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GEOCHEMICAL SURVEY OF THE WESTERN ENERGY REGIONS

July 1978

Fifth annual progress report describing current work in a broad-scaled reconnaissance geochemical study of landscape materials in the major coal-, uranium-, and oil shale-bearing lands of the western United States.

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This is the fifth in a series of annual reports describing studies in environemental geochemistry of the western energy region. A wide variety of work has been undertaken, much of it focusing on background geochemical studies in rocks, soils, stream sediments, vegetation, and water. Collectively, these studies constitute an attempt to define and quantify the regional geochemical background or baseline in the area. Most of the summary baseline data have been reported in the two previous annual reports (U.S. Geological Survey, 1976, 1977). Baseline data for soils in the San Juan Basin and for rocks of the Fort Union Formation in the Northern Great Plains and the Garden Gulch Member of the Green River Formation in the Piceance Basin appear in this report.

A broad spectrum of topical studies continued, many of which were first conceived during the regional background surveys. Much of this work has focused on two broad problem areas: 1) geochemical change in native vegetation due to powerplant opeations or strip-mine reclamation, and 2) availabiliy to native plants of elements in soils and in rock materials that may become plant-growth media in areas of mine-spoil reclamation. Six of the eleven papers in this report cover specific aspects of these problems. Guidelines developed from both the baselines studies and these topical studies contribue to environmental impact evaluation and to effective reclamation and restoration of disturbed areas.

Spatial Variation in Total Element Content in Soils in Northwest New Mexico and Differences in Soil Composition at the Great Group Taxonomic Level

by

R. C. Severson

Samples of A- and C-horizon soils were collected at 47 locations in northwest New Mexico (fig. 1) from an area underlain by the Kirtland Shale, Fruitland Formation, and Mesaverde Group of Cretaceous age (Dane and Bachman, 1965). Sampling locations were selected randomly and fit into a five-level, unbalanced, nested, analysis-of-variance design (Leone and others, 1968). The sampling design is as diagramed in figure 2. Within the irregular boundaries of the selected area, cells 50 km on a side were arranged to provide maximum coverage (fig. 3). Each of the eight 50-km cells was divided into areas of decreasing size, as follows: four 25-km cells, each of which was divided into 25 5-km cells, which were then divided into 25 1-km cells. Cells to be sampled were randomly selected, as follows: all four 25-km cells, two 5-km cells in a 25-km cell and one 5-km cell in each of the three other 25-km cells, two 1-km cells in one 5-km cell and one 1-km cell in each of the four other 5-km cells. This nested arrangement of cells to be sampled is shown in figure 3, and it resulted in 48 sampling locations; however, only 47 locations were actually sampled because one location was inaccessable. A sample of A- and C-horizon soil was collected from each location.

This work was undertaken to (1) provide background information on element content in soils of the area before large scale surface mining of coal occurs, (2) assess variability in element content in soils at various geographic distances, (3) determine the feasibility of preparing reliable maps of element content in soils on a regional basis, and (4) assess differences in soil composition at the great group taxonomic level and to relate, if possible, soil taxonomy and spatial variability.

Variation due to all laboratory procedures was estimated from replicate analysis of 16 samples selected randomly from the total of 94 samples collected. Eight A-horizon and eight C-horizon samples were split and randomly placed among the samples. This procedure insures that any systematic error in analysis would be effectively converted to random error.

All samples were dried at ambient temperature under forced air and then were disaggregated in a motor-driven ceramic mortar and pestle to pass a 2-mm stainless steel sieve. The samples were further ground to minus-100 mesh in a ceramic mill, and splits of this material were used for all chemical determinations.

