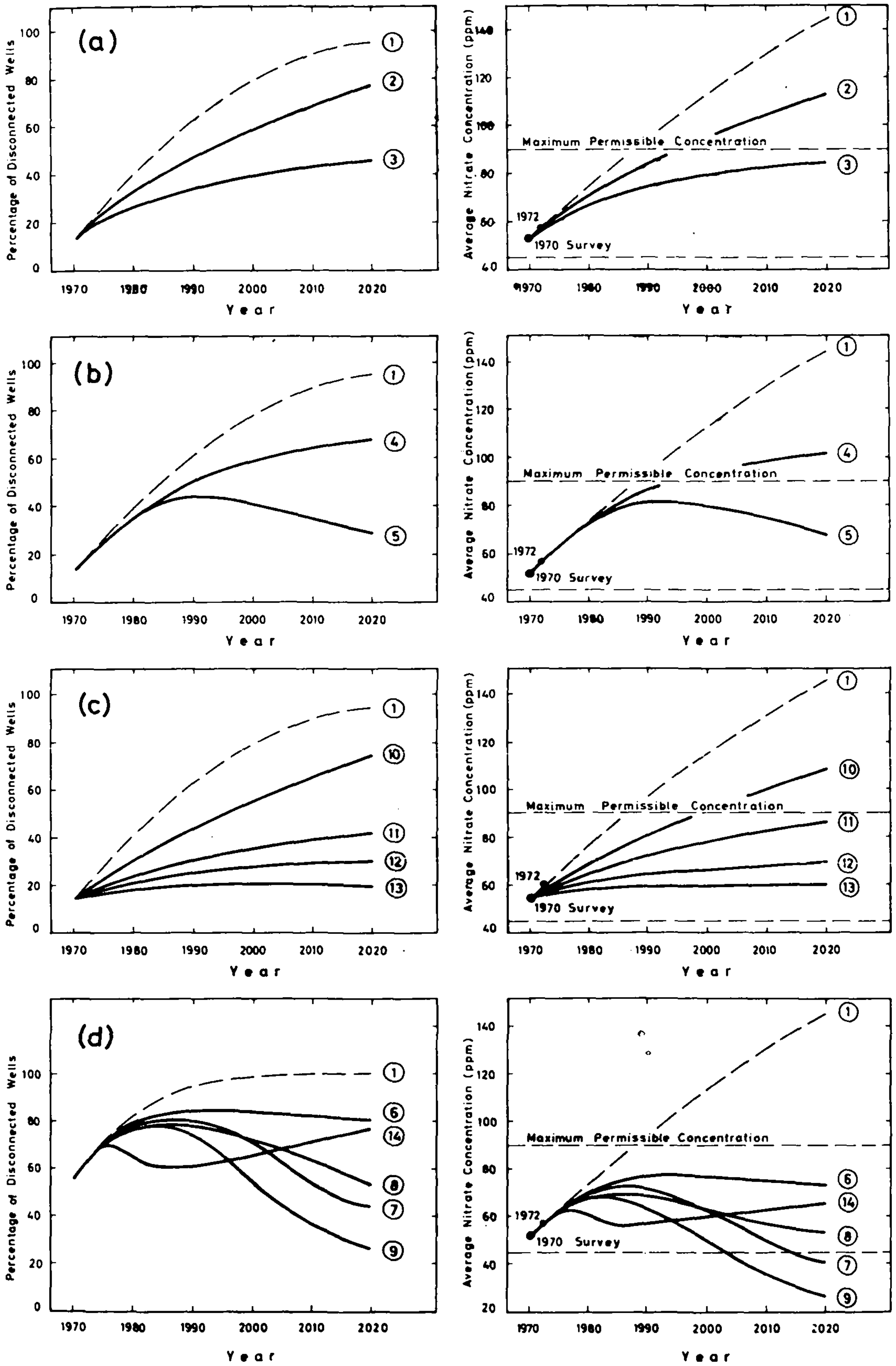


Figure 6. The effect of alternative protection measures on future average nitrate concentrations and expected disconnection of nitrate-contaminated wells

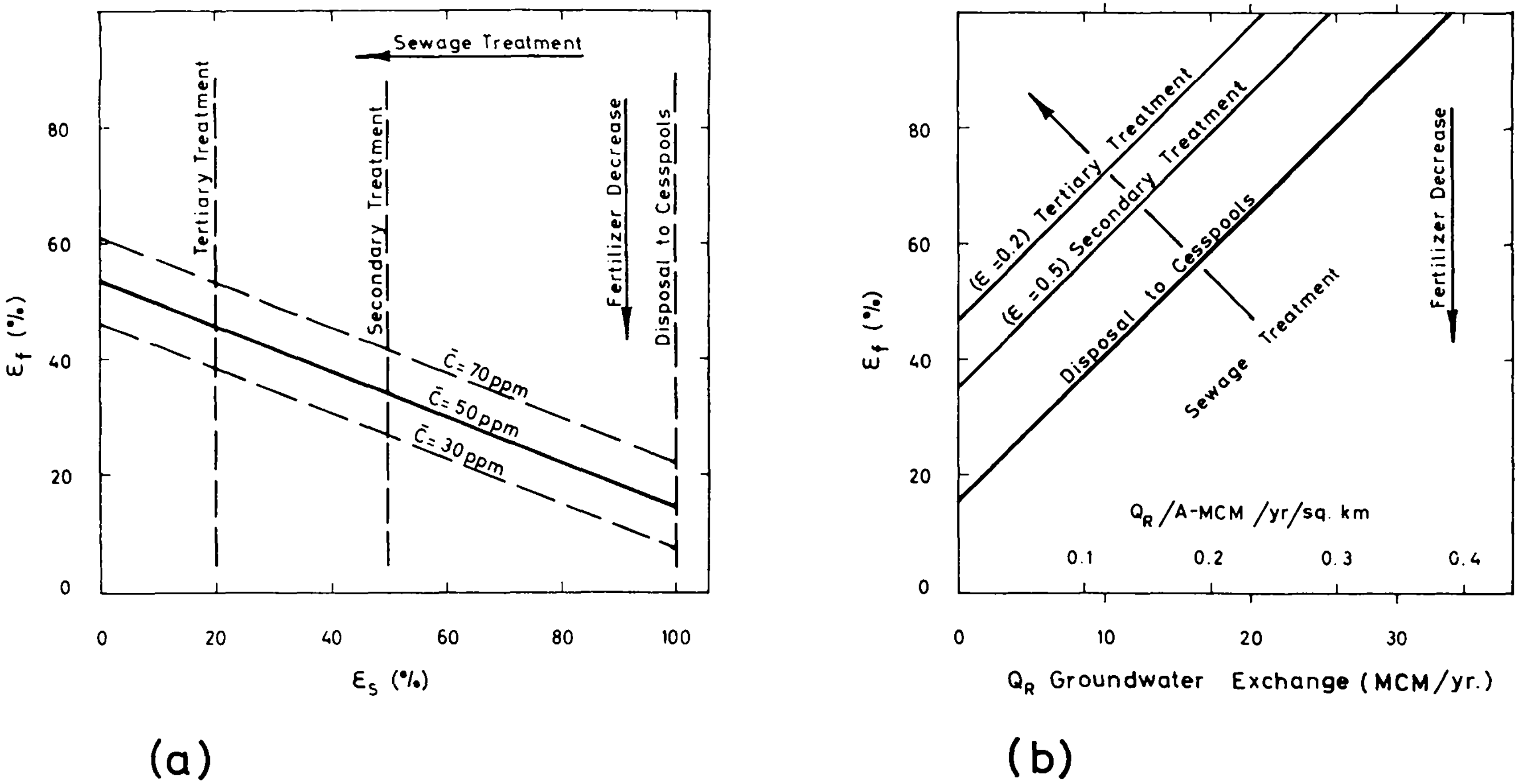
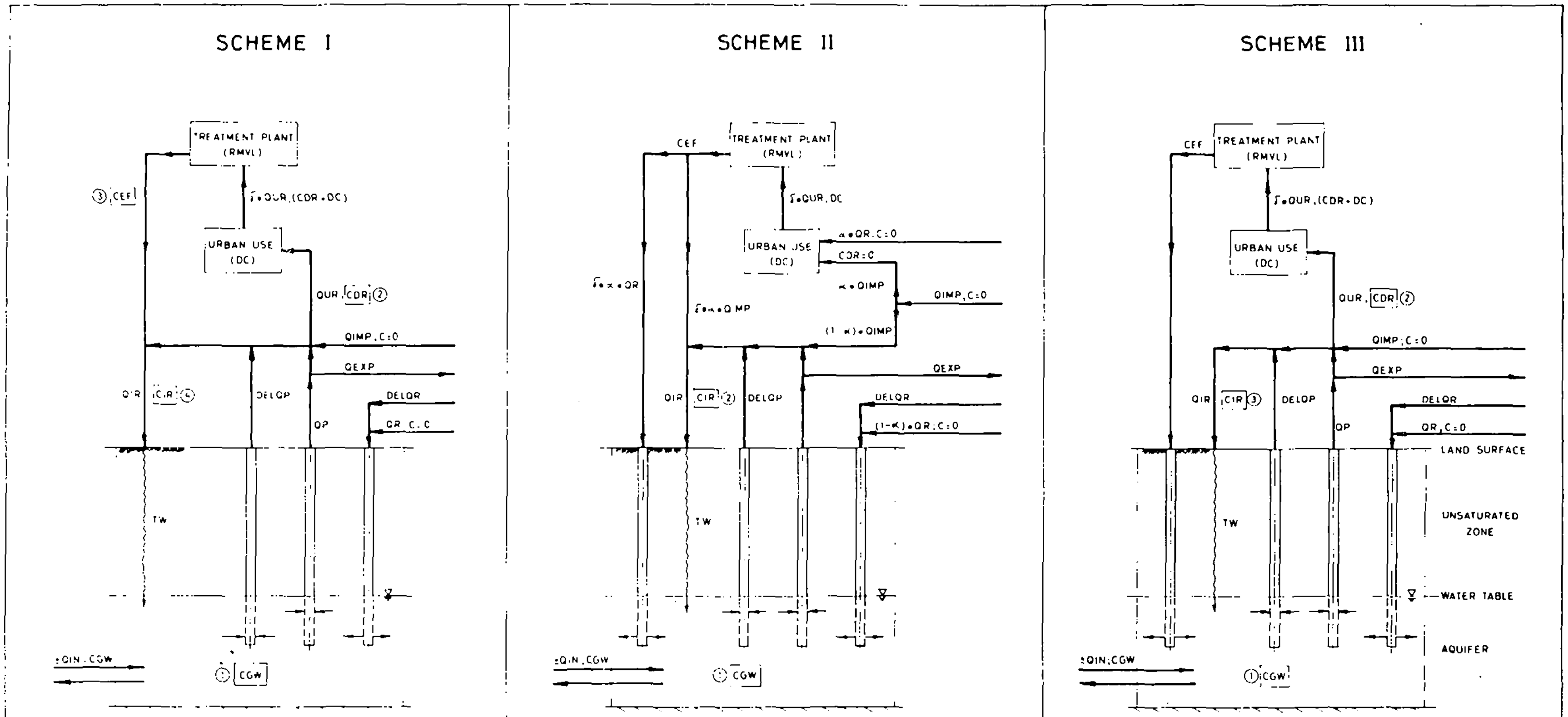


Figure 7. Exchange relationships between protective measures to prevent nitrate pollution



SCHEME I

$QIR = QP-QEXP+QIMP$
$QUR = \alpha*QIR$
$DELQP = DELQR = (1-\delta)*QUR$
$CDR = CGW*(QP-QEXP)/QIR$
$CEF = (DC+CDR)*(1-RMVL)$
$CIR = \delta*\alpha*CEF+(1-\alpha)*CDR+(1-\delta)*\alpha*CGW$

SCHEME II

$QIR = QP-QEXP+QIMP$
$QUR = \alpha*(QIMP+QR)$
$DELQP = (1-\delta)*\alpha*QIMP$
$DELQR = DELQP+(1-\delta)*\alpha*QR$
$CDR = 0$
$CEF = (1-RMVL)*DC$
$CIR = [QP-QEXP+DELQP)*CGW+\delta*\alpha*QIMP*CEF]/QIR$

SCHEME III

$QIR = QP-QEXP+QIMP$
$QUR = \alpha*QIR$
$DELQR = (1-\delta)*QUR$
$DELQP = DELQR+\delta*QUR - QUR$
$CDR = CGW*(QP-QEXP)/QIR$
$CEF = (DC+CDR)*(1-RMVL)$
$CIR = (1-\alpha)*CDR+\alpha*CGW$

LEGEND

α	- Proportion of urban water use	DELQP	- Complementary pumpage	RMVL	- Removal efficiency of treatment plant
δ	- Return flow coefficient of urban use	DELQR	- Complementary recharge	CGW	- Groundwater concentration
QP	- Pumpage	QUR	- Urban water supply	CDR	- Drinking water concentration
QEXP	- Export	QIR	- Total water demand	CEF	- Effluents concentration
QIMP	- Imported water	QIN	- Groundwater inflow (+) and outflow (-)	*CIR*	- *Irrigation water*
QR	- Artific recharge	DC	- Pollutant conc. increase by urban use	TW	- Transit time along unsaturated zone

Figure 8. Alternative schemes for recycling sewage effluents in the aquifer system

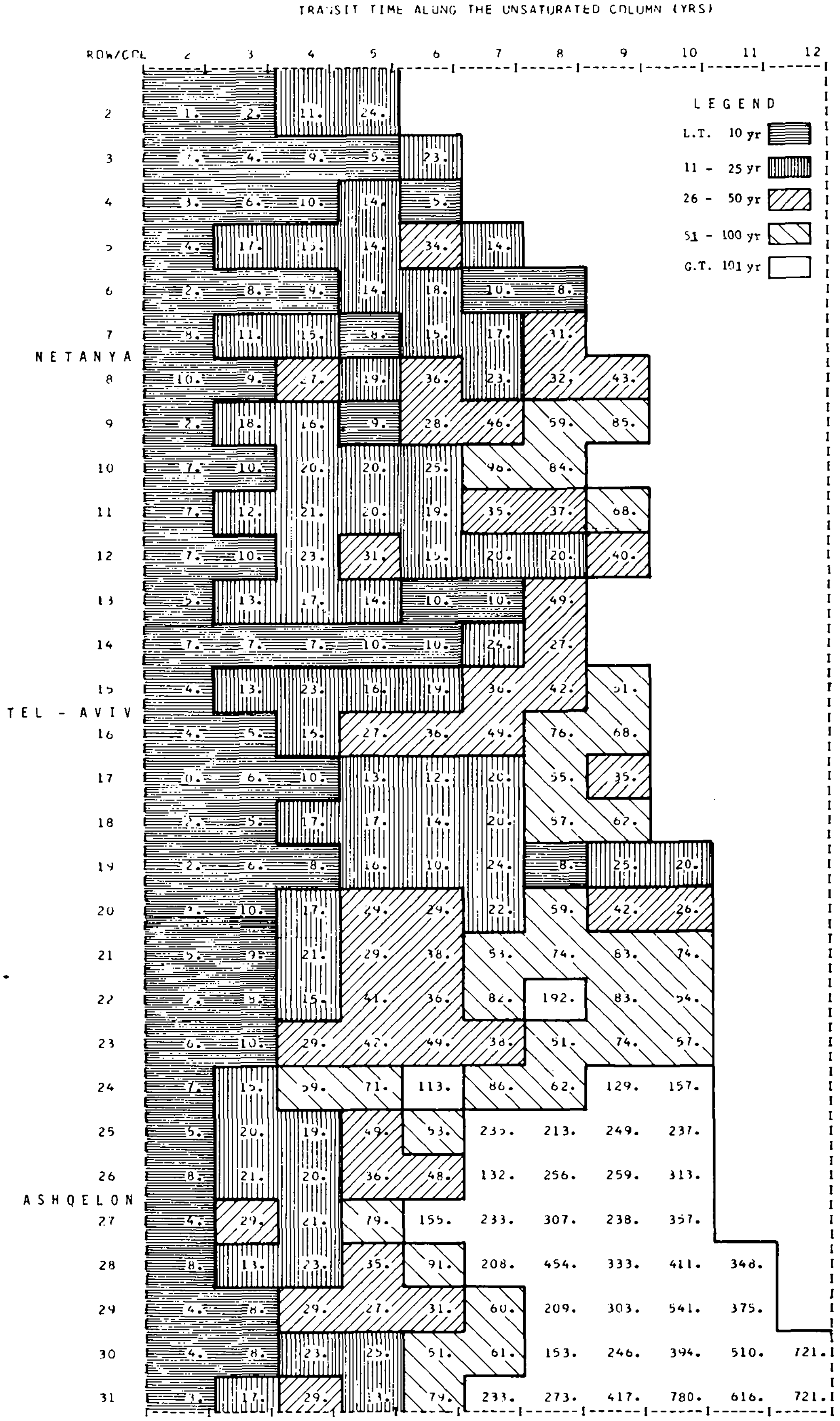


Figure 9. Transit-time of chemically -inert solutes from land surface to the coastal plain aquifer

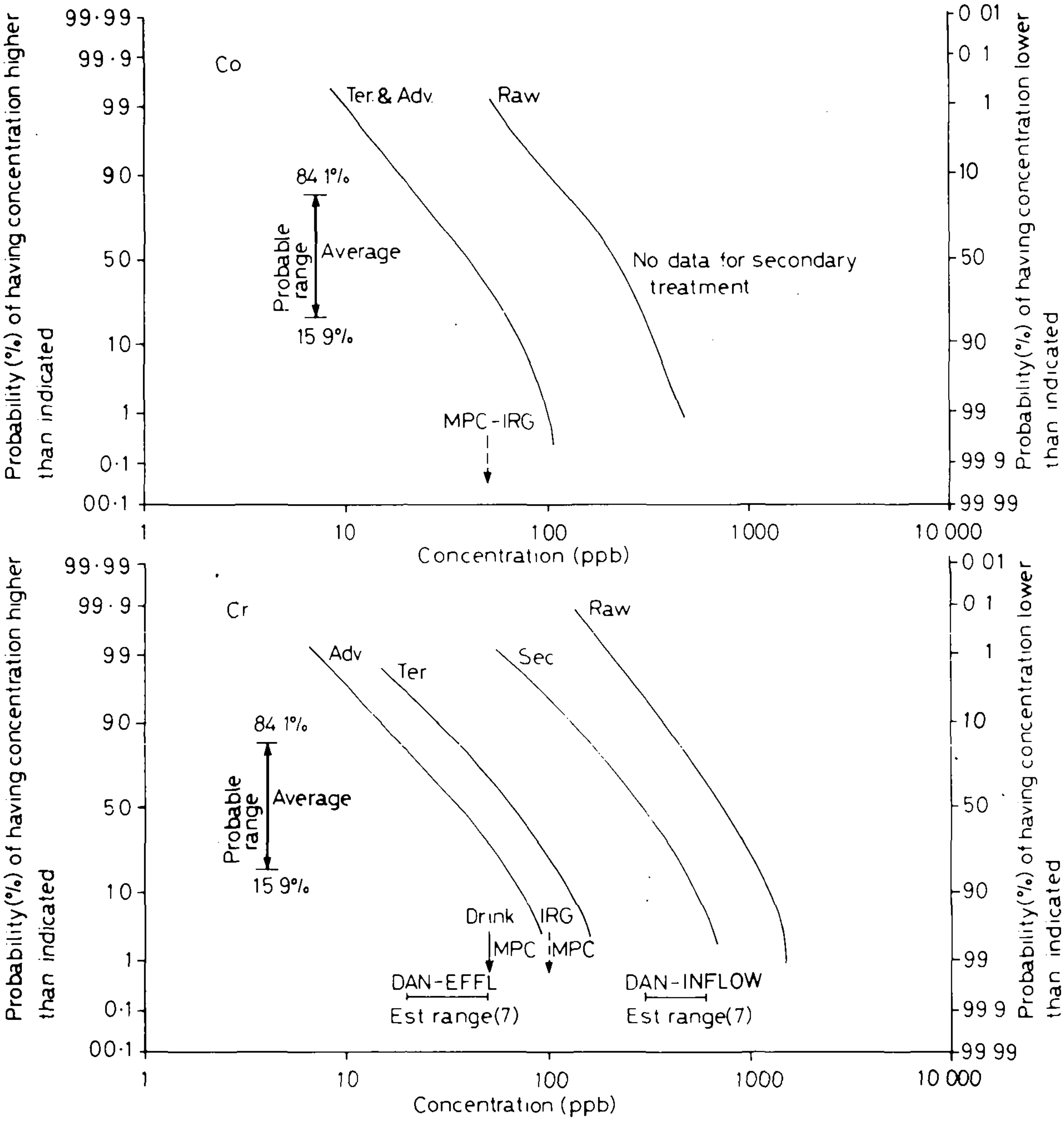


Figure 10. Probability distributions of cobalt and chromium concentration in sewage effluent

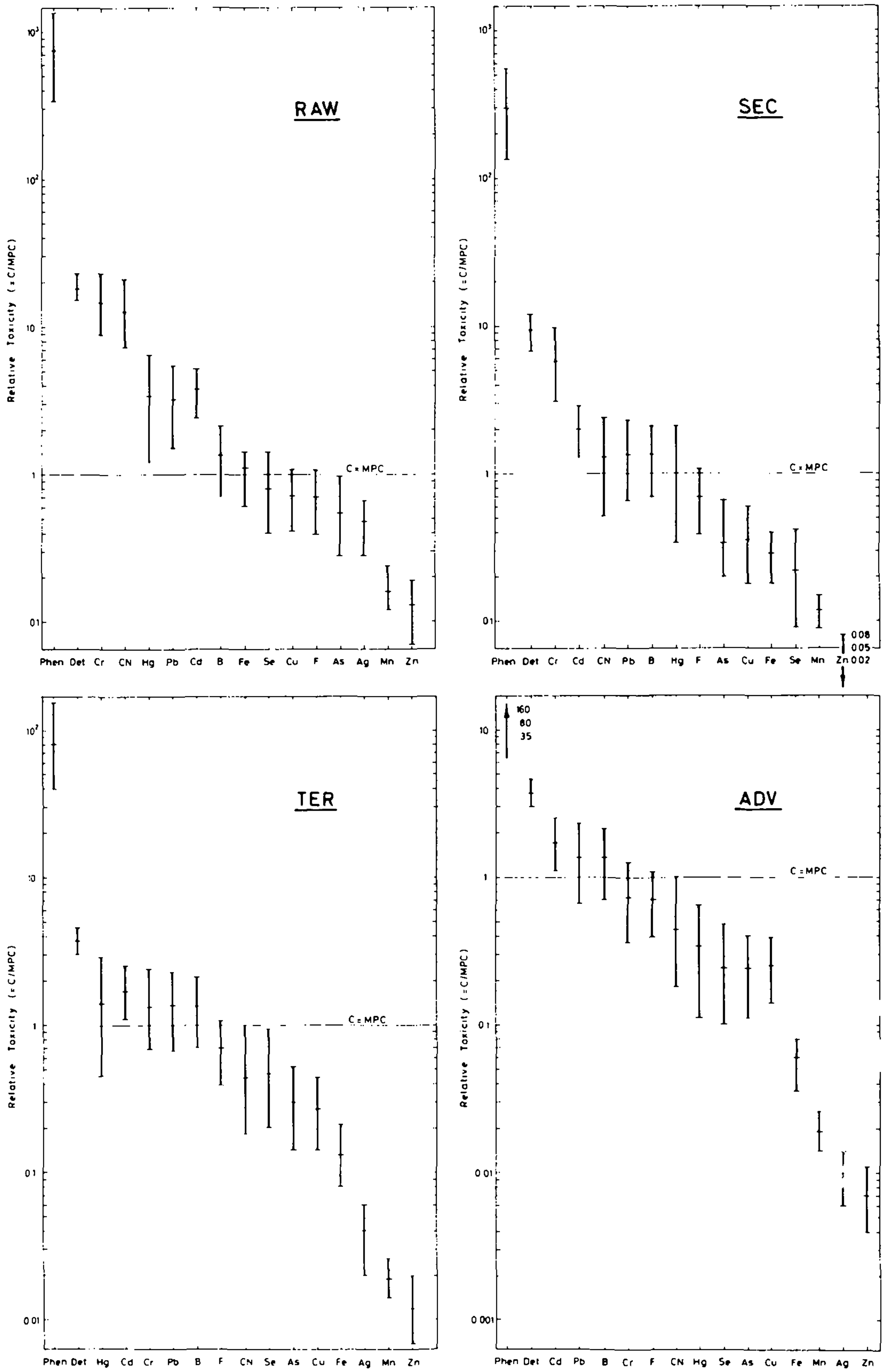


Figure 11. Classification of trace elements in sewage effluents according to their 'relative toxicity' (drinking water standards)

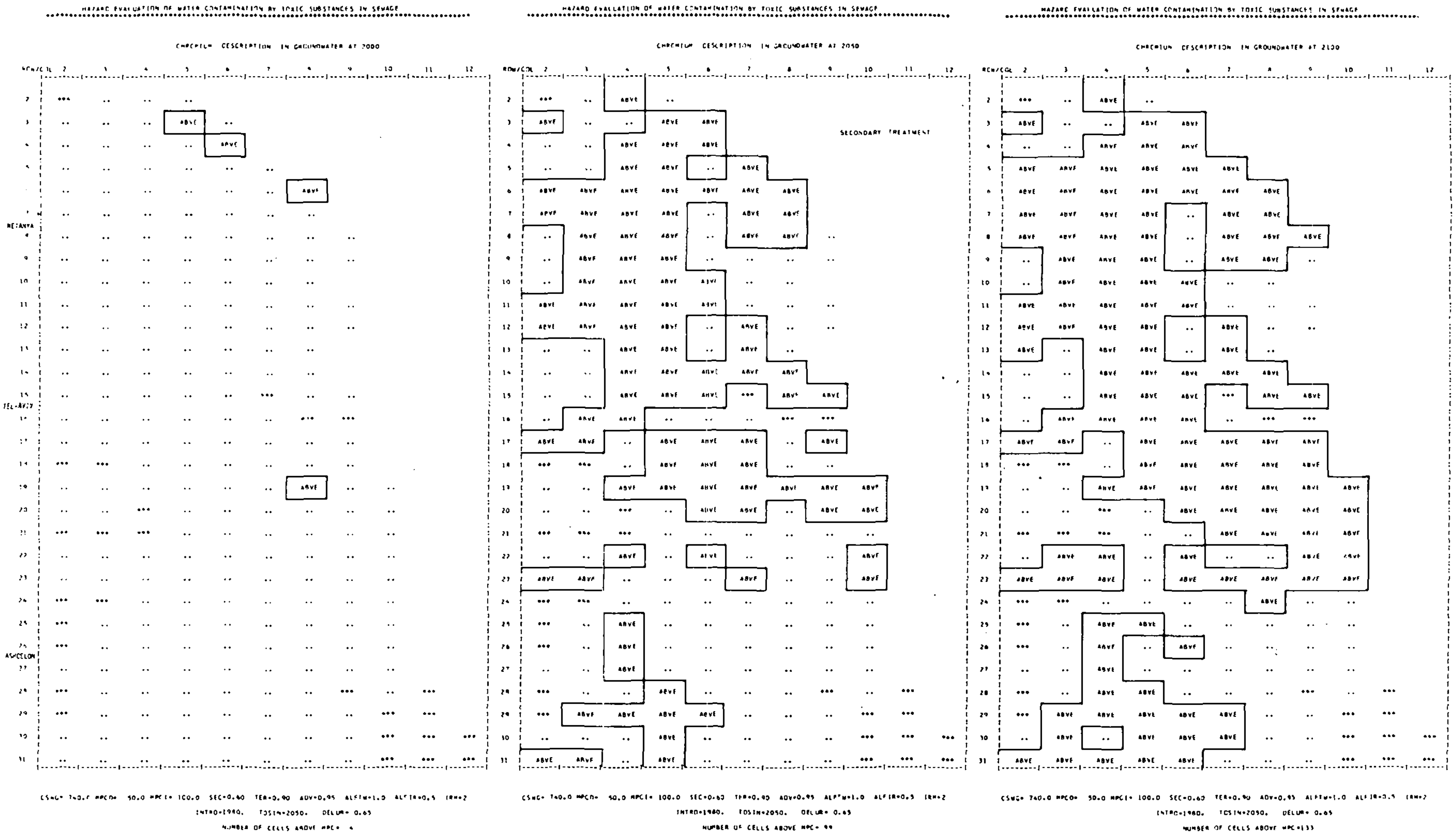


Figure 12. Descriptive maps of possible groundwater pollution by chromium in secondary effluents

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HAZARD EVALUATION OF GW CONTAMINATION BY TOXIC SUBSTANCES IN SEWAGE - AVEARAGE ASSUMPTION
*******************************************************************************************

                 RECOM. TREATMENT TO REACH CHROMIUM MPC IN GROUNDWATER

ROW/COL  2        3        4        5        6        7        8        9        10       11       12
        I--------I--------I--------I--------I--------I--------I--------I--------I--------I--------I--------I
        I                                                                                                   I
        I                                                                                                   I
   2    I  ***      RAW      TER      RAW                                                                   I
        I                                                                                                   I
        I                                                                                                   I
   3    I  TER      RAW      RAW      TER      ADV                                                          I
        I                                                                                                   I
        I                                                                                                   I
   4    I  SEC      SEC      ADV      TER      TER                                                          I
        I                                                                                                   I
        I                                                                                                   I
   5    I  SEC      SEC      TER      TER      SEC      TER                                                 I
        I                                                                                                   I
        I                                                                                                   I
   6    I  TER      TER      TER      TER      TER      TER      ADV                                        I
        I                                                                                                   I
        I                                                                                                   I
   7    I  TER      TER      TER      TER      SEC      TER      TER                                        I
NETANYA I                                                                                                   I
   8    I  SEC      TER      TER      TER      SEC      TER      TER      SEC                               I
        I                                                                                                   I
        I                                                                                                   I
   9    I  RAW      TER      TER      ADV      SEC      SEC      SEC      RAW                               I
        I                                                                                                   I
        I                                                                                                   I
  10    I  SEC      TER      TER      TER      TER      RAW      RAW                                        I
        I                                                                                                   I
        I                                                                                                   I
  11    I  TER      TER      TER      TER      TER      SEC      RAW      RAW                               I
        I                                                                                                   I
        I                                                                                                   I
  12    I  TER      TER      TER      TER      SEC      TER      RAW      RAW                               I
        I                                                                                                   I
        I                                                                                                   I
  13    I  SEC      SEC      TER      TER      RAW      TER      RAW                                        I
        I                                                                                                   I
        I                                                                                                   I
  14    I  RAW      SEC      TER      TER      ADV      TER      TER                                        I
        I                                                                                                   I
        I                                                                                                   I
  15    I  RAW      RAW      TER      TER      TER      ***      TER      TER                               I
TEL-AVIV I                                                                                                  I
  16    I  SEC      TER      TER      SEC      SEC      RAW      ***      ***                               I
        I                                                                                                   I
        I                                                                                                   I
  17    I  TER      TER      SEC      TER      TER      TER      SEC      TER                               I
        I                                                                                                   I
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  18    I  ***      ***      RAW      TER      TER      TER      RAW      SEC                               I
        I                                                                                                   I
        I                                                                                                   I
  19    I  SEC      RAW      TER      TER      TER      TER      ADV      TER      TER                      I
        I                                                                                                   I
        I                                                                                                   I
  20    I  RAW      RAW      ***      RAW      TER      TER      RAW      TER      TER                      I
        I                                                                                                   I
        I                                                                                                   I
  21    I  ***      ***      ***      SEC      SEC      RAW      RAW      RAW      RAW                      I
        I                                                                                                   I
        I                                                                                                   I
  22    I  RAW      SEC      TER      RAW      TER      RAW      RAW      RAW      TER                      I
        I                                                                                                   I
        I                                                                                                   I
  23    I  TER      TER      SEC      SEC      SEC      TER      SEC      RAW      TER                      I
        I                                                                                                   I
        I                                                                                                   I
  24    I  ***      ***      RAW      RAW      RAW      RAW      RAW      RAW      RAW                      I
        I                                                                                                   I
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  25    I  ***      RAW      TER      RAW      RAW      RAW      RAW      RAW      RAW                      I
        I                                                                                                   I
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ASHQELONI                                                                                                   I
  27    I  RAW      SEC      TER      RAW      RAW      RAW      RAW      RAW      RAW                      I
        I                                                                                                   I
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  28    I  ***      SEC      SEC      TER      RAW      RAW      RAW      ***      RAW      ***             I
        I                                                                                                   I
        I                                                                                                   I
  29    I  ***      TER      TER      TER      TER      RAW      RAW      RAW      ***      ***             I
        I                                                                                                   I
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  30    I  SEC      SEC      SEC      TER      SEC      RAW      RAW      RAW      ***      ***      ***    I
        I                                                                                                   I
        I                                                                                                   I
  31    I  TER      TER      SEC      TER      RAW      RAW      RAW      RAW      ***      ***      ***    I
        I--------I--------I--------I--------I--------I--------I--------I--------I--------I--------I--------I

    CSWO= 740.0 MPCD=  50.0 MPCI= 100.0  SEC=0.60  TER=0.90  ADV=0.95  ALFTN=1.0  ALFIR=0.5  IRM=2
                              INTRO=1980.   TDSIN=2050.   DELUR= 0.65
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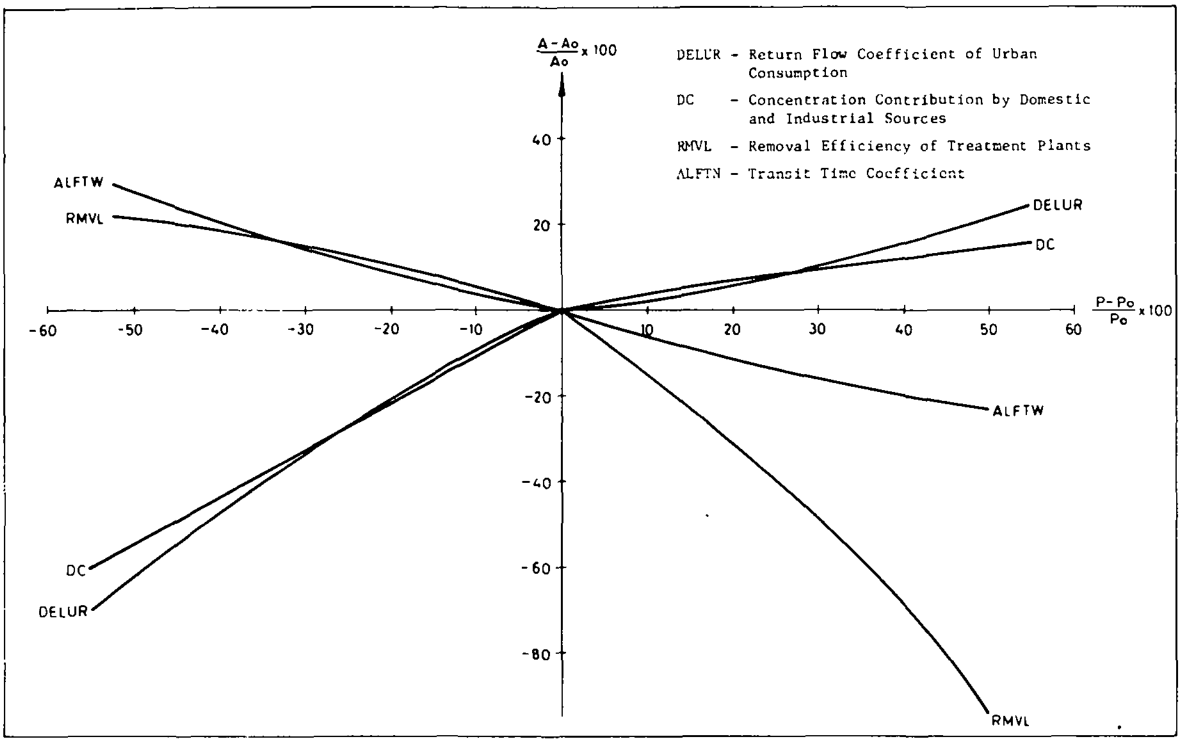
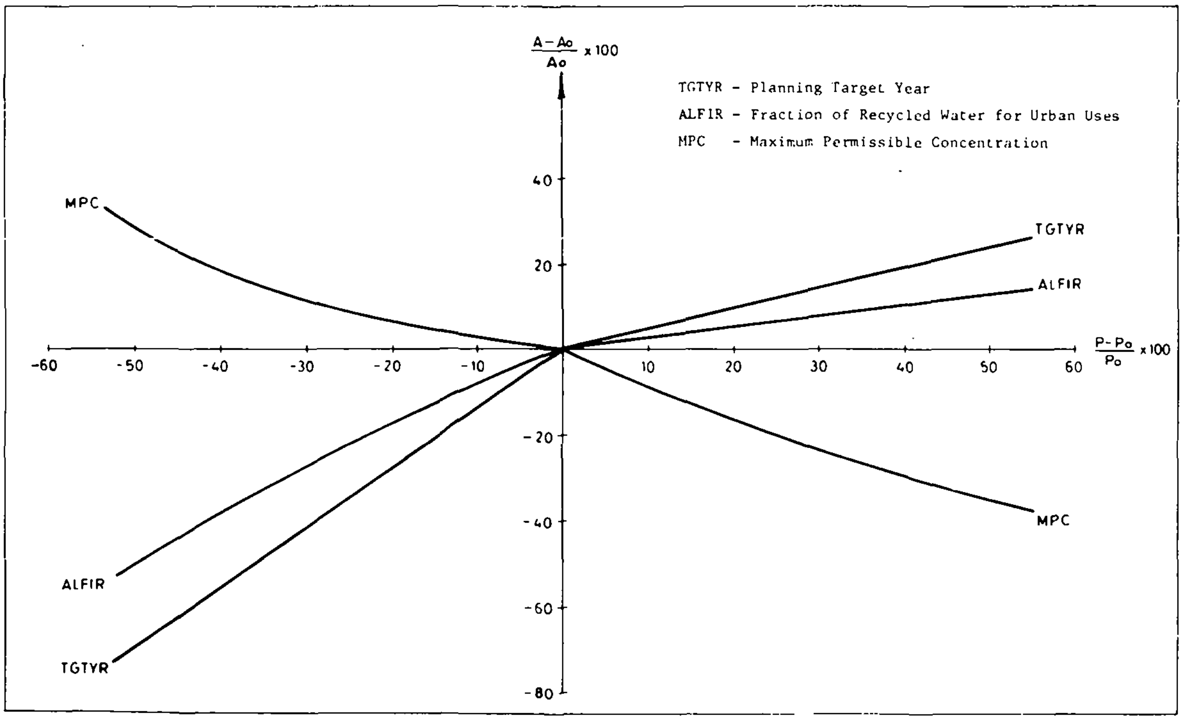
Figure 13. Recommended treatment levels of sewage effluents to conserve groundwater quality till 2050





A - Contaminated Area
P - Parameter (DELUR, DC, etc.)

REFERENCE ALTERNATIVE (Chrome)

DELUR	= 0.65	ALFTW	= 1.0
DC	= 740 ppb	TGTYR	= 2050
RMVL	= 60% (sec)	ALFIR	= 50%
Ao	= 97 cells out of 216 (45%)		

Figure 14. Sensitivity analysis of possible pollution to parameter variations

PAPER 19

A COMPARISON OF GROUNDWATER QUALITY MODELLING TECHNIQUES

Prof. L. W. Gelhar

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1. INTRODUCTION

Groundwater quality modelling techniques can be classified according to the flow field, mixing process and reaction phenomena which are implicitly included in the mathematical model. The objective in this discussion is to develop comparisons of these various techniques and identify practical field conditions for which a given form of model will be suitable.