All analyses were done in the laboratories of the U.S. Geological

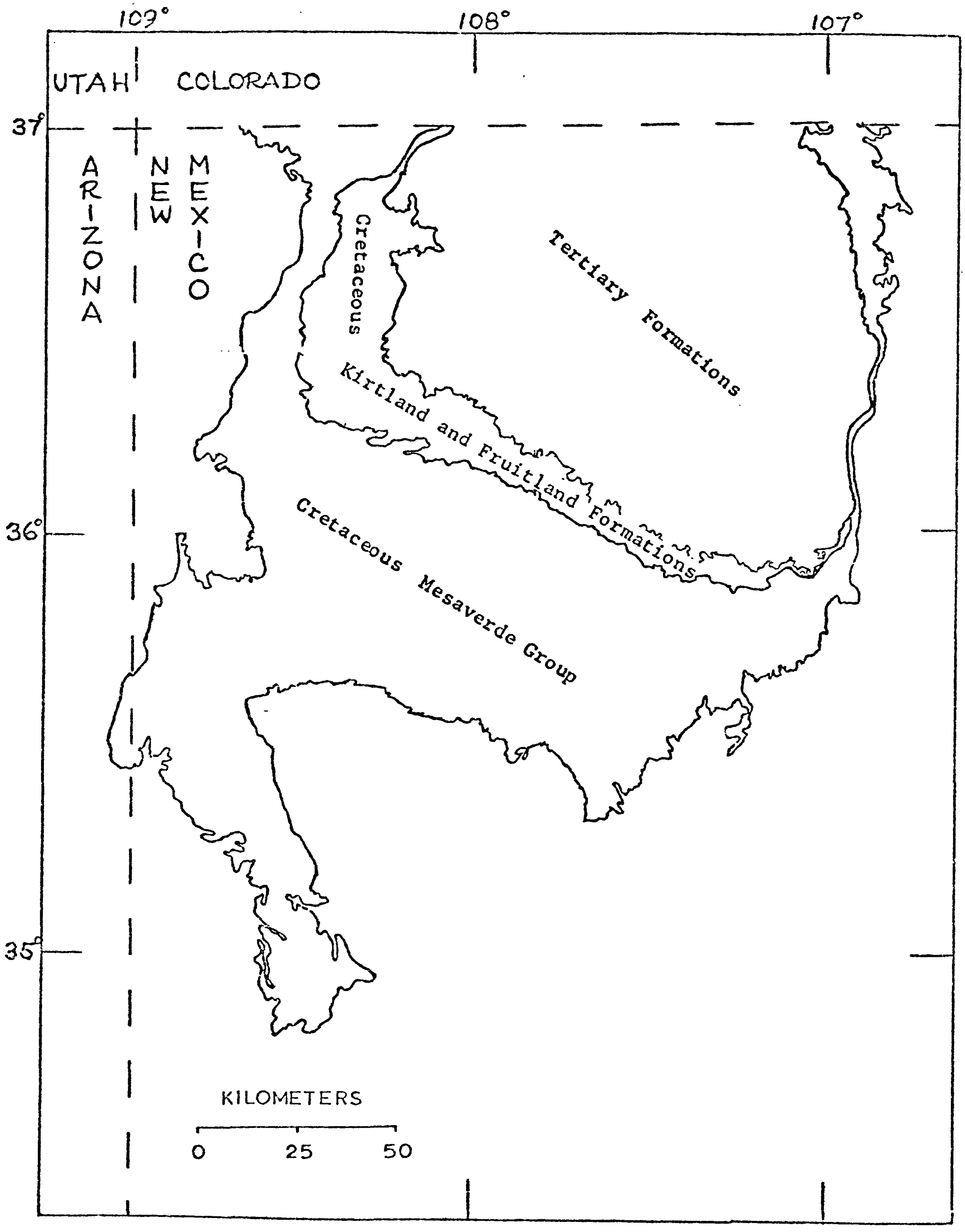


Figure 1.--Location of the study area in northwest New Mexico. Geology adapted from Dane and Bachman, 1965.

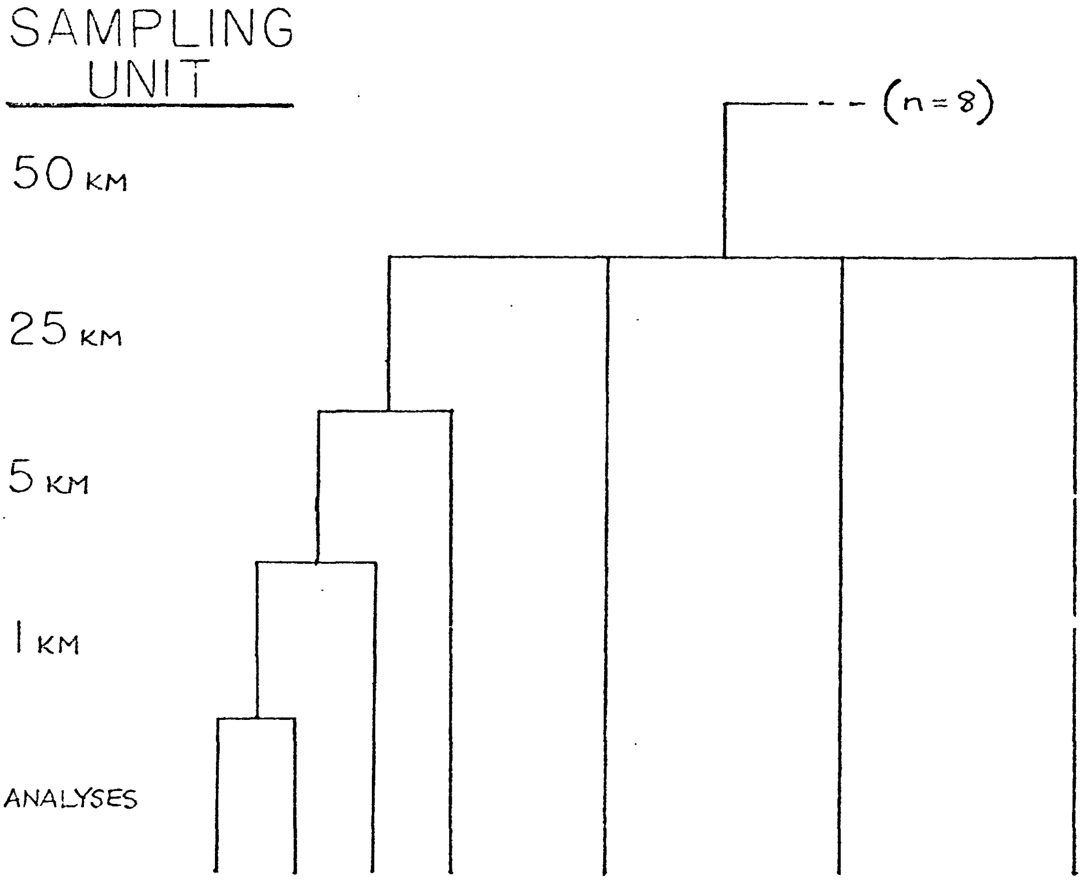


Figure 2.--Diagram of the unbalanced, nested, analysis-of-variance sampling design.