The physical basis for the various types of models is outlined; included are lumped parameter mixing cell models, one-dimensional flow models with dispersive mixing and chemical reaction, two-dimensional horizontal flow models with dispersive mixing, two-dimensional flow models representing displacement in a vertical plane and chemical reaction, and three-dimensional flow models including dispersive mixing. Also discussed briefly are the various solution techniques including finite difference and finite element numerical methods, as well as appropriate analytical methods. The data requirements for each of the types of models are outlined, especially as related to practical applications of the models.

For purposes of specific comparison, the application of several different types of models to the prediction of irrigation return flow water quality is reviewed. The results of several studies using a two-dimensional horizontal flow model with dispersive mixing, a lumped parameter mixing cell model with chemical equilibrium reactions, and two-dimensional models of vertical circulation with chemical equilibrium reactions are compared and discussed.

2. STRUCTURE AND MODEL EQUATIONS

Groundwater quality models can be classified in terms of the physical structure that is represented in the statement of mass balance that forms the physical basis for all such models. This structure is reviewed in terms of a hierarchy of models beginning with the simplest and evolving through to the more complex. The structure is also related to the type of reaction or source term which is involved in the overall mass balance. Summarized in Table 1 are several recent groundwater quality modelling studies described in terms of their physical structure, the solution technique and the type of application involved.

The simplest type of model is the lumped parameter model, which deals with spatial averages of the variables. Models of this type have been used by Gelhar and Wilson, 1974, and Mercado, 1976 . The essential mass balance statement can be written in the following form (see Gelhar and Wilson, 1974):

$$\frac{d}{dt}(nhC) = \varepsilon C_o - qC + nhr \qquad \ldots\ldots\ldots 1$$

where n is the average effective porosity of aquifer, h is the average saturated thickness, and C is the concentration (mass of the contaminant/ unit volume of solution). The terms on the right hand side of Equation 1 represent the net input of contaminant to the model as follows:

ε = recharge rate per unit area
C_o = concentration of recharge
q = outflow rate per unit area
r = volumetric source (mass of contaminant per unit volume of water per unit time)

The primary assumption involved in Equation 1 is the form of the outflow term. This form implicitly assumes a completely mixed system in which the concentration of the water flowing out of the aquifer is identical to the average concentration within the aquifer. Gelhar and Wilson, 1974, show that this assumption is appropriate because of the nature of convection through a phreatic aquifer. The lumped parameter model is depicted schematically in Figure 1. This model is most suited to groundwater quality problems in which contaminant sources are widely distributed throughout the aquifer, and for which aquifer conditions or conditions in the ouflow from the aquifer are of concern.

One-dimensional groundwater quality models are used to describe the longitudinal and temporal variation of the water quality in aquifers. The governing equation is a convective-dispersion type equation including a longitudinal dispersion term as follows (see Bachmat and Bear, 1964; Gelhar and Collins, 1971):

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = \alpha_L u \frac{\partial^2 C}{\partial x^2} + r \qquad \ldots\ldots\ldots 2$$

where x = longitudinal co-ordinate

u = seepage velocity = specific discharge/porosity

α_L = longitudinal dispersivity

This equation applies to the concentration variation along a streamline in steady flow or to the longitudinal variation of the depth averaged concentration in a confined aquifer of constant thickness. The fluid density and the porosity are assumed to be constant in Equation 2. Examples of applications of the one-dimensional equation are given in Table 1 (14, 19, 22).

The two-dimensional horizontal representation of water quality variations is used in connection with the usual two-dimensional horizontal flow description of applied groundwater hydrology. In this case, the governing equation represents the depth-averaged concentration over the aquifer thickness, h, stated in the following form:

$$\frac{\partial}{\partial t}(hC) + \frac{\partial}{\partial x_i}(u_i hC) = \frac{\partial}{\partial x_i}\left(hD_{ij}\frac{\partial C}{\partial x_j}\right) + rh + \varepsilon C_o, \quad i, j = 1, 2 \qquad \ldots\ldots\ldots 3$$

where x_i = horizontal co-ordinates ($i = 1, 2$)

u_i = components of the seepage velocity

D_{ij} = dispersion coefficient tensor

ε = rate of inflow/unit area (recharge)

C_o = concentration of the inflow

Equation 3 was given by Bredehoeft and Pinder, 1973, in a somewhat more general form which includes variable porosity and the effect of aquifer and fluid compressibility. Note also that their dispersion coefficient is based on the gross area and thus is smaller than D_{ij} in Equation 3 by the factor porosity. The form of dispersion coefficient used in Equation 3 is consistent with the traditional three-dimensional form (see Bear, 1972 or Fried, 1976) although the actual form is arbitrary. The two-dimensional horizontal modelling format has been widely used in applied field studies of groundwater quality (see 1, 2, 7, 9, 11, 16, 20, 21, 22, 27 and 28 in Table 1). The typical configuration of a two-dimensional horizontal flow model is indicated in Figure 1.

Two-dimensional models, which consider the circulation within a vertical plane as in the classical regional groundwater circulation system, are also used to describe groundwater quality in aquifers. As depicted in Figure 1, the concentration variation within a vertical plane is described. The following equation will, in general, describe that distribution (Bear, 1972):

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x_i} (u_i C) = \frac{\partial}{\partial x_i} (D_{ij} \frac{\partial C}{\partial x_j}) + r \qquad \ldots\ldots\ldots 4$$

where i, j = 1, 2 and x_2 is the vertical co-ordinate. A few modelling studies have used this general dispersion equation (see 10, 15, and 24 in Table 1). In many other studies only the convective transport effect is described (see 3, 4, 8, 13, 23, and 25 of Table 1).

The most detailed description of water quality distribution in an aquifer is based on a three-dimensional representation which is governed by Equation 4 but in this case the indices i and j range over 1, 2, and 3. Because of the fundamental natural complexity of three-dimensional systems and the inherent difficulty in obtaining solutions in this case, truly three-dimensional models have seen very little use. Recently, however, Gupta <u>et al.</u>, 1975, have described a three-dimensional numerical transport model.

The entire hierarchy of models described in this section can be developed by appropriate averaging or integration of the three-dimensional transport equation. It is important to recognize this inherent averaging process because it influences the character of the dispersion coefficient that may appear in a given equation. For example, the dispersion coefficient in the horizontal flow models (Equation 3) implicitly involves the effects of vertical stratification of the aquifers in the dispersion coefficient as discussed by Fried, 1975 . The magnitude of the dispersion coefficient will depend on the structure of the model selected to describe the process.

The source term identified by the symbol r in the various equations can be important in several water quality systems. However, it is evident from Table 1 that few models consider specific source terms. Two forms of the source term which are quite widely used are the first order decay

$$r = -kC \qquad \ldots\ldots\ldots 5$$

where k is a rate constant, and the linear adsorption form

$$r = -\frac{(1-n)}{n} K_d \frac{\partial C}{\partial t} \qquad \ldots\ldots\ldots 6$$

where K_d is the so-called distribution coefficient or a constant of proportionality relating the concentration in the solid phase to the concentration in solution. More complex source terms involving chemical equilibrium (25 and 26 in Table 1) and chemical kinetics (14 and 23) have also been used.

The model equations described above provide only a partial description of the water quality model. In each case a compatible flow field description must also be obtained. This is found from the appropriate combination of the conservation of total mass and some form of the Darcy equation. In most cases flow field calculations are independent of the quality considerations; however, when density changes are significant, as in the case of sea-water intrusion in coastal aquifers, the flow system and contaminant transport system must be coupled (see 10 and 24 in Table 1).

3. SOLUTION TECHNIQUES

Several methods of solving the various governing equations, including analytical, numerical and analogue techniques will be summarized. The emphasis will be on the decoupled system and on practical techniques whose use has been demonstrated under field conditions.

The lump parameter or mixing cell models as described by an ordinary differential equation of the form of Equation 1 can be solved for some simple inputs by analytical methods (Gelhar and Wilson, 1974). However, for most realistic inputs, a numerical solution is required. The ordinary differential equation can be represented in an elementary finite difference form (Gelhar and Wilson, 1974) which can be solved explicitly with a very simple computer program. Analogue computation methods have also been used to solve lumped systems (Thomas et al., 1972). Digital simulation with a recursive expression has been used to represent multi-cell lump parameter models (Przewlocki and Yurtsever, 1974).

The one-dimensional transport equation (Equation 2) has, for the case of constant velocity and dispersivity, classical analytical solutions (Ogata, 1970; Bear, 1972; Fried, 1975) which may be useful for preliminary estimates under field conditions. Rabinowitz et al., 1976, have applied a one-dimensional analytical solution in the case of the movement and dispersion of atmospheric tritium pulses in a confined aquifer. More general analytical solutions are available for the case when the convection velocity u is spatially variable (Dagan, 1971; Gelhar and Collins, 1971). These solutions involve a direct integration of the velocity field which may be obtained from numerical or analogue flow models, or estimated from flow nets constructed from field observations. This technique was applied by Sauty, 1974, using a two-dimensional horizontal flow field obtained from a finite difference model.

Convection patterns in two-dimensional vertical circulation systems have been found by numerical integration of analytically derived streamline patterns (e.g., Jury, 1975). The flow field generated by an electric analogue was used to calculate the displacement in a regional groundwater circulation system on Long Island, New York (Franke and Cohen, 1972), and observations of dye displacement in a viscous analogue were used to simulate the displacement of contaminants in the Long Island systems (Gelhar, 1972). Schwartz and Domenico, 1973, carry out numerical integrations along several streamlines in a regional vertical circulation system, neglecting the effect of dispersion but including hydrochemical changes.

Several two-dimensional horizontal systems have been simulated using simultaneous mass balances for several interconnected finite cells (Water Resources Engineers, 1969; Maddaus and Aaronson, 1972; Hassan et al., 1974). In these models, no attempt is made to represent the system in terms of the governing partial differential equation. This approach has the advantage that it allows more direct physical insight; however, it introduces an artificial mixing effect which is related to the cell structure.

Several finite difference techniques have been used to solve the transport equations in one- and two-dimensional systems. The books by Remson et al., 1971, and Fried, 1975, give considerable detail on such finite difference schemes in the context of subsurface hydrology. Explicit schemes (e.g., Hoopes and Harleman, 1967) are direct, but require very small time increments to satisfy the usual stability requirement. Implicit schemes, which require matrix inversion, appear to be computationally more efficient and have been widely used (e.g., Shamir and Harleman, 1967; Bresler, 1973; and Tagamets et al., 1975) in idealized one-dimensional problems. These standard finite difference schemes involve a truncation error in the convection term. This error, which is referred to as numerical dispersion, can be minimized by using higher order finite difference schemes (Lantz, 1971; Bresler, 1973; VanGenuchten and Wierenga, 1974).

In an effort to avoid this numerical dispersion, Gardner et al., 1964, introduced the method of characteristics, which essentially calculates the displacement of water through the system and then superimposes the effect of dispersion on that displacement. The method of characteristics was adapted to groundwater flow systems by Reddell and Sunada, 1970, and has been extensively used in field simulations (9, 20 and 21 in Table 1).

The finite element method based on the variational formulation has been applied to an idealized two-dimensional system by Guymon et al., 1970. The Galerkin formulation was applied by Pinder, 1973, for two-dimensional problems and Rubin and James, 1973, in one-dimensional systems with chemical equilibrium reactions. A three-dimensional Galerkin formulation of the transport equation has been developed by Gupta et al., 1975.

A feature which seems to be common to all finite difference and finite element methods is the numerical oscillation or overshoot which develops when a step input is introduced. This was reported by Shamir and Harleman, 1967, using an implicit finite difference scheme, by Reddell and Sunada, 1970, with the method of characteristics, by Rubin and James, 1973, and Gupta et al., 1975, using the Galerkin finite element method. These oscillations are usually eliminated by trial adjustment of the space-time increments. Because of the potential errors associated with this oscillation, it is important to check a numerical model with a step input to be sure that the oscillations are eliminated before applying the model to field conditions involving continuously invariable inputs.

Ahlstrom and Foote, 1976, have introduced a Markov-type random walk model to simulate the dispersion superimposed on the mean motion in an aquifer flow system.

4. DATA REQUIREMENTS

Extensive data may be required to implement many of the water quality models discussed above. The data requirements fall into two primary categories, the first being that of mathematical initial or boundary conditions. The configuration of the aquifer and boundary fluxes of water and contaminant or head must be prescribed. Some starting conditions, including initial distribution of head and water quality, are required in addition to information on the quantity and quality of inflows and withdrawals in the form of recharge and pumping.

A second category of information which is required from model implementation is that of model parameters. These may be developed from independent observations or may evolve from analysis of the initial and boundary data. In the case of the two-dimensional horizontal model, the required flow parameters are the storage coefficient or specific yield and the aquifer transmissivity. These may be obtained from independent pumping tests in the area or through some automated or trial calibration of the model based on historical water level data.

Some type of mixing parameter must also be specified. For several of the models, longitudinal and lateral dispersivities are required but there does not seem to be a suitable independent method of determining the required dispersivities. It is recognized that the dispersivities are dependent on the scale of the contamination problem (Fried, 1975, Chapter 4). Thus, dispersivity estimates based on local single or two well tests may not be suitable for the larger scale regional systems which are most often of applied interest. In cases where a long term history of contamination is available, dispersivities are estimated by adjusting to provide a suitable representation of the data. In the case of the lumped parameter models, the mixing characteristics are somewhat simpler and they are not explicitly dependent on dispersion characteristics. Only a response time, which is the ratio of the volume of water in the system to the rate of flow through the system, is required. If non-conservative contaminants are to be considered, parameters relating to adsorption or chemical reaction within the aquifer will also be required. Such parameters are difficult to estimate from direct data because of the high degree of variability of most natural deposits.

Related to the question of data requirements is that of model evaluation of some type. Typically a so-called verification is performed by comparing the model prediction with historical information on some important output feature in the model. In addition, it is usually desirable to test the sensitivity of the model results to changes in model parameters and input data. In many actual field applications, data availability will be a severe limitation on actual model capabilities. The type of data that is available will often dictate the model structure that can be adapted to the given problem.

5. APPLICATION - IRRIGATION RETURN FLOW MODELS

The results of several different types of modelling efforts dealing with salinity effects in irrigated areas will be summarized. The contaminant in this case is the dissolved solids associated with the applied water as well as soluble material in the soil and aquifers underlying irrigated areas. Salinity increase as a result of irrigation is of major concern in terms of impact on surface water quality as well as groundwater quality. For example, in the Colorado River Basin major salinity control programmes are under way (Flack and Howe, 1974).

A lumped parameter model was applied by Thomas et al., 1972, using electric analogue computations for the hydrologic simulation and the digital simulation of chemical equilibrium reactions within the unsaturated zone. The groundwater complement of this model is simply a conservative mass balance. The chemical model considers exchange of calcium, magnesium and sodium and dissolution or precipitation of gypsum and lime. The model is applied to an irrigated area in the Little Bear River Basin in Utah. Typical results (Figure 2) show the predicted quality of the outflow from the basin.

A two-dimensional vertical circulation model was applied by Jury, 1975, to describe the movement of solutes from agricultural areas to drains. He compared data on the leaching of chloride from a small field plot with model results (Figure 3). A more detailed model of this type has been used by Shaffer et al., 1976. It includes a stepwise chemical equilibrium calculation carried out as water is displaced through the aquifer under steady flow conditions. A typical result (Figure 4) shows the quality of the effluent from an aquifer as a result of 75 years of irrigation in a 2200-acre area in south western Colorado. The required input data on the initial chemical characteristics of the aquifer material were estimated from samples taken in an adjacent non-irrigated area. From additional runs without chemical reactions in the aquifer (a conservative tracer) Shaffer et al., 1976, concluded that chemical effects were significant in this case (Figure 4).

A two-dimensional horizontal representation has been used by Konikow and Bredehoeft, 1974a, to simulate groundwater quality in an irrigated area along the Arkansas River in south eastern Colorado. The method of characteristics was used to solve the transport equation in which dissolved solid concentration was taken as a conservative tracer. Simulations were carried out for a one-year period and compared with the field data for that period; results for the quality variation of two wells are shown in Figure 5. Additional results show that the model also reasonably represents the spatial water quality pattern which was observed. A longitudinal dispersivity of 100 feet was used in the final simulations, but it was found that results were insensitive to changes in the dispersivity. It was concluded that the water quality distribution is controlled primarily by convection and mixing with the recharge waters. This model is also used to evaluate irrigation management alternatives (Konikow and Bredehoeft, 1974b).

A two-dimensional horizontal representation was also used to simulate water quality conditions in the Santa Ana Basin in Southern California (Water Resources Engineers, 1969). The aquifer, which encompasses 500 square miles, was decomposed into several hundred finite polygonal cells in which simultaneous conservative mass balances were performed for dissolved solids by a digital computer. There was some salt load from municipal and industrial sources, but the predominant contribution was from agricultural sources associated with irrigation. This model also simulates the movement and storage of salts in the unsaturated zone. Extensive input data were required and a special data management system was developed to process the data. Some results for a ten-year simulation are shown in Figure 6. After testing, the model was used to simulate management alternatives for the period 1965 to 2015.

Gupta et al., 1975, have demonstrated the computational feasibility of a three-dimensional model in using the Galerkin finite element method. They applied the model in the Sutter Basin of California's Central Valley, but the water quality simulations were not tested with field data.

6. CONCLUDING REMARKS

This summary of modelling results for irrigation return flow water quality shows that several types of models have been used successfully to simulate this process. If only the outflow quality is desired, the lumped parameter model is suitable and produces reliable results. The results for the two-dimensional vertical circulation systems indicate that convection is a predominant factor, and that the chemical reactions can also play an important role. The two-dimensional horizontal models require very extensive input data. These models generally reproduce the spatial and temporal patterns observed, although there are some significant differences. Again, the convective effects seem to be a predominant transport mechanism.

In cases of localized contamination sources two- and three-dimensional dispersive models are obviously required to represent the phenomenon. However, in the case of widely distributed contaminants, the lumped approach or possibly a simple convective model may be appropriate. This would appear to be the case for the irrigation return flow problem.

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TABLE 1. SUMMARY OF RECENT GROUNDWATER QUALITY MODELING STUDIES

Legend: FDM = finite difference method; FEM = finite element method; MOC = method of characteristics; N-D = N-dimensional

No.	Authors	Physical Structure	Source Effects	Solution Technique	Applications & Remarks
1	Ahlstrom and Foote, 1976	2-D horizontal dispersive	Ion exchange, precipitation	FDM (flow) + random walk	Radioactive waste movement
2	Bredehoeft and Pinder, 1973	2-D horizontal dispersive	None	MOC	Chloride contamination of artesian aquifer, Brunswick, Georgia
3	Franke and Cohen, 1972	2-D vertical section convection only	None	Electric analog	Long Island, New York, septic tank contamination
4	Gelhar, 1972	2-D vertical non-dispersive	None	Viscous analog	Regional contaminant movement, Long Island, New York
5	Gelhar & Wilson, 1974	Lumped	None	FDM	Regional highway salt contamination
6	Gupta, et al., 1975	3-D dispersive	None	FEM, Galerkin	Preliminary field simulations
7	Hassan, et al., 1974	2-D horizontal multiple mixing cells	None	Digital computer	TDS simulation for Santa Clara-Callegnas Basin, California
8	Jury, 1975, I & II	2-D vertical section convection only	None	Analytical & numerical integration	Agricultural drainage
9	Konikow and Bredehoeft, 1974a	2-D horizontal dispersive	None	MOC	Irrigated area along Arkansas River in Colorado
10	Lee and Cheng, 1974	2-D vertical dispersive	None	FEM	Saltwater intrusion; Florida
11	Maddaus & Aaronson, 1972	2-D horizontal non-dispersive	None	FDM	Management 1200mi^2 basin in California

No.	Authors	Physical Strucuture	Source Effects	Solution Technique	Application & Remarks
12	Mercado, 1976	Lumped	None	FDM	Nitrate and chloride contamination, coastal plain aquifer, Israel
13	Miyamoto and Warrick, 1974	2-D vertical section, convection	None	Analytical & numerical integration	Salt leaching from soils
14	Palciauskas & Domenico, 1976	1-D dispersive	Linear chemical kinetics	Analytical	Ca & Mg in Floridian aquifer, qualitative
15	Pickens and Lennox, 1976	2-D vertical with dispersion	Linear adsorption	Galerkin FEM	Hypothetical regional flow, sensitivity analysis
16	Pinder, 1973	2-D horizontal dispersion	None	Galerkin FEM	Chromium plume on Long Island, New York
17	Przewlocki & Yurtsever, 1974	Lumped; multiple mixing cells	Radioactive decay	Recursive equation	Tritium output of basins in Austria and Czechoslovakia
18	Reddell & Sunada, 1970	2-D with dispersion	None	MOC	Hypothetical problems
19	Rabinowitz et al., 1976	1-D dispersive	First order decay	Analytical	Tritium tracing carbonate aquifers, New Mexico
20	Robertson, 1974	2-D horizontal dispersive	Linear adsorption Sr^{90}	MOC	Radioactive waste distribution in Snake River plain aquifer
21	Robson, 1974	2-D horizontal dispersive	None	MOC	Effect of waste disposal basins in Barstow, California
22	Sauty, 1974	2-D horizontal dispersive	None	Dispersion analytical and flow by FDM	Several stream-aquifer-lake configurations

No.	Authors	Physical Structure	Source Effects	Solution Techniques	Application & Remarks
23	Schwartz & Domenico, 1973	2-D vertical nondispersive	Chemical kinetics	FDM	Natural water quality distribution in a regional flow system, Ontario
24	Segal, et al., 1975	2-D vertical dispersive	None	Galerkin FEM	Saltwater intrusion, Florida
25	Shaffer et al., 1976	2-D vertical nondispersive	Chemical equilibrium	FDM	Irrigation return flow, Colorado
26	Thomas, et al., 1972	Lumped	Chemical equilibrium	Hybrid, analog & digital computer	Little Bear River Basin, Utah; irrigation return flow
27	Water Resources Engineers, Inc., 1969	2-D horizontal multiple mixing cells	None	Digital computer	Water management 500 mi^2 basin in Southern California
28	Willis, 1976	2-D horizontal dispersive	Linear adosrption	FDM	Optimal waste water management

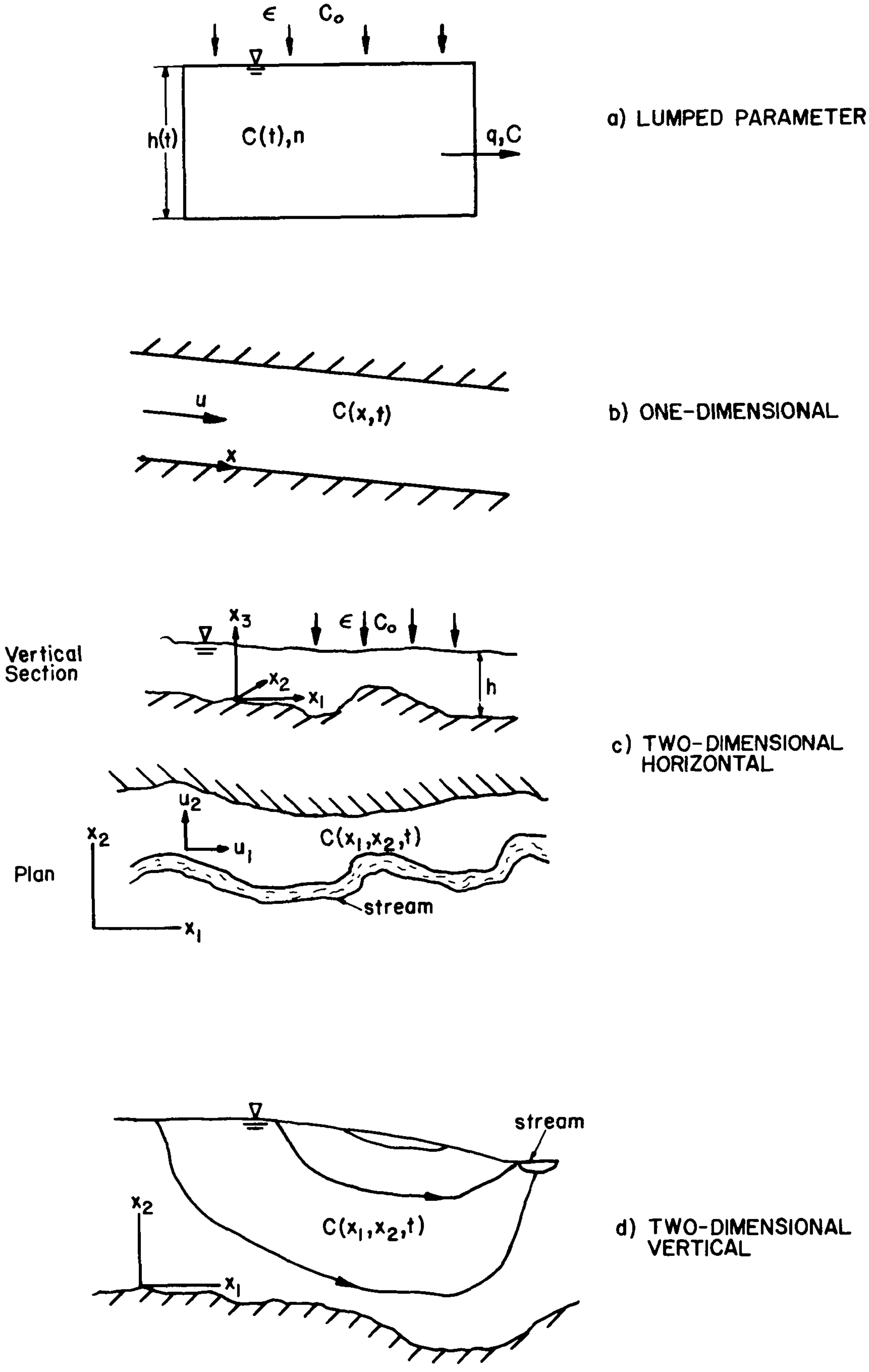

Figure 1. Schematic illustrations of model structure

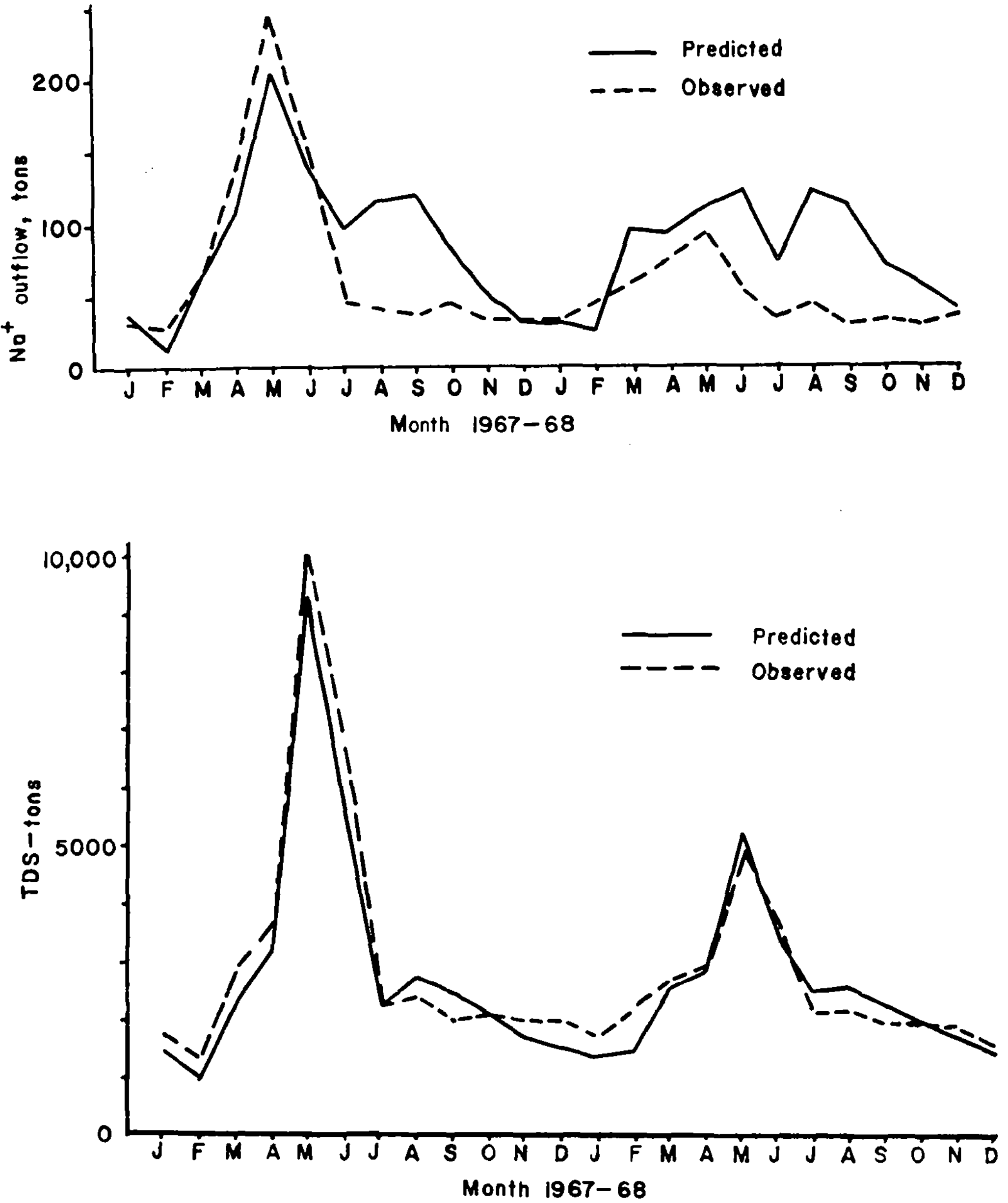

Figure 2. Comparison of results of the lumped parameter model by Thomas, et al., 1972, with observation for the Little Bear River Basin, Utah

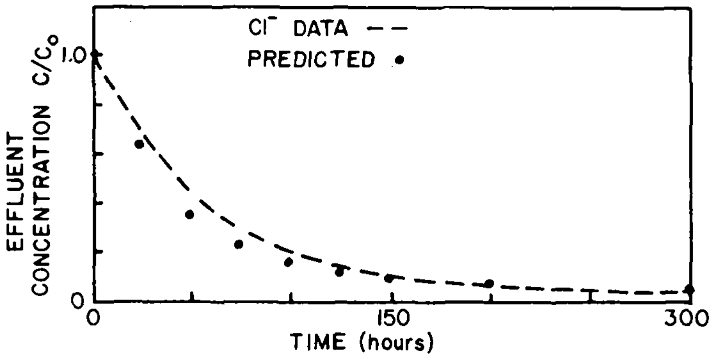

Figure 3. Comparison of results of two-dimensional vertical convective model by Jury, 1975, with observed leaching from a small field plot

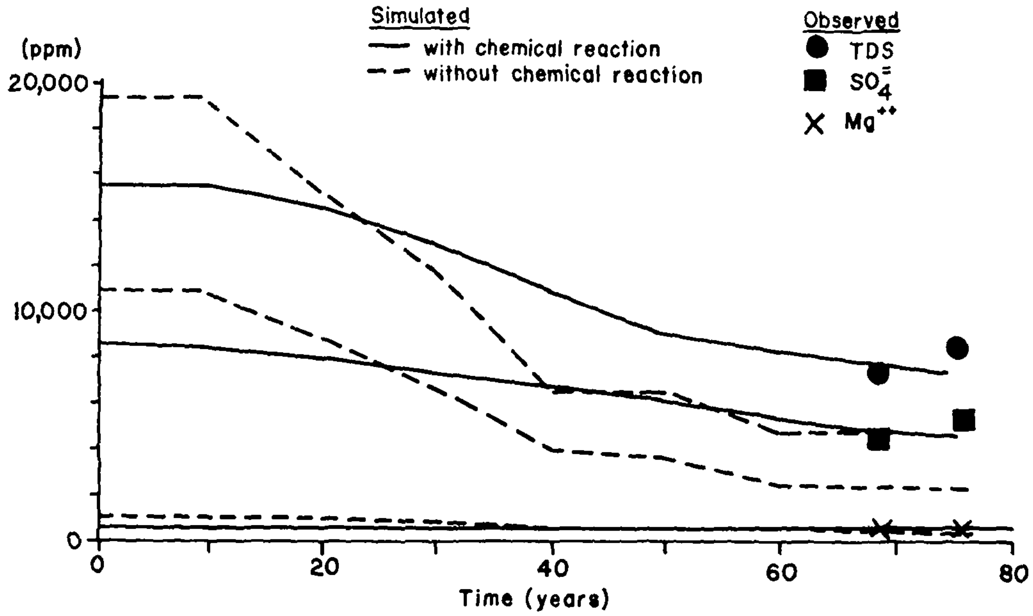

Figure 4. Modelling results by Shaffer et al., 1976, using a two-dimensional vertical representation with chemical equilibrium reactions

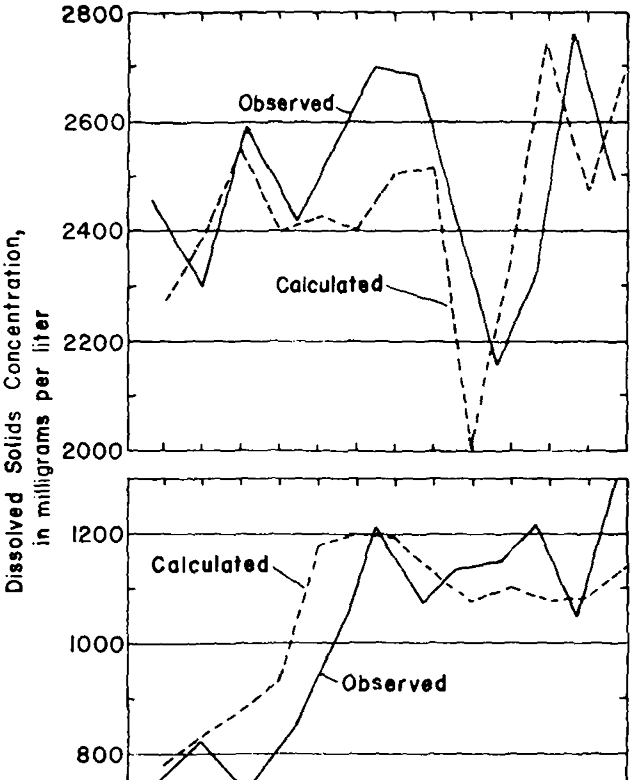

Figure 5. Results of the two-dimensional horizontal simulations by Konikow and Bredehoeft, 1975, compared with the observed dissolved solid concentration in two wells

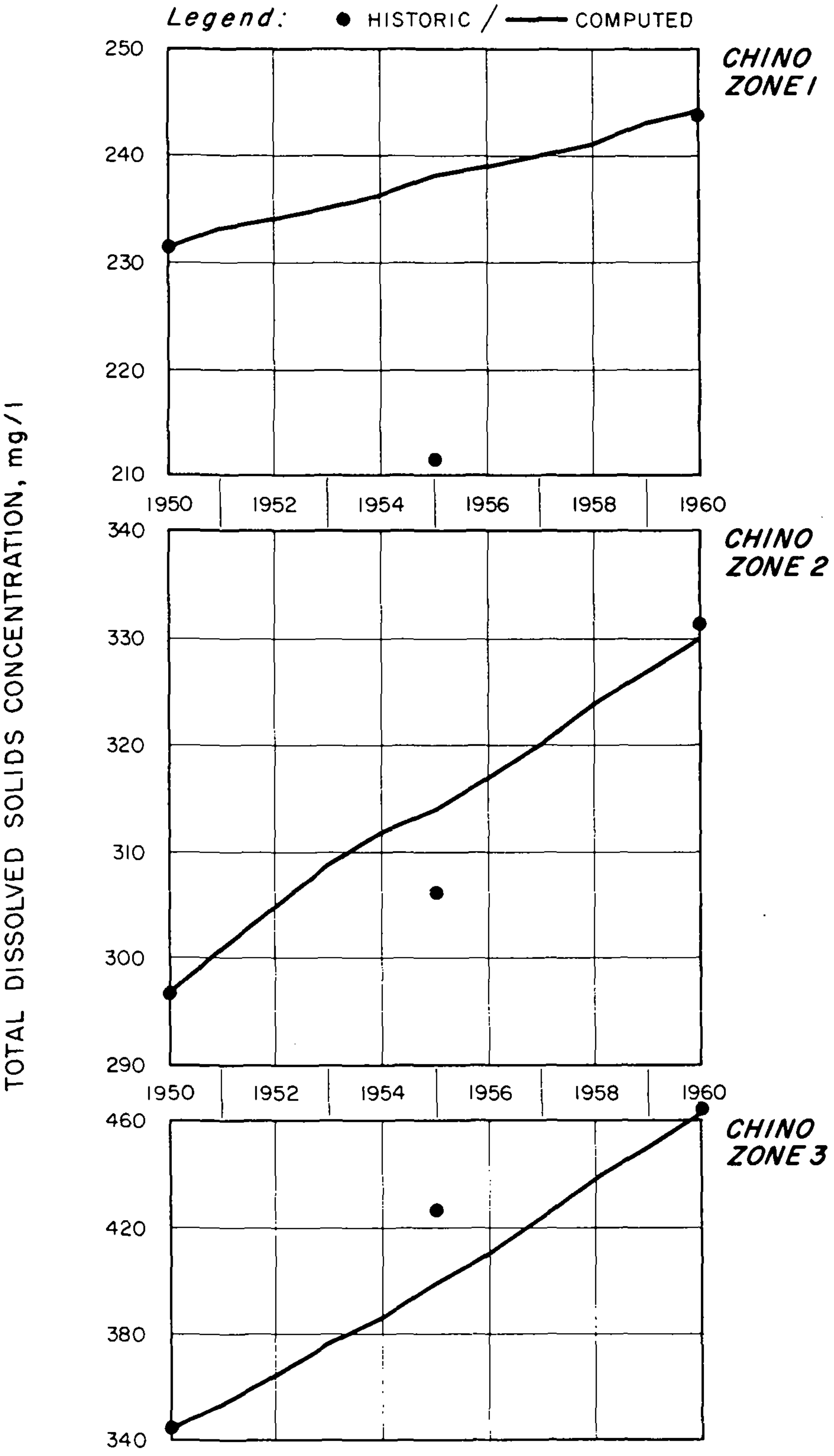

Figure 6. Results of the two-dimensional horizontal simulation by Water Resources Engineers, 1969, compared with average TDS in three sub-basins of the Santa Ana Basin, California

SUPPORT PAPER T

GROUNDWATER BASIN WATER QUALITY SIMULATION TO STUDY ALTERNATIVE MANAGEMENT PLANS

T. Clark Lyons

1. INTRODUCTION

The pumping of water from a groundwater basin depletes the natural outflow and flushing. The concentrated, returning, non-consumptively used water carries all the water quality constituents pumped, as well as new wastes added during use. Time and again experience has shown that the intensive development of a groundwater basin can lead to a dramatic degradation in pumped water quality.

In order to analyse this water quality degradation process and to provide a predictive planning and management tool, a groundwater-basin water quality model has been developed. This groundwater-quality model is coupled with a groundwater hydraulics model and solves the basic advection equations for conservative chemical constituents. The dissolved constituents are routed vertically downward from the ground surface to the water table through the unsaturated zone, and then horizontally throughout the saturated zone. The non-conservative effects of the upper portions of the unsaturated zone are accounted for in a data management system developed to work with the groundwater models. A stream system model has also been coupled with these models to account for the impact of influent-effluent base flow and of direct discharges from sewage treatment plants and industries to the stream system.