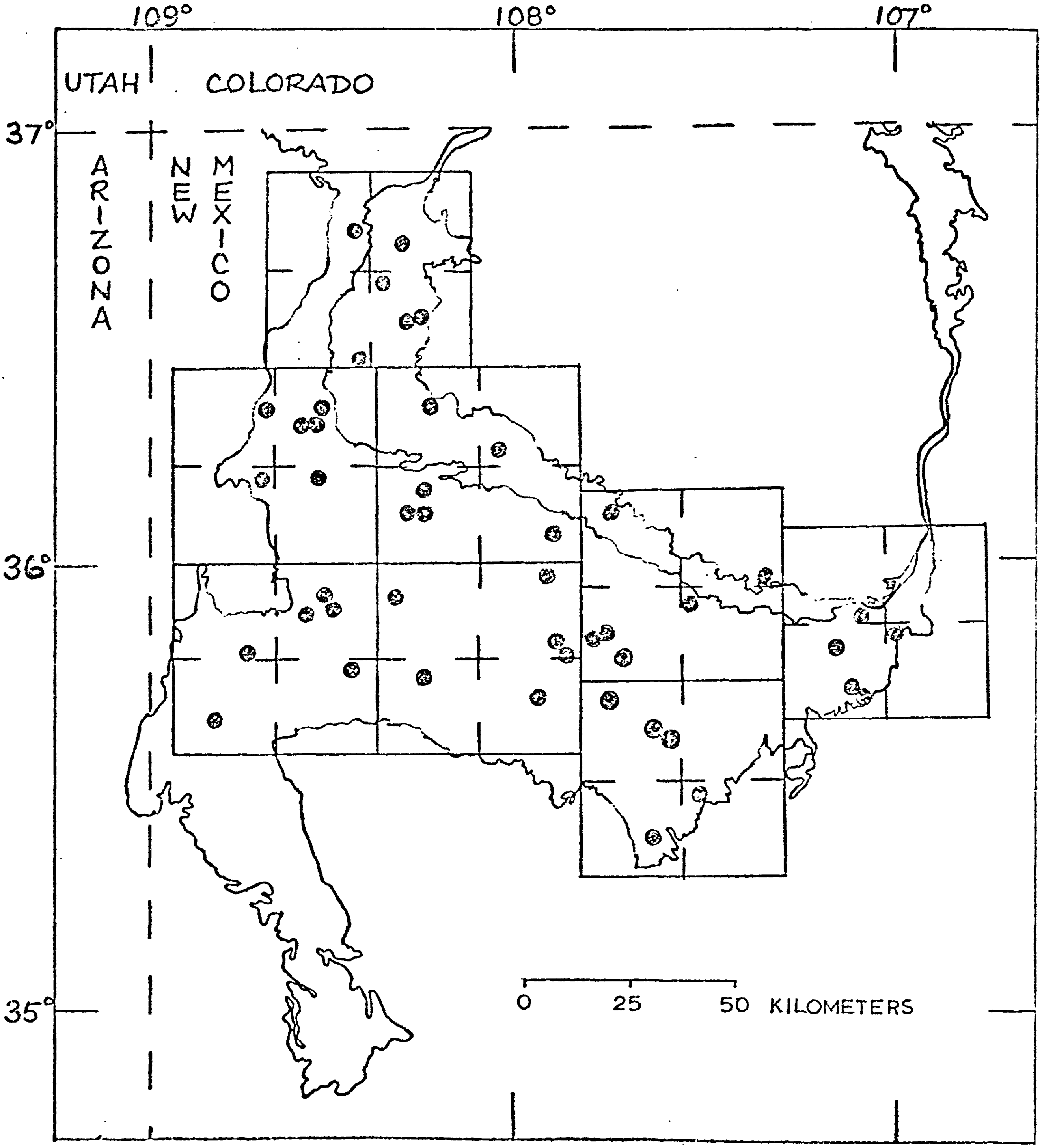


Figure 3.--Soil sampling localities in northwest New Mexico. Large squares (solid lines) are 50 km on a side; smaller squares (dashed lines) are 25 km on a side, Dots are sampling sites.

Survey at Denver, Colorado. The analytical methods employed are described in U.S. Geological Survey (1975) by J. S. Wahlberg (p. 69), Claude Huffman, Jr. (p. 71), and H. T. Millard, Jr. (p. 79); and in U.S. Geological Survey (1976) by A. L. Sutton, Jr. (p. 131). Analyses were performed by J. W. Baker, A. J. Bartel, P. H. Briggs, J. G. Crock, C. M. Ellis, Carol Gent, K. E. Horan, R. G. Havens, Claude Huffman, Jr., Fred Lichte, J. G. McDade, C. McFee, H. T. Millard, Jr., V. Merrit, Harriet Neiman, F. D. Perez, S. E. Prelipp, George Riddle, V. E. Shaw, A. L. Sutton, Jr., J. A. Thomas, M. L. Tuttle, R. E. Van Loenen, J. S. Wahlberg, and W. J. Walz.

Concentrations of some elements in some samples were below the limit of determination by a given analytical method. When more than one-third of the determinations for an element were below this limit the element was omitted from analysis of variance. For elements with less than one-third censored values, the censored values were replaced by small, arbitrary values. The use of replacement values is thought to not affect, in any substantial way, the geochemical interpretation of the data, because of the generally small number used. Baseline summary statistics of such censored data were estimated using the technique of Cohen (1959).

Voucher specimens of the 47 soils sampled were saved and later classified taxonomically by J. E. Ruiz and Leroy Hacker, soil scientists with the United States Department of Agriculture, Soil Conservation Service in Aztec and Albuquerque, New Mexico, respectively. Differences in chemical content were evaluated at the great group taxonomic level. Taxonomic criteria at the great group level consider the nature of all soil horizons collectively. Moisture and temperature regimes are the main criterion, and they are the cause of many differentiating soil properties as well as being properties of the whole soil rather than specific soil horizons. Further information on soil taxonomy can be found in Soil Survey Staff (1975).

Variance Components

Sampling was designed to measure variation over increments of distance expressed in terms of cell size. Total variation was subdivided into components, each associated with a predetermined cell size. These components for 39 elements, each expressed as percent of total variance, are shown in table 1 for A-horizon soils and in table 2 for C-horizon soils.

A principal interest in variance components is their use in calculating the minimum number of samples (n_r) required to estimate a cell mean with a certain degree of reliability and to determine the presence and magnitude of regional variation as a basis for constructing maps. The conventional F-test at the 0.05 probability level is used to test each variance component to determine if variation between cells is significantly different from variations within cells at each level of the sampling design. If a component fails to be significantly

Table 1.--Variance components, for A-horizon soils, expressed as a percentage of total variance.

[v, variance ratios for 25-km cells; n_r, number of random samples needed to map element distributions at the 25-km cell level at an 80 percent confidence level; *, is used to denote significance of variance components at the 0.05 probability level; ---, not determined]