2. BACKGROUND OF MODEL DEVELOPMENT AND APPLICATION

In response to a serious continuing degradation of the groundwater and base flow stream quality in the Upper Santa Ana River Basin, the California State Water Resources Control Board initiated a salt balance investigation of the basin in 1967. This investigation (1) led to the original development of the model described in this paper. The Upper Santa Ana River Basin is located in an arid region of Southern California with a total drainage area of 1500 square miles (390 000 hectares). The groundwater basin is 560 square miles (140 000 hectares) in size and is composed of unconfined alluvium traversed by many semipervious and impervious faults. During this study the computational efficiency of the groundwater hydraulics model developed previously by the California Department of Water Resources (2) was improved and an unsaturated zone added to it. The groundwater quality model was coupled to this hydraulics model and calibrated against ten years of recorded water quality records. Once calibrated, these models were used to evaluate three basic alternative basin management plans.

Upon completion of this first groundwater quality modelling effort by the State of California in 1970, a regional planning agency, the Santa Ana Watershed Planning Agency (SAWPA) was formed to continue the work further towards developing a total water resources development and management plan. As a first step SAWPA had the model data management procedure improved to better facilitate investigations of alternative management plans (3) and had a stream quality model coupled with the groundwater models. This improved groundwater - surface water interfacing was needed to better simulate the interaction between the groundwater basin, stream base flow, releases of imported water for recharge, and waste discharges to the stream system (4). This improved version of the groundwater basin hydrologic and quality models was then used extensively by SAWPA in a two phased planning effort spanning the period 1971 to 1974. Around ten alternative management plans were simulated and evaluated for the total basin, as well as an equal number of sensitivity analyses on several of the hydrologic and planning variables (5).

During the second phase of its planning effort, SAWPA decided also to develop a groundwater model of the adjacent San Jacinto Groundwater Basin. The San Jacinto Groundwater Basin is similar to the Upper Santa Ana River Basin but smaller, 46 square miles (12 000 hectares). This basin has a very deep aquifer (average depth is about 8000 feet (2400 metres)) and a significant portion of it is confined. The developed model node-link structure consisted of 63 nodes and 116 links. This model was first calibrated by the same hand trial-and-error procedures as used on the Upper Santa Ana River Basin. Later, the calibration of this model was further improved by the use of a new non-linear optimization automatic calibration procedure (6). As with the Upper Santa Ana River Basin model, the San Jacinto model was used extensively by SAWPA to evaluate alternative water resource management plans and to plan sensitivity analyses.

The final application of the groundwater quality model involved planning a further extension of its capabilities. The model was adapted to the Salinas Valley on the coast in Northern California for the Association of Monterey Bay Area Governments (AMBAG). The total watershed is considerably larger than in the first two applications, 4500 square miles (1 170 000 hectares), and the alluvial groundwater basin covers an area of 1000 square miles (260 000 hectares). The lower portion of this groundwater basin is strongly confined, two overlaying independent aquifers; and it is hydraulically connected with the Monterey Bay. This confined hydraulic connection with the ocean was incorporated into the model and it was able to successfully represent the existing seawater intrusion conditions of the lower valley. This model was used by AMBAG to predict the future quality of pumped groundwater for agriculture. Two alternative management plans were considered, and they both showed a continuing decline in the quality of the delivered water.

3. MODEL SYSTEM PACKAGE

The groundwater quality model by itself is relatively useless; to take advantage of its broad capabilities it must be used in conjunction with a set of other models. As a result of the described modeling experience, a set of computer programs has been developed that can greatly assist in the groundwater basin planning and management. This set of programs is built around the groundwater quality model and its ability to predict pumped and stream base flow water quality. The three components of this package are depicted in Figure 1. This figure illustrates how these components are used to evaluate groundwater basin management plans. Each component shown in this figure consists of several computer programs.

All basin or watershed wide planning studies require an effective data management system to describe present and future land use, water demands and waste loads. The data management system developed to support the quality model (see Figure 2) is composed of three major subsystems; these are:

1) a preprocessor that verifies and refines unit water supply and waste return factors, and projects future water demands and waste returns;

2) DMS2 which generates a complete data bank of all unique user-induced water transfers between ground and surface water source and disposal locations,

and

3) MERGE which adds hydrologic input data to the detailed water transfers generated by DMS2.

The groundwater basin hydraulics model simulates the movement and distribution of water in unconfined and confined aquifer systems. The model calculates the movement of water downward through the unsaturated zone, the horizontal flow throughout the saturated zone and the resulting rise and fall of the water table within the basin. It also simulates base flow in streams. Inputs to the model are the nodal extractions and returns computed by the data management system, the basin geometry and geologic properties, and initial aquifer unsaturated moisture and water table conditions.

The quality model simulates the movement and distribution of conservative water quality constituents throughout a groundwater basin and its overlying interconnected stream system. Model input includes the basin water table and flow conditions computed by the hydraulics model, user induced water transfer information from the data management system, information on waste treatment plant discharge into the stream system, and initial basin quality levels.

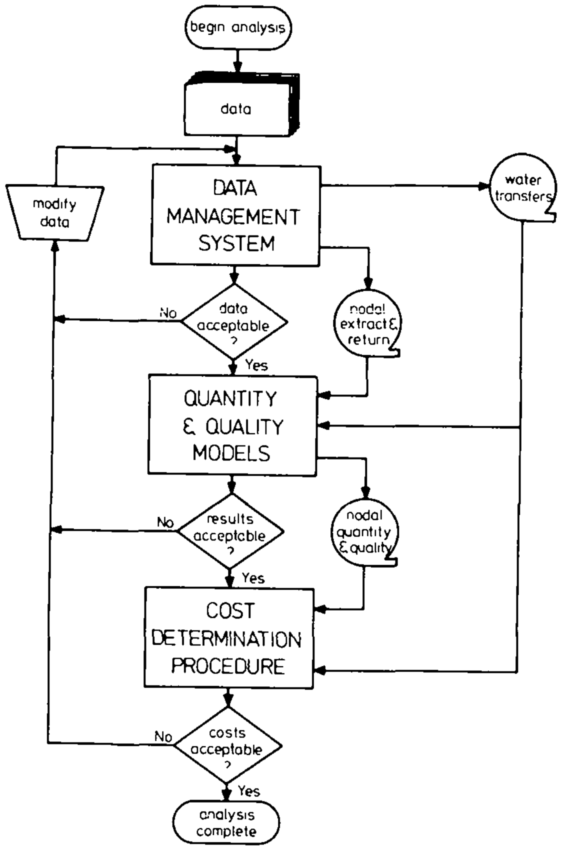

Figure 1. Groundwater basin management package

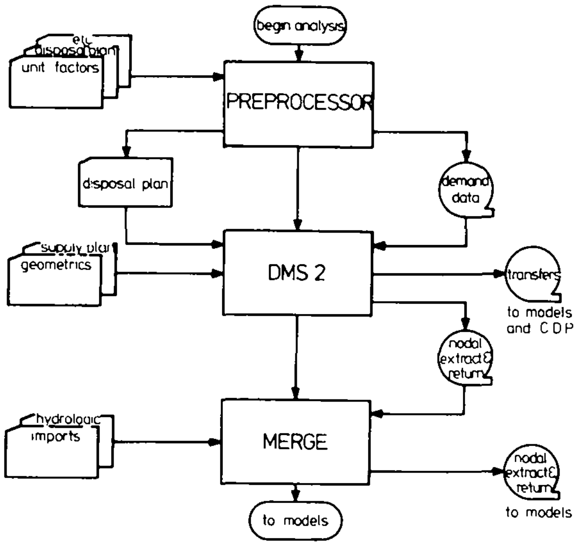

Figure 2. Data management system

The cost determination procedure is the final component of the computer programs to evaluate alternative basin management plans. This program computes capital costs as well as operation, maintenance and replacement costs for each 'operational-area' in the basin. An operational-area is an area of the basin that has similar water supply and waste collection characteristics, e.g. a water supply agency. Input to the cost determination procedure comes from groundwater models, the data management system, and a special data file that contains basic cost information. This information includes such items as tax rates, cost curves for water and wastewater treatment plants, and unit costs for water production, delivery, and waste collection. This data is used to compute operational-area costs for four water use groups: agriculture, industry, residential-commercial inside, and residential-commercial outside. In addition to operational-area costs, the cost determination procedure determines costs for each water and wastewater treatment plant and for each agency that imports water into the basin.

4. MATHEMATICAL REPRESENTATION

This section describes the basic concepts of the groundwater quality model. Although described with reference to an irregular polygonal pattern, the equations also apply to other patterns. In the case of a polygonal pattern, each node and each link have certain water quality properties of the physical system. Basically, a node stores quality constituents, while links transfer quality constituents between nodes. These basic properties, along with the geometric descriptions of the nodes and links, the hydrologic flows and inputs, the average concentration of all percolating waters, and the initial conditions, provide the basic input for modelling the dynamics of groundwater quality. To develop a model with this information, consider a typical node as illustrated in Figure 3. Its change in mass in a time interval, Δt, can be described as:

$$\Delta M_j = \Delta M_{uj} + \Delta M_{sj} = (V^*_{uj} C^*_{uj} - V_{uj} C_{uj}) + (V^*_{sj} C^*_{sj} - V_{sj} C_{sj})$$

$$= (Q_{rj} \bar{C}_{rj} - Q_{pj} \bar{C}_{pj} + \sum_i Q_{ij} \bar{C}_{ij}) \Delta t \qquad \ldots\ldots 1$$

where

M_j = mass contained in node j,
M_{uj} = mass contained in the unsaturated zone of node j,
M_{sj} = mass contained in the saturated zone of node j,
V_{uj} = volume of water in the unsaturated zone,
V_{sj} = volume of water in the saturated zone,
C_{uj} = constituent concentration in the water in the unsaturated zone;
C_{sj} = constituent concentration in the water in the saturated zone;
C_{rj} = constituent concentration in the water recharging the node;
C_{pj} = constituent concentration in the water being pumped from the node
C_{ij} = constituent concentration in the water flowing between adjacent nodes i and j;
Q_{rj} = rate of recharge
Q_{pj} = rate of pumping, and
Q_{ij} = flow rate between adjacent nodes.

An asterisk (*) over a term indicates that it is referenced to the end of the time interval, Δt, and a bar ($\bar{}$) denotes that the term is the average of its values at the beginning and end of the interval.

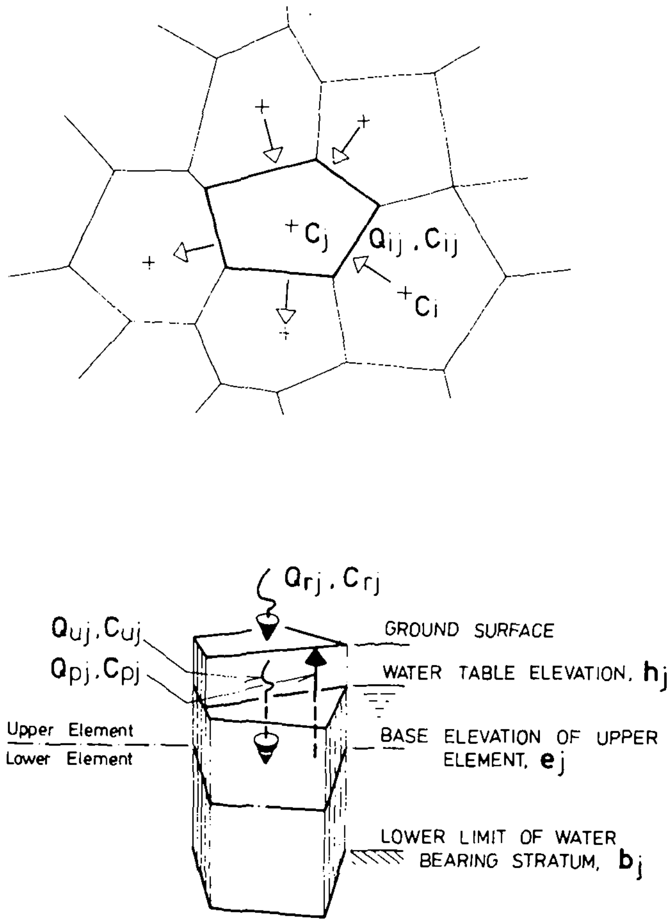

Figure 3. Typical node for water quality model

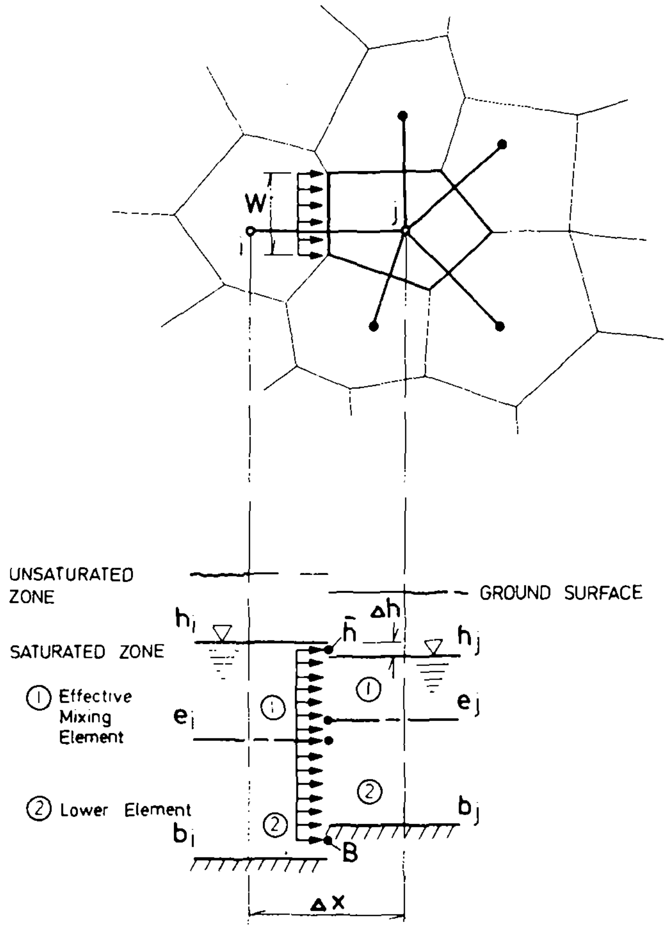

Figure 4. Geometric and flow properties of a typical link

By introducing the mass of a quality constituent that leaves the unsaturated zone and enters the saturated zone, this equation separates into its two basic components: the unsaturated and saturated zones.

4.1. UNSATURATED ZONE

By assuming the concentration of the water that leaves the unsaturated zone is equal to the average concentration of all water in this zone, a mass balance can be approximated as:

$$\Delta M_{uj} = V^*_{uj} C^*_{uj} - V_{uj} C_{uj} = (Q_{rj} C_{rj} - Q_{uj} \bar{C}_{uj}) \Delta t \qquad .....2$$

where

Q_{uj} = flow leaving the unsaturated zone, and

$\bar{C}_{uj} = (C^*_{uj} + C_{uj}) / 2.$

Since the hydraulics model provides the volumes and flow rates, the data management system provides the recharge concentration and either the starting condition or a previous solution provides the initial concentration, the concentration at the end of the time interval, C^*_{uj}, can be calculated directly. Rearranging Equation 2, this concentration can be expressed as:

$$C^*_{uj} = \frac{\left[\left(V_{uj} - \frac{Q_{uj} \cdot \Delta t}{2} \right) C_{uj} + \bar{Q}_{rj} \cdot C_{rj} \cdot \Delta t \right]}{\left(V^*_{uj} + \frac{Q_{sj} \cdot \Delta t}{2} \right)} \qquad \ldots\ldots 3$$

Thus, once the hydraulics are known, the average concentration of the water contained in the unsaturated zone can be approximated by Equation 3.

This equation is, of course, only an approximation. Two major assumptions were made: both the moisture level and the concentration were uniform throughout the unsaturated zone. The validity of these assumptions depends primarily on the depth of the unsaturated zone, its permeability, and the time interval. If these assumptions are invalid, the number of elements representing this zone may be increased until approximate validity is achieved.

4.2. SATURATED ZONE

This zone is separated into upper and lower elements for modelling purposes. The upper element, designated as the zone of 'effective' mixing, represents that portion of the saturated zone from which water is pumped. It also receives the water that leaves the unsaturated zone. The lower element is the portion that is not directly affected by pumping and recharge. In the equations that follow a subscript 1 refers to the upper element and a 2 refers to the lower element.

A mass balance of a conservative quality constituent for a typical node, j, that considers pumped withdrawals and inflows from the unsaturated zone and adjacent nodes, can be written for a two element system as:

$$\Delta M_{sj} = \Delta M_{1j} + \Delta M_{2j} = (V^*_{1j}C^*_{1j} - V_{1j}C_{1j}) + (V^*_{2j}C^*_{2j} - V_{2j}C_{2j})$$

$$= (Q_{uj}\bar{C}_{uj} - Q_{pj}\bar{C}_{1j} + \sum_i Q_{ij}\bar{C}_{ij})\,\Delta t. \qquad \ldots\ldots 4$$

In the development of this equation, it is assumed that the concentration of the water pumped, C_{pj}, is equal to the time average concentration of the water in the upper element, $\bar{C}_{1j}$. All the terms in this equation are relatively straightforward except the flow between nodes, Q_{ij}, and the average concentration of the water flowing, $\bar{C}_{ij}$. First, we will consider the flow term. Flow can occur between 1) adjacent upper elements, 2) adjacent upper and lower elements or adjacent lower and upper elements, and 3) adjacent lower elements. The choice in the second item depends on the direction of flow and the base elevation of the upper element of the adjacent nodes. Figure 4 illustrates these flow paths.

With reference to Figure 4 and assuming a direction of flow from node i to node j, flow equations for each path can be written as:

$$Q_{ij,1} = Q_{ij}\left(\frac{\bar{h} - e_i}{\bar{h} - B_{ij}}\right)$$

$$Q_{ij,2} = Q_{ij}\left(\frac{e_i - e_j}{\bar{h} - B_{ij}}\right) \qquad \text{if } e_i \geq e_j$$

$$Q_{ij,3} = Q_{ij}\left(\frac{e_j - B_{ij}}{\bar{h} - B_{ij}}\right)$$

or $\qquad\ldots\ldots 5$

$$Q_{ij,1} = Q_{ij}\left(\frac{\bar{h} - e_j}{\bar{h} - B_{ij}}\right)$$

$$Q_{ij,2} = Q_{ij}\left(\frac{e_j - e_i}{\bar{h} - B_{ij}}\right) \qquad \text{if } e_i < e_j$$

$$Q_{ij,3} = Q_{ij}\left(\frac{e_i - B_{ij}}{\bar{h} - B_{ij}}\right)$$

where

$$Q_{ij,1} + Q_{ij,2} + Q_{ij,3} = Q_{ij},$$

and

$$\bar{h} = (h_i + h_j)\ /2.$$

A similar set of equations can be written when the flow is in the opposite direction, that is, from node j to node i.

In addition to this horizontal distribution of flow, there is a vertical component that transfers mass from the lower element to the upper element or vice versa. Since the volume of the lower element is constant (assuming the upper element is not pumped dry), this horizontal flow must be equal to the sum of all the flows into and out of the lower element. This flow, Q_{hj}, can be expressed algebraically as:

$$Q_{hj} = \sum_i (\phi_i Q_{ij,2} + Q_{ij,3}), \qquad \ldots\ldots 6$$

where

$$\phi_i = 1, \text{ if } e_i \geq e_j,$$

and

$$\phi_i = 0, \text{ if } e_i < e_j.$$

Flow goes from the lower element to the upper element when this sum is positive. The opposite is true when the sum is negative.

All of these flow terms transfer water at some concentration. It is assumed that the concentration of water that flows between nodes i and j can be expressed as follows:

$$C_{ij} = \delta C_i + (1 - \delta) C_j$$

where δ is an interpolation factor that can vary between 0.5 and 1.0

Assuming the flow is from node i to node j a set of equations that describe the transfer of mass across the vertical plane between adjacent elements can be written as:

$$\Delta M_{ij,1} = Q_{ij,1} \left[\delta \bar{C}_{1i} + (1 - \delta) \bar{C}_{1j} \right] \Delta t$$

$$\Delta M_{ij,2} = Q_{ij,2} \left[\delta \bar{C}_{2i} + (1 - \delta) \bar{C}_{1j} \right] \Delta t \qquad \text{if } e_i \geq e_j$$

$$\Delta M_{ij,3} = Q_{ij,3} \left[\delta \bar{C}_{2i} + (1 - \delta) \bar{C}_{2j} \right] \Delta t$$

or 7

$$\Delta M_{ij,1} = Q_{ij,1} \left[\delta \bar{C}_{1i} + (1 - \delta) \bar{C}_{1j} \right] \Delta t$$

$$\Delta M_{ij,2} = Q_{ij,2} \left[\delta \bar{C}_{1i} + (1 - \delta) \bar{C}_{2j} \right] \Delta t \qquad \text{if } e_i < e_j$$

$$\Delta M_{ij,3} = Q_{ij,3} \left[\delta \bar{C}_{2i} + (1 - \delta) \bar{C}_{2j} \right] \Delta t$$

A similar set of equations can be written for the case when the flow is from node j into node i.

For the flow component across the horizontal plane the equations are much simpler. When the flow is from the lower element to the upper element, the concentration is assumed to be that of the lower element. The reverse is assumed when the flow is downward. Algebraically this horizontal mass transfer, ΔM_{hj}, can be written as:

$$\Delta M_{hj} = Q_{hj}\bar{C}_{2j}\Delta t, \quad \text{if } q_{hj} > 0$$

or

$$\Delta M_{hj} = 0 \qquad \text{if } Q_{hj} = 0 \ , \qquad \ldots\ldots 8$$

$$\Delta M_{hj} = Q_{hj}\bar{C}_{1j}\Delta t \quad \text{if } Q_{hj} < 0 \ .$$

Equations 7 and 8 describe the transfer mechanisms resulting from flow between nodes. Thus, for a typical node, j, this net result can be written as:

$$\sum_i Q_{ij}\bar{C}_{ij} \ \Delta t = \sum_i (\Delta M_{ij,1} + \Delta M_{ij,2} + \Delta M_{ij,3}) + \Delta M_{hj} \qquad \ldots\ldots 9$$

When these equations are substituted into the basic mass balance equation for the saturated zone, Equation 4, a set of simultaneous linear equations result. The coefficients in these equations are dependent on the direction and magnitude of the flow terms. Hence, they must be evaluated for each time interval. These equations are then solved using an iterative technique. Iteration stops when the assumed answer is within 1 mg/l of the calculated answer at all nodes. Experience indicates that less than five iterations are required for convergence.

5. EXPERIENCE GAINED

To date much experience has been gained in the use of groundwater quality models in real world engineering, planning and management. Previous authors have already summarized the role and difficulties of using models in groundwater management (7) as well as the general capabilities and problems of quality models (8). In general it is fairly well accepted that groundwater quality modelling is something here to stay even in the light of the existing models' limitations. A few short words based on the experience of applying the model described here are in order, nevertheless, concerning some of the significant aspects of using groundwater models that are frequently overlooked. In general the problems or deficiencies of the present state-of-the-art in groundwater modelling can be broken down into three basic areas; 1) data measurement, 2) data management, and 3) model limitations.

The single largest problem today in the application of quality models to groundwater basins is lack of data. This data deficiency is particularly strong during the model calibration and validation phases, but it is also persistent throughout the model application phases. Basically, the independent inputs as well as the dependent response of the groundwater basin are at best only generally known. At present direct measurement of return water quality to a basin is not feasible and it must be indirectly computed from overlying land use and supply water quality. It is possible to measure the direct water quality response of a basin, but there are few data collection programs that gather enough data to be of much value for model development. Even the best data collection programs leave room for large areas of improvement in their statistical reliability. The unreliability of data available for groundwater quality modelling is far more significant than the mathematical deficiencies of today's models.

There has been some significant progress recently, however, in the use of optimization calibration techniques and statistical filtering to improve the usability of existing data (9). Optimization techniques are being used to achieve the maximum benefit of parameter adjustment in matching simulated results with calibration data sets. Errors in measured basin responses and spacial and temporal deficiencies can be reduced by the use of a statistical Kalman Filter.

Another large problem area in using quality models in basin wide planning is data management. The input data requirements for groundwater quality modelling are at least an order of magnitude greater than with hydraulic modelling. The quality of the recharge water in all parts of the basin is needed, which requires that a close track must be kept of all movements and uses of water. This means that the quality of all water supplies must be known and this is a feed-back loop problem with groundwater supplies. Moreover, all changes in supply quality through water treatment, use and waste treatment must be accounted for as well as the impact of land use on the quality of percolating return waters. To handle these data effectively an organized scheme of information processing is essential. When such a data handling scheme is correctly formulated it increases the accuracy of the quality modelling activities by reducing the number of assumptions necessary in determining return water quality and it very significantly reduces the effort associated with evaluating various management plans. For a groundwater modelling project to be a success, great care and effort should go into the planning and development of a data management system.

At present, under most conditions, the mathematical limitations of existing models are not as significant a problem as the calibration data inaccuracies. Mathematical models are available that can simulate much better the basic advection-diffusion equations than the model presented here, or can incorporate the non-conservative chemical reactions in the unsaturated and saturated zones. We do not yet in most circumstances, however, have data collection programs instituted capable of providing the data necessary to warrant the additional development and application of such sophisticated modelling techniques in basin wide planning.

6. SUMMARY

The mathematical groundwater quality model described here has been applied to several complete basins and used in real-world water quality management planning. While the model is not mathematically the most sophisticated available, its accuracy is still greater than the calibration and planning input data normally available. Taken as a whole, however, the calibrated model is a very capable and powerful tool in water quality management studies.

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SUPPORT PAPER U

MODELLING GROUNDWATER FLOW NEAR LANDFILLS AND GRAVEL PITS FOR WATER QUALITY STUDIES

W. E. Kelly

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1. INTRODUCTION

Pollution of groundwater by waste disposal in gravel pits, by disturbance of the natural chemical balance due to removal of sand and gravel, and by landfills, is common. To assess the extent of pollution at a particular site an accurate picture of groundwater flow is needed. Because a gravel pit or landfill may seriously distort groundwater flow patterns, the collection of meaningful water level data and the determination of directions of flow and gradients may be difficult. If an investigator can estimate flow patterns prior to installing wells, optimum locations may be selected. In making initial estimates of the flow pattern all available data as well as any anticipated distortion of the flow pattern should be considered. Geo-electric surveys may be especially useful for initial estimates of flow directions and modelling for predicting distortion of the flow pattern and movement of contaminants.

2. BACKGROUND

Groundwater flow in the vicinity of gravel pits and landfills has received some attention in the literature. Freeze (1) demonstrated how computer modelling might be used to study regional groundwater flow patterns for the purpose of landfill siting; Hughes et al. (2) reported mounding of groundwater beneath a number of landfills in north-eastern Illinois and attributed it to decreased permeability around the edges of the landfills. Peaudecerf(3) observed and modelled the effects of gravel pits on groundwater flow. Studies of the relation between lakes and groundwater aquifers (4) (5) are also relevant since gravel pits may become, or in fact be, artificial lakes. In any case the mechanics of flow between gravel pits or landfills and aquifers is similar to that which occurs between lakes and aquifers.

The direction of groundwater flow may be difficult to determine from water level measurements when flow conditions are distorted. In such cases, the average flow direction may be more easily determined using geo-electric methods and tracers or in the case of a landfill the resistivity anomaly accompanying the movement of leachate (6). There are a number of examples in the literature of the successful use of geo-electrical methods for determining the extent of groundwater contamination and hence average flow directions in connection with landfill studies suggesting that the most timely use of geo-electrics is prior to installation of any monitoring wells. Flow directions and water quality may be estimated from the geo-electric survey followed by installation of monitoring wells to collect water quality data and to verify and extend the initial interpretation.

An excavation below the water table can increase local permeability, while filling an excavation with relatively impervious material will lower it. In cross-section it is apparent that both the depth of excavation and the changed permeability will combine to change transmissivity.

The effects of such changes may be evaluated using various methods, listed here in order of increasing complexity.

(a) Flow nets.
(b) Conducting sheet analogue models.
(c) Digital computer models.

Only the last method may be applied conveniently to transient problems.

3. RESULTS

To illustrate the preceding, a case study will be reviewed. Figure 1 shows the location of a landfill monitored from October 1973 to September 1974 (7) and intermittently since then. The landfill has been in operation for more than 25 years and occupies part of an operating gravel pit. Filling and excavating below the water table is occurring at the landfill as well as at an adjacent site just to the north. Groundwater flow in the vicinity of the landfill under natural conditions was in a south-westerly direction towards Thirty

Acre Pond as can be seen from the water table map shown in Figure 1 (8). Based on the apparent flow direction and because of concern that the Universi of Rhode Island's supply wells at Thirty Acre Pond might be affected by leachate, monitoring wells were installed just south-west of the landfill. Initial water quality measurements outside the landfill indicated little or no impairment of groundwater quality and it was not until a pumping test was ma near the eastern edge of Hundred Acre Pond that it was suspected that leacha might be moving in that direction.

A geo-electric survey made between Hundred Acre Pond and the landfill indicated the presence of a resistivity anomaly. Two additional monitoring wells drilled along the axis of the anomaly between the landfill and Hundred Acre Pond confirmed that leachate was moving from the landfill towards Hundred Acre Pond (9). The direction of flow at the landfill determined fron water level measurements at wells in and just outside the landfill was genera towards Hundred Acre Pond. The average direction of flow from the geo-electric survey and the water level measurements are in reasonable agreeme

Although evidence for the direction of flow is overwhelming the reason for the apparently altered flow pattern is not. Various reasons for the altered flow pattern are being investigated including:

(a) an error in the original water table map;
(b) increased evapotranspiration due to the adjacent gravel pits;
(c) an altered recharge pattern;
(d) modified transmissivity in the vicinity of the landfill.

Although all of these factors except the first appear to be contributing, only th last will be considered in this paper.

To illustrate qualitatively the effect of a change in transmissivity an example of a conducting sheet analogue simulation will be used. The natural water able configuration around the landfill taken from the water table map in Figure 1 was used to provide boundary conditions for the analogue. Water able contours and flow lines constructed perpendicular to the contours were aken at some distance from the landfill as constant head and no flow boundaries espectively. With these boundary conditions various changes due to the resence of the landfill were considered. An impervious zone was simulated y cutting out an area in the shape desired (severe change) and an excavation vhich tended to increase transmissivity by covering the appropriate area with layer of Aquadag*.

igure 2 shows the effect of an excavation (cross-hatched) behind the landfill; he direction of flow within and just down-gradient from the landfill becomes pproximately perpendicular to the long leg of the excavation and the effect of he distortion diminishes down-gradient. Also shown are directions of flow letermined from measurements of water levels at the landfill during April 1974 nd the average flow direction estimated from the geo-electric survey. emoval of gravel from below the water table is modifying the flow pattern; owever, additional water level measurements and modelling results indicate hat the lower permeability landfill material is also affecting the flow pattern. nitial estimates indicate that transmissivity in the landfill area is about half ts original magnitude. Preliminary results of digital modelling indicate that ncreased evapotranspiration and modified recharge patterns are of lesser mportance in altering the flow pattern, a conclusion also reached by Hughes t al. (2) for landfills in north-eastern Illinois.

4. CONCLUSIONS

low patterns around landfills and gravel pits penetrating the water table may e altered. Geo-electric methods are especially useful when distortion is nticipated for determining average groundwater flow directions. Relatively

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Aquadag is the trade name for a mixture of graphite in water manufactured by the Acheson Colloids Company, Port Huron, Michigan 48060, USA.

simple analogue computer techniques can be used to make rapid qualitative assessments of possible flow patterns and when data is available digital computer models may be used to make more refined predictions of flow patterns.

ACKNOWLEDGEMENT

The work on which this paper is based was done in co-operation with the Rhode Island Water Resources Board.

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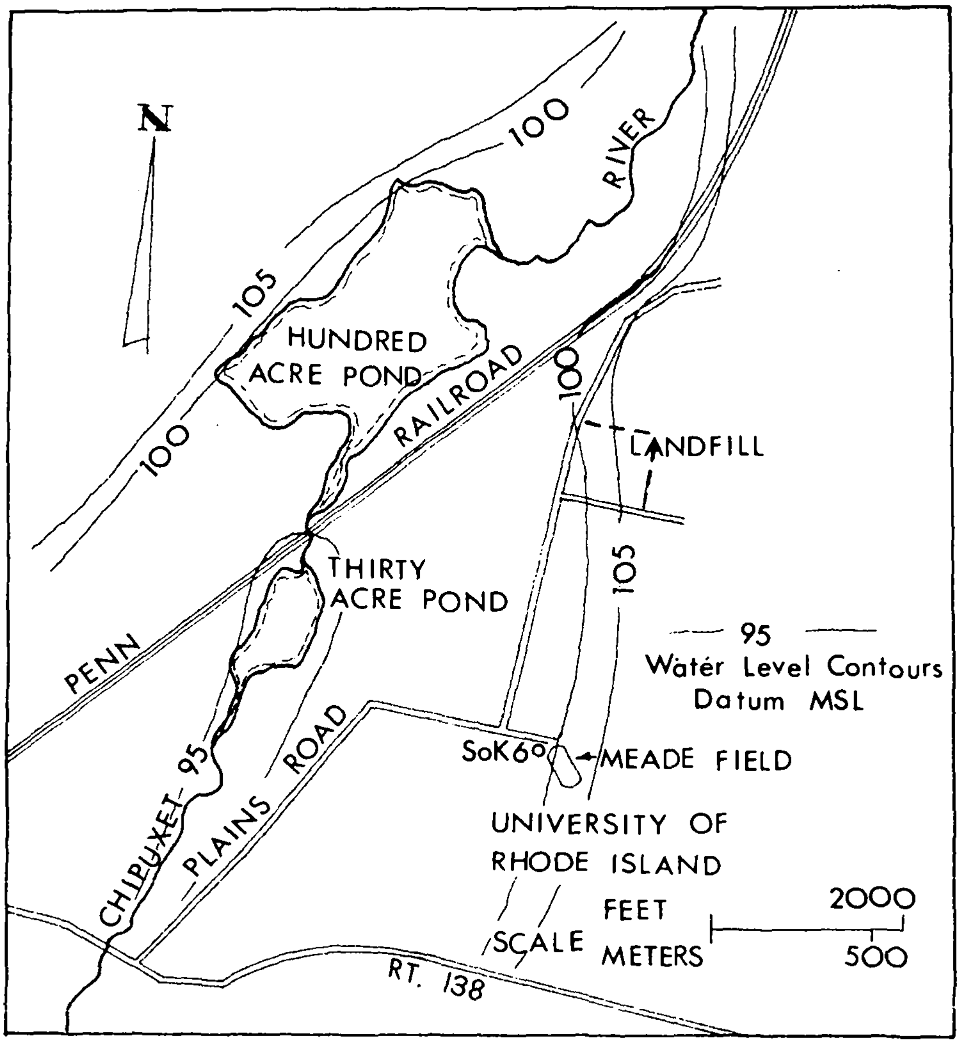

Figure 1. Location

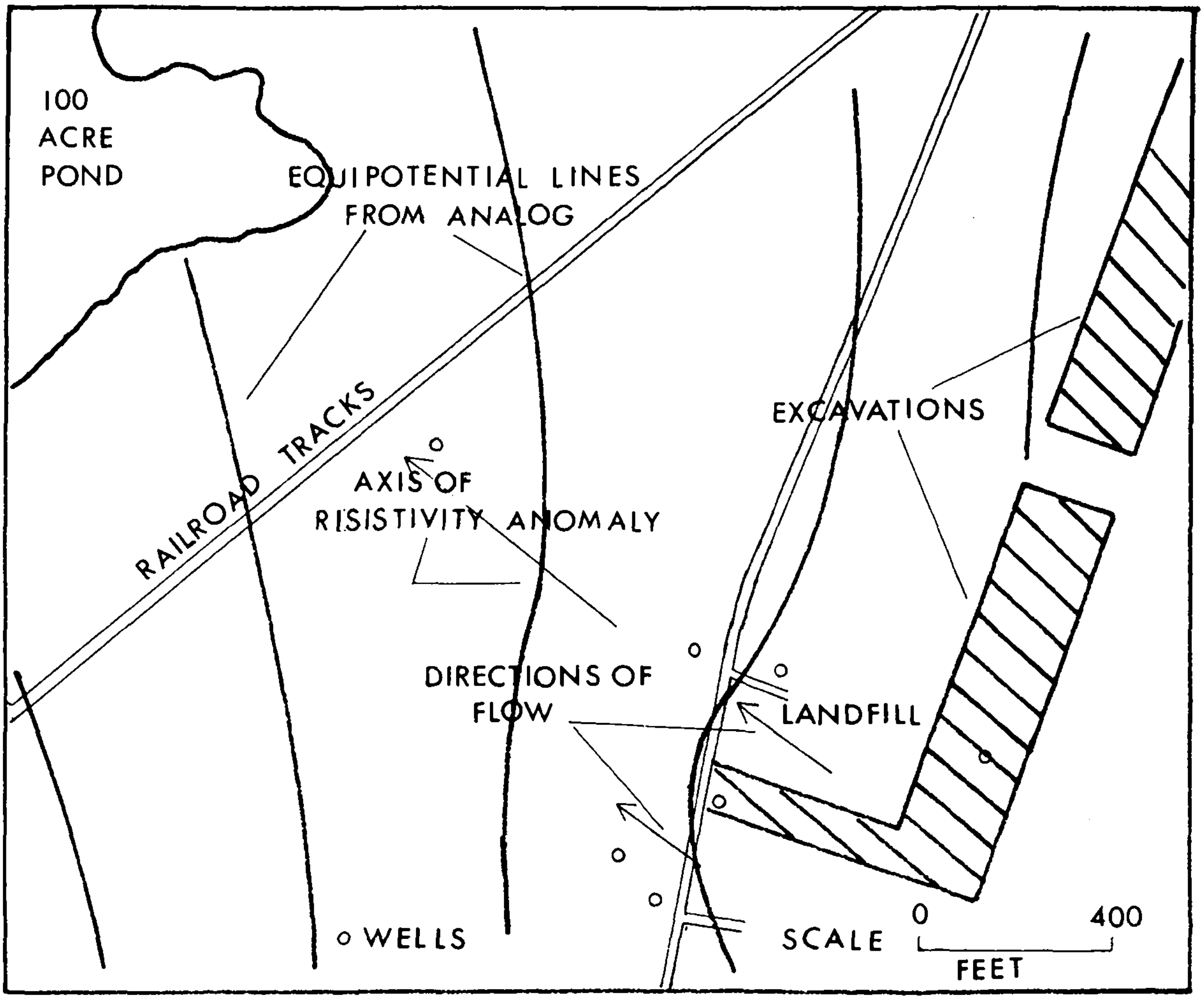

Figure 2. Effect of excavation on groundwater flow in the vicinity of the West Kingston landfill

DISCUSSION - SESSION 5

This discussion formed part of a 'workshop' session. Delegates divided into three groups and moved between two lecture rooms (where computer groundwater models were demonstrated on an interactive computer terminal) and the Conference Hall (where the main discussion was held). The Chairman, Mr J. A. Cole, arranged the proceedings so that the first part of the session was taken up with a discussion of the papers. He then suggested that the following topics should be considered:

(a) ways of selecting the model appropriate to a particular problem

(b) kinds of data required for various models

(c) methods and costs of collecting such data.

Dr J. HOEKS was surprised by the statement in Mr Oakes' paper that horizontal flow in the aquifer was assumed and no account was taken of streamlines when modelling the mixing of leachate in the groundwater.

Mr D. B. OAKES replied that such considerations were immaterial to the result of the model except in cases where the abstraction well was partially screened. He pointed out that in most aquifers in the United Kingdom flow was almost horizontal, and that in the landfill sites investigated to date there was evidence that leachate was convecting along the water table.

Dr HOEKS made the observation that in field studies in deep aquifers he had used screens at different depths to locate flow paths of pollution.

Professor J. BEAR said that for local problems where the length of aquifer modelled is three or four times the thickness, it may be necessary to adopt a three-dimensional approach and consider streamlines, but for regional problems where the length of aquifer modelled is many hundreds of times the thickness, a two-dimensional approach is the most sensible.

Mr T.C. LYONS asked all the authors how accurate they felt their models were in view of the fact that they were calibrated using historical data which usually contained errors and was often incomplete.

Dr L.F. KONIKOW suggested that models should only be calibrated against point data because it is easy to put a false interpretation on data when drawing water-table maps, etc. He also mentioned methods for solving the inverse problem which assigned reliabilities (in terms of means and standard deviations) to observed data points.

Professor L.W. GELHAR drew attention to the work of statisticians at Fontainebleau on errors in estimating the spatial distribution of variables from point data.

Dr A. MERCADO pointed out that a model could be useful in deciding which data were required in order to solve a particular problem, and how best to collect them.

Professor A. VERRUIJT said that head levels calculated by most models are not very sensitive to changes in permeability, and hence the inverse problem is very difficult to solve.

Mr D. BAILEY felt that the models described were of no value for routine evaluation of sites for tipping hazardous wastes. The data required for the models are not readily available and even if they were, he felt that the presence of undetected fissures would make the model predictions unreliable.

In reply to Mr Bailey, Dr W.B. WILKINSON said that idealized models, of the type described in the paper by Mr Oakes, were likely to be used by the DOE when preparing guidelines on landfill site evaluation, once the present investigations on hazardous waste in landfills are completed. These investigations had passed well beyond the halfway stage, but he understood that the 'guidelines' would not be available for at least 12 months.

He agreed with Mr Bailey that groundwater models should not be used to evaluate, routinely, the pollution risk for every landfill site. However, in a situation where a landfill contained a particularly noxious substance, and the hydrogeological setting of the site threatened the security of local groundwater supplies, he was sure that groundwater quality models could help in assessing the risks. It would, of course, be necessary to collect appropriate data. He said that an understanding of groundwater quality problems in the Yorkshire Water Authority area could also be obtained by the use of models. He listed the mineralized water in the Permo-Triassic sandstones in the Vale of York, and the high concentrations of nitrate that had recently been observed in some groundwater sources.

Mr D. L. BROWN asked whether it would be possible to model the deterioration of permeability (50 to 60%) which he had observed, when injecting freshwater into a clay aquifer containing saline groundwater.

Professor A. VERRUIJT, Mr OAKES and Dr MERCADO all thought it would be possible if the mechanism causing the blocking was understood and it was possible to derive a relationship between permeability and sodium absorption ratio (SAR).

The CHAIRMAN suggested that the discussion should move on to the consideration of costs of data collection, including specific cases. For example, how much did it cost to sink an observation borehole?

Dr MERCADO said that preliminary data were needed before decisions about the procurement of further data could be reached. The obtaining of data was indeed expensive. It cost about £2, 500 to sink a 100m exploratory borehole.

It was suggested by a number of speakers from the floor that cost in the UK could range between twice and ten times the amount quoted by Dr Mercado.

Dr MERCADO imagined that these higher costs referred to boreholes of six inches diameter. Such diameters were only necessary for BOD measurements; for most purposes two-inch diameter holes were sufficient.

Mr D. B. OAKES said the value of the data should be considered rather than the cost. The value should be related to the cost of having no data at all.

In presenting his paper, Mr RICHARDS had said that a 'quality network' of boreholes should resemble a 'quantity network'.

Mr OAKES disagreed with this; quality changes occurred more rapidly in space so that, for quality measurements, a denser network should be used or pollution plumes may be missed.

Mr L.F. ANDERSEN said that a 'quality network' should be designed to give the earliest possible warning of pollution. It should also be noted that although some aquifers may not be stratified in terms of hydraulic properties, they may be in terms of pollutant concentrations.

Mr M. T. JONES pointed out that public pumping wells were in themselves monitoring boreholes. Weekly or monthly samples have to be taken by law, so they can show the first signs of pollution. For example, saline intrusion is no new problem, it is only necessary to consult the records to see the initial appearance of the phenomenon.

Mr J.J. FIELD was anxious to know whether organizations, when seeking planning approval for new waste disposal sites, would be asked to provide models of pollution spread. He felt that many organizations did not have the necessary expertise for this requirement. In the Devon County Council area, the main concern was with contamination of surface water, rather than groundwater. Who would carry out the necessary field work required?

Mr H. G. HEADWORTH thought that monitoring-boreholes should be sunk by the waste disposer, but the monitoring would be carried out by the water authority. He thought that in situations where a model was necessary the disposers would have to approach the WRC for advice since nowhere else in the UK did the necessary expertise exist.

Mr R. E. JACKSON mentioned models developed in Canada in the 1950s for radioactive wastes and salt-water intrusion. In those circumstances the loss of major coastal aquifers was threatened; the scale of this threat was and is larger than that of the local rubbish tip. The degree of threat should be great before one resorted to modelling.

Another example of a large-scale threat was the leaching of nitrates into the Great Lakes. He felt that few modellers would be available anywhere in the world to deal with the sort of small-scale work described by Mr Field.

Mr J. A. COLE said that a distinction should be drawn between the acuteness of pollution and the severity of the danger caused by pollution. Pollution near tips might be intensive but not important.

Mr D. B. OAKES said that of the ten sites examined by the Water Research Centre only two could be modelled by the techniques described. The others were too complex and effort was restricted to investigation and monitoring.

Dr L. F. KONIKOW referred to data acquisition costs in the Arkansas river valley of South Eastern Colorado (see Section 4. 2. of Paper 17). Over an 11 mile reach of river all inflows, outflows, and storage of water and salt were monitored for one year so that seasonal variation might be detected. Continuously recording sream and conductivity meters were placed on all inflows and outflows. There were 30 observation wells in the network; 15 were already in existence and 15 new wells were drilled. The network was sampled on a monthly basis. The one year programme cost between US $50 000 and $100 000. The well density was about two per square mile, average depth being 40 feet (12m) in gravel and each cost about $6/foot to drill. Fifty-three separate head gates had to be monitored and there were 65 irrigation wells in the area whose output was assessed from recorded monthly power usage. The major part of the project expense was data reduction but maintenance of the network was also expensive.

Dr A. MERCADO said that indeed the costs of data acquisition constituted a real problem, in particular, he felt, because this was where more effort should be placed. A quantity of good dispersion data is already to hand, but data are needed on adsorption properties of soils and particularly on the concentrations of heavy metals in sewage. Dr. Mercado stressed that relatively simple common sense models should be used, and emphasis should not be placed on further model refinement.

Mr T.C. LYONS mentioned the costs of collecting data in the St. Anna watershed (catchment), California. A model was developed in the early 1960s to describe this highly mixed urban and agricultural area. They gathered all data from other agencies, i.e. imports and water movements, sewage and industrial effluents including those from the only major steel plant in the Western United States. Even at that time the analysis of the data alone cost US $1 million. Major problems were encountered in the determination of who used what water. In comparison, the aquifer properties were quite well understood.

Dr J. SIDENVALL showed transparencies illustrating tests near Uppsala in Sweden (see Support Paper O). The tests were performed to determine the properties of the aquifer when recharge is employed as a means of supplementary water supply to Uppsala. One hundred wells were used to determine water table levels and the direction of flow, while tracer tests were used near areas favoured for recharge. They needed to know the velocities of recharged water and also the changes in chemistry which took place on its way to the well gallery. It would also be interesting to know the quantity of sewage sludge which could be safely administered to fields in the area.

Professor L. W. GELHAR suggested that groundwater specialists should work more closely with geochemists as there are many interesting geochemical phenomena that should be combined with flow models.

Mr J. A. COLE asked what new work was being done by the United States Geological Survey in this field.

Dr L. F. KONIKOW said that the USGS was directing effort into looking at chemical reactions, particularly those occurring as a result of landfills. There was also much laboratory work designed to determine reaction rates and ways by which the chemistry thus described could be incorporated into mathematical models. It would be necessary then to return to the field in order to see how the 'laboratory' models matched reality.

Dr W. B. WILKINSON said that ideally models should be capable of making sound predictions but that, even in the absence of that ideal, models are still able to help the crystallization of ideas; in that sense alone they amount to powerful thinking tools.

Mr J. A. COLE in bringing the discussion to a close, said that models are developed in response to a need. Drawing a diagram is a form of model-building. Model-building ranges from the quick calculation on the back of an envelope to the serious pursuit of composite models produc from the ideas of many experts. The art lies in deciding which model to apply to a particular problem.

Session 6

PROTECTION AND REHABILITATION

Chairman:

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Assistant Director of Scientific Services,
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Presented Papers:

PAPER 20

LEGISLATIVE ASPECTS OF GROUNDWATER QUALITY

A. H. Goodman and M. J. Beckett

1. INTRODUCTION

In the past the United Kingdom has relied heavily on groundwater for its potable supplies, although the occurrence of vast quantities of upland water in areas suitable for impounding reservoirs meant that we did not develop groundwater resources to as great an extent as some countries in Europe. About one-third or rather less of our public supply is derived directly from wells or boreholes. The quality of groundwater is usually extremely good so that it is suitable for potable supply with the minimum amount of treatment, usually disinfection only or filtration when iron and manganese contents are too high. This outstanding quality of groundwater is surprising when one considers that it has percolated from the surface where large quantities of decaying organic vegetable matter and faecal matter, which may have been deliberately spread on the soil as manure and millions of bacteria are present in the top few inches of soil. Yet by the time the water has reached the water table, pollutants are almost completely removed. The ground, therefore, is an excellent purifying medium and a valuable resource if properly used.

It is surprising then that there has been little legislation concerned directly with the protection of groundwater. Our recent legislation pays regard mostly to its protection indirectly and concentrates more on the prevention of pollution of surface waters. Possibly one reason for this is that groundwaters are relied upon implicitly to be pure and free from pollution. However, few strata are perfect and almost all water undertakers know of wells affected badly immediately after heavy rainfall, when polluted surface water reaches the aquifer through 'swallow holes'. The Steering Committee on Water Quality of the Department of the Environment in its first and second reports expressed concern over the disposal of industrial waste by means of soakaways, although cases of evidence of pollution of groundwater because of such practice are few. The investigation carried out by the Society of Water Treatment and Examination and the Institution of Water Engineers through a symposium revealed no evidence of pollution of groundwater due to the disposal of waste material in tips on the surface. However, a recent case of pollution by the product of pyrolysis of rubber tyres of a spring feeding a reservoir showed that groundwater can be polluted and test boreholes showed that the pollution was moving underground in the aquifer. A problem when such an occurrence does take place is the length of time that it takes for the aquifer to become free from pollution again. A case of accidental leakage of polluted water and oil from a gas works in 1938 resulted in pollution of a well in the chalk about half a mile away and this well had to be abandoned for potable supply purposes. Another well about a quarter of a mile yet further away from the source of pollution was in continuous use, and up to 32 years later in one of the author's experience it was found that during dry weather with the draw-down of the water table it was possible still to detect thiocyanate in the water. Thus the time scale is quite considerable and this makes the pollution of groundwater a matter of serious concern.

2. LEGISLATION RELATING TO GROUNDWATER

Looking at legislation we may start with the rather morbid Cemeteries Clauses Act of 1847 Sections 20 and 22. Section 20 states 'if the Company at any Time cause or suffer to be brought or to flow into any Stream, Canal, Reservoir, Aqueduct, Pond, or Watering Place, any offensive Matter from the Cemetery, whereby the water therein shall be fouled, they shall forfeit for every such Offence the Sum of Fifty Pounds'. Section 21 said that the penalty must be sued for while the offence was taking place or within six months thereafter, and Section 22 stated that a penalty of £10 per day was recoverable from a time 24 hours after the time of the notice of the offence had been served on to the Cemetery Company. The point about this reference is that when the penalties are considered it can be seen how very much they were in relation to a working man's wage of a few shillings per week and so it gives us a measure of the degree of severity with which such pollution was viewed.

This Act was incorporated into the Public Health Acts of 1875 and 1879. These Acts gave provision for the prohibition of houses being constructed within 200 yards of a burial ground. In those days it was likely that many houses had their own wells, and this would have meant that the wells themselves would have been a reasonable distance from the burial ground. Section 2 of the

Burial Act 1906 reduced this distance of a dwelling from a burial ground to 100 yards. It is believed that these provisions of 1847 included in the Public Health Acts of 1875 and 1879 would have been extended to pollution of wells. Before we leave this subject it may be said that its consideration is topical still. It is believed that although the Public Health Act of 1875 was repealed largely by the Public Health Act of 1925, and this was repealed in turn by the Public Health Act of 1936, the clauses relating to burial grounds as amended by Section 2 of the Burial Act of 1906 are in force still.

An unpublished memorandum on the sanitary requirements of burial grounds was prepared by the Ministry of Housing and Local Government in, it is believed, about 1958. It was likely that the topic was under consideration for inclusion in the Public Health Bill 1961 although it was not included in the Act. If we may quote from that memorandum it says that 'the degree to which the purity of neighbouring wells is endangered by a burial ground, and the distance to which contamination may extend, will depend in each particular case upon the relative elevation of the respective sites of burial ground and well, and upon the nature and dip of the intervening strata and the direction and amount of flow of underground water, so that it is impossible to lay down a general rule for all cases. Fissured rock might allow foul matter to traverse a considerable distance, while the inter-position of a bed of clay or a water-tight fault would shut them off, or their passage through an acrated stratum of finely divided earth would oxidize and destroy them on their way. The risk of pollution would seem to be greatest when graves and wells are sunk close together in a shallow superficial water bearing stratum of loosely porous nature resting on impervious clay, the water in the superadjacent bed being stagnant. It does not appear, however, that the risk to which wells are exposed from the proximity of a properly managed burial ground is in ordinary cases great. It is probably less than that to which in unsewered villages they are exposed by soakage into the subsoil from cess pools and privies.

In 1847 it became compulsory to drain houses into sewers where they were provided. Up until 1815 sewers had been constructed to convey surface water, and it had been illegal to discharge excrement to sewers. Most houses had middens, ash pits, or cess pits into which all wastes were put, and the household well was probably dug close by. Conditions had become dreadful with the increasing urbanization. The problem was that streams and rivers became intolerably foul and the Public Health Act 1875 prohibited the passage of sewage into streams from sewers until it had received treatment to remove 'excrementitious or other foul or noxious matter'. The relevance to undergroundwater in this was that in 1857 the first Sewage Commission had recommended that 'the right way to dispose of town sewage was to apply it continuously to the land'. The amazing thing is that the subsequent numbers of sewage farms which were set up, and some of which were in operation until recent years, did not bring about noticeable deterioration of groundwater; which illustrated what was said earlier about the excellent capacity of the soil to purify foul water. It can only be assumed that cultivation prevented cracks in the top soil and that any below the immediate surface became plugged rapidly by bacterial and fungal growths, when the sewage was applied. Of course, properly carried out, the soil should not have become waterlogged. Perhaps today with more refined methods of analyses we would be able to detect some changes in the quality of groundwater in increases in chloride, nitrate and sulphate, if the practice were to be started again. The practice of land treatment continues on a smaller scale today on farms where animal wastes have to be disposed of and the private wells on farms are examined by the Ministry of Agriculture, Fisheries and Food officers to see that the water supply is satisfactory when milk is processed in dairies on these farms. Otherwise the quality of private wells used for potable water are the responsibility of local medical officers (now Community Health Physicians).

We find reference to wells in the Public Health Act 1936 in Sections 124, 125 and 140. Section 124 put the ownership of public wells, giving a gratuitous supply of water to the inhabitants, into the hands of the local authority. If the local authority was satisfied that the water obtained from such a well was polluted and it was not reasonably practicable to remedy the cause of pollution they could close that well. Section 125 gave a Parish Council power to utilize any well, spring or stream within their Parish and to provide a facility for obtaining water therefrom and so on. Section 140 gave the local authority powers to prevent a water supply not being vested in their control from being used if they thought that it was polluted. Upon issuing a summons a Court could make an order directing the source of supply to be permanently or temporarily closed or cut off or for the water from that source to be used for certain purposes only, but this was a case of shutting off the supply, not of protecting it.

So we pass to the Water Act of 1945 where underground water was mentioned specifically in Section 7, which came under the general title of facilities for obtaining information as to underground water. It was this section which required anybody sinking a well to a depth more than 50 ft below the surface to give details of pumping tests to an appropriate authority. Then we find in Sections 18 and 21 the first steps to prevent pollution of underground water. Section 18 allowed for byelaws to be made to prevent pollution of the water of a water undertaker. Section 21 laid down the penalty for polluting water used for human consumption and it said that if any person 'is guilty of any act or neglect whereby any spring, well or adit, the water from which is used or likely to be used for human consumption or domestic purposes, or for manufacturing food or drink for human consumption, is polluted or likely to be polluted he should be guilty of an offence against this Act: provided that nothing in this section shall be construed as prohibiting or restricting:

a. any method of cultivation of land which is in accordance with the principles of good husbandry; or

b. reasonable use of oil or tar on any highway maintainable at the public expense, so long as the highway authority take all reasonable steps for preventing the oil or tar, or any liquid matter resulting from the use thereof, from polluting any such spring, well or adit'.

The section also gave right of entry to any officer of a local authority or statutory water undertaker to investigate to see that there was no contravention of this section. This was quite a step forward, and Section 22 gave power to statutory water undertakers to acquire land for the purpose of the undertaking and 'there shall be deemed to be included amongst those purposes the purpose of protecting against pollution any water, whether on the surface or underground, which belongs to the undertakers or which they are for the time being authorised to take'. The statutory water undertakers were also given the powers to acquire the necessary easements or rights 'to construct and maintain drains, sewers, watercourses, catchpits and other works for intercepting, treating or disposing of any foul water rising or flowing upon that land or for otherwise preventing water which belongs to the undertakers for which they are for the time being authorised to take from being polluted' with certain protections for fishery and navigation authorities. Section 14 of the Water Act 1945 prevented any person from abstracting underground water from any well, borehole or other work for purposes other than his domestic needs until he had obtained, in accordance with the regulations under this section, a licence from the Minister. This was amended in Section 5 of the Water Act 1948 which allowed for experimental boreholes to be sunk.

The owners of wells and boreholes were protected under Common Law up till this time and also groundwater was protected to a considerable extent by the various Planning Acts which would not allow works to take place which would be likely to interfere with water supplies. In 1963, however, river authorities had their powers extended to give control over discharges to underground strata. These powers were complementary to those they had already over discharges to watercourses. The most obvious thing about these powers is that they were limited to discharges made 'by means of any well, borehole or pipe', 'into any underground strata'. Discharges made, for instance, to the surface of the ground did not require consent. This was one of the sources of concern to the Steering Committee on Water Quality mentioned earlier. However, if at that time all discharges to the surface of the soil had had to receive consent it would have meant a burden of work on the river authorities which would have been untenable. This was because every farmer allowing his cows to graze in the fields or applying fertilizer or manure or pesticides to his fields would have been likely to have been judged guilty of pollution. The legislation also recognized that pollution was far less likely to reach groundwater if it was spread on the surface than if it was introduced down to the aquifer by means of a well, borehole or pipe. It did not take account, however, of the fact that when the underlying rock was open, and particularly when it was fissured, conditions were not favourable to the discharge on the surface and trouble could be expected. There are instances of pollution of groundwater from silage liquor from pea vines stacked on porous limestone having been noted (1). These powers were given to the authorities in the Water Resources Act 1963. Direct references to wells are given in Section 18 which allowed for the investigation of water in underground strata, Section 24 allowed an individual to abstract water from an underground strata for domestic purposes of his household without having to obtain a licence as laid down under Section 23 and further exceptions were given in Section 25. It was Section 72 which gave the powers to the river authorities to control 'discharges by means of any well, borehole or pipe into underground strata within their area, over trade effluents or sewage effluents or any poisonous, noxious or polluting matter, except consent be given and that consent should not be unreasonably withheld subject to any conditions which the river authority should wish to impose'. Section 73 gave transitional exemption of certain discharges and Section 74 gave river authorities power to vary consent given under Section 72. In addition, in Section 68 the river authorities were given the powers which had been given to water undertakers in the Water Act of 1945, that is they could purchase land for the purposes of protection against pollution of water in any reservoir or any underground strata from which they were authorized to abstract water.

It seems strange, considering the escalation of interest in the protection of underground water supplies up to the passing of the Water Resources Act 1963, that when we come to the Water Act of 1973 there is no reference at all to underground waters. All the emphasis appears to be concerned mostly with recreation, amenity and the financial aspects of water, but the protection of underground water was maintained still through previous legislation. The new proposals for the protection of underground water were introduced in the Control of Pollution Act 1974. Here Section 31 of Part 2 of the Act refers to specified underground water and the definition of this given in Section 56 states that this is 'underground water in the area of a water authority which is specified as water which is used or is expected by the authority to be used for any purpose in a document which is in a form described for the purposes of this definition and contains prescribed particulars and of which a copy is kept available, and has for not less than one month been kept available, at the principal office of the authority for inspection by the public, free of charge, during office hours'. This reference 'specified underground water' comes in the clause which says that a person shall be guilty of an offence if he 'causes or knowingly permits any poisonous, noxious or polluting matter to enter any stream or controlled waters or any specified underground water', and with the rather narrow definition of a specified underground water it would appear that the protection is confined to only those aquifers which are used or which have been declared in a published document to be likely to be used by the water authority.

However, a further look at this shows that it is intended to replace Section 18 of the Water Act of 1945 which gave powers to statutory water undertakers to protect only those waters which they were authorized to take. So that although the definition appears to be narrow, in fact it extends the control of pollution of underground water. Much of the recent legislation controls the disposal of solid toxic wastes.

3. PROTECTION OF GROUNDWATER AGAINST POLLUTION CAUSED BY WASTE DISPOSAL

In 1964, the Technical Committee on Disposal of Solid Toxic Wastes was appointed to consider disposal practices used for such wastes and to advise what measures were necessary to ensure that the wastes were disposed of safely and without risk of polluting water supplies and rivers. In its report (the Key Report) published in 1970, the Committee attempted specifically to deal with the pollution of water supplies, especially of underground water.

Although it examined a number of case histories of water pollution, the Committee found that the proportion which resulted in underground water being so contaminated in quality as to be unfit for drinking was extremely small. In a few isolated instances, small private supplies (such as shallow wells) had been affected and had needed replacing. There had been no significant pollution, due to tipped toxic wastes, of drinking water from underground sources supplied by water undertakings. The importance of the protection provided by water undertakings for larger sources was probably partly responsible for this favourable position, though the likelihood of leachate from a tip affecting a large source would also, by dilution, tend to be reduced.

There had been rather more cases of surface water pollution resulting from waste disposal, though often this had been due to poor site selection or failure to provide adequate precautions to prevent pollution. The Committee concluded that although there was at least a theoretical risk of water pollution involved in the disposal of wastes to land, in most cases the actual risks, especially of groundwater pollution, were small and experience did not justify the prohibition of tipping. Similar conclusions were reached by a joint research panel of the Society for Water Treatment and Examination and the Institution of Water Engineers, based on a survey of refuse tips located in the vicinity of water supply boreholes in a number of important aquifers. Experimental investigations into methods of depositing household refuse had been carried out at Bushey by staff of the Government Chemist, and at Egham by a local authority; the results obtained supported the view that risks to water supplies could be minimized by suitable site selection and, where necessary, the provision of appropriate protective measures.

In the early years of the present decade, a number of cases of unsatisfactory disposal of hazardous wastes gave rise to renewed concern about the risk of water pollution; one such case, involving the dumping of cyanide waste in drums at a site in the Midlands where groundwater pollution could have resulted, achieved particular notoriety via the various news media. The first two reports of the Royal Commission on Environmental Pollution (1971, 1972) thus referred to the tipping of dangerous wastes as a matter for urgent attention.

With this in mind, and to curb abuses such as those reported, the Deposit of Poisonous Wastes Act (DPW Act) was passed in the spring of 1972. This Act, which was intended principally as an interim measure pending the introduction of more comprehensive legislation, is described as: 'An Act to penalise the depositing on land of poisonous, noxious or polluting waste so as to give rise to an environmental hazard, and to make offenders liable for any resultant damage; to require the giving of notices in connection with the removal and deposit of waste; and for connected purposes'.

The DPW Act operates in two main ways: firstly by penalizing unsafe disposal, and secondly via a notification procedure. These will now be briefly considered in turn.

Under the Act (Section 1(3)) the presence of waste on any land is to be treated as giving rise to an environmental hazard if the waste has been deposited in such a manner, or in such quantity (whether that quantity by itself or cumulatively with other deposits of the same or different substances) as to subject persons or animals to material risk of death, injury or impairment of health, or as to threaten the contamination of any water supply (whether on the surface or underground).

Although this definition of an environmental hazard has been criticized, principally on the grounds of its general nature, it does have an important advantage in that, as far as the wastes themselves are concerned, it eliminates the necessity for specifying what constitutes a hazardous waste in terms of the physical, chemical and biological properties of a material. In other countries, attempts have been made to categorize wastes on the basis of their environmental behaviour (as inferred from the properties of their constituent substances) but such systems as have been evolved in this way have often proved extremely difficult to operate, principally because of the considerable difficulty in specifying exactly what is subjected to the hazard(s) associated with the waste.

The implementation of the more general type of definition, as used in the DPW Act, allows room for consideration of the particular disposal route concerned - for landfill disposal it would primarily refer to possible contamination of water supplies. The definition was, therefore, retained in the Control of Pollution Act 1974 which is discussed later on in this paper.

The second main feature of the DPW Act, i. e. the notification procedure (Section 3), requires those concerned to give local and water authorities at least three clear days notice of their intention to deposit notifiable waste. There are additional notification requirements once the deposit has been made. This procedure came into effect via the Deposit of Poisonous Waste (Notification of Removal or Deposit) Regulations in August 1972. The Regulations operate on an exclusion basis by listing many commonly occurring wastes which need not be subject to notification to the appropriate authorities provided they do not contain any hazardous quantity or concentration of any poisonous, noxious or polluting substance. In general, the list of exempted wastes though not exhaustive seems to have been reasonably appropriate. The notification procedure has resulted in information becoming available, often for the first time, on the magnitude and locations of the arisings of many toxic or hazardous wastes. It has also probably in many cases resulted in the use of improved disposal methods for such wastes.

During the Parliamentary stages of the DPW Act it was emphasized by the Secretary of State for the Environment that, so long as no environmental hazards were created it was not the intention to generally prohibit the disposal of wastes on land. In particular it was recognized that industry must be able to dispose of its wastes, and in so doing should not be forced to adopt complex practices which might not be necessary and which might be prohibitively expensive. Subject to careful control, much industrial and other waste could be deposited in tips without serious harm to the environment, and could thus play a useful part in land reclamation schemes.

The more comprehensive controls which were foreseen at the time of the DPW Act were eventually incorporated in the Control of Pollution Act (CP Act), which received royal assent in July 1974. This Act reformed the law relating to the deposit of wastes on land, the control of water pollution, control of noise emissions, and made some amendments to the law on air pollution. To date, only certain sections of the Act have been implemented and for the purposes of this paper only Parts I and II need be considered.

Part I of the CP Act, dealing with wastes on land, established a new system of responsibilities for the collection and disposal of all controlled waste, i.e., household, commercial and industrial waste, including wastes which are considered to be hazardous and to require special care and consideration in their disposal, and will thus be subject to more intensive control.

The primary method of establishing control of waste disposal operation is by means of a site licensing system, introduced in June 1976, whereby all persons intending to operate waste disposal sites are required to obtain a licence from the relevant waste disposal authority. These authorities are empowered to impose operating conditions on sites, and have extensive powers of supervision and enforcement to ensure that the conditions are met, and that operation of sites is maintained at a high standard. No waste controlled by the Act is allowed to be disposed of at an unlicensed site and there are heavy penalties for unlicensed dumping.

Before issuing site licences, waste disposal authorities have a statutory duty to consult the water authority in whose area the site is located. In certain circumstances they are also required to consult the Institute of Geological Sciences. It is also the duty of the waste disposal authority to revoke a site licence should it appear that continuation of the operations to which the licence relates would cause pollution of water, unless the danger of pollution could be avoided by modifying the conditions specified in the licence.

The operation of controls under the DPW Act is unaffected by the introduction of the site licensing system, and this Act will not be repealed until regulations made under Section 17 of the CP Act have established new controls over difficult and dangerous wastes, in addition to those provided by the licensing system. The Department has established a number of sub-groups, each comprising representatives of industry, waste disposal and water authorities, to review the arisings and disposal of specified categories of difficult wastes. From the report of each sub-group, a technical memorandum incorporating a code of practice for the disposal of the waste is prepared for publication in the Waste Management Papers series available from HMSO. At a later date, it is envisaged that, where necessary, disposal of particularly diffficult wastes would be controlled by regulations introduced under Section 17 of the CP Act, and that the recommendations contained in the technical memoranda would form the basis for these regulations.

When implemented, Part II of the CP Act dealing with water pollution will require all discharges of trade and sewage effluent to land, lakes, underground water, rivers and the sea to be made only with the consent of the appropriate water authority (Section 32). It will also be an offence to cause any poisonous, noxious or polluting matter to enter any stream or controlled waters or any specified underground water (Section 31).

Although these provisions are not yet in force, it may be of interest to give some preliminary indication of their implications for authorities. Whilst it will be necessary for the operator of a waste disposal facility to obtain consent from the water authority if his operations involve the making of a discharge of trade effluent, whether it be to water, land or underground, so long as he is operating within the terms of any relevant disposal licence or consent which he has obtained under the CP Act, he will not by virtue of Section 31(2)(a) be at risk of prosecution under Section 31.

The protection extended to specified underground waters replaces the more limited controls provided by Sections 72-76 of the Water Resources Act 1963, and those sections will be repealed. For the purposes of the CP Act, specified underground water is defined in Section 56(1) as meaning underground water in the area of a water authority which is designated as water which is used, or is expected by the authority to be used, for any purpose, in a document which is in a form prescribed for the purpose of this definition, and which contains prescribed particulars and is available for inspection by the public.

Although the CP Act provides for statutory consultations between waste disposal and water authorities where protection of water is concerned, those two types of authorities have differing responsibilities. Their respective interests will thus need to be adequately balanced if the provisions of the CP Act are to operate satisfactorily and without conflict. The basic objective of the site licensing system is to ensure that waste is disposed of with the least practicable risk of damage to the environment and the minimum expenditure needed to enable this to be done. In some cases the risk to water supplies, or some other environmental hazard, will render the use of a proposed site unacceptable for certain wastes. At other sites, the risk may be slight but will nevertheless still need to be considered. In all situations, water authorities will be able to offer advice, based on their experience and expertise, while waste disposal authorities will have opportunities to discuss the disposal of controlled waste both at existing and proposed new sites. Both sets of authorities, by discussing problems as they arise and by exchanging relevant information, should profit by these opportunities for informal discussion and by giving full consideration to their respective interests should thus be able to reach joint decisions on how difficulties can best be resolved. This subject is discussed at greater length in DOE Circular 39/76 'Balancing of Interests between Water Protection and Waste Disposal'.

4. INTERNATIONAL ASPECTS

So far groundwater protection has figured very little in international discussions. The EEC Directives, discussed and submitted for approval to the Council of Ministers have been concerned largely with surface waters. The Council of Europe programme of intergovernmental activities for 1976 includes provision for a survey on automated monitoring of groundwater. There appears to be an increase in interest in the exchange of phreatic waters in the Rhine Valley with the water of the River Rhine leading to a study, and storage and protection of water in underground strata in The Netherlands is studied fully. It appears likely that restrictions being imposed more widely on discharges of wastes to surface waters are leading to increased disposal to underground, e.g., the Alsace Potash Mines disposal of waste brines, and protection of groundwaters on an international basis is likely to become more urgently required. Without knowing the laws of other countries it is not possible to say what controls over pollution or protection of groundwaters exist, but it is believed that it is likely that the legislation of the United Kingdom must be as far advanced as any.

There is a proposal for an EEC Directive to control discharges to underground strata and to protect underground waters. This is through the implementation of Article 4 of the Directive on Pollution Caused by Certain Dangerous Substances Discharged into the Aquatic Environment. Section 4 of Article 4 states that 'this Directive relating to ground water shall no longer apply upon the implementation of a separate Directive on ground water'. So at the present, an interim measure exists for groundwater. One plenary meeting has been held to discuss the provisions of this Directive on dangerous substances as they apply to groundwater (for which a definition has not been agreed). The points at issue were: whether the point of discharge was directly to the aquifer, or to the soil above from where it could percolate; whether the substances in lists I and II for surface water discharges ought to be adopted directly without amendments when considering underground waters. The difficulties associated with this part of the Directive could be considerable and many further discussions will have to take place before agreement.

The full text of Article 4 of the Directive on Pollution Caused by Certain Dangerous Substances Discharged into the Aquatic Environment states:

Section 1. Member States shall apply a system of zero emission to discharges into ground water of substances within List I.

Section 2. Member States shall apply to ground water the provisions of this Directive relating to the substances belonging to the families and groups of substances in List II.

Section 3. Paragraphs 1 and 2 shall apply neither to domestic effluents nor to discharges injected into deep, saline and unusable strata.

and Section 4. Referred to already above.

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PAPER 21

MEASURES FOR THE PROTECTION AND REHABILITATION OF AQUIFERS IN THE UNITED KINGDOM

H. G. Headworth and W. B. Wilkinson

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1. INTRODUCTION

At present about 30% of public water supply in the United Kingdom is derived from groundwater sources, and regional schemes for future development are now being planned and implemented. However, there is an increasing demand for these aquifers to fill a multiple role in water supply, waste disposal, and as sources of construction material. It is, therefore, appropriate that authorities concerned with water supply and waste disposal, and the associated organizations, are now directing their attention towards the best use of these aquifers while attempting to resolve the problems arising from their conflicting functions.

The biodegradation, chemical and dilution processes that occur as water infiltrates through the surface layers of soil and the body of an aquifer make groundwater much less vulnerable to pollution than a surface water source. Groundwater has thus provided water engineers in the United Kingdom with a good quality, relatively cheap source of supply for many years. In view of this high and relatively constant quality, there appeared in the past to be little reason to install observation boreholes adjacent to abstraction wells and there are many major groundwater abstraction sources which are not monitored in this way. However, if monitoring wells are not available to give warning of the approach of polluted water, bacterial or chemical contamination of the abstracted water may suddenly occur and the engineer may be given no opportunity to take protective action or, in the short term, to identify the source of pollution. Once the well has become polluted, remedial measures to return the water to its former, or lower but acceptable, quality may be uneconomic and the well source may thus be lost.

It is probable that only a small proportion of the instances of groundwater contamination that have occurred over the last few years have been discovered. The incidence of well pollution in the future is, however, likely to increase due to the following factors:

(a) groundwater may move so slowly that a pollutant may take several years before it reaches a water supply well;

(b) some pollutants may take a long time to decay in the groundwater system;

(c) the ability of the soil to absorb or degrade pollutants may, with time, be reduced;

(d) the increasing quantity and variety of chemicals that are continually being produced represent a threat from spillage during storage or transport and as potential waste materials;

(e) the pressure to dispose of wastes underground and

(f) the increased use of aquifer outcrops for constructional materials, e.g. sand, gravel, chalk, etc.

Water authorities have a statutory duty and are currently engaged in reviewing the use and management of their water resources and in drawing up future plans. Thus there is an opportunity to prepare a long-term policy for the protection of groundwater quality.

This paper firstly categorizes the principal sources of pollution and the groundwater development conditions that will lead to contamination of underground resources. The control and rehabilitation measures that may be adopted for existing and potential pollution situations are described and illustrated by a number of case histories.

2. SOURCES OF POLLUTION

The sources of groundwater pollution generally encountered in the United Kingdom are as follows:

Sewage effluent discharges
- domestic sewage receptacles
- sewage treatment works

Agricultural activities
  - inorganic fertilizers
  - animal wastes
  - crop sprays
  - silage

Domestic and industrial wastes
  - landfill sites
  - lagoon storage
  - mine workings
  - deep wells

Surface drainage and accidental spills
  - soakaways from highways, housing, industry
  - storage tanks
  - road and rail tankers
  - highway salt

Coastal saline intrusion

Mining activities
  - colliery drainage
  - colliery and power station spoil heaps

Mineralized water

The nature of the pollutants resulting from these activities and possible control and rehabilitation measures are described in Sections 3 to 9. Case histories dealing with waste disposal, mining activities and saline intrusion are reported in Section 10.

3. SEWAGE EFFLUENTS DISCHARGES

The discharge of untreated and partially treated sewage into the ground is widely practised in the UK and can give rise to microbial contamination of nearby abstraction wells. In addition ammonia is present in sewage and the aquifer can suffer an overall increase in nitrates if this ammonia becomes nitrified. The presence of nitrogen in the form of ammoniacal nitrogen and albuminoid nitrogen does not in itself prove contamination by sewage, but an increase of these in groundwater would suggest such a source of pollution, as would an increase in the proportion of ammoniacal nitrogen to albuminoid nitrogen. While chlorination will deal with most bacteria and viruses, the presence of ammonia can give rise to taste problems, excessive chlorine demand, and growths in water mains.

There are many reports (Holden, 1970) of wells being removed from service owing to contamination by sewage. Usually the source has been found to be a broken pipe or concealed cesspool or septic tank. Springs are also at risk, particularly after heavy rainfall.

It has been estimated that in 1970 about 6% of the population of England and Wales, being unconnected to main drainage, used septic tanks and cesspools (Hunter Blair, 1972). Septic tanks normally discharge their effluents into permeable strata whereas cesspools store the effluent which is periodically emptied by tanker. Badly constructed or maintained units with uncontrolled leaks are not uncommon. Montgomery and Wheatland (1972) showed that the suspended solids content of septic tank effluents varied between 15 and 700 mg/l. They considered that emptyings should be carried out more frequently than once a year.

In some parts of the country sewage works serving small towns or villages are not linked to arterial foul drainage systems and dispose of crude, partially-treated, or fully-treated sewage via soakaways into an aquifer. Such situations are not uncommon on the Permo-Triassic sandstones of the Midlands and Chalk of south and east England. Nicolson (1972) has reported that along the Chalk outcrop of the Thames Water Authority area, from the Marlborough Downs to the Chilterns, there are 36 discharges of domestic sewage effluent, exceeding 23 m^3/d, from small treatment plants to which more than one dwelling is connected; four of these exceed 450 m^3/d. They do not include many hundreds of septic tank discharges from individual properties. In Hampshire there are eight such disposal works sited on the Chalk outcrop, of which all but two dispose of up to 640 m^3/d of biologically treated effluent into the Chalk via soakages and in one case,a shallow borehole. In two cases the only treatment consists of settlement of suspended solids, and the effluent is discharged into the ground via lagoons; in the largest of these serving a town of 31 000 people, the dry weather discharge is 5700 m^3/d. Only in one or two cases has some evidence of pollution been detected in groundwater samples from wells in the vicinity.