Element	Total $\log_{10}$ variance	Percent of total variance between					v	n_r
		50 km	25 km	5 km	1 km	Analyses		
Al--------	.0133	0	36.3	0	61.9*	1.8	.6	3
As--------	.0358	18.9*	44.1	0	19.6	17.4	1.7	2
B---------	.1384	3.0	0	37.1	11.8	48.1	<.1	>20
Ba--------	.0306	0	0	57.2	33.9*	8.9	---	---
C, organic	.0959	10.9	13.6	0	57.6*	17.9	.3	4
C, total--	.0869	0	23.3	0	76.6*	.1	.3	4
Ca--------	.1201	2.9	21.0	13.9	62.0*	.2	.3	4
Co--------	.0264	0	10.6	37.1	40.0*	12.3	.1	8
Cr--------	.0406	0	22.1	0	0	77.9	.3	5
Cu--------	.1021	1.0	14.3	0	81.4*	3.3	.2	6
Er--------	.0185	0	30.2	6.8	0	63.0	.4	4
Fe--------	.0467	0	49.6	22.2	27.9*	.3	.9	3
Ge--------	.0144	0	41.0*	0	0	59.0	.7	3
Hg--------	.0555	8.7*	7.1	17.9	0	66.4	.2	6
K---------	.0079	0	84.5*	.9	14.1*	.5	5.5	2
La--------	.0277	0	17.6	41.9*	0	40.5	.2	6
Li--------	.0436	0	59.5	13.9	10.5	16.1	1.5	2
Mg--------	.0546	0	46.0	14.8	38.9*	.3	.9	3
Mn--------	.0740	0	29.2	24.3	37.8*	8.7	.4	4
Mo--------	.0615	0	53.0	17.0	0	30.0	1.1	3
Na--------	.0910	2.2	16.2	0	0	81.6	.2	5
Nb--------	.0235	0	31.2	5.1	0	63.7	.5	4
Ni--------	.0461	0	34.4	27.8	33.8*	4.0	.5	4
Pb--------	.0116	0	24.0	10.6	37.5	27.9	.3	5
Rb--------	.0760	0	39.3*	0	0	60.7	.7	3
S---------	.0328	4.9	0	0	67.5*	27.6	.1	15
Sc--------	.0423	0	13.2	45.3	36.1*	5.4	.2	7
Si--------	.0019	0	40.6	0	57.1*	2.3	.7	3
Sn--------	.1669	6.3	9.4	26.6	0	57.7	.2	6
Sr--------	.0218	0	69.8*	0	24.2*	6.0	2.3	2
Th--------	.0190	0	39.1	17.8	15.2	27.9	.6	3
Ti--------	.0205	7.3	0	14.8	75.2*	2.7	.1	11
U---------	.0162	0	45.5*	0	50.2*	4.3	.8	3
V---------	.0349	4.5	37.9	0	53.8*	3.8	.7	3
Y---------	.0185	0	21.2	34.5	16.3	28.0	.3	5
Yb--------	.0200	5.3	0	49.4	.1	45.2	.1	14
Zn--------	.0299	0	40.9	11.5	37.0*	10.6	.7	3
Zr--------	.0642	3.7	8.1	27.9	0	60.3	.1	7

Table 2.--Variance components, for C-horizon soils, expressed as a percentage of total variance.

[v, variance ratios for 25-km cells; n_r, number of random samples needed to map element distributions at the 25-km cell level at an 80 percent confidence level; *, is used to denote significance of variance components at the 0.05 probability level; ---, not determined]

Element	Total $\log_{10}$ variance	Percent of total variance between						
		50 km	25 km	5 km	1 km	Analyses	v	n_r
Al----------	.0156	0	53.2	11.3	33.4*	2.1	1.1	3
As----------	.0371	2.2	51.0*	0	38.2*	8.7	1.1	3
B-----------	.2015	0	7.2	28.2	0	64.6	.1	11
Ba----------	.0404	0	59.6	21.6	8.0	10.8	1.5	2
C, carbonate	.4027	0	75.1*	0	20.3*	4.6	3.0	2
C, organic--	.1619	17.3*	5.7	0	60.2*	16.8	.3	4
C, total----	.1152	6.5	55.6*	0	37.8*	.1	1.6	2
Ca----------	.1539	0	65.0*	0	34.9*	.1	1.9	2
Co----------	.0550	0	12.8	0	84.6*	2.6	.2	7
Cr----------	.0496	0	29.9	0	40.9	29.2	.4	4
Cu----------	.0900	0	30.1	18.4	25.3	26.2	.4	4
Er----------	.0168	0	7.5	0	50.3	42.2	.1	11
Fe----------	.0471	0	36.4	0	63.2*	.4	.6	4
Ge----------	.0118	0	18.5	0	28.2	53.3	.2	5
Hg----------	.0758	0	51.0	2.4	23.7	22.9	1.0	3
K-----------	.0212	0	44.4*	0	54.9*	.7	.8	3
La----------	.0176	0	28.8	8.3	24.3	38.6	.4	4
Li----------	.0551	1.3	27.0	0	50.0*	21.7	.4	4
Mg----------	.0918	0	67.1*	0	32.7*	.2	2.0	2
Mn----------	.1332	0	8.7	0	84.2*	7.1	.1	9
Mo----------	.0409	0	0	6.3	50.4	43.3	---	---
Na----------	.0522	0	57.9*	0	41.0*	1.1	1.4	2
Nb----------	.0162	0	15.8	0	51.5	32.7	.2	6
Ni----------	.0631	0	51.7	0	45.8*	2.6	1.1	3
Pb----------	.0182	0	19.8	15.2	35.7	29.3	.3	5
Rb----------	.0416	3.1	24.5	0	42.0	30.4	.4	4
S-----------	.2387	0	48.5*	0	50.9*	.6	.9	3
Sc----------	.0420	0	18.5	17.4	55.4*	8.7	.2	5
Si----------	.0028	0	53.7*	0	39.9*	6.4	1.2	3
Sn----------	.1637	0	25.2	37.8	7.2	29.8	.3	4
Sr----------	.0315	0	52.0*	0	42.6*	5.4	1.1	3
Th----------	.0191	0	25.2	36.1	25.7	13.0	.3	4
Ti----------	.0233	0	5.0	65.1*	27.6*	2.3	.1	15
U-----------	.0244	0	40.3	42.3*	14.8*	2.6	.7	3
V-----------	.0412	0	29.4	0	62.9*	7.7	.4	4
Y-----------	.0247	0	35.9	11.6	29.3	23.2	.6	4
Yb----------	.0373	0	5.9	0	86.3*	7.8	.1	13
Zn----------	.0500	0	44.3	6.4	48.9*	.4	.8	3
Zr----------	.0526	0	47.0	0	24.4	28.6	.9	3