Generally discharges of sewage effluents to permeable strata do not constitute a serious hazard because of the removal of bacteria and biodegradation of organic matter which occurs in the upper few metres of soil and bedrock. A possible long-term consequence of the discharge of sewage effluents is a gradual increase in the concentration of nitrate in the groundwater. In the Southern Water Authority area it is estimated that there are 100 000 domestic properties not connected to a public sewer, and that only 8.3% of the contents of their cesspools and septic tanks is received for treatment by the Authority. Assuming the remainder to be discharged evenly over the 5700 km^2 of permeable strata, and assuming 2.5 persons/household, 160 litres/day/person discharge, an average ammonia value (as N) of 100 mg/l, and 270 mm annual infiltration, then the groundwater would suffer an increase in nitrate concentration of 0.9 mg/l as N. Although this figure would appear to be small, it has to be remembered that it represents only an average over a wide area and local concentrations will occur. Moreover, repeated cycles of abstraction and discharge would tend to cause some increase in this concentration. However, in an investigation of nitrate pollution of Chalk boreholes in Lincolnshire, Davey (1970) shows that the amount of nitrate from sewage or animal faeces was insufficient to account for recent increases in nitrate in groundwater.

The dangers of sewage discharges polluting an aquifer and contaminating boreholes and wells can only be lessened by connecting cesspools and septic tanks to sewage treatment works which discharge treated effluent into surface streams. However, a measure of improvement can be achieved by ensuring that pipes and joints are watertight and that installations are properly constructed and maintained.

Although some powers to control discharges into underground strata have been available to water authorities, or their predecessors, they were used rather sparingly. Section 31 (5) of the 1974 Control of Pollution Act will, when implemented, allow areas to be designated within which activities likely to give rise to pollution can be prohibited or controlled, but it remains to be seen how water authorities will use these powers. It is likely that the requirement for obtaining consent for all septic tank discharges will impose a crippling administrative burden, and that only specific areas in the vicinity of abstraction wells will be do designated.

It is interesting to note that under Section 18 of the 1945 Water Act, Brighton Corporation passed bylaws in 1970 which made it an offence to make any discharge from sewage receptables into underground strata within a distance of approximately 3.2 km from each pumping station. Regular emptying of septic tanks and cesspools was carried out at a nominal charge. As long ago as 1930 Brighton Corporation pursued a policy of buying up farms on the gathering grounds so as to control discharges into the Chalk, but it can only be conjectured whether this, and the later bylaws, have been the reason for the low bacterial content of their groundwater supplies.

Clearly it is desirable for householders to have their cesspools and septic tanks emptied regularly, and financial inducement rather than legal sanctions is likely to be a more effective way of achieving this in the long term. However, the consequences of the Daymond Case (judgement by the House of Lords in December 1975 upholding appeal by Daymond against the South West Water Authority for levying a general service charge on an unsewered property) is not likely to assist this objective, since authorities will be obliged to recoup the money by a greatly increased charge for the disposal of cesspool contents at their sewage works.

This problem has been recognized in the Government's recent consultative document 'Review of the Water Industry in England and Wales', which proposes that the regional water authority should be made directly responsible for the collection and disposal of cesspool contents. This would enable the RWAs to exert greater control over the use of cesspools and septic tanks, particularly on permeable catchments. Operation, emptying and charging policies could then be kept under optimum conditions conducive to pollution control.

4. AGRICULTURAL ACTIVITIES

Potential sources of groundwater pollution resulting from farming practices are: applications of organic and inorganic fertilizers, disposal of manure from intensive animal rearing compounds, ploughing of pasture land, spraying of pesticides and herbicides, and liquors emanating from silage clamps. Changes in traditional farming methods may tend to exacerbate pollution from the above causes.

In recent years several authors have reported increasing concentrations of nitrate in groundwater sources. (Davey, 1970; Greene and Walker, 1970; Foster and Crease, 1974; Foster, 1975; Young et al, 1976.) The nitrate content in the groundwater of about 100 public water supply wells in the UK now exceeds, at least intermittently, the WHO recommended limit of 11.3 mg/l, (as N). As a result extensive investigations are being undertaken to determine the sources of this pollution. This work has suggested that certain agricultural practices, including the application of inorganic fertilizer, tend to increase the nitrate load in the underlying aquifer.

Although nitrate is the ultimate stable form of nitrogen under atmospheric conditions, it is only produced naturally following the generation of nitrogenous organic matter by nitrogen fixation (Hall, 1972). This is not true when ammonia is introduced artificially as in the application of fertilizer, when nitrate formation merely involves bacterial oxidation. Denitrification of nitrates to nitrogen gas and the breakdown of protein to ammonia occur in the presence of organic matter. Intensive cereal cultivation requires not only heavy application of inorganic fertilizers (predominantly ammonium nitrate) but frequent ploughing, and this favours aeration of the soil, the breakdown of soil humus, and the oxidation of ammonia in the soil to nitrate.

Some authors claim that no significant leaching of nitrate from the soil takes place on well-managed farms when the optimum application of fertilizers of between 145 to 302 kgN/ha/a is applied (Burford and Pain, 1972). However, Foster and Crease (1974) note that between 1957 and 1971 the application rate for inorganic fertilizer in Yorkshire increased from 20 to 93 kgN/ha/a and over the same period the nitrate content of abstracted groundwater rose from about 4 to 11 mg/l.

The introduction of intensive animal rearing units in recent years has also led to increased nitrate contamination. Manure is concentrated at disposal points and leachates from these contain coliform organisms as well as inorganic nutrients. The spreading of slurry, derived from these units, on to farmland can increase the danger of high nitrate leachates where applications are excessive, and where the spreading is carried out during winter months when recharge to the aquifer takes place.

The seriousness of the nitrate problem lies not only in this but in the coincidence between the location of large arable farms and the outcrop of the Permo-Triassic sandstone of the Midlands, and the Chalk Downs of eastern and southern England. Many communities in these areas are almost totally dependent on groundwater derived from these aquifers. A further problem is that appreciable quantities of nitrates already exist in the unsaturated aquifer zones as a consequence of former farming practice (Young et al, 1976). The apparently slow downward movement of these 'high nitrate zones' may continue to contaminate the groundwater for many decades. A change in farming practice now will therefore have little or no immediate beneficial effect.

The use of herbicides and pesticides presents a potentially serious problem since only very minute concentrations in water supplies are needed to make the water unfit for drinking. The substances may be toxic, accumulate in body fat, or persist in the ground for many years, e.g. DDT. They can be detected only by the use of very sophisticated analytical techniques which do not form part of routine chemical analyses. However, samples from 74 underground water supplies in Kent, where market gardening and fruit growing give rise to intensive use of herbicides and pesticides, showed no contamination from these sources, (Croll, 1972), although they were subsequently detected in river water. However, cases of groundwater contamination have been reported in other parts of the world (Miller and Scalf, 1974).

Silage liquors can constitute a distinctive and serious pollution threat. One tonne of unwilted silage can produce 273 litres of strong polluting effluent with a BOD of 12 000 to 160 000 mg/l. Silage clamps holding over 300 tonnes are not uncommon. Between 1970 and 1972, Richards (1972) investigated the movement of silage leachates from a clamp in Dorset by means of two boreholes drilled into the Upper Chalk to depths of 38m, with the water table 20-26 metres below ground level. During the two sampling seasons a consistent pattern attributable to silage leachates was not obtained. Wide natural seasonal variations were evident in all the constituents: phenols, 0 to 0.3 mg/l; sulphate, 9 to 30 mg/l; total hardness 250 to 600 mg/l; pH, 6.25 to 7.6 mg/l; COD, 1.5 to 28 mg/l; BOD, 0.5 to 11.5 mg/l; alkalinity, 150 to 850 mg/l. All except pH showed an increase with natural recharge. This apparent lack of gross pollution from silage liquor should not give rise to complacency as it may be stored in the unsaturated zone of the Chalk to be released in later years. The highly noxious nature of silage effluent means that there is always the danger of a nearby groundwater source becoming contaminated in fissured or granular aquifers. When such a danger exists, silage clamps need to be underlain by an impervious base, and the liquors collected and disposed of by spraying over farmland. Rarely would a water authority accept them for treatment at a sewage treatment works.

Practical measures for the protection of aquifers against contamination resulting from farming activities are difficult to formulate. It does appear that the increase in nitrates in groundwater in recent years is due to the ploughing up of grassland for the cultivation of arable crops, and to the application of increasing amounts of inorganic fertilizers. It is now widely recognized that agriculture is one of the principal causes of nitrate pollution, and it is hoped that farmers' attention may be drawn to this so that they apply no more fertilizer to their crops than is strictly required.

The disposal of slurry from intensive animal units and silage liquor is more amenable to control than fertilizer application, and this can best be achieved by an improvement in farming practice through the auspices of the MAFF than by enforcement of pollution laws by water authorities.

5. DOMESTIC AND INDUSTRIAL WASTES

The leachate from waste disposal sites may present a hazard to the quality of groundwater supplies. The problem is clearly related to the amounts of industrial and domestic wastes which continue to be generated, the composition of the waste, the location and hydrogeological setting of the sites, and the degree of control employed during site operation. It is estimated that in 1974 domestic solid wastes totalled about 20 m tonnes in the United Kingdom. A lesser quantity of industrial wastes are produced annually but this still amounts to several million tonnes of which about 30% are solid and 70% liquids and sludges. These estimates exclude coal mining wastes and those arising from electricity generating stations, (Section 8). In 1971, the DOE undertook a survey of waste disposal sites in England and Wales. The preliminary results of this, described by Gray et al (1974), were based on 2494 landfill sites; a 62% response to the survey. The sites are, in general, widely distributed over England and Wales, but some concentration occurred adjacent to major conurbations. On the basis of a desk study, 51 of these sites were considered to present a pollution risk to groundwater sources. The actual pollution risk for a number of these sites has since been assessed differently by the water authorities and this underlines the importance of site visits together with detailed local knowledge and the limitations of working from the geological maps only (Dowse and Selby, 1975).

Domestic wastes are largely biodegradable and their constituents change very slowly with time. In general, leachate is produced from the waste if there is a source of water equal to or greater than about 133 mm per metre of of fill (HMSO 1961 and Qasim and Birchinall, 1970). This may result from precipitation or other inflow at the surface, or groundwater being in contact with the fill. This water requirement for leachate production is equivalent to about 60% moisture content by weight, whereas an average refuse may only contain about 20% moisture (Bell, 1963; Kaiser, 1966). Thus, if the water can be eliminated, domestic refuse will decompose slowly and little leachate will be produced. It is clearly difficult, however, to exclude water in every circumstance and where it enters the fill, so as to generate leachate, a highly polluting liquid is produced with a contaminating ability some 10 or even more times greater than sewage. A typical analysis for a domestic leachate is given in Table 1, below:

Table 1. Characteristic composition of leachates derived from domestic refuse tipped above the water table

Ammoniacal N	Albuminoid N	NO_2	NO_3	Organic N	Organic C	BOD	SO_4	Sulphide	pH	Cl
300-600	30 - 70	0-0.2	0-40*	20-60*	200-2000	100-3000	c.800	10 - 20	7-8	c.1500

* high during initial stages of decomposition, declining thereafter.

There is evidence however, to suggest that the polluting load may decrease markedly over a period of two to three years (Salvato et al, 1971; Fungaroli 1971). The quality of the leachate that reaches the groundwater depends on the depth and the type of strata overlying the water table. If the leachate passes downward into a granular unsaturated aquifer and the rate of release of leachate is such that aerobic conditions may persist, then organic polluting matter may be greatly reduced in quantity, (Aggar and Langmuir, 1971). If, on the other hand, clogging of the strata develops, leading to an anaerobic condition, or if the fill is in direct contact with the water table, a highly contaminated leachate may result (Hassan 1971). A potentially serious polluting hazard clearly exists in fissured strata where the rapid movement of the leachate down to the water table and horizontally within the body of groundwater may take place.

While the composition of domestic refuse will vary from one tip to another and is likely to vary during the life of the tip the problem of assessing the nature of leachate likely to be generated is greatly exacerbated if industrial wastes are included in the refuse. Industrial wastes may include, for example, metal sludges, acids, oils, tarry wastes, phenols, pharmaceutical wastes and many other materials, of which some may be inimical to underground water quality. Some of these materials may be rendered harmless if carefully placed in domestic refuse. Industrial waste may be deposited in liquid form directly into pits and, as such,may present a particularly dangerous source of contamination.

In the past abandoned quarries have frequently been used as sites for the disposal of both domestic and industrial waste. In these situations the layers of upper soil or weathered rock which may have afforded a degree of protection against leachate are likely to have been removed. Lack of detailed records, and in some cases illegal tipping, may mean that the source material of the leachate which has emanated from a landfill or lagoon is unknown unless detailed site exploration work involving drilling is undertaken.

In view of the potential pollution of leachates that can be generated from domestic waste at unsatisfactory landfill sites and of the nature of some of the industrial wastes that are deposited in landfills, lagoons, or pits it is somewhat surprising that there have been so few reported cases in the UK of well supplies being contaminated from such sources. There may be a number of reasons for this (Aspinwall, 1975) as follows:

a) Groundwater flow rates are generally very slow and it may be several years before a body of contaminated groundwater reaches an abstraction well, by which time dilution, dispersion, biological and chemical interactions may have lowered the concentrations of pollutants to an acceptable level.

b) In analysing groundwater, more attention may be paid to the biological rather than the chemical analysis, so that the slower rise in inorganic constituents may go unnoticed.

c) The expense and technical difficulties that the abstractor may face in proving that pollution results from a specific source and the legal actions that may result.

The recent DOE investigations (DOE, 1975) have clearly demonstrated that groundwater contamination does occur below some waste disposal sites. Information on the widespread movement of pollutants away from waste disposal sites is less readily available in the UK, although measurements made overseas have shown that contaminants may be transported by groundwater flow over considerable distances (Exler, 1972; Miller and Scalf, 1974).

The measures to be adopted to control leachate from waste sites will, in the first instance, depend on the nature of the waste material. This may vary from relatively inert substances, such as builders rubble, to soluble toxic materials. The former materials will have little or no effect on water quality while the latter, unless deposited in a safe site, may leach into the groundwater and in time gain access to boreholes or surface waters. Domestic wastes are intermediate between these two extremes.

The measures which can be adopted to control leachate from solid wastes are those which:

a) Exclude as far as possible the entry of water to the site.

b) Prevent leachate from percolating to the groundwater table or control the rate of flow, so that some removal of organic and inorganic matter occurs in the unsaturated zone, followed by a satisfactory degree of dilution in the groundwater.

c) Collect the leachate for treatment at a sewage works.

Liquid industrial wastes present a particularly complex problem. They may contain a wide variety of materials, some possibly toxic, and it may not always be possible to predict or to make the appropriate laboratory experiments to assess the degree of chemical interaction that will occur, should they come into contact with the bedrock or groundwater. Control measures to be adopted involve:

a) Pre-treatment for the removal of toxic chemicals.
b) Impermeable linings to those pits that contain toxic substances, and provision for the collection and treatment of noxious overflow.
c) The addition of chemicals to react with and bind the waste into an impermeable matrix with a long term stability (Young, 1975).

Clearly these measures can be incorporated in a new waste disposal site but at an existing site control will be much more limited. Little consideration was given in the past to site selection and preparation in order to control groundwater contamination. The new waste disposal authorities have now inherited many sites which give rise to pollution of groundwater and/or surface water. Nevertheless, it may be possible at existing operational sites to change the method of placement of the fill, improve surface drainage facilities or even close down the site. However, pollution of the groundwater may already have occurred.

The removal of pollution from an aquifer is difficult and expensive. The pollutants, if they threatened the quality of existing wells, may be intercepted by the use of scavenging wells. Alternatively, it may be possible to arrange the pumping rates and regimes of existing abstraction wells in such a way that natural groundwater flow causes dilution of the contaminants so that the pollutants no longer present a hazard to supply. The authors are, however, unaware of any situation in the UK where such policies have been adopted.

Although it must be recognized that the requirements of the waste disposal authorities and the water authorities may frequently be divergent, it is to be hoped that good initial site selection will minimize groundwater contamination problems arising in the UK in the future. Good sites that are near to the source of waste and which do not require expensive site preparations are, however, not easily found. Hydrogeological site investigations should be undertaken if it is felt that the pollution of groundwater supplies is likely to result from a proposed waste disposal site. The cost of such investigations are small in relation to the site engineering works and the site operation. Depending on the results of the drilling and sampling both short and long term monitoring of surface leachates and of groundwater quality by means of boreholes may be necessary.

It is beyond the scope of this paper to discuss other methods of disposal such as incineration, disposal at sea, etc. other than to say that they are not without their problems and are generally more expensive than disposal on land.

Preliminary guidelines to be used in new site selection have been proposed (Gray et al, 1974). However, at the present time the degree of purification that will result as a leachate passes through various strata and into the groundwater body is, to a large degree, unknown. Comprehensive guidelines are currently being prepared by the DOE which will draw on the results from a wide range of field and laboratory studies which they have commissioned over the last three years. These are eagerly awaited. The range of drilling, sampling, analytical and monitoring techniques that have been used in the course of these studies have been described by Barber, et al, 1976.

New waste disposal sites which could cause pollution of minor aquifers should not be rejected out of hand by the water authorities. Economic and environmental studies of the current and future value of the water resource in relation to the value of the aquifer for waste disposal purposes may lead to the conclusion that the aquifer should be sacrificed to the latter use.

Industrial wastes, frequently with a highly toxic content, have been directly disposed of underground in the UK for many years. Old mine workings have generally been used but in some cases boreholes have been specially constructed. Disposal depths are relatively shallow, usually less than 300m. If the waste is placed in an uncontrolled manner and the hydrogeological setting is not fully taken into account in the choice of the disposal site, a contamination of groundwater may result or the effluent may appear at the surface. A number of such occurrences have been reported (Henton, 1975; Dowse and Selby, 1975).

Deep well disposal methods are used in the USA, Canada, and elsewhere in the world. The technique of drilling a borehole possibly to a depth of 2000 m and injecting the liquid waste under pressure into a permeable strata has so far not been used in the UK. There is the possibility, however, that the method could be used in the future as industry finds increasing problems in disposing of its more difficult wastes or of keeping treatment costs to a minimum. This disposal method is, however, not without its problems and requires the installation of a monitoring system (Edworthy, 1976).

6. SURFACE DRAINAGE AND ACCIDENTAL SPILLAGES

Surface drainage by soakaways and accidental spillages from a variety of sources can constitute serious pollution hazards to unconfined aquifers. In areas where no watercourses or sewage treatment works are conveniently available, soakaways comprise the only practical alternative for the disposal of surface waters. Furthermore where development is substantial, the run-off from impervious surfaces could constitute a significant loss to resources and it may be desirable to discharge such water to the aquifer.

Discharges from soakaways can originate from a variety of sources, principally urban and industrial development, urban highways, motorways and trunk roads. Run-off from each class of development is liable to be contaminated to some extent. Surface water from new housing developments will contain dirt-wash from roads, oils and detergents from washing and possibly servicing of cars, oils from spillages and leakages from domestic heating systems. Urban run-off may contain, additionally, wastes from shops and industrial yards and sewage from overloaded soil sewers. Run-off from industrial development is likely to contain oils, a wide variety of organic and/or toxic substances resulting from spillages and leakages, and possibly cooling waters which may be contaminated. Highway drainage is liable to contain much the same pollutants as indicated above for urban development, but would be subject also to spills from traffic accidents in which oils and a wide variety of chemicals, some hazardous, may be involved.

Methods of disposal may be by means of soakaways, single or linked, varying in depth up to 3 metres, depending on the volume to be disposed of and the permeability of the ground. Exceptionally, where the surface soil layer is of low permeability, disposal may be via boreholes into underlying permeable strata. Motorways and trunk roads running through permeable strata are often drained through porous pipes terminating in dug soakaways or open soakage pits. The extent to which contaminants will be removed or neutralized in an aquifer depends on many factors, and in fissured rocks it will depend largely upon the degree of dilution afforded.

Where it is likely that surface water will contain trace amounts of oil, provision should be made for this to be removed prior to final discharge. An oil interceptor is appropriate for most small installations. The dimensions will vary according to the volumes to be treated,but adequate storage should be provided to cope with a rainfall intensity of 13 mm/h (Ministry of Technology, 1967). Provision will need to be made to allow excess flows to bypass the trapped chambers so as to prevent retained oil from being flushed out. Arrangements should be made to ensure that the trap is regularly emptied of oil and the pea gravel is replaced as necessary. Where discharges are liable to contain more than trace quantities of oil or the oil is immiscible, the area at risk should be restricted as far as possible and be drained to the foul sewer, after treatment as necessary by means of an oil separator. Discharges which may contain toxic substances should similarly be drained to the foul sewer, after treatment, as may be necessary to protect the sewers, treatment processes and the receiving waters. Large discharges containing oil are best treated by means of a gravity separator to the specification of the Manual of Disposal of Refinery Wastes of the American Petroleum Institute (American Petroleum Institute 1959) or by inclined-plate separators. However, these installations would not normally be required for the relatively small flows dealt with by soakage.

In addition to aquifers being at risk from polluting matter discharging from soakaways, they are particularly vulnerable to spillages and leaks from industrial plants, fuel storage tanks and pipelines. Day (1972) describes contamination of chalk boreholes by organic solvents due to leaking underground drains, which necessitated the boreholes being shut down for a year, and the scavenging of contaminated water from eight dug pits. As a remedy the underground drains were replaced at the factory site by a pumped overhead effluent system. Dowse and Selby (1975) report a similar occurrence in the Midlands where a canal was contaminated with fuel oil leaking from storage tanks. Eight boreholes and a 3.3 m diameter shaft and heading were subsequently required to locate and clear the contamination. Dracos (1972) detailed measures taken to prevent a shallow alluvial aquifer becoming polluted from spillages and leakages at a rail shunting yard in Switzerland. Rather than lay the rail-track ballast on an impermeable layer and thereby lose the recharge to the groundwater, the ballast was laid on a 'delaying' layer of low permeability material 1.5 m thick, and equipment provided for the speedy isolation of any spillages and the digging out of this layer. More complicated measures were adopted at an oil refinery in Cressier, Switzerland, which is located on a filled canal. Plant and tanks are sited on concrete basins. Seven wells have been drilled along the line of the filled canal to keep the water levels depressed beneath the plant to prevent natural outflow of contaminated groundwater, and as a further measure concrete and bentonite cut-off screens have been inserted to a low permeability layer at each end of the fill to prevent natural outflow. A code of practice, published by the Institute of Petroleum (1967) recommends measures for the avoidance of oil pollution which, if followed, will appreciably lessen the likelihood of oil losses, while a report by the same body (Institute of Petroleum 1972) sets out emergency procedures and action for dealing with inland oil spills.

Stockpiles of rock salt for de-icing highways constitute a potential source of pollution and the South Warwickshire Water Board (1972) instance a borehole in Keuper Sandstone in which an increase in chlorides from 30 to 375 mg/l over a period of nine years was attributed to this cause. It recommends that salt stockpiles should be housed in concrete holding bays and covered with polythene sheeting to exclude rainfall.

It can be seen that measures to prevent contamination arising from surface drainage and spillages are both diverse and necessary. The remedial works associated with the clearance of the contamination from organic solvents, described above, cost the Company nearly £200 000.

7. COASTAL SALINE INTRUSION

The major aquifers in the UK (the Chalk and Permo-Triassic sandstones) are partly bounded by coastal waters, (Figure 1). Saline intrusion has occurred in these coastal regions where large urban and industrial developments have made use of groundwater resources.

Along the Thames Estuary in Essex, between Purfleet and Tilbury, groundwater derived from riverside boreholes contains chloride up to 8000 mg/l, and is to be compared with the chloride in the river at low and high tide of 6100 and 10 200 mg/l respectively (Houghton 1962). Saline intrusion now extends along the line of the River Thames to central London, and reaches inland for a distance of approximately 4 km on the north side of the river and 1 km on the south side (Water Resources Board, 1972). On the south side of the Thames estuary in Kent between Northfleet and Gravesend, industrial abstraction from the Chalk outcrop for cement and paper manufacturing has produced a saline intrusion front, along a 3 km-wide shoreline, where chlorides exceed 1000 mg/l. Chlorides reach 2500 mg/l on both flanks of this front, of which the western one at Northfleet extends for a distance of 1.5 km inland.

On the east coast of England sea water has locally invaded the Magnesian Limestone beneath the industrial towns of Sunderland and Hartlepool. Further south in the Humber estuary serious saline intrusion has occurred beneath Hull and Grimsby. At Grimsby the Chalk is confined by Pleistocene boulder clay and superficial deposits totalling about 20 m in thickness (Gray, 1964). Between 1948 and 1957 public water supply and industrial abstraction increased from 40 Ml/d to 70 Ml/d. Over a period of 40 years the piezometric surface has been lowered by 7 m. In 1923 only isolated areas existed at Grimsby with a piezometric surface below sea level, but by 1962 this had increased to an area of approximately 3 km radius, with a depression to -10m OD in some parts where chlorides reach 6000 mg/l. Electrical conductivity measurements in boreholes have shown that a saline wedge has built up to 2 km inland, while the vertical profiles show sharp interfaces between the freshwater zone, an intermediate saline zone and a highly saline zone.

A similar situation is present on the north side of the Humber beneath Kingston-upon-Hull (Foster et al, 1976) where the estimated groundwater resources in the Chalk are over-committed. A zone of saline water of 1000 mg/l chloride extends along a coastal frontage beneath the city for 10 km and for a distance inland of 3 km. Although the area with groundwater of this salinity has not changed greatly since 1951, the area of mixed fresh and saline water has increased noticeably in 25 years. Geochemical analysis indicates that the salinity originated from the River Hull and the estuary which probably have access to the confined Chalk where sandy post-glacial river bed deposits lie directly on the Chalk.

Probably the most serious occurrence of saline intrusion in the UK is in the Permo-Triassic sandstones of the Mersey area of Lancashire, (Mersey and Weaver River Authority 1971, Hibbert 1956). In this area groundwater abstraction exceeds natural replenishment by up to 40% and in five districts (Liverpool, Warrington, Wirral, Gowry and Manchester) chlorides have now risen to between 2720 and 14 200 mg/l. In the Warrington and Manchester districts it is possible that the salinity is attributable to the upconing of groundwater at depth, possibly derived from the solution of evaporite deposits (Howell 1965). In the coastal districts bordering the Mersey estuary chloride concentrations up to 1000 mg/l occur for a distance of 2 km inland from the coast where they are associated with groundwater levels more than 25 m below sea level.

Along the east coast of Suffolk and Norfolk a wide belt of high chloride groundwater occurs in the Chalk beneath the overlying Tertiary and Quaternary deposits (East Suffolk and Norfolk River Authority, 1971). The impermeable deposits on the sea floor and the high piezometric levels in the Chalk indicate that this cannot be due to sea water intrusion but to connate sea water trapped in the deposits from an earlier geological period. However, some limited coastal saline intrusion does occur at Ipswich and at the mouth of the River Orwell at Felixstowe. The chlorides in a borehole located in the centre of the saline zone at Ipswich have increased from 194 mg/l in 1936 to 2020 mg/l in 1970. At Felixstowe four boreholes have chlorides ranging from 4000 to 11 000 mg/l, although the area of contamination is very restricted.

On the south coast of England around Brighton, Sussex, careful control of groundwater abstraction has prevented serious encroachment of saline water into the highly fissured Chalk aquifer. A number of boreholes within 2 km of the sea can have chlorides exceeding 300 mg/l, but since 1945, despite a large increase in the quantity of water pumped, a policy of controlled abstraction based on pumping inland 'storage' stations most heavily in the summer, and coastal 'leakage' stations in the winter, has prevented the situation deteriorating. A detailed account of the application of this technique for controlling saline intrusion is given in Section 10.2. This method offers a good solution to the problem where the aquifer outcrop is broad enough to permit the development of inland groundwater storage and when ownership and location of abstraction boreholes permit central control.

In the Isle of Thanet, East Kent, groundwater has been abstracted from the Chalk for public water supply since the early 1800s, but over-pumping between 1850 and 1900 caused several sources to be shut down (Rampling 1974). In Thanet the nine public water supply sources and their 13 km of headings (tunnels approximately 2 m high driven horizontally just below the water table) lie on a concentric arc approximately 2 km from the sea. Three of these are pumped only during the period May to September to meet the large holiday demand of the seaside towns of Margate, Ramsgate, and Broadstairs, which is 70% greater than the average daily demand. During the summer season chlorides can reach 250 mg/l in one borehole 1 km from the coast at Margate, but elsewhere a saline zone of up to 100 mg/l chloride is limited generally to between 1 and 2 km from the coast. The well and heading system was a highly favoured method of developing groundwater resources of the Chalk until about 1940. In Thanet the wells and adits penetrate the unconfined Chalk aquifer to a depth of only 3 m below the groundwater level and this has been instrumental in lessening the possibility of saline water entering the boreholes from greater depth.

The use of borehole recharge to reduce or control saline intrusion is, of course, used in many other parts of the world. It is not carried out in the UK although a desk study of the feasibility of using a line of recharge wells to the north of the Thames has been made (Water Resources Board, 1974). An experiment into borehole recharge was carried out in 1951 at an industrial plant in the Grimsby district (Buchan, 1955) when between February and April of that year about 70 megalitres was recharged into the confined Chalk at a rate approaching 3.0 Ml/d. The experiment ceased because of the high concentration of iron and titanium in the recharge water.

Scavenger pumps offer a technically attractive method of limiting inflow of saline water into abstraction wells (Long, 1965). The method can be used in a single borehole where the scavenger pumps are set at the bottom of the borehole, below a packer, with the less saline water being abstracted at the higher level. It is more suited to separately constructed boreholes penetrating the aquifer to different depths. The technique is not thought to have been used in this country to remedy sea water intrusion, but it has been used inland to deal with upconing mineralized water (see Section 9).

Coastal barriers involving impermeable curtains are not likely to be utilized extensively in this country because of the fissured nature of the aquifers. Steel sheet piling is, however, to be used later this year in an attempt to seal springs in the banks of the River Arun in Sussex. These are thought to be the points of entry by which, during high tides and low groundwater conditions, Burpham Pumping Station (Warren, 1972), 2 km distant, is contaminated by turbid water with chlorides reaching 300 mg/l.

Unlike many other sources of contamination, methods are available for lessening or overcoming saline intrusion. The use of a large number of dispersed smaller-yielding boreholes would allow a greater proportion of the seaward-flowing groundwater to be abstracted, and lessen the intrusion of localized tongues of saline water which can occur when a number of high-yielding boreholes are grouped together and large drawdowns develop. Where the aquifer is wide enough the intermittent use of inland storage stations and coastal wells (leakage stations) according to the seasonal variation in groundwater levels will reduce intrusion. Coastal barriers, whether by artificial recharge or impermeable curtains, are not thought likely to be widely adopted in the UK. Scavenger pumping offers a good method of lowering high chlorides in boreholes already suffering the effects of saline intrusion.

8. MINING ACTIVITIES

A wide range of minerals have been mined in the UK but of these coal predominates. Figure 2 shows the locations of the principal coalfields, stock piles of colliery shale, and power stations producing pulverized fuel ash, in relation to the outcrop of two principal aquifers in the UK, the Chalk and Permo-Triassic sandstones. The degree of coincidence is apparent.

The problems of the pollution of surface water from highly mineralized or acidic waters from both working and disused coal mines are well known. The mineralization appears to result principally from the oxidation of iron pyrites to ferrous sulphate and sulphuric acid. Pollution of groundwater may occur when a productive aquifer overlies coal measures and abandoned coal mines are flooded. Surface streams carrying mineralized mine drainage water may infiltrate and cause pollution of groundwater where streams flow over the outcrop of an aquifer and are influent. It has been reported (Cairney and Frost, 1975) that careful regulations of water levels in mine workings by pumping may be used to reduce the degree of mineralization in the discharged waters. This approach is clearly worth further investigation.

Of the 9 million tonnes per year of fuel ash waste produced by the power stations burning pulverized coal,about 3 million tonnes are disposed of in old workings or in lagoons. These have a countrywide distribution (Figure 2). Pulverized fuel ash, although considered to be relatively inert, contains about 2% soluble material and trace metals (for example, germanium and selenium have been recorded). Pollution may also occur from lagoons used to store effluent from coal washing plants.

About 50 million tonnes of colliery spoil are produced annually, the major proportion of which is tipped on land. It was estimated that in 1970 there were some 3000 million tonnes of spoil stock-piled, occupying some 15 000 hectares (Gutt et al, 1974).

A highly mineralized leachate can result, containing chloride, sulphate, iron and manganese, if the permeability of tipped material allows infiltrating rainfall to react with the unweathered spoil. If tips are located on an aquifer outcrop, leachate may enter the aquifer over a period of years causing long term progressive pollution. Nicholls (1972) describes such an occurrence in the Bunter Sandstone aquifer to the east of Doncaster.

Modern methods of constructing spoil heaps include the formation of a relatively impermeable base to the tip and provision of facilities for the collection, treatment, or safe disposal of the tip leachate and surface drainage. These measures should prevent the occurrence of major groundwater pollution problems from this source in future. However, there still remains the problem of the colliery spill tips which are already contributing a mineralized leachate to groundwater. Nationally the scale of the problem is difficult to assess as there are few tip sites where detailed investigations to establish the extent of the pollution have been made.

Where pollution of groundwater has occurred from coal mining activities and this threatens an underground water supply, it may be possible to remove the pollution by scavenging wells or contain it by controlling the hydraulic gradient with recharge wells or basins. Clearly, before adopting any such measures it is necessary to assess the present and future value of the endangered resource in relation to the cost and probability of success of any remedial works. Pollution of an area of the Kent Chalk resulting from coal mine drainage waters and the steps being taken to assess the rehabilitation prospects for this area of the aquifer are described in Section 10.3.

9. MINERALIZED WATERS IN INLAND AQUIFERS

Large volumes of mineralized water occur particularly in the Permo-Triassic sandstones (Mersey and Weaver River Authority, 1969; Bow et al, 1969; Crook and Howell, 1971; Anon. 1974; Severn-Trent Water Authority, 1975) but also in other aquifers in the United Kingdom. The origin of the high salinity content may be the remnant of an ancient depositional sea, a high sea level at some later geological time, or it may be due to widely disseminated or discrete layers of saliferous matter within the body of the aquifer or adjacent strata. Geologically recent freshwater recharge may have flushed out the saline water from near the surface of aquifer but it may still exist at depth or in zones where the natural movement of groundwater has been restricted.

An example of a typical situation in the Permo-Triassic sandstones is given in Figure 3 which shows a diagrammatic section across the Vale of York (Anon., 1974). Poor quality water with a high sulphate content is observed towards the west of the aquifer and is believed to be associated with gypsum layers within the Permian marls at its base. To the east, the Keuper Marl is thought to be responsible for the high sulphates, while the zone of water below the thick boulder clay has a high sodium chloride content. A somewhat similar picture has been observed in parts of the North Shropshire Permo-Triassic sandstones (Severn-Trent Water Authority, 1975).

With the abstraction of groundwater mineralized water moves into the formerly freshwater zones. A typical situation is shown diagramatically in Figure 4a. As the abstraction rate from the well is increased the cone moves progressively upwards until it may eventually be drawn into the well and contaminate the freshwater. If the pumping rate is reduced the mineralized water will, due to its density difference, tend to subside and the well may still be able to maintain a freshwater supply, albeit at a reduced rate. Ingress into the pores and fissures of the aquifer adjacent to the abstraction well may have occurred, however, and it may take some considerable time for the mineralized water to subside under the small density difference which is now the only driving hydraulic head.

Although contamination of supply wells due to this cause has been rather limited in the UK to date, it could develop as a problem in the future. A number of schemes have been and are being investigated to use groundwater resources for river regulation or conjunctive use purposes (Great Ouse River Authority, 1972; Thames Conservancy, 1972; Anon. 1974; Severn-Trent Water Authority, 1975). In such schemes the groundwater will be used intermittently as the need arises and while the long-term average rate of withdrawal will not exceed the natural recharge rate, during dry periods heavy demands will be imposed on groundwater storage and a major, albeit temporary, reduction in groundwater levels will occur. Such conditions favour the movement of mineralized water by upconing from depth or by lateral displacement as shown diagramatically in Figure 3. Clearly, well fields must be carefully designed in terms of well numbers, location and abstraction rates if such problems are to be avoided (Schmorak and Mercado, 1969). Monitoring boreholes close to the abstraction wells with their screen sections set in the deepest freshwater zone could be periodically sampled to reveal the onset of the intrusion of mineralized water. Should intrusion occur control measures such as changing abstraction patterns or rates may then be adopted. Artificial recharge could also be used to reverse the situation. It may be noted, however, that should mineralized water enter a well in such a scheme, it may possibly be utilized for river regulation or conjunctive use, due to the dilution it will receive, whereas it would be of unsuitable quality for a more conventional direct supply.

Saline water moves into a freshwater zone in response to an imposed pressure gradient and a means of control is to reduce the pressure in the saline zone. This can be accomplished by means of scavenger wells (Figure 4b). The method has been successfully employed in the Permo-Triassic aquifer of North Shropshire at the Woodfield Pumping Station (Tate and Robertson, 1971). There are three abstraction boreholes with depths between 65 and 95 m at the site, which was originally developed in 1930. Limited records on one of the boreholes show that the chlorides had increased from 266 mg/l in 1948 to 520 mg/l in 1965. Small capacity scavenger pumps were set in the bores below the main pump suction levels and following a series of experiments it was shown that a yield of 45 Ml/d to 60 Ml/d could be obtained from the main wells by pumping about 1 Ml/d to waste. At the Woodfield site the waste water was pumped to a local stream, but clearly in some situations the high chloride content of this water may present disposal problems. The waste water had a chloride content in the range 1000 to 1600 mg/l, while the supply water concentration was reduced from its original value of approximately 350 down to 158 mg/l. The report by Tate and Robertson stresses the importance of undertaking detailed hydrogeological measurements at the site including downhole geophysical logging and of understanding the flow mechanism before remedial measures are attempted. Surface geophysics have also been successfully used in determining the presence and defining the extent of saline water bodies (Severn-Trent Water Authority, 1975).

10. CASE HISTORIES

10.1. POLLUTION OF A WELL - POSSIBLE CAUSES

The case reported below in which a public water supply well suffered pollution is probably typical of many where the source of the pollutant may be a landfill site. The evidence is, however, by no means unequivocal and the source of pollution is only likely to be positively established by further site investigation.

A well has existed at the site in Surrey for more than 60 years. A geological cross-section (Figure 5) shows the Gault, a clay of low permeability, overlying the poorly cemented sands of the Folkstone Beds. The strata are relatively undisturbed and dip northwards at an angle of 2° to 3°. A major clay horizon 3 m thick occurs about 15 m below the top of the Folkstone Beds and this has been identified at the borehole site and in a sand pit at outcrop 380 m to the south of the bore (Dines and Edmunds, 1933). The clay layer appears to act as an aquiclude separating the sands into an upper and lower aquifer.

The modern borehole, which is about 600 mm in diameter, obtains water from 380 mm diameter screened and sand packed section in the Folkstone Beds which extends from 46.5 m to 96 m below ground level. The bore is used as a standby and has supplied water during the last 15 years on an intermittent basis at rates up to about 3.5 Ml/d. The transmissivity and confined storage coefficient of the Folkestone Beds have been estimated from pumping tests on the bore to be about 290 m^2/d and 3×10^{-3} respectively. Lithological and geophysical logs suggest the presence of a band of relatively higher permeability between 55 and 60 m below ground level and above the clay layer. Tritium concentrations in the pumped water more than doubled between 1966 and 1973 indicating that by 1973 some relatively modern water was being drawn into the bore.

In 1973 ammonia was detected in the borehole water and in 1974 a peak value of 3.0 mg/l was recorded and the water on occasions acquired an odour of 'onions'. Regular analyses are available from 1961 both for the polluted borehole A and nearby bore 1400 m to the west marked B in Figure 6. The rise in levels of potassium, alkalinity and ammonia (comparative results between boreholes A and B are shown in Table 2), all suggest that organic pollution has increased rapidly since 1971. Bacteriological samples have all proved satisfactory.

Table 2. Comparison of chemical analysis on samples from Wells A and B

		Well A mg/l	Well B mg/l
Calcium	Ca	101	-
Sodium	Na	21.5	-
Potassium	K	8.4	2.1
Alkalinity	$CaCO_3$	180	135
Sulphate	SO_4	112	85
Chloride	Cl	29.2	22
Nitrate	N	4.97	8.4
Nitrite	N	0.02	-
Ammonia	N	1.22	Zero
Phosphate, total	P	0.222	0.3-0.4
TOC	C	4.3	-
Anionic detergents	Manoxol OT	0.2	-

A number of possible sources of pollution were examined (Figure 6) as follows.

(a) A sandpit in the Folkestone Beds of 20 hectares, of which 12 hectares are filled with 650 000 tonnes of domestic rubbish. Tipping at this site commenced in 1960. Sand had been excavated to the top of the clay layer (Figure 5), and the exposed northern wall of Folkstone Beds rises 12 to 15 m and is unprotected. Although a careful sanitary tipping regime was specified in the consent conditions it appears from inspection that the standard of tipping declined over the years and there is some doubt whether the refuse is entirely of domestic origin.

(b) A small sewage works with a throughput of 25 m^3/d discharges its effluent to the bed of a local stream and its sludge to an adjacent field. Despite this the stream showed only slight contamination when samples were taken in 1974.

(c) The mucking of a small stables is piled some 150 m from the head of the borehole. This appears to drain to a generally dry ditch which joins the stream that flows past the sewage works mentioned above.

(d) The surrounding fields (Figure 6) have had applications of inorganic fertilizers, including ammonia, over the past few years.

(e) It is likely that there are a number of disused wells in the area and the local people recall the presence of 'two rain-water sumps 80 feet deep' which have been filled in and their positions are now lost.

Simple calculations based on the abstraction history of the bore and the aquifer properties show that some of the water now entering the bore will have originated from the outcrop area adjacent to the domestic landfill within the last ten years or so, and this would seem to be confirmed by the tritium measurements previously referred to.

It is difficult to be categorical about the source of pollution. The sewage works has been operating over a long period of time and the effluent could have been drawn in from the lower reaches of the stream at a time when its quality may have been at a lower standard than it is today. The riding stable effluent and muck-out is likely to contain high concentrations of potassium and ammonia but the small local nature of both these potential pollution sources and the thick cover of impervious Gault above the borehole make them unlikely contributors. Fertilizer applications to the fields have not caused pollution of the stream and it is difficult to see how they could pollute the aquifer. Only one field (No. 6) is on the outcrop, the others being on the Gault. If fertilizer applications are the source of pollution then some explanation must be found for the rise in level of TOC in the borewater and the rise in hardness and alkalinity; factors which are more commonly associated with domestic refuse tips, sewage works and feed lots. There is no direct evidence of the abandoned 'boreholes' and if they are present there is little chance of finding them. If they do exist they could of course provide an easy path for the entry of pollutants to the Folkestone Beds.

The calculations of the rate of movement of groundwater suggest that the waste in the sandpit is potentially a major source of pollution. Increasing potassium concentrations and the potassium/sodium ratio in the bore-water point to domestic refuse as a possible source as does the high ratio of ammoniacal to nitrate nitrogen in the tip leachate which could explain the changes in concentration of ammonia and nitrate in the bore water.

The case described is like many others in that although the waste in the sandpit appears to be the source of the pollution, this cannot be positively established without additional investigations including the drilling of observation boreholes between the borehole and the sandpit site (Figure 6) and a series of controlled pumping tests. If the landfill could be established at the source of pollution it might be possible to use one or two scavenging boreholes to intercept the polluted groundwater (Figure 6) in addition to improving drainage facilities at the landfill site, and so rehabilitate the existing groundwater source.

10.2. CONTROL OF SALINE INTRUSION IN THE SOUTH DOWNS COASTAL CHALK AQUIFER

The Chalk escarpment of the South Downs extends for a distance of 95 km, of which the most eastern 45 km in Sussex is bounded directly by the English Channel. The Chalk dips due south at an angle of 2^{o}. At the coast the Upper Chalk, a flinty fine-grained fissured white limestone, reaches a thickness of 210 m and is underlain by the Middle and Lower Chalk, each being approximately 60 m thick. Over 50% of the population of the counties of East and West Sussex live in seaside towns of which the largest are: Brighton (162 000), Hove (73 000) and Worthing (81 000)(Figure 7). The South Downs are dissected by a number of tidal rivers into isolated 'blocks', and the problems of saline intrusion encountered in the Brighton Chalk Block, which lies between the rivers Adur and Ouse, are described below.

The first pumped water supply in Brighton was provided in about 1825 when a new well was sunk to the north of the town, nearly 2 km from the sea. In 1853 a heading was added to this well which, together with a second well and adit system constructed in 1872, supplied 13 Ml/d to a population of 103 000 people. By 1918 Brighton Corporation had constructed, or taken over, six more sources of supply in and around Brighton, Hove and Shoreham, which provided 33.6 Ml/d. No further wells were sunk until 1936, when following a most severe dry spell in 1932-34 a new source at Balsdean, yielding 27 Ml/d, was commissioned. Since 1936 the demand for water has risen from 43 Ml/d to the present demand of 90 Ml/d, and this is now met from a total of twelve boreholes and well sources. The demand is likely to reach 125 Ml/d by the end of the century.

Since its introduction in 1872 the Goldstone well, located 2 km from the sea, has experienced problems with high chlorides. These have risen to 600 mg/l when the output of the station reached 27 Ml/d. The problem lessened when additional stations were introduced between 1900 and 1910. Similar problems were encountered at the Balsdean well, 10 km to the east of Goldstone and 2.5 km from the sea, during the dry year of 1949. At this time the station was being used to meet summer demand in Brighton and chlorides reached 300 to 400 mg/l. Studies of the groundwater flow into the boreholes at Balsdean were carried out between 1957 and 1961 (Warren, 1962) and it was established that during periods of low groundwater levels the chlorides exhibited a cyclic pattern which had the highest amplitude and reached the highest levels during spring tides. It was shown that pumping at high rates during periods of low groundwater level drew saline water into the borehole via one or two fissures only, of which the one at -21m OD was large enough to provide nearly the total supply of the well.

It was realized in 1945 that the rather haphazard way in which the wells were operated would have to be modified. A system was adopted in which heavy groundwater abstractions were imposed on the coastal wells during the winter and the burden of the summer abstraction was shifted to wells further inland. These coastal wells abstracted surplus winter water which would otherwise discharge into the sea and were termed 'leakage stations', while the inland wells utilized groundwater storage and were termed 'storage stations'. In order to control the abstraction data on pumping, reservoir levels were telemetred on a sequential scan basis to a central control point. Since this was installed in 1957 the leakage stations are pumped heavily through the winter and into the spring until chlorides reach approximately 100 mg/l. At this point the quantity abstracted is reduced, but is increased at the storage stations where groundwater levels have been allowed to rise during the recharge period. The same principle applies to wet and dry years with as much groundwater being pumped from the leakage stations as possible to conserve groundwater storage (Figure 8). As a result of this controlled abstraction, groundwater levels in the Brighton area have recovered by up to 5 m in the last 20 years, despite the 25% increase in consumption.

By 1972 the amount pumped annually represented 48% of the average annual recharge considered to be available for abstraction (150 Ml/d) and 97% of that in a 2% drought period. With a 50% increase in demand forecast by the year 1991 it was clear that detailed studies were needed to establish the full yield of the South Downs while at the same time controlling saline intrusion. A programme of investigations was initiated involving theoretical resource studies, thermal infra-red linescan aerial surveys, drilling and borehole logging, and mathematical modelling (Sussex River Authority, 1973).

In February 1971 a thermal infra-red linescan aerial survey was carried out along the Sussex coast between Bognor Regis and Eastbourne (Davies, 1973; Brereton and Downing, 1975) to try to detect fresh-water springs arising in the foreshore below low-water mark. No submarine springs were identified but numerous springs were detected on the foreshore around the low-water mark. They were found to be issuing from the Chalk through overlying superficial deposits, particularly west of the River Adur where groundwater is thought to be diverted by the edge of a syncline of Eocene strata. The picture which emerged was that groundwater discharges on the foreshore through a multitude of small fissures and that groundwater is moving towards the sea on a broad front.

The geophysical logging of coastal boreholes, started by the former Water Resources Board, is now being continued and extended by the Water Research Centre (Monkhouse and Fleet 1975). As part of the investigation, six 200 to 250 m deep boreholes were sunk within 500 m of the Brighton shoreline. Formation resistivity, temperature, differential temperature, and fluid conductivity logs have been run as part of a continuing programme, but the nature of the saline intrusion has been most clearly demonstrated by the fluid conductivity logs. The picture which has emerged is one of fresh water flowing seaward, and salt water moving landward along discrete horizontal fissures which can extend to a depth of approximately 100 m below sea level. One borehole, for instance, showed that saline water is moving inland along four distinct fissure zones between 70 and 130 m below the surface but that the Chalk between the zones is relatively fresh (Figure 9). Below a depth of about 130 m the geophysical logging suggests that a stagnant but predominantly fresh-water zone exists. Analysis of seasonal changes in salinity in these boreholes shows that the salinity increases in response to the natural depletion of groundwater storage of the Chalk during the summer, and can respond rapidly to changes in the abstraction rate from wells located as much as 6 km inland.

A mathematical model has been constructed of the Brighton Chalk Block (Nutbrown 1975; Nutbrown et al 1975) which has been of value in understanding the response of the aquifer to seasonal recharge and the patterns of abstraction. The model paints a rather pessimistic picture of an aquifer of high transmissivity (1000 m^2/d) and relatively low storage coefficient (2%) (but typical of the Chalk) in which the rate of groundwater outflow from the catchment is sufficiently rapid so as not to allow inland groundwater storage to be utilized during dry years to the extent which was hoped. Nevertheless, as more water level and pumping test data become available, it will be possible to refine the model and use it to provide guidance on the present and future management of the aquifer.

10.3. CONTAMINATION OF A CHALK AQUIFER FROM MINE DRAINAGE AT TILMANSTONE, EAST KENT

Between 1906 and 1973 Tilmanstone Colliery disposed of mine water onto the ground surface at a number of points around the Colliery, and this seeped into the Chalk. Approximately 13 km^2 of the unconfined Chalk aquifer has become contaminated, and in an area of near-fully committed groundwater resources it is desirable to see if the aquifer can be rehabilitated.

The Coal Measures lie in an elongated basin 100 km^2 in an area which plunges gently south-eastwards beneath the coast (Forster Brown 1922). Three water-bearing sandy formations abut directly onto the Coal Measures. These are the Lower Oolites of the Jurassic series and the Folkestone Sands and Hastings Beds of the Cretaceous series. Gault Clay 50 m thick separates and, it is believed, effectively seals these underlying strata from the water-bearing Chalk.

When the first shafts were being sunk at the Tilmanstone Colliery between 1907 and 1913 flows of 1.4 Ml/d were encountered in the Folkestone Sands and 10.8 Ml/d in the Oolites. Attempts to open up new coal faces in 1914 and 1922 encountered large inrushes of water which have been a serious and continuing problem at Tilmanstone. Even in 1962 11.8 Ml/d was being pumped from the mine, of which 9.8 Ml/d was derived from the shaft and the remainder from the coal workings themselves. Workings of the Kent No. 6 (Millyard) Seam since 1952, at a depth of 450 m below the No. 1 seam has produced less water but of greater salinity (Plumptre 1959).

Precise data on the pumped quantities and chloride contents is scant but Figure 10 shows trends in both parameters from 1906 to 1973 when the discharge onto the Chalk, of all but a very small quantity, ceased. Using these figures it is estimated that the total quantity of chloride discharge onto the Chalk is 318 000 tonnes.

The sites at which the mine water was discharged are located approximately 10 km from the coast,and groundwater flow spreads in a north-easterly direction discharging as base flow in the North and South Streams. These streams then join and flow over alluvial flats before discharging to the sea at Sandwich. The assessment of natural recharge to these streams indicates that virtually no underflow occurs beneath the superficial coastal deposits. Since 1961 the chlorides in the streams have risen from about 100 to 230 mg/l (Figure 11). The limited data on flows and chloride concentrations prohibits other than a crude estimate of the amount of chloride which has discharged from the aquifer via streamflow; however, calculations indicate that 47 000 tonnes of the pollution has been lost in this way, only 15% of the quantity discharge from the mine.

Determination of three-dimensional distribution of chlorides in the Chalk aquifer is difficult. Twice-yearly groundwater salinity surveys have been carried out since 1948 in an area of 90 km^2 around the Tilmanstone Colliery and the nearby Snowdon Colliery. Water samples have been obtained from 70 wells and springs. These surveys show that the contamination has spread from the points of discharge, and 13 km^2 of the surface of the aquifer is contaminated with chloride in excess of 750 mg/l (Figure 12). At the nearest sampling point to the discharge lagoons chlorides reach 5800 mg/l. A clearer picture of the three-dimensional extent of the contamination resulted from a surface resistivity survey which showed that the surface topography has had a strong influence on the movement of the discharged mine drainage.

A total of nine boreholes have been drilled at three separate sites, in order to understand more about the three-dimensional distribution of the contamination in the aquifer. One of these, at Eastry, is an 840 mm diameter production borehole. The boreholes were sunk to depths of 50, 100 and 150 m. Resistivity logs in the first hole indicated three zones of differing salinity and consequently casing was inserted to depths of approximately 20, 60 and 115 m. Pore-water samples from the Chalk showed that in the 100 m deep borehole at the site closest to the discharge point chloride concentrations varied from 4900 mg/l near the surface to 1180 mg/l at 85 m depth. In the 150 m deep hole at the same site the pore-water chloride concentration decreased from 1400 mg/l at 35 m depth to 100 mg/l at 130 m depth.

Each of these boreholes was pumped for one week between November 1975 and January 1976. Only minor fluctuations in chloride concentration occurred during this period. There was thus no evidence that the concentration of chlorides in one layer changed in response to pumping from a different layer. From the results of the various analyses shown in Table 3, it is seen that the chloride concentrations in pore-water were approximately half those in fissure water.

Table 3. Details of observation boreholes - Tilmanstone rehabilitation study

Site	Borehole No.	Depth (m)	Lining depth (m)	Depth to water table (m)	Chloride concentration during week test (mg/l)			Aquifer properties for test pumping rate of 54.6 m^3/d	
					Start	End	Porewater sample	Storage coefficient	Transmissivity (m^2/d)
Thornton Farm	5	36	24	12.8	2880	3100		0.47	63
	1	100	55	12.8	2150	2250	1180	0.35	184
	6	148	130	12.3	330	390	112	17.7	0.9
Lower Venson Farm	3	46	20	6.0	1170	1180	490	6.8	2.4
	4	90	65	6.8	1600	1600	955	0.4	143
	2	150	100	6.8	590	560		1.2	29
Eastry	8	30	10	6.5	1620	1600			
	7	73	30	6.3	820	800		20.0	0.9
	9	76	30	5.5	1600	1605			

While much has been learned about the extent and nature of the contamination in the aquifer, it is not possible to evaluate the potential for rehabilitation until prolonged pumping tests have been undertaken. A pumping main is being laid to allow the contaminated groundwater to be removed from the site and the production borehole to be pumped at a rate of 4.5 Ml/d. It will then be possible to determine whether the chlorides are rapidly removed from the Chalk.

An analogous situation has occurred at a nearby Southern Water Authority abstraction well lying in the path of a contaminated plume from the Snowdon Colliery. This ceased to discharge onto the Chalk in 1935 when a river outlet was constructed. Since then the rate of pumping from the well has increased from 8.4 to 22.7 Ml/d while the concentration of chlorides in the abstracted water has diminished from 270 mg/l to 48 mg/l. This latter value is close to the natural level of chloride in the Chalk of this area. The chloride concentration has decayed exponentially over a period of 40 years. In the Eastry borehole, with its initial chloride concentration of 1600 mg/l and which behaves in a similar way, a considerable amount of pumping may be required to rehabilitate the aquifer.

Once the pumping of the Eastry production borehole has been carried out for several months it should be possible to assess whether the aquifer can be rehabilitated and how this could best be achieved. Water may be disposed of in three ways; piped into the sea through the new main, discharged into the rivers as compensation flow, or abstracted for supply. A biological survey of the North and South Streams indicates that discharge of groundwater containing up to 500 mg/l chloride, and possibly 1000 mg/l chloride, should not have too adverse an effect on animal and plant life.

The results of the pumping tests are eagerly awaited and if the aquifer can be successfully rehabilitated the techniques will have application elsewhere.

11. CONCLUSIONS

1. Sources of aquifer contamination can be grouped into two broad categories having either (a) a local or (b) a regional effect.

   (a) Local contamination can result from spillages and surface drainage, certain agricultural activities such as silage clamps, sewage effluent discharges and landfill sites. These may, without warning, pollute individual wells and boreholes.

   (b) Regional contamination may gradually develop from sewage effluent discharges, agricultural activities such as the application of inorganic fertilizer and ploughing in of certain crop residues, and saline intrusion.

2. Two principal measures can be adopted to protect aquifers from contamination: (a) containment at source prior to entry into the aquifer, or (b) containment by controlled groundwater pumping.

   (a) Local sources of pollution can be controlled by proper construction and maintenance of containers, pipelines, etc or isolation and treatment of effluents. For example, fuel storage tanks can be bunded and oil interceptors installed for highway drainage. Septic tanks can be emptied regularly and cesspools made watertight. Landfill sites can be appraised more thoroughly from a hydrogeological point of view, preventive measures taken if need be, and tipping can be more closely supervised. No measures will entirely eliminate groundwater pollution, but the incidence of pollution can be greatly reduced.

   (b) On a regional scale measures using controlled groundwater pumping, for instance to prevent saline intrusion, may require very large capital investment in resiting boreholes, mains networks and service reservoirs. In other cases, for example nitrate pollution, such preventative measures may be inapplicable.

3. Rehabilitation of aquifers, and the replacement of contaminated wells and boreholes, is almost always expensive and time consuming. Success is frequently uncertain. In addition disposal of the contaminant may present problems. The cost of a thorough hydrogeological investigation, and of properly designed and constructed protective measures will invariably be a fraction of the penalties of ignoring them.

4. Aquifers are now under a great deal of pressure; for water abstraction, for waste disposal sites and for mineral extraction. Schemes for developing groundwater resources on a regional scale are being tested, or being introduced, in several parts of the country. These involve the sinking of a large number of boreholes on the aquifer outcrop, which will be more vulnerable to the many varieties of groundwater contamination. It will therefore be necessary for the water authorities to work in close collaboration with local authority planning and highway departments, and the waste disposal authorities, to agree measures which will prevent contamination of existing and new underground water supplies.

5. The new Control of Pollution Act 1974 will allow water authorities to define 'protective zones' for aquifers. Protective zones, centred on abstraction wells, have been adopted in a number of European countries, within which a range of activities likely to lead to pollution is prohibited (Food and Agriculture Organization of UN 1964, Noring 1974). Such measures have not been adopted on a formal basis in this country and water authorities will consider carefully the desirability of their introduction and their efficacy. The latter factor is particularly relevant in the UK where the most important aquifers are fissured and where complex hydrogeology or high rates of groundwater flow could nullify the merits of a prescribed protective zone.

6. Water authorities will need to consider whether certain minor aquifers can be 'written off' to provide waste disposal sites, and the merits (financial and environmental) of rehabilitation of already-polluted aquifers.

7. Advantage can be taken of the increased understanding of the hydrogeological and physio-chemical processes governing the movement of contaminants through aquifers that have been aquired in recent years and of the mathematical models that have been developed. The level of laboratory and field investigations and the effort in modelling will clearly depend on the size and importance of the source or of the aquifer unit that is under consideration. With a single well a simple flow analysis is perhaps all that is required, whereas with developments involving many wells more detailed field and laboratory studies and sophisticated modelling may be needed so that the overall cost of control measures or remedial works may be kept to a minimum. All this must be based on a first-rate monitoring network to procure the maximum amount of data and to act as an early-warning system for deteriorating groundwater quality.

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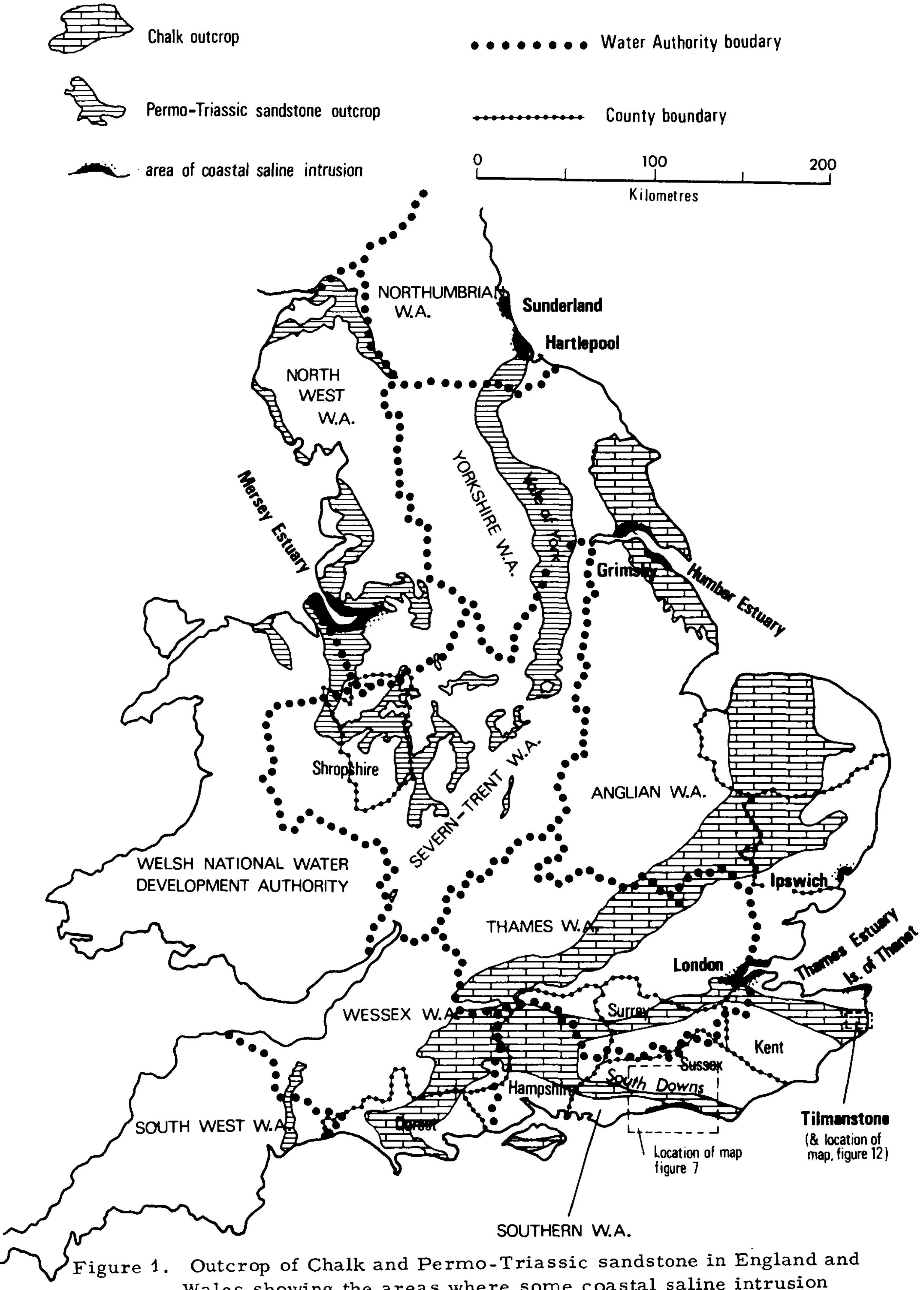

Figure 1. Outcrop of Chalk and Permo-Triassic sandstone in England and Wales showing the areas where some coastal saline intrusion has occurred and other important place names referred to in the paper

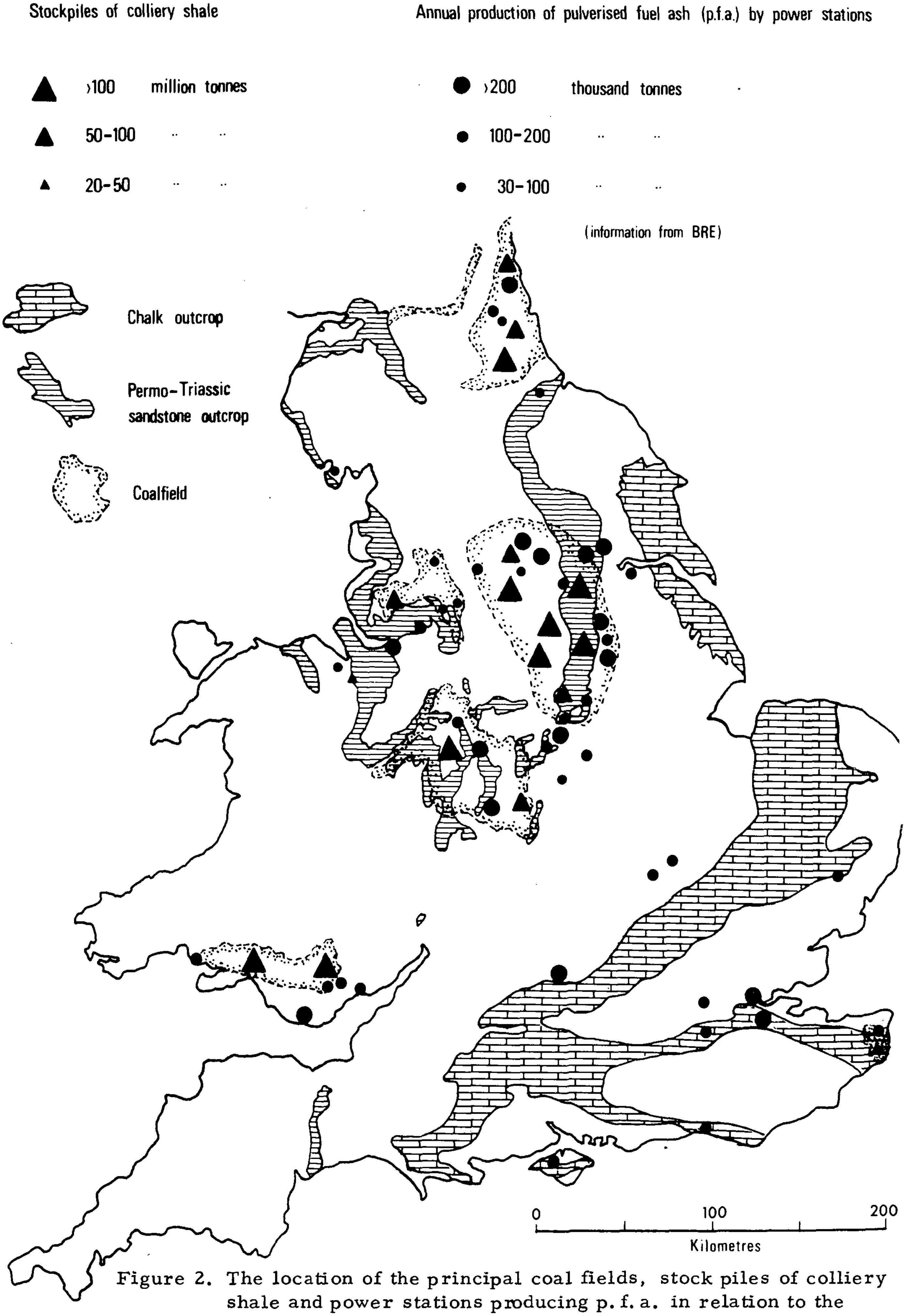

Figure 2. The location of the principal coal fields, stock piles of colliery shale and power stations producing p. f. a. in relation to the Chalk and Permo-Triassic sandstone aquifers.

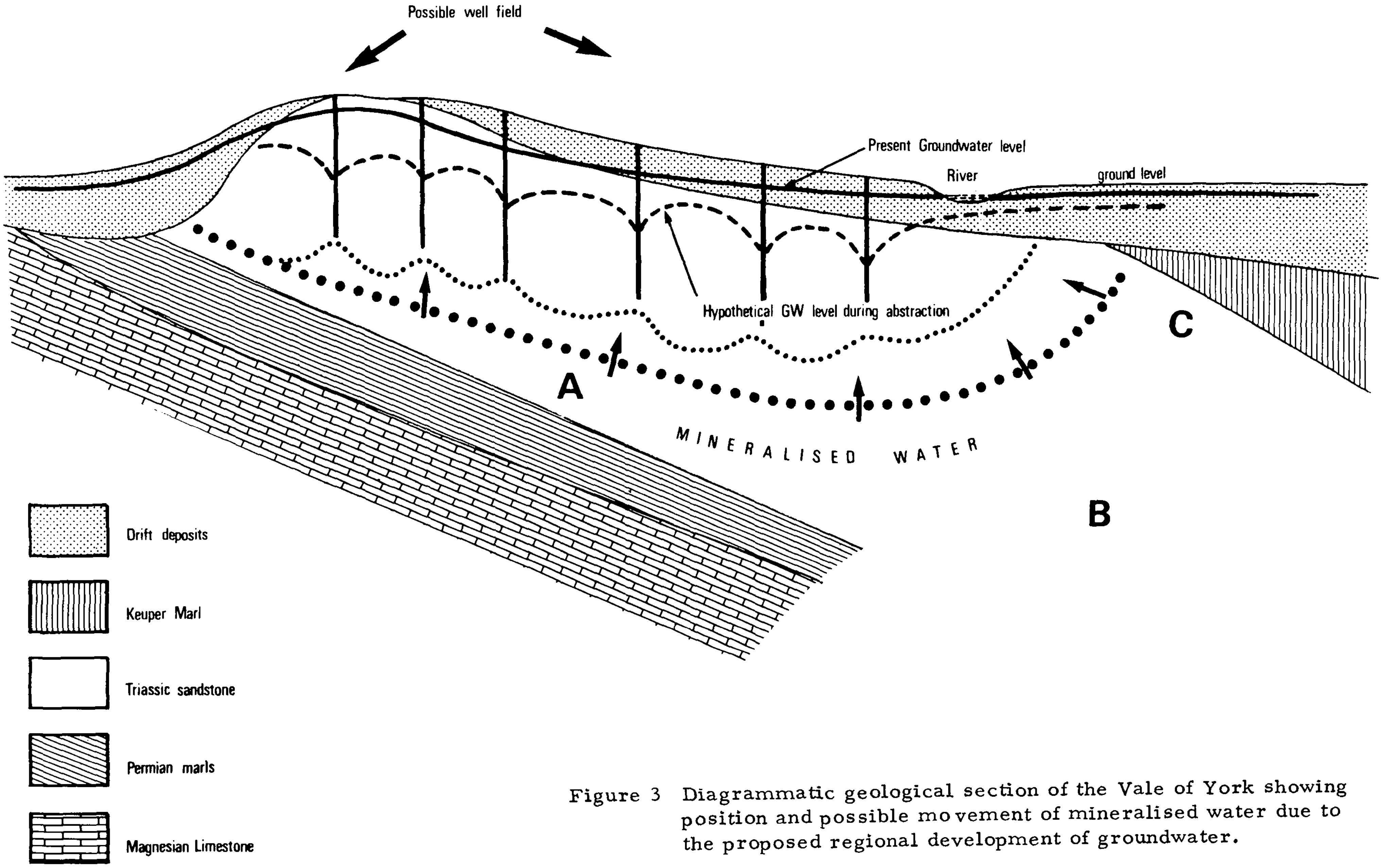

Figure 3 Diagrammatic geological section of the Vale of York showing position and possible movement of mineralised water due to the proposed regional development of groundwater.

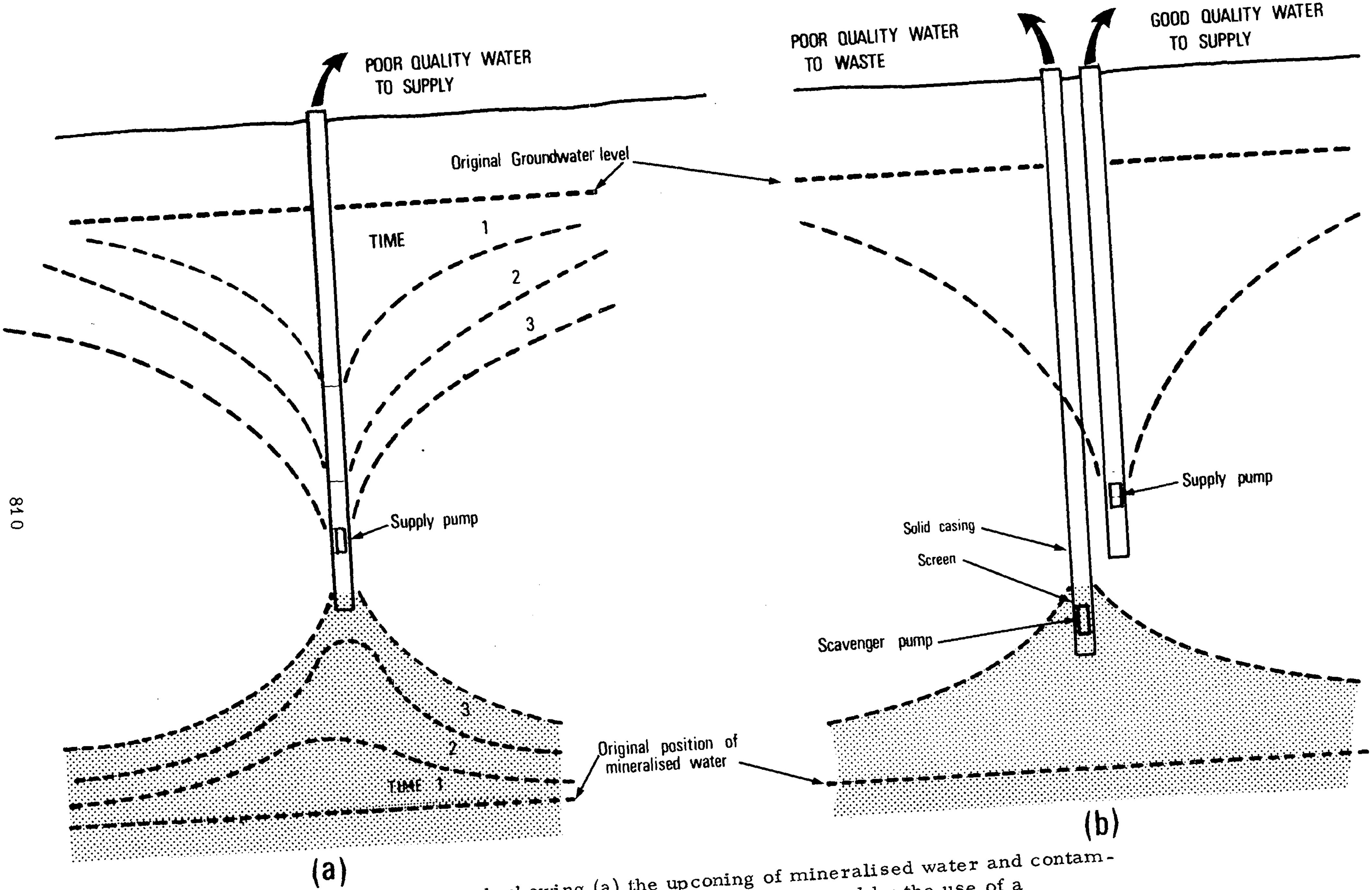

Figure 4 Sketch showing (a) the upconing of mineralised water and contamination of a supply well and (b) its control by the use of a scavenger pump

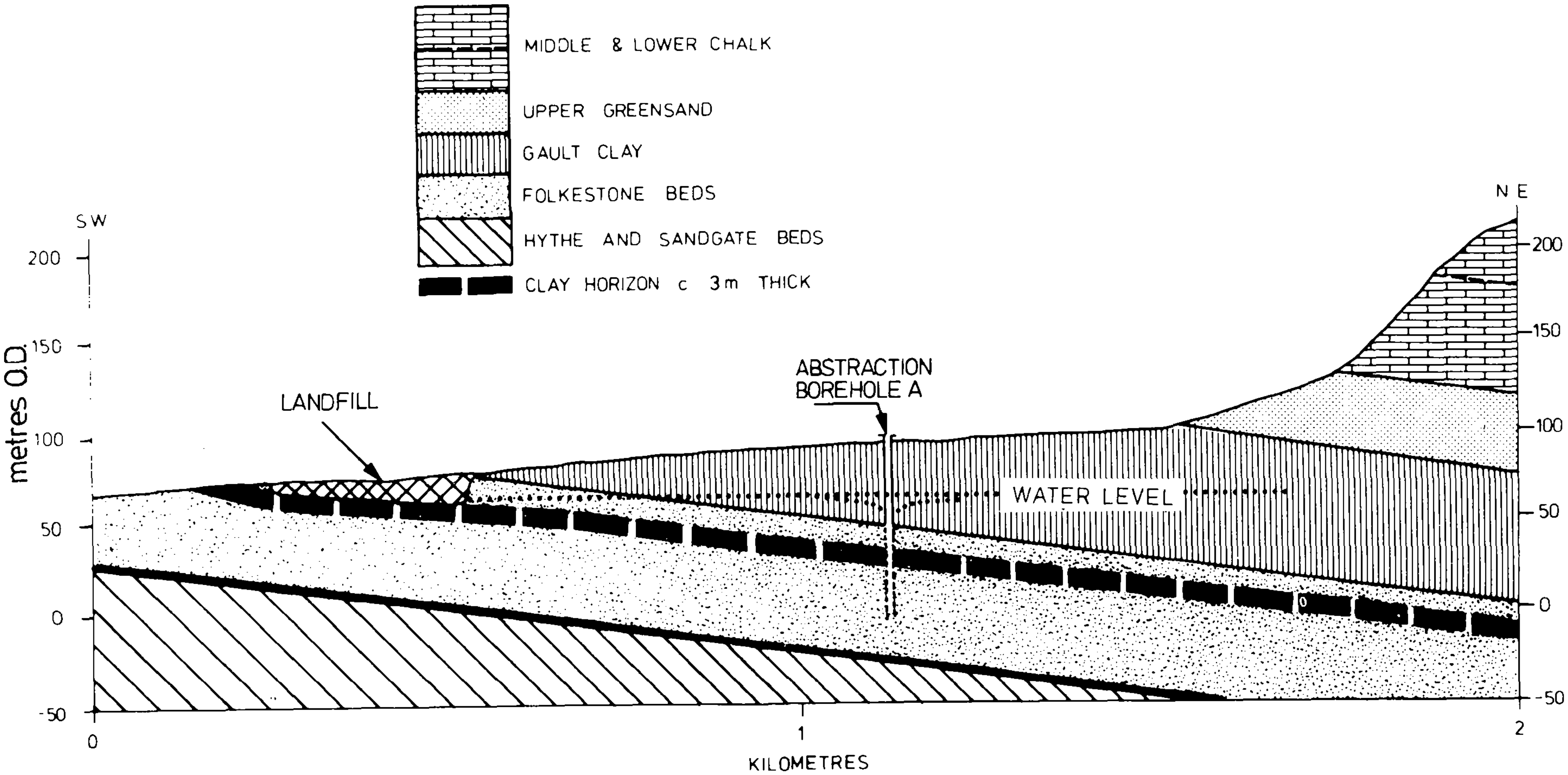

Figure 5 Geological section between abstraction borehole A and the landfill site

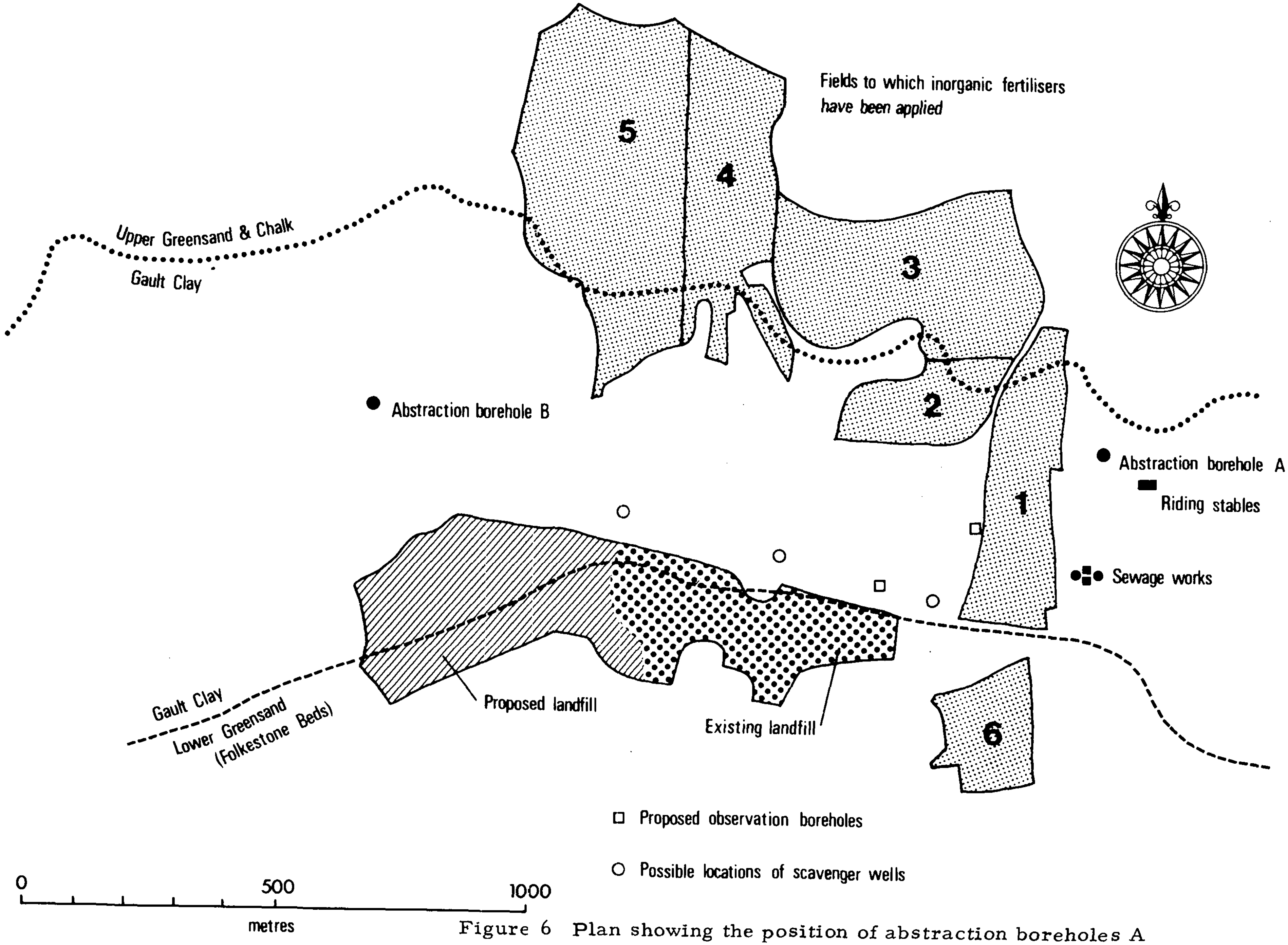

Figure 6 Plan showing the position of abstraction boreholes A and B in relation to landfill site, sewage works and riding stables

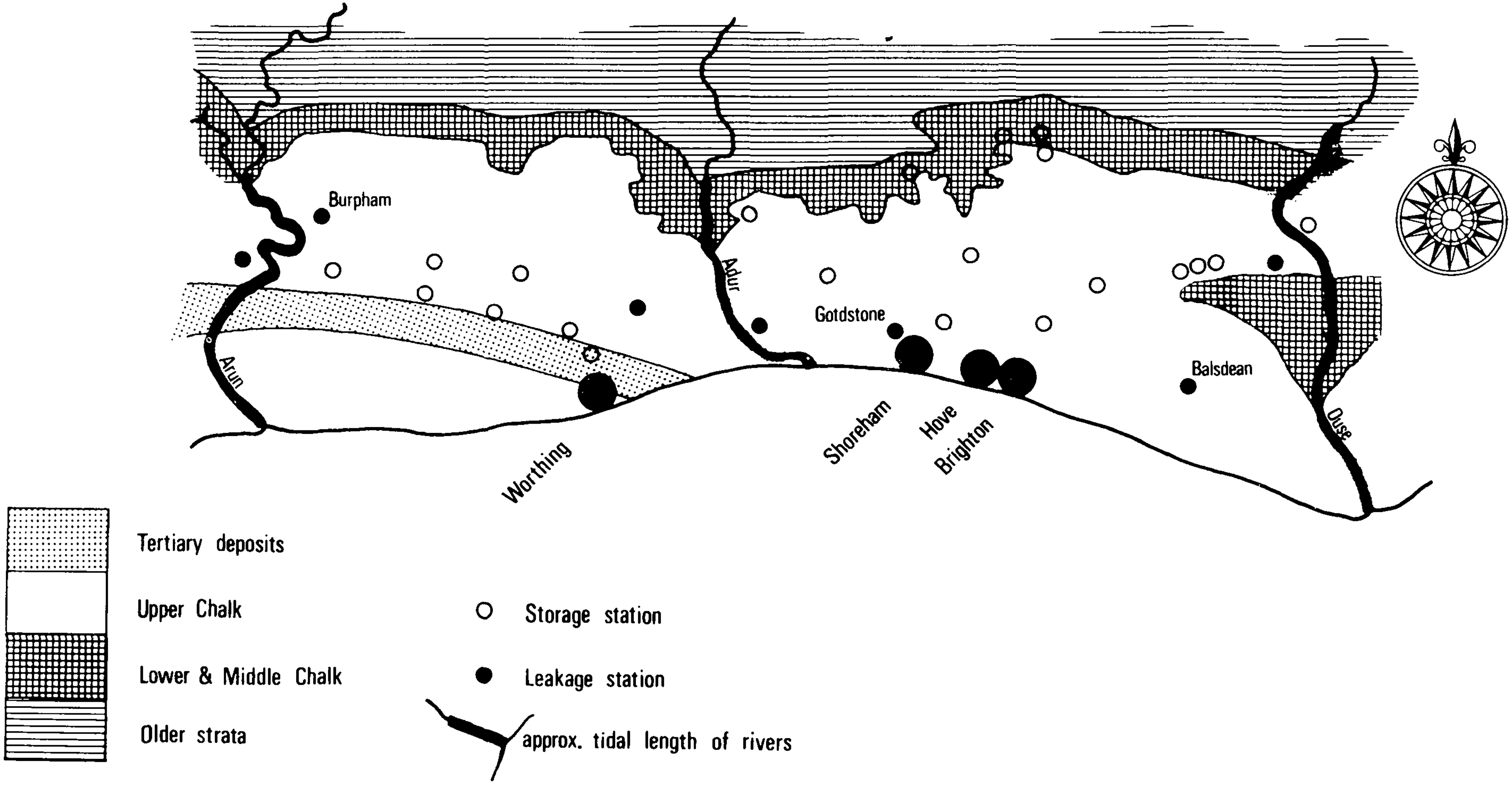

Figure 7 'Leakage and Storage' stations along part of the South Downs of Southern England (For location see Figure 1)

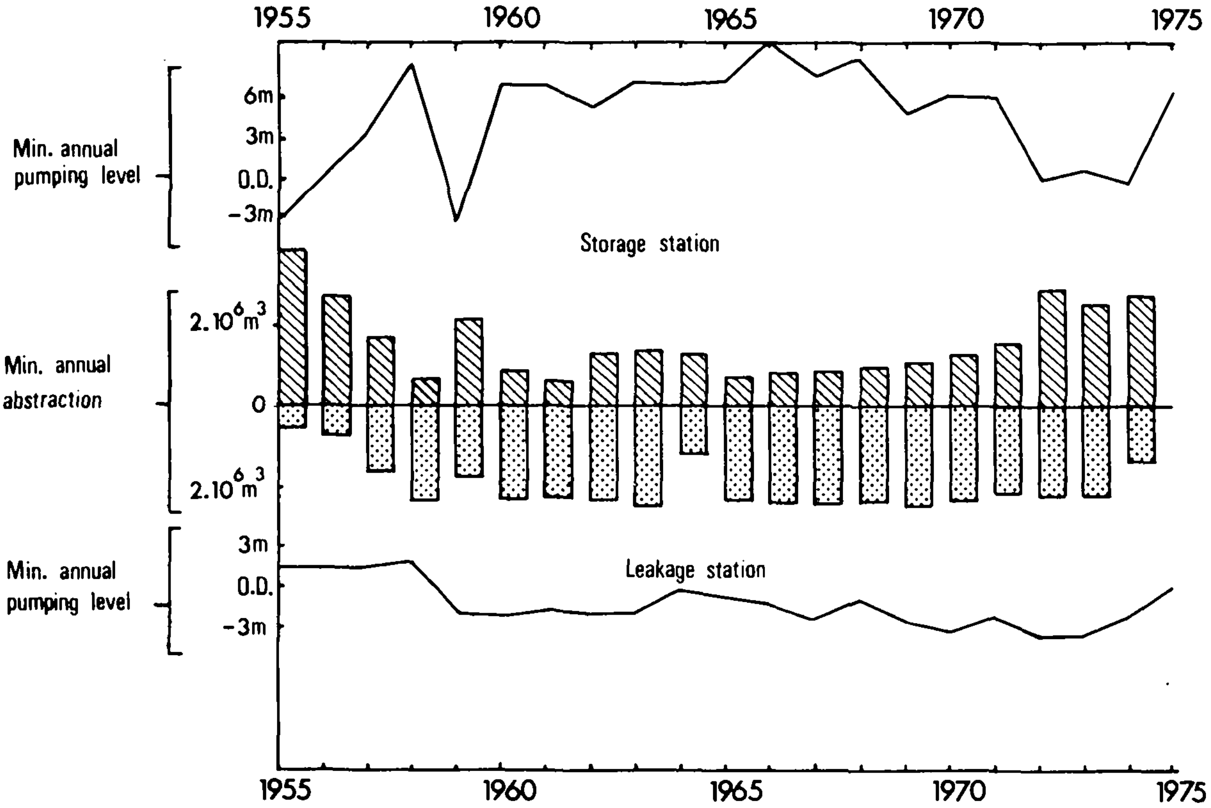

Figure 8 Pumping volumes and water levels in two typical 'storage and leakage' pumping stations - South Downs

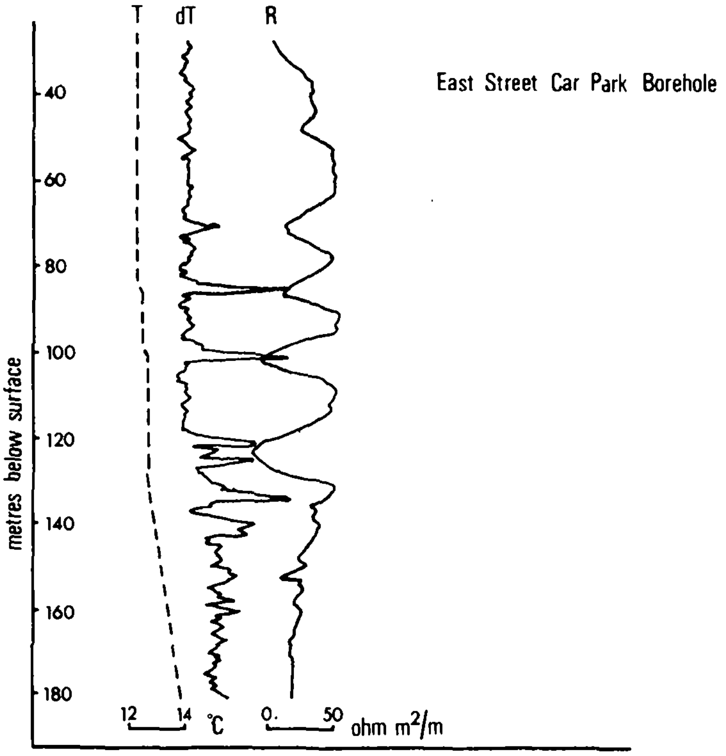

Figure 9 Temperature, differential temperature and formation resistivity logs (T, dt, R) in a coastal borehole at Brighton (after Monkhouse and Fleet, 1975)

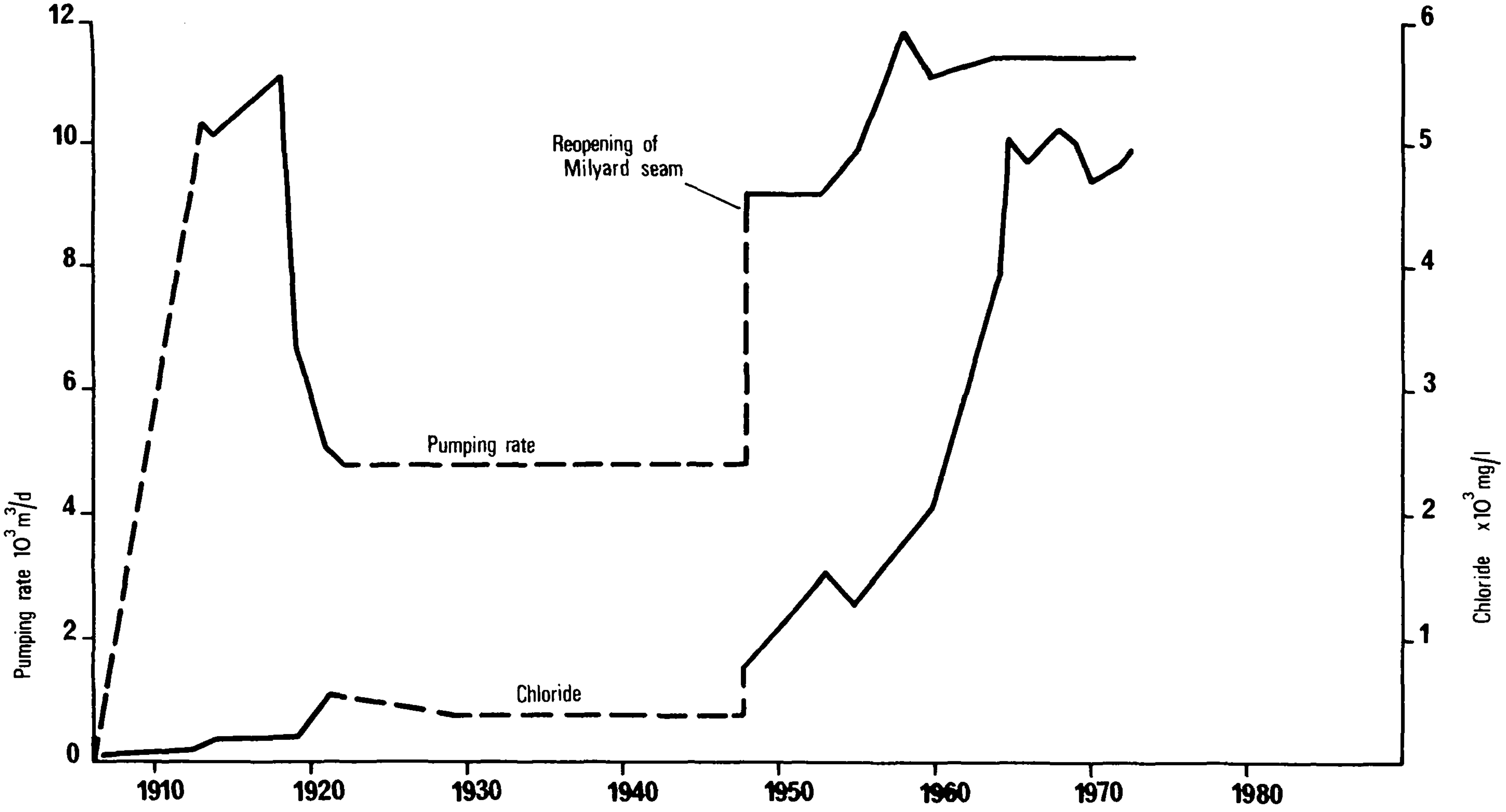

Figure 10 Rates of pumping from Tilmanstone Colliery and Salinity of Minewater

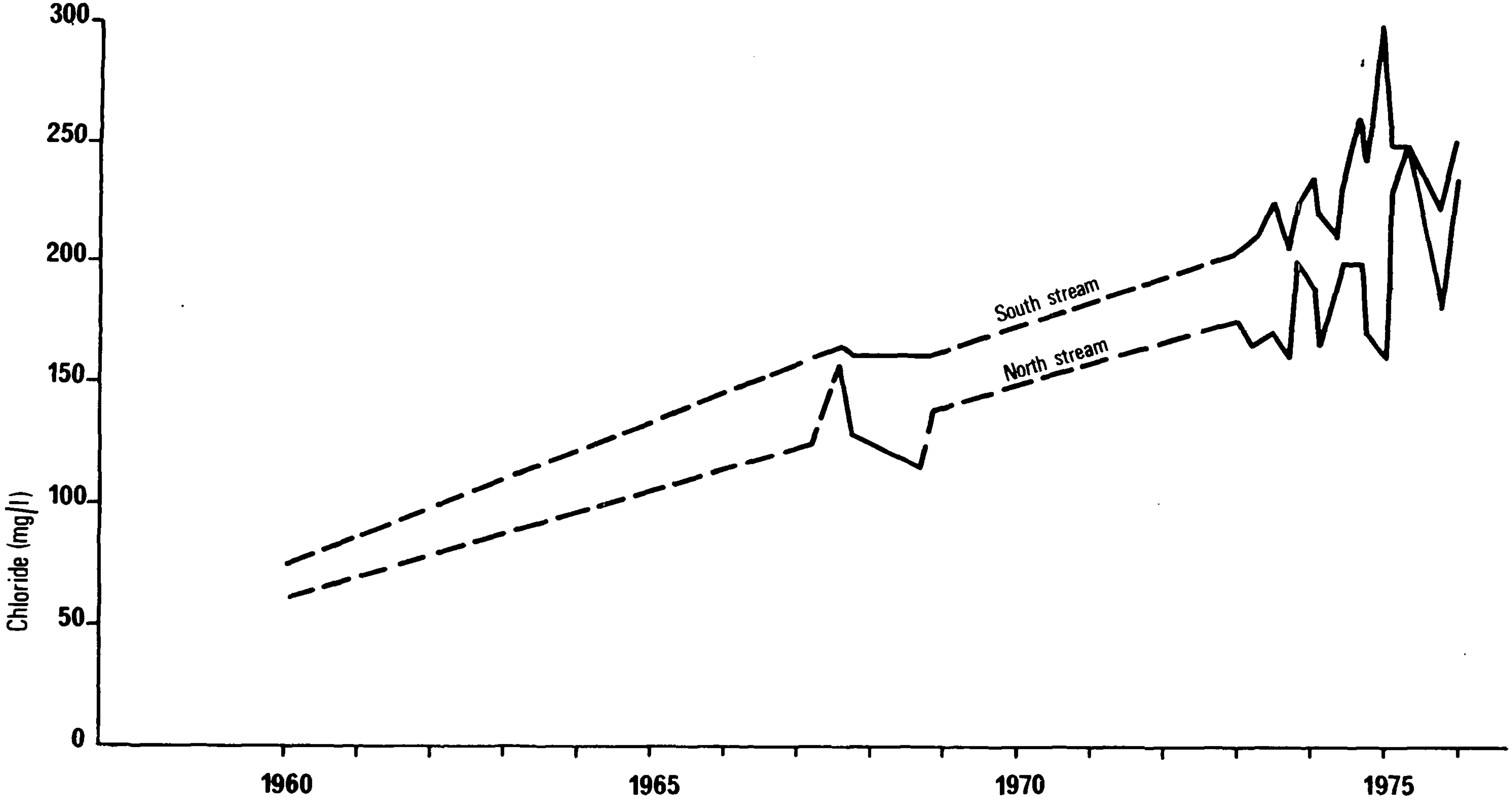

Figure 11 Chloride concentrations of North Stream and South Stream - Tilmanstone Investigation

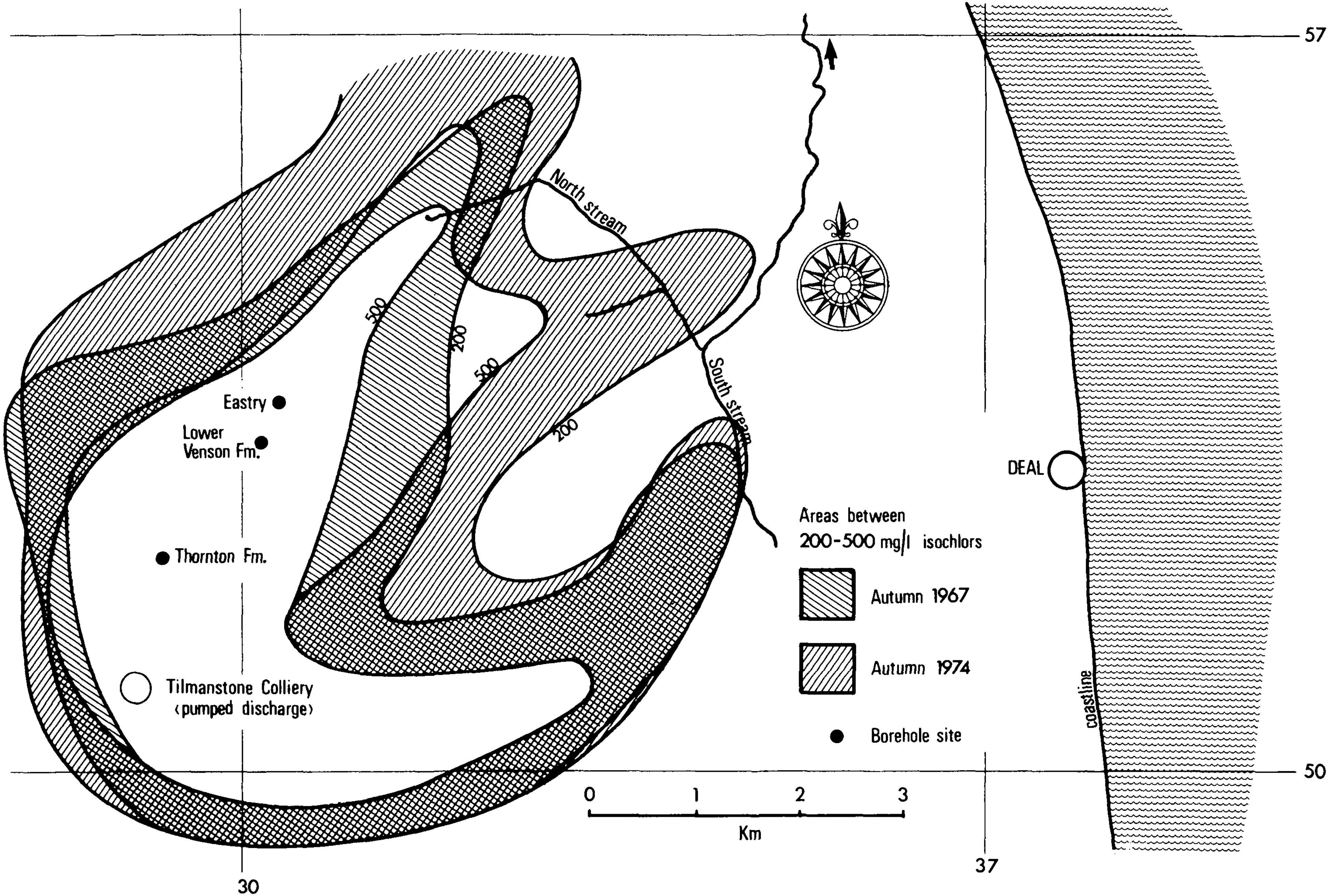

Figure 12 Expansion of Plume of saline water resulting from minewater discharge from Tilmanstone (For location see Figure 1)

PAPER 22

GROUNDWATER PROTECTION IN GERMANY

H. J. Exler

1. INTRODUCTION

As water became recognized during the last century as a cause of sickness and even epidemics through chemical or bacterial impurities, a start was made in the larger towns in providing inhabitants with wholesome water supplies. The first public water undertakings were built, using spring sources to begin with, but because these had mostly highly variable yields, they were superseded by wells. For a time, the mostly small water requirements could be developed in the immediate vicinity of the user, but with increasing industrialization and growing population the water requirement increased steadily. More water had to be developed and the fact was faced that sufficient quantities of water could not be obtained everywhere. In other words, it was necessary to develop water, supplied where the required quantities and quality were available as governed by geological conditions. Therefore, one could not do as one wished. Again and again during the course of the decades, building schemes of various kinds conflicted with existing or projected water supply schemes. Not infrequently, the water came off worse. Those having responsibility for water supply had difficulty in making clear to those representing other interests that water had to have priority in every case.

Today, we have long been aware that water is essential to life. For it to be at the disposal of the steadily increasing demand in sufficient quantities and with the quality of drinking water, the available and useful groundwater must be protected from impurities of every kind, even if this means that other plans have to be changed. It is possible that in the future not only existing catchments will be protected, but also groundwater reserves in potentially useful aquifers as yet unused.

2. LEGAL FUNDAMENTALS

In Germany, during the middle of the last century, a water law was passed which, in the course of time, was built upon further and which was variously administered in the different states and elsewhere. The historical developments of the law, however, will not be considered here in further detail, but merely its eventual definition.

According to Article 75 of the Land Statute of the Federal Republic of Germany, the Federation is authorized to enact enabling laws which become comprehensive and effective through detailed regulations promulgated in the separate state. This was implemented particularly in the case of the water budget, the water regulations of the 10 states and West Berlin, completing the federal framework legislation (WHG). The states of the Federal German Republic are:

Baden - Württenberg
Bayern
Bremen
Hamburg
Hessen
Niedersachsen
Nordrhein-Westfalen
Rheinland-Pfalz
Saarland
Schleswig-Holstein
(West Berlin has a similar legislative authority)

and their state laws take account of their respective regional requirements. The WHG allows the ownership of waters, including that of groundwater to be established. To whom it belongs is established by the state laws. The use of water, e.g. the requirement for groundwater, nearly always requires permission or a consent (Art. 2 WHG). Usually the landowner qualifies as the owner of the groundwater.

The following lie within the scope of the WHG:

Art. 1. The law is valid for the undermentioned waters:
 *1.
 2. Groundwater.
Art. 2. A use of waters requires an appropriate permission or consent (as far as no exceptional circumstance occurs).
Art. 3. (1) Uses, within the terms of the law are:
 * 1 - 4;

5. introduction of substances to groundwater;
6. abstraction, exposing, bringing to the surface and distribution of groundwater.

(2) Use also includes:

1. the raising, lowering or transfer of groundwater through plant intended or suitable for the purpose;
2. measures which are liable to cause lasting or not insignificant adverse changes in the physical, chemical or biological properties of the water.

Art. 19 concerns the establishment of water protection zones:

(1) For the common good:

1. to protect waters from adverse effects in the interest of existing and potential public water supply;

* 2.

3. water protection regions can be established.

(2) In water protection regions:

1. certain processes can be forbidden or declared permissible only with limitations;
2. the owner and authorized user of a piece of land can be obliged to conform to a tolerance in certain measures. These include measures for the observation of waters and of the soil.

(3) Compensation has to be made where the application of a regulation, according to Clause 2, represents an expropriation.

(4) Establishment of a water protection region requires a formal enquiry.

Clause 1, No. 1 applies to all waters, i.e. water courses, lakes, impounding reservoirs, springs and groundwater. However, water protection regions can be established only in the interest of a public water supply for existing plants and those having a definite prospect of construction.

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* Sections thus marked do not relate to groundwater.

However, under Section 19, it is possible to protect potential groundwater abstraction in the pursuit of a planning policy. Of significance is the fact that in the event of Section 19 colliding with the Federal Building Law where land has been designated for building or for the utilization or disposal of effluents, the provisions of Section 19 take preference.

The establishment of water protection regions involves their demarcation and the protective measures applicable therein. Nearly all the state water laws state that water protection regions can be divided into zones having different protective measures applicable. These are mostly based upon the 'Guidelines for Drinking Water Protection Regions' formulated by the Deutsche Verein von Gas - and Wasserfachmännern (DVGW). These are described in Section 3 of this paper.

The question of compensation for a land owner or authorized land user, who could eventually suffer from the protection regulations, is also stated in Section 19, para. 3, and in Section 20, with particular reference to expropriations.

The protection of spa waters, including mineral and thermal waters developed by drilling, is not regulated by the WHG but through the corresponding state laws. For example, Article 40 of the Bavarian Water Law (Bay WG) says:

> Spring protection regions can be established as far as is required for the protection of spa waters within the scope of the Water Budget Law recognized by the state.

Because the 'Guidelines of the DVGW' do not extend this far, the Länderarbeitsgemeinschaft Wasser (LAWA) brought together the highest authorities from the realms of water law and management and commissioned the Spa Water Working Group to draw up corresponding guidelines. These exist today as 'Guidelines for Protection Regions for Spa Waters', and serve as a foundation for the establishment of protection regions. However, this applies only to state-recognized springs.

3. DRINKING WATER PROTECTION REGIONS

The 'Guidelines for Drinking Water Protection Regions' are issued as one of DVGW's work sheets. These were formulated in co-operation with representatives of LAWA and therefore serve as a reference basis for those authorities responsible for defining protection zones. Since drinking water in Germany is obtained not only from groundwater, the 'Guidelines' come in three parts: for groundwater, impounded reservoirs and lakes respectively (Nos. W101, 2 and 3). Although the latter two are of great significance, we are concerned here only with that relating to groundwater.

3.1. POTENTIAL RISKS FOR GROUNDWATER

In the latest issue of Worksheet W101 (Feb. 1975) the risks are listed against which groundwater should, at present, be protected in order to maintain both quality and quantity:

(1) substances and organisms which are dangerous to health;

(2) substances and organisms which, while not dangerous, can impair the properties of water and should therefore be kept away;

(3) adverse changes of temperature (e.g. by cooling water) should be prevented;

(4) the reliable yield of a groundwater should be maintained. (For example, a variation of yield can occur through variation of underground discharge from additional abstraction elsewhere or by a diminution of infiltration area by buildings).

Possible impurities and adverse influences are then listed and their corresponding risks named. Risks that can bring about a lasting change in the properties of groundwater cannot be tolerated within a groundwater catchment. However, consideration is given to impurities being partially destroyed and partially retained by purification effects underground. For example, essential points are:

(1) physical processes, such as the filtration effect of pore spaces, dilution (e.g. through groundwater replenishment) and adsorption;

(2) physico-chemical processes, e.g. the coating of soil particles (adsorption) and ion-exchange;

(3) chemical processes, such as oxidation and reduction;

(4) biological and biochemical processes, e.g. the removal of substances by plants and microbial degradation. Bacteria or other micro-organisms that have reached the groundwater system which, being unlike their natural habitat, does not generally support their survival after 50 days.

The so-called self-purification capacity of the subsurface is not a uniform property but is dependent upon hydrogeological, biological and climatological factors. The following, for example, play a part:

(i) the type, quantity, duration and frequency of an impurity;

(ii) land use and methods of culture applied to the soil overlying the groundwater as well as its thickness and properties. Unfavourable circumstances exist if, for example, the surface is penetrated by animal burrows or by large roots.

Groundwater flow is governed by whether it moves through pores, fissures or karst formations and also by the pressure gradient and permeability. With increasing abstraction, the flow velocity increases with the drawdown.

Flow velocity is of great significance because all processes in the movement of groundwater which are subject to a definite time-span (death of organisms, chemical reactions, microbial degradation, etc.) can be related to a definable path length.

3.2. PURPOSE AND RANGE OF PROTECTION ZONES

The risk for an abstracted groundwater generally falls off with the distance of a pollution source from the point of abstraction. For this reason protection of the immediate vicinity of a point of abstraction is particularly important. Therefore, there is an agreed organization of the protection region into the following three protection zones:

Far zone, Zone III
Intermediate zone, Zone II
Abstraction area, Zone I.

The arrangement of protection regions result from various hydrogeological circumstances that vary from place to place. The borders of the catchment area have to be considered as well as the properties and thickness of the surface cover, meteorological and climatological conditions, the type of abstraction plant and the quantity abstracted. However, other features also play an essential part, such as nearby buildings, land use, mining, sand and gravel workings, traffic arrangements, etc. Depending upon region and locality, there is no limit to what may need to be taken into consideration.

3.2.1. Far protection zone, Zone III.

Zone III stretches from the edge of the catchment area to the periphery of Zone II. If the area extends more than 2 km, an approximate 2 km length is designated as Zone IIIA and the remainder as Zone IIIB. Zone III has to be protected against a wide range of adverse influences and particularly from impurities that degrade only slowly or not at all. In this zone the following, amongst others, are considered dangerous and generally not allowed:

> housing estates, hospitals and industrial operations if effluents are not completely removed from Zone IIIA by sewers; effluents, sewage and refuse disposals; airfields, military manoeuvres and exercises and military installations; automobile breakers, boreholes for oil prospecting, natural gas, carbonated and mineral waters, salt, etc.

The list is not complete.

Normal agricultural use of the land concerned is allowed, except for intensive animal farming. If the catchment region is very extensive, Zone IIIB can in practice be reduced on appropriate hydrogeological grounds.

3.2.2. Intermediate protection zone, Zone II.

The intermediate protection zone includes the area between Zone I and Zone III (A & B) up to a line marking a 50-day retention period in the movement of groundwater to the abstraction plant. Zone II should guarantee the protection of groundwater from contaminants or particular adverse influences that derive from human activities and equipment.

The list of activities and equipment that are generally regarded as dangerous and not to be tolerated near to the abstraction plant include those listed for Zone III and in addition, the following:

> industrial and agricultural buildings, building sites, builders yards, streets, car parks, railways, camping sites, sports tracks, cemeteries, gravel, sand, peat and cement excavations, stone quarries, smallholdings, storage of heating oil, routing of effluents, etc.

A very important requirement, for example, is that organic manuring is allowed only by the spreading of manure immediately following its production. Moreover, the danger of possible excessive manuring or washing away in the direction of the abstraction plant must not occur. For this reason, the open storage and improper application of inorganic fertilizers is also not allowed. All encroachments into the ground by which the living soil zone can be damaged or its thickness diminished are forbidden. Only normal agriculture and forestry are allowed.

Zone II disappears only if deeper groundwater levels are used which are sealed from infiltration from above. This case applies mostly with deep boreholes. Indeed, Zone II does not require restrictive measures if, for example, impermeable layers of extensive thickness stretch from the point of abstraction to the 50-day line.

3.2.3. Abstraction area, Zone I.

In the abstraction area, which is subject in large measure to all kinds of contamination, everything listed for Zones III and II is forbidden.
Every agricultural use or application of chemical agents for plant protection and pesticides is forbidden; as are pedestrians and road traffic.

These strict regulations have the result that Zone I is fenced in and usually turfed. For legal reasons this piece of ground is owned by the appropriate public water authority. The minimum recommended distance of the Zone I boundary from the abstraction point is 10 m. However, the abstraction area is considered to extend far enough that organic manuring can be permitted anywhere outside the boundary. Moreover, the entire cone of depression should be covered.

3.3. APPLICATION OF GROUNDWATER PROTECTION ORDERS

As described in Section 2, groundwater protection is governed by a federal enabling law which is enacted through water regulations of the separate states. The latter permit implementation regulations which control such details as the dimensions of the individual zones and the practices proscribed therein. They are brought up to date from time to time with additions or amendments. For these reasons the standards used in defining the zones and the compilation of the list of proscribed functions certainly differ between states. In order to give some indications about the possibility of defining individual zones, some propositions can be considered which have been proved in practice to be generally applicable.

3.3.1. Establishing Zone III.

To be able to establish Zone III, it is necessary to know the subterranean catchment region of the groundwater (see Section 3.2.1.). This is usually set by the water shed occurring by a variation in hydrogeology such as the groundwater path being blocked by silt, tapering off or intersected by faults. It is the region in which groundwater replenishment takes place and from which groundwater arrives at the abstraction plant. The boundaries here should be set for abstraction rates which are maximum and water tables at their lowest. If the range of this region is greater than 2 km, the subdivision into Zones IIIA and IIIB is instituted. This means that the proscribed operations are reduced for the greater distance from the abstraction plant. There are cases where the catchment is so large that is is sensible to demarcate Zone IIIB, but not the whole catchment area. The following considerations are relevant to this:

Zone III should be protected from impurities or adverse influences which decay slowly or not at all and the zone should cover a layer of the catchment in which it is guaranteed that all such impurities are so diluted (e.g. by groundwater replenishment) that they are harmless, i.e. are less than a given level of tolerance.

3.3.2. Establishing Zone II.

Zone II is established according to a 50-day retention time to the abstraction point. Since normal groundwater movement increases in velocity in the vicinity of the cone of depression it would be expedient to undertake tracer studies to be able to establish empirically the required distance. In practice this is not always possible on the grounds of expense and one is forced to rely upon experience. This is possible for aquifers of similar permeability and yield. Since each borehole drilling is followed by a pumping test to determine the specific yield (Q) and the coefficient of permeability (k_f), the groundwater velocity can be roughly calculated.

According to Darcy,

$$V = \frac{k_f \ I. \ 86400}{n} \quad \text{m/day}$$

or according to Smreker-Holler,

$$V = \frac{Q}{n \ BH} \ . \ 86400 \quad \text{m/day}$$

where V = field velocity of groundwater (m/day)
I = natural groundwater gradient (e.g. 0.003)
n = pore volume, porosity (e.g. 0.25)
B = assumed width of recharge zone (m)
H = height of useful water level above basal layer (m)
Q = abstraction rate (m^3/sec) (pumping test maximum)
K_f = coefficient of permeability (Darcy) (m/s)

There are different ways for evaluating the width, B, of the recharge zone. The simplest is Sichard's formula for the width, R, of the cone of depression:

$$R = 3000\ s \sqrt{k_f} \text{ metre,}$$

where s is the drawdown (m). The width Zone II is then taken as 1.2B. The recommended length of Zone II follows for a 50-day retention, with a safety factor of 5 to 10% added to take account of the greater velocity in the cone of depression.

3.3.3. Establishing Zone I.

It was mentioned earlier that the abstraction area should have a minimum radius of 10 m. Consideration is given, of course, to the cone of depression being covered. In view of the various methods of construction of the covering, the area varies between 10 X 10 and 50 X 50 m.

3.3.4. Scope and limitation of protection zones.

If the size of the necessary areas can be ascertained, the boundaries of the protection zones are so drawn on a contour map that wherever possible the boundaries coincide with boundaries in the terrain. These can be streets, water courses, woods or property boundaries. They should be clearly recognizable in the terrain in order to avoid mistakes, such as the institution of differing protective regulations for the same piece of ground.

It should be emphasized that only porous aquifers have been considered so far, for with fissured and karstic aquifers the evaluation of the required hydrogeological values is incomparably more difficult. Moreover, the flow velocities in karsts are much higher than in porous aquifers. In these cases the existing circumstances have to be investigated in order to establish the boundaries of the protection zones as effectively as possible.

4. PROTECTION REGIONS FOR SPAS

Mineral springs are naturally evolved or artificially enclosed water and gas formations which, due to their chemical composition, physical properties or from experience, are suitable for curative purposes. Mineral springs, whose preservation appears to be in the common good, can be recognized by the state. This recognition is incumbent upon the individual federal states who enact appropriate laws and regulations. Thus, for example, the Bavarian Water Law (Bay WG) protects only state-recognized spas, and the same is true in other states. 'Guidelines for Protection Regions for Spas' was therefore formulated by representatives of provincial water authorities, balneology, mining, geology, and the German Spa Associations (Deutscher Bäderverband and Verband Deutscher Mineralbrunnen, e.V.) as a result of the application of the DVGW's 'Guidelines for Drinking Water Protection Regions' (W101).

4.1. TYPES OF SPA PROTECTION ZONES AND THE DIVISION OF SPA PROTECTION REGIONS

Since no two spas are the same, the arrangement of their protection regions and the consequent protective regulations do not arise systematically. Two essential kinds of spa protection are based respectively upon Qualitative and Quantitative Protection Regions. Since mineral springs in most cases (or predominantly) are prescribed for drinking, they must be covered by drinking water protective regions. In addition, the dissolved contents and/or temperature should be protected against adverse (i.e. undesired) changes. However, a variation in the content of dissolved carbon dioxide can even be brought about by a variation in yield or spring discharge.

Spas of various types are distinguished according to the origin of the water. In this, one recognizes the existence of horizontal migration at various depths, otherwise there would be mixing between the mineral or thermal water with groundwater nearer to the surface. All of these features play a part in the laying out of spa protection regions.

4.1.2. Protection zones against qualitative impairment.

The occasional and persistent sources of adverse influence upon quality are practically the same for spa waters as for drinking water. The qualitative protection regions are organized in a similar way:

Zone 1 (Abstraction area)
Zone II (Intermediate)
Zone III (Far zone, inner)
Zone IV (Far zone, outer)

Their measurement and respective protective regulations follow throughout those for drinking water.

The assignment of Zones III and IV, for the protection of the catchment of a spa water, requires hydrogeological knowledge about the type of water. The catchment region may be exceptionally far distant, as with mineral springs which rise from more than 100 m deep, but have travelled 10 km or more. The same is true for juvenile water which has never taken part in the water cycle. Such water comes mostly from many km depth. Its catchment region can be influenced from the surface at the most by deep boreholes. In this connection, mining can have an influence, if it runs up against the water-bearing fissure zone.

4.1.3. Protection zones against quantitative adverse effects.

Causes of adverse effects upon mineral waters include unaccounted-for water abstractions, groundwater recharge, measures which can hinder infiltration in the catchment area, various underground activities (e.g. compaction, drift and tunnel excavation), gas abstraction and storage.

Protection zones against quantitative effects do not necessarily coincide with those for qualitative protection. There are four zones designated by the letters A to D. Since the type of spa source has to be considered for protective measures, the geological circumstances are of dominant importance.

Zone A, as a rule is the area in which excavations more than 30 cm deep and variations of soil use are prohibited. It includes the immediate vicinity of the abstraction plant and should preserve the hydraulic situation of the spa water.

Zone B, prohibits excavations beyond 3 to 5 m depth; i.e. it permits normal excavations for building and pipe laying, etc.

Zone C, prohibits excavations beyond 10 to 20 m depth. This is therefore the area in which wells to a depth of 20 m can be permitted.

Zone D, permits excavations to a depth of 100 m.

If it is required, further zones with corresponding stages of depth can be instituted. Zones which prove to be unnecessary can be rescinded.

5. SUMMARY

In the Federal Republic of Germany, water is protected through Federal enabling law together with supplementary water regulations of the separate states. Although groundwater is the property of the landowner, he can freely dispose of it only in exceptional circumstances. The law states that the abstraction, recharge, impoundment, lowering and transport of groundwater, requires an authorized consent or grant. The same is true for discharge of substances into groundwater. As far as the common good requires, water protection regions can be defined in which certain processes are prohibited or permitted only under stated conditions, in order to protect groundwater for public supply from adverse effects of a chemical, physical or biological nature.

Groundwater protection regions are organized into various zones. The hazard associated with an impurity diminishes generally with increasing distance of the impurity source from the point of abstraction. For this reason, the list of processes which, in Zone I, are forbidden or only conditionally allowed is particularly extensive. Zone II has the foremost objective of protecting against impurities which originate from human activities and equipment. Its extent is so chosen that the groundwater has a 50-day retention from the perimeter of the zone to the pumping station. Zone III covers the remaining catchment and should protect it against impurities which are not degradable or only slowly so.

State recognized mineral springs can likewise be protected, with a distinction made between qualitative and quantitative protection regions. The qualitative protection zone corresponds throughout to groundwater protection zones described previously, except that they have also to hinder variations occurring in temperature and dissolved chemical constituents. The qualitative protection zone should guarantee an unchanging yield or spring discharge rate. Variations in these could cause undesirable changes to occur in temperature or concentration of dissolved constituents. The establishment of quantitative protection regions and the appropriate protection regulations requires an exact knowledge of the geological circumstances as these are particularly relevant to the source and underground flow pattern of the water to be protected.

6. REFERENCES

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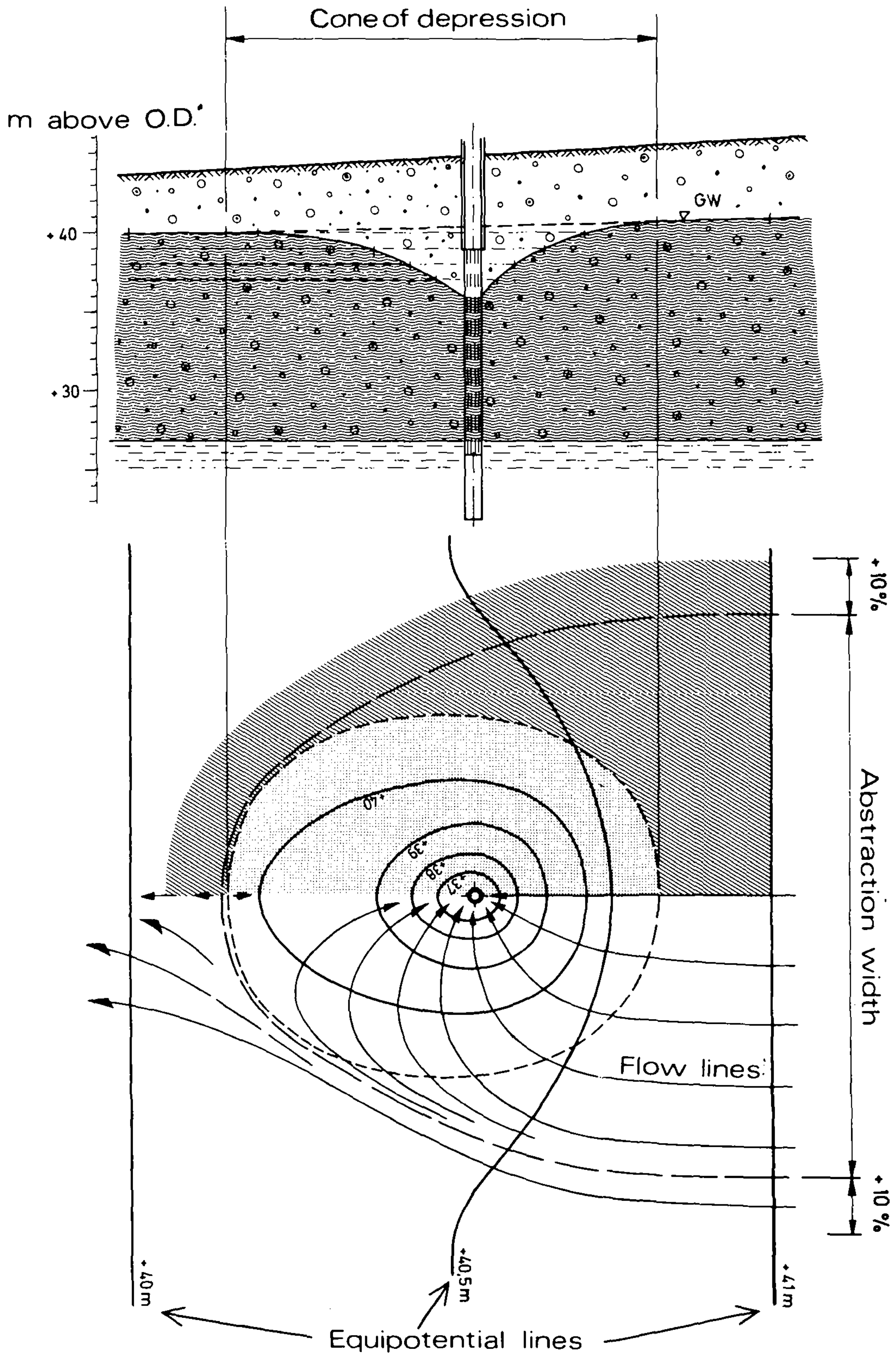
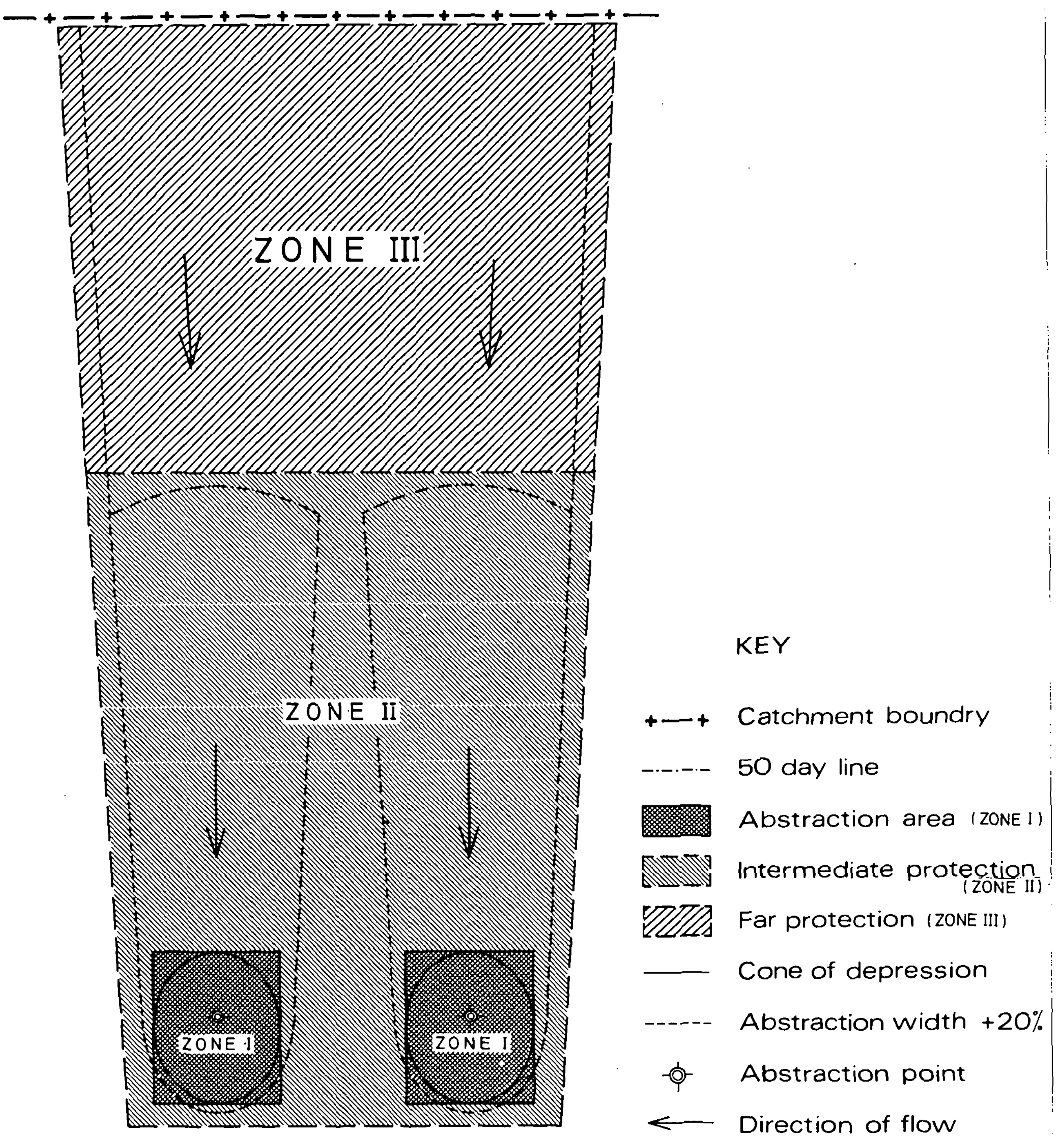

Cone of depression
m above O.D.
+40
+30
GW
+40
+39
+38
+37
+10 %
Abstraction width
+10 %
Flow lines
+40 m
+40,5 m
+41 m
Equipotential lines


ZONE III
ZONE II
ZONE I
ZONE I
KEY
Catchment boundry
50 day line
Abstraction area (ZONE I)
Intermediate protection (ZONE II)
Far protection (ZONE III)
Cone of depression
Abstraction width +20%
Abstraction point
Direction of flow

DISCUSSION - SESSION 6

Mr J. A. NAYLOR said his comments related to the licensing of waste disposal sites. The Control of Pollution Act (1974) requires that there should be statutory consultation between the waste disposal authorities and the regional water authorities, and he asked Mr Goodman and Mr Beckett whether they felt that a balance of interests could be obtained without undue conflict. The paper by Headworth and Wilkinson had referred to protection zones and indeed the Severn Trent Water Authority's aquifer protection proposals had recently been published. He asked whether such proposals would pre-empt the Department of the Environment's (DOE) forthcoming guidelines or Codes of Practice for waste disposal which were to be based on their current landfill research programme.

Mr Naylor asked what were the implications of such aquifer protection policies both for the waste disposal authorities and the water authorities who grant site licences. Are such policies likely to lead to the concentration of wastes in a few very large sites?

Mr M. J. BECKETT, in reply to Mr Naylor, said he did not think such aquifer protection proposals would pre-empt the DOE's landfill report. What is understood by the 'balancing of interests' is that discussion into all the broader aspects of site licensing should occur at an early stage. As Mr Headworth had already pointed out, in certain cases aquifers are already unsuitable for potable water supply, because for example, of saline intrusion. In such, and similar, situations there ought to be sensible discussion between the water authority and waste disposal authority as to the use of some of the land for landfill disposal. Mr Beckett said that the DOE's landfill research programme report is really a report on a scientific investigation; the implications for landfill practice will be evolved by the DOE at a later date.

At present a situation exists where waste is concentrated at a few large disposal sites and as a result there are many examples where waste is transported over long distances. It is accepted that industry must have the opportunity to dispose of waste more locally, and it is for this very reason that discussions are being conducted at a local level to develop more suitable sites. Such discussions clearly involve a 'balance of interests .

Mr H. G. HEADWORTH and Dr W.B. WILKINSON, in reply to Mr Naylor's comments, considered it was a pity that the final report of the DOE's landfill research programme was not available at a time when water authorities were drafting, and even implementing, policies for aquifer protection. These policies were needed as a matter of urgency because the water authorities were already receiving waste disposal licence applications to consider from the waste disposal authorities. However, it should be stated that such policies were designed to provide guidance to waste disposal authorities, local authority planning departments, etc., on the reactions that could be anticipated from the water authorities to proposals for waste disposal which were referred to them.
Such aquifer protection policies would be sufficiently flexible to be modified in the light of the results of research which became available. The variability of site hydrogeology and of the waste itself meant that hard and fast rules for site selection were likely to be inappropriate and the aim of the aquifer protection policies was to eliminate speedily the clearly acceptable or clearly unacceptable sites to allow staff to give greater attention to those sites which required detailed consideration. The choice of a few large sites was more likely to result from economic factors, but the need to safeguard water supplies was more likely to favour a large number of small sites. There was an obvious association between mineral abstraction, sites attractive for waste disposal, and aquifers used for groundwater supplies. Water authorities would not lose sight of the comparative value of minor aquifers for water supplies and their value for waste disposal sites.

Mr D. D. YOUNG (Chairman) said that the Severn Trent Water Authority's aquifer protection policy document is a statement of where the Authority's interests lie; indeed if a water authority does not state its own interests, it is difficult to see how a balance can be reached with the other parties. He asked Dr Skinner to comment on this document.

Dr A. C. SKINNER said he did not consider that the Severn Trent Water Authority's aquifer protection policy pre-empted the work of the DOE in its landfill investigations. The policy document had been prepared so that the Authority's priorities for the protection of aquifers could be made known. It seeks to ensure that the greatest protection is given to the most important aquifers by means of a series of protection zones. The various, often unwritten, policies of the Authority's predecessors have been incorporated and standardized, except that the emphasis has been shifted from the protection of sources to the protection of resources. The policy has been welcomed by many planning and waste disposal authorities as a clear statement of Severn Trent's position, even though it does not always meet with their full agreement. Publication of the policy has led to a constructive debate on the general principles. The policy is not a substitute for detailed site investigation and it is recognized that individual consideration is due in each situation through the consultation procedures now in operation. In this sense the policy is complementary to the DOE investigation which, it was hoped, would provide the detailed guidelines to assist the Authority in considering individual situations.

As this was the middle of the first year of implementation of the Control of Pollution Act, the Authority would have liked to have had the benefits of the full results of the investigations to assist it during this critical period, rather than at the end as seemed likely.

Mr P. H. GARNETT considered that the Conference had been extremely useful in providing an up to date collection of information and current research knowledge under specific headings in a 'handy form'. He said the paper by Headworth and Wilkinson was notable in this respect.

Mr Garnett went on to pose a number of questions. He recalled a suggestion that treated domestic sewage was going to be used along the South Coast of the UK to prevent saline intrusion. He gathered from the paper by Headworth and Wilkinson that this was no longer being considered and he would value their comments. Their paper implied that treated effluent, or even crude sewage, could enter underground waters and become suitable for public supply. This was of particular interest to him as at present he was concerned with defending a proposal to the EEC that in future good quality domestic effluent might well be discharged to underground waters in order to supplement potable supplies. The practice is, of course, carried out extensively overseas.

In order to protect groundwater it is necessary to have a legal definition, particularly in relation to an EEC directive, and it was felt that the best and simplest definition was 'water found underground'. The title of this conference makes no reference to potable water, nor incidentally does the new EEC directive on controlling discharges to underground strata. The UK point of view has been that a protection policy should be defined in relation to 'use'. It is only water that is being or is likely to be used for public supply that requires protection. This, however, is a minority view, the general view being that all water should be protected. Mr Garnett said he would welcome views as to whether the UK attitude at Brussels should be that only sources suitable for public supply are protected or all sources are protected. It was proving difficult to define 'use' as the spectrum was very wide, ranging from drinking water to industrial treatment. Finally, he said, it should be borne in mind that water today,which is considered to be of no value, may tomorrow be of considerable importance.

Mr H. G. HEADWORTH and Dr W. B. WILKINSON thanked Mr Garnett for his kind comments about their paper. They had not heard of suggestions for the use of treated domestic sewage along the South Coast of the UK to prevent saline intrusion. Recent research work had shown that the very strongly developed fissuring which was present in the Chalk permitted very speedy movement of fresh and saline water in response to tides, abstraction, and winter recharge. Consequently they felt it unlikely that water supplies would be put at risk by discharges of treated sewage effluent. In their paper they did not advocate the discharge of semi-treated or untreated sewage effluents into underground strata. It was necessary to acknowledge, however, that biological and bacteriological degradation took place relatively quickly in the aerobic and saturated zone and that cases of groundwater becoming contaminated were limited to sources of sewage effluents very close to the abstraction source. Nevertheless the long-term resultant rise in nitrate levels and other contaminants in groundwater resulting even from fully-treated sewage effluents, was a factor that could not be disregarded. The question as to whether aquifer protection should be afforded to public water supply sources or all sources of abstraction, was a difficult one. The answer probably lies in affording specific protection to the larger private sources, which by the nature of their size have a 'catchment', and to protect smaller private sources within an overall policy related to the nature of the aquifer.

Mr C. CHUMBLEY raised the issue of the disposal of silage liquors, which had been discussed in the paper by Headworth and Wilkinson. He said that impervious bases to silage lagoons were becoming much more common, as was the thin application of effluent to farmland. The paper had suggested that silage effluent may be disposed of in a sewage treatment plant; however he understood that such sudden shock loading of the facilities in June and October was discouraged.

The Ministry of Agriculture, Fisheries and Food does not advise the liquors to be pumped to sewage works. They recommend that the liquor be sprayed rather than allowed to soak away.

Mr H. G. HEADWORTH and Dr W. B. WILKINSON, in reply to Mr Chumbley, said that the statement in their paper which suggested that silage liquor effluents should be disposed of at sewage treatment plants was in fact misleading, and the paper would be modified in terms of the Ministry of Agriculture, Fisheries and Food's recommended practice.

Mr. D. D. YOUNG (Chairman) said he did not wish to enter the controversy too deeply, but generally the disposal of silage liquors at sewage treatment works was an uneconomic proposition, although it may be technically feasible. In some places it may still be used.

Mr K.H. SELBY said he wished to raise some points with Mr Goodman and Mr Beckett regarding the implementation of the Control of Pollution Act (1974). Although the Act will strengthen the legal powers of the water authorities, as the body responsible for groundwater and surface water protection, it is the implementation of these powers which is important in controlling pollution.

His Authority had received many circulars, instructions, etc. from the DOE both before and after the introduction of Part One of the Act. He said there were many points in the mass of information with which he would take issue, and there were certain ambiguities. For the present discussion he would, however, consider only the 'Balancing of Interests' document. This was produced in April when the Government were under strong pressure to reduce public expenditure and he thought that this was reflected in the ideas presented in the document. His interpretation of the document was that, in the interests of economic waste disposal, water authorities should be prepared to sacrifice certain aquifers. He quoted a brief extract from the document as follows:

> 'Strata with limited groundwater resources may not be rated as significant on water supply grounds and thus the need to protect them may not be so important. Factors which would need to be considered include any problems relating to the degradation of existing abstraction rights, the question of compensation and the number of people depending upon the aquifer, since the fewer the number the cheaper would be the alternative water supply.'

However, while the Government were under pressure to reduce expenditure in April, they are now under other pressures in this unprecedented drought situation to conserve water supplies. He asked Mr Goodman and Mr Beckett whether they would, in the light of this new situation, like to recommend to the Minister that he revise his views on this particular aspect.

Mr M.J. BECKETT said he agreed with Mr Selby that the 'Balancing of Interests' document was written with the object of avoiding unnecessary public expenditure. Perhaps a need exists for the provision of more scientific background to the guidelines provided, and it was hoped that the final report on the landfill research programme would meet this requirement. On the other hand he was doubtful if it was ever possible to say that a groundwater resource was completely safe if a landfill site was located on it. It is very much a question of balancing the cost of waste disposal against the cost of alternative supplies. He did not think Mr Selby's interpretation of the document was correct in suggesting that there are examples where one outweighs the other solely for economic reasons. The water authorities are in the best position to assess these risks in conjunction with the waste disposal authorities. If the problem is approached in an inflexible way a series of public enquiries, etc.,are likely to develop, and Mr Beckett hoped this situation would not arise.

Mr A.H. GOODMAN said in response to Mr Selby that this was a very difficult area to deal with. Some years ago he was called to assess the risks of pollution likely to occur through an application to construct a tip site, before any controls of pollution were even thought about. As a water chemist he would not have liked any waste to be deposited in that area as it was on an extensive exposure of Bunter Sandstone. The evidence of the waste disposal authorities suggested strongly that the leachate would be reduced in volume and would decrease in strength with time. He said he had had to reconsider his views in the light of their application and the scientific evidence. He went on to say that in any proposal for a waste disposal site it is important to examine all the evidence, and it is difficult to find a definite connection between <u>controlled</u> tipping and groundwater pollution. Soil has a very large adsorption capacity and even Chalk appears to have a major modifying influence on pollutants. Thus scientific as well as financial considerations must be examined, and a fair assessment made of the likely risks. It is also important to recognize that the waste disposal engineer has a job to do as well as the water engineer/scientist.

Mr M. MORGAN-JONES asked Mr Goodman and Mr Beckett when does a site licence cease to be effective; and who then pays for any remedial action. He was also interested to know the date on which Part Two of the Control of Pollution Act is likely to be implemented.

Mr A.H. GOODMAN and Mr M.R. BECKETT prepared the following written reply to the questions raised by Mr Morgan-Jones.

The circumstances in which a disposal licence ceases to be effective are laid down in Part I of the Control of Pollution Act. A licence can be revoked by the waste disposal authority under Section 7(4) or Section 9(4) of the Act, and the notice served on the licence holder to revoke the licence states the time at which the revocation is to take effect. A licence can also be cancelled by the licence holder and it ceases to be operative once it has been surrendered to the issuing authority. No prior notification is required in this case. A licence lapses ten weeks after the licence-holder has transferred occupation of the licensed site to someone else; if disposal operations are to continue a new licence must be obtained.

If remedial work is carried out by the waste disposal authority under Section 9 of the Act after the licence has ceased to be operative, the costs cannot be recouped from the former licence holder. However, if remedial measures under this section are carried out by the authority while the licence is still in force, any expenditure incurred can be recovered from the holder of the licence even after this has been revoked or cancelled. There is, of course, far greater scope for recovery of costs for remedial action if the disposal activity was undertaken in contravention of Section 3; Sections 16 and 88 would then be relevant. The assumption has been that a site operated in accordance with appropriate licence conditions would be unlikely to require later remedial work.

The implementation of Part II of the Control of Pollution Act has been deferred due to the current economic situation. The introduction of the major provisions of Part II would place the regional water authorities in a position where they would have to incur substantial capital expenditure at a time when they are operating under increasingly severe capital investment restrictions, and when they are under pressure to keep their charges as low as possible. In these circumstances it would not be reasonable to introduce the major provisions of Part II. The situation is however under constant review and the whole of Part II will be implemented as soon as the circumstances are judged to be right.

Mr J. B. JOSEPH submitted the following written discussion for consideration by Messrs Goodman and Beckett. In his reply to a question, Mr Beckett suggested that some parts of aquifers could possibly be written off from a water supply viewpoint, and their outcrops used for landfill purposes. As an example, it was suggested that areas around the coast and subject to saline intrusion might be treated in this way.

Saline intrusion is in most, if not all, cases the result of overpumping of the aquifer in the area. This would suggest that locally the supply of water is insufficient to meet the demand and that, far from abandoning the aquifer, these are the very areas which should be considered for remedial action such as artificial recharge.

Mr A. H. GOODMAN and Mr M. J. BECKETT replied to Mr Joseph's discussion as follows.

Where saline intrusion had been so extensive that recovery of the aquifer would take an excessively long time and might require expensive pumping to waste over a long period, and where development of an alternative source of supply was reasonable in effort and expense, it would be acceptable to write off part of an aquifer, although possibly temporarily. If it was critical to retain the aquifer for potable supply, in the near future the situation might be considered differently and all attempts made to effect the recovery and to protect it. They did not accept the view that the use of land above an aquifer for waste disposal would inevitably mean that the aquifer would be written off for all time. Once equilibrium had been established between the introduced material and the outcrop or catchment, it was quite possible that the aquifer might be found suitable to be redeveloped. Leachates from wastes of organic origin become much less polluted within a reasonable period of time, although in the early period of disposal a strongly polluting leachate would most likely occur. They considered that although some inorganic industrial wastes might take longer to become stabilized, it was likely that the risk of pollution of underground water would decrease markedly with time. Investigations were being carried out on the changes occurring in tipped wastes with time, and he thought that the time scales might not be so very different from those necessary for recovery of an aquifer from severe saline intrusion, which could be over a decade. Every situation needed to be studied separately, and generalities were not wise. He thought that it was not intended to suggest that the example quoted should be taken as a general guide, but only to draw attention to a possibility. A point not often considered was that if it was necessary to use water from an aquifer which was known to have been exposed to a risk of pollution, there might also be a need for provision of treatment for the water. The usual attitude was that groundwaters ought to be of a quality such that little or no treatment was required. Perhaps this attitude would have to change in some of our more intensely developed areas.

Mrs M. P. HENTON submitted the following written questions for consideration by Messrs Goodman and Beckett.

The authors have covered in some detail the legislative situation as it applies to England and Wales, but some people may not be aware that the legislation is not necessarily the same throughout the UK. The Water Resources Act applies only to England and Wales, whilst the Control of Pollution Act combines both English and Scottish sections in the one Act. Because of the regrettable lack of emphasis which has been placed on groundwater in Scotland in the past, there has never been any legislation (apart from the ineffective Water Act (Scotland) 1946) to protect it until 1972 when the Clyde River Purification Board Act was passed which applied only to the area of that Board. The Act covers all underground strata within the Board's area and works on a consent procedure similar to that for surface water discharges.

When the Control of Pollution Act is eventually brought into force in Scotland, its relevance to groundwater will be different to that in England and Wales. The site licensing procedure (which is also awaiting enforcement) will be the same but the proposals for the protection of underground water from 'poisonous, noxious or polluting matter' will be different. The Scottish definition of these waters says simply 'such underground water as may be specified'. It does not say by whom or at whose instigation it will be specified, neither does it give any guidelines such as the English definition which places the emphasis on the present or future use of the water. Not much groundwater is used at present in Scotland for potable supply, although this is changing and the potential for future use is very good, but knowing the opposition there has been in certain quarters to the introduction of any legislation to protect groundwater in Scotland, difficulties can be foreseen in getting any groundwater classified as specified. Several people in Scotland have stated publicly that they would have preferred a system similar to the Clyde River Purification Board Act consent procedure to have been incorporated in the recent new legislation.

She wanted to know whether the authors considered the present Act in the UK, with different legislation for England and Scotland, to be too 'bitty'. Did they think that a good opportunity had been missed during the drafting of the Control of Pollution Act to incorporate the best parts of the legislation from both sides of the border into one Act, equally applicable to both countries.

Mr A. H. GOODMAN and Mr M. J. BECKETT prepared the following replies to the questions from Mrs Henton.

Basically, the same controls over water pollution apply in Scotland as in England, albeit under differently-named statutes, and most of the Control of Pollution Act 1974 will also apply to Scotland. However, because of the historical legal backgrounds of the two countries, in some respects there are differences as, for example, in the laws relating to sewerage. To apply a single form of sewerage law to the whole of the United Kingdom would involve the complete reorganization of one of the existing legal systems, and this is not considered to be a worthwhile or practical proposition.

Much less reliance is placed in Scotland on groundwater as a source of potable supply - in 1975 less than 100 Ml/day was derived from boreholes and springs, compared with over 3000 Ml/day from other sources. So far as the licensing of discharges to underground sources is concerned, only one area of Scotland is covered by legislation, and that is the area of the former Clyde River Purification Board, where a system of licensing applies to underground discharges similar to that of discharges on the surface.

As and when those sections of the Control of Pollution Act dealing with underground water are brought into force, it will be possible for the Secretary of State to prescribe by regulations 'specified underground water'. Once such waters are prescribed, a river purification board will be in the same position to deal with discharges into that water as it will be to deal with discharges to surface waters. It is not yet possible to define the criteria which would apply before the Secretary of State would prescribe underground water, but it seems likely that underground water would only be prescribed where there was a real need to do so, for example to prevent the pollution of an underground water source.

FORWARD LOOK: PROFESSOR J. BEAR

Professor Bear began by expressing his gratitude for being invited to participate in the Conference. He said that he was honoured by the further invitation to try and look into the future, although he felt that this had already been done by all the speakers in their individual summings up. The Conference had been very successful in achieving its objectives of transferring information and reviewing methods; this exchange between participants from different disciplines should help to define areas of common concern and of deficient knowledge.

Water is a very precious resource; without it life is impossible. This Conference has been concerned with the aspect of groundwater quality and, more especially, the problems of groundwater pollution and contamination.

The proper management of our water resources must be viewed in terms of quantity, quality and cost, and it must be remembered with respect to this latter factor that society has alternative uses for its financial resources. Although one may be looking at some particular detail of a system, such as molecular exchange at the interface of clean and polluted waters, it is essential that the overall view relating this to good resource management should remain in mind.

Management, or decision-making, is really the setting up of social objectives. It is our job to provide the basic data to aid the decision-making process in the water industry. The Conference has dealt specifically with groundwater quality, but quality is not a detachable sub-set of the whole system; quality and quantity must be considered together. For example, one must have some knowledge of flow velocities in order to understand and quantify the dispersion of plumes of pollution. Management problems, in the water industry are multidisciplinary and for their solution require the knowledge and co-operation of people from different backgrounds.

The point of view that has been expressed throughout the Conference is the practical one of dealing with problems which require solutions at local, regional or national level. This is said in the knowledge that research is also important for its own sake, for the advancement of science. The Conference participants have taken the engineering approach, i.e. their approach is oriented towards finding the most efficient solution to problems which are of practical interest to society. In order to do this they must use the accumulated experience and practical knowledge that is expressed in the form of scientific information.

It is the manager who must decide, on behalf of society, whether or not to implement particular proposals. The function of the engineer is to provide possible solutions to problems - and it must be remembered that one course of action which is almost always available is to do nothing.

Solutions depend upon the use of the correct methodology; the correct analysis of the problem must be made before the tools for prediction are set up. It is seldom possible to work on a trial and error basis when dealing with groundwater quality as it is a 'real time system'. If a mistake is made, the processes needed to reverse the quality changes that have occurred may take a very long time. This is not necessarily so important in quantity work where one can, for instance, stop pumping.

Groundwater quality comprises an exceedingly complex natural system, involving inter-relationships between geology, hydrology and climate. Man may also have superimposed his activities on the natural system. We live in a time of very rapid change and are therefore concerned not only with the present but also with the future, a future containing an increasing number of presently unknown chemical compounds with equally unknown degradation products.

Situations may arise where what is desirable for the public is uneconomic. It is important to be able to predict the response of the system in the future under any form of excitation, such as pumping, artificial recharge, effluent disposal etc., and to decide which outcome is to be preferred.

The discussion has centred on the tools rather than the management; the tool that is required is modelling. The very complexity of the system dictates the use of models, but they must be handled with care. Any model used must be valid within the assumptions on which it is based or, to put it another way, the system must be simplified so that the basic elements and objectives of the model are not lost. It is important to find the correct balance between the model's sophistication and the user's capabilities. If the model is too sophisticated it may not be possible to collect the necessary data for it, or to calibrate it; conversely if it is too simple it may fail to answer the problem.

In essence all models are balances, using numerous coefficients to deal with various forms of inflow and outflow. There are many types of models, differing according to their design objectives, and it is important to build and use one that conforms to the problem in hand. In some cases a single cell model will be sufficient; in others a multi-cell model must be used. All models should be easy to operate and calibrate, and the results should be easy to check and understand, and conform to the original objective.

Our work must be based on a scientific knowledge of elemental behaviour which can be described by a set of laws. Once the basic ideas related to an individual point are understood and expressed as laws they can be used to build up complex models. It is the basic ideas, however, that are the essential building blocks; the mechanism is all-important, and the 'black-box' approach should never be used. It is impossible to overemphasize the need to determine coefficients and calibrate the model using field data.

The calibration of models is usually carried out by a process of trial and error, fitting against historical data. Once a fit has been made, it is assumed that one can extrapolate into the future. Calibration is, however, a continuous process. A precise fit between the model and reality should not be expected, partly because a model is a simplification in which a number of factors and details existing in reality must be ignored. There is, then, an intrinsic difference between the model and the modelled. One should, however, aim for the best fit and the optimal solution. It is important in this context to recognize the more and less important factors; to the scientist everything is of equal interest, while to the engineer cost outweighs almost every other factor - from the engineering viewpoint the less important factors may be ignored.

It is time to take stock of existing knowledge and abilities. What planning and management tools are available and what are still lacking? A common effort will be needed to close the gaps. Not that we should sit by in the meantime. At any time full use should be made of everything that is known or even estimated; it may be possible to calibrate a system, but if not it may be necessary to proceed even without this check.

Models of groundwater flow in aquifers.

Almost all of the information required for a complete knowledge of flow in the saturated zone is available, and it is possible to build mathematical models of regional phenomena. However, the importance must be recognized of three-dimensional data on the local scale, as against two-dimensional data on the regional scale. More work, and so a greater depth of knowledge, is needed on the true nature of flow in fractured rocks; this is very important in relation to pollution.

Double porosity systems, i.e. those in which fractures as well as intergranular interstices have a part to play, also need further investigation; at what stage, for instance, is averaging permitted? It should be noted that much has already been done on this topic in the field of oil reservoir engineering where, if the correct operating procedures are not followed, water may rush through the fissures into the system and prevent full recovery of the oil. The importance of the microstructure to local phenomena is still the subject of some debate.

The introduction of increasing numbers of probabilistic factors into quantitative models should be attempted. Poor results are often obtained because it has not been possible to model all the relevant factors. It might be better to look at and use the distribution of coefficients rather than an averaged value, and at probable rather than point specific results. As a corollary, sensitivity tests on the model are important.

Groundwater quality models

Quality should be defined in terms of standards related to both the source and the use of the water. The decision must be made as to which are the most important constituents, and whether they are representative. It is not possible to study everything, so simplified models of the system must be sought; for example, if we are examining solutes that are not affected by adsorption, tritium measurements could perhaps be used to aid in understanding the flow of such solutes through the system.

Adsorption is known to occur in the field, but the details are not known, let alone understood; for instance, how is adsorption related to the structure of the pore walls and what complex interactions are involved? Eventually basic information on adsorption must be expressed in relationships which can be built into models.

Changes in groundwater quality.

There are many unknowns in this field. What, for instance, are the interplay effects of flow through fractures, ion exchange, diffusion, reaction and decay, or even simply flow of pollutants? What is the effect of anisotropy, or the degree of saturation in the unsaturated zone? The unsaturated zone is extremely important but little is known about the relationship of dispersion and degree of saturation. The more important constituents of the system must be isolated and studied and typical patterns of behaviour and environmental effects established. Once this is done it should be possible to model local and regional problems.

Data collection.

Data collection must be directed towards use in models both now and in the future, and the objectives of that collection must be defined with a view to calibration. Observations are required for monitoring purposes, but there must be a follow-up and warning system. There is work still to be done on network design, so that the greatest efficiency is obtained for the least cost, although it must not be forgotten that costs also affect accuracy. Guidelines on the spatial and temporal distributions of measurements and determinations are required by those carrying out these operations in the field and the laboratory.

All of this information must be translated into guidelines needed by legislators and administrators, and acceptable to users making decisions at a social and political level. A methodology is required for turning our knowledge of phenomena into rules and regulations, and this is available in the form of predictive excitation/response models. It is worth remembering that it is necessary to provide management techniques to reduce damage where protection techniques have failed, as well as protection at the source, and that there are circumstances in which one must accept deterioration of quality as a trade-off for quantity.

This 'forward look' has been very optimistic. Much has been achieved in the past ten to twenty years and, by extrapolation, much will be achieved in the future. Some powerful tools are available now; they should be used even though they may be imperfect and based at least in part on assumptions. If a job needs doing do not wait for exactly the right tool to be developed; you might wait for ever.

Groundwater is an important resource with great advantages, and it should be incorporated into our water supply systems. With respect to pollution, protection and prevention are better than restoration. When pollution is occurring or has occurred it may not necessarily be a question of total prevention or restoration, but rather of minimising damage. We have accumulated a vast store of knowledge, and although much remains to be done we are closing the gaps. We can look forward in hope.

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Additionally the Centre would like to thank Professor Jacob Bear, Israel Institute of Technology, for his closing 'Forward Look' address.

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