different, it is not practical to attempt to map variation at the interval associated with that component because of the high probability that the variation within the cell masks the variation between the cells. Analytical-error variance components in excess of 50 percent are considered to be excessive. Any interpretations of the data for these elements must be made with caution.

The largest portion of the measured variation occurs, for most elements in both soil horizons, at two levels of the sampling design--between 25-km cells and between 1-km cells. Variation among 50-km cells is virtually nonexistent in both soil horizons. Variation between 5-km cells is nonexistent for some elements but is substantial for other elements. Cells 25 km on a side have been chosen as a manageable mapping interval.

In order to test the feasibility of using the data to prepare a map of element content based on 25-km means, a variance ratio ($\underline{v}$) is computed (tables 1 and 2). For 25-km cells the ratio is as follows:

$$\underline{v} = \frac{P_{50} + P_{25}}{P_5 + P_1 + P_e} \qquad (1)$$

where P is the percent of total variance between cells of the size indicated by the subscript (P_e = variance between samples).

This ratio is defined by Miesch (1976, p. 8) as a "relative measure of the compositional heterogeneity among, and the compositional homogeneity within, mapped units of the population being studied." A value of $\underline{v}$ equal to 1.0 is chosen as the value below which a reliable map could not be prepared. If the $\underline{v}$ is greater than one, then there is some basis for preparing a map that will reliably depict the true geochemical pattern, because the relatively large variation among the 25-km cells tends to obscure or mask the smaller variation measured within each 25-km cell.

In addition to using $\underline{v}$ to indicate reliability of data for presentation in the form of a map, it can also be used to estimate the number of samples that would need to be collected at random from each 25-km cell in order to prepare a reliable map. Values of $\underline{n_r}$ (number of random samples) are tabulated for each element for A- and C-horizon soils in tables 1 and 2, respectively.

As, K, Li, Mo, and Sr in the A horizon meet the minimum requirements for representing their variation at the 25-km cell level on a map (table 1). In the C horizon, Al, As, Ba, Be, carbonate C, total C, Ca, Hg, Mg, Na, Ni, Si, and Sr also meet the minimum requirements (table 2). These elements are represented on maps in figures 4-20. The values used to construct the maps are arithmetic means of 25-km cells. The cell means are not contoured because there are no apparent regional trends (the variance at the 50-km level is nonsignificant). Only for As in the A horizon (fig. 4) and C horizon (fig. 10) are such trends suggested. Overall, however, there is generally no regional pattern because of the lack of variation measured for the 50-km cell.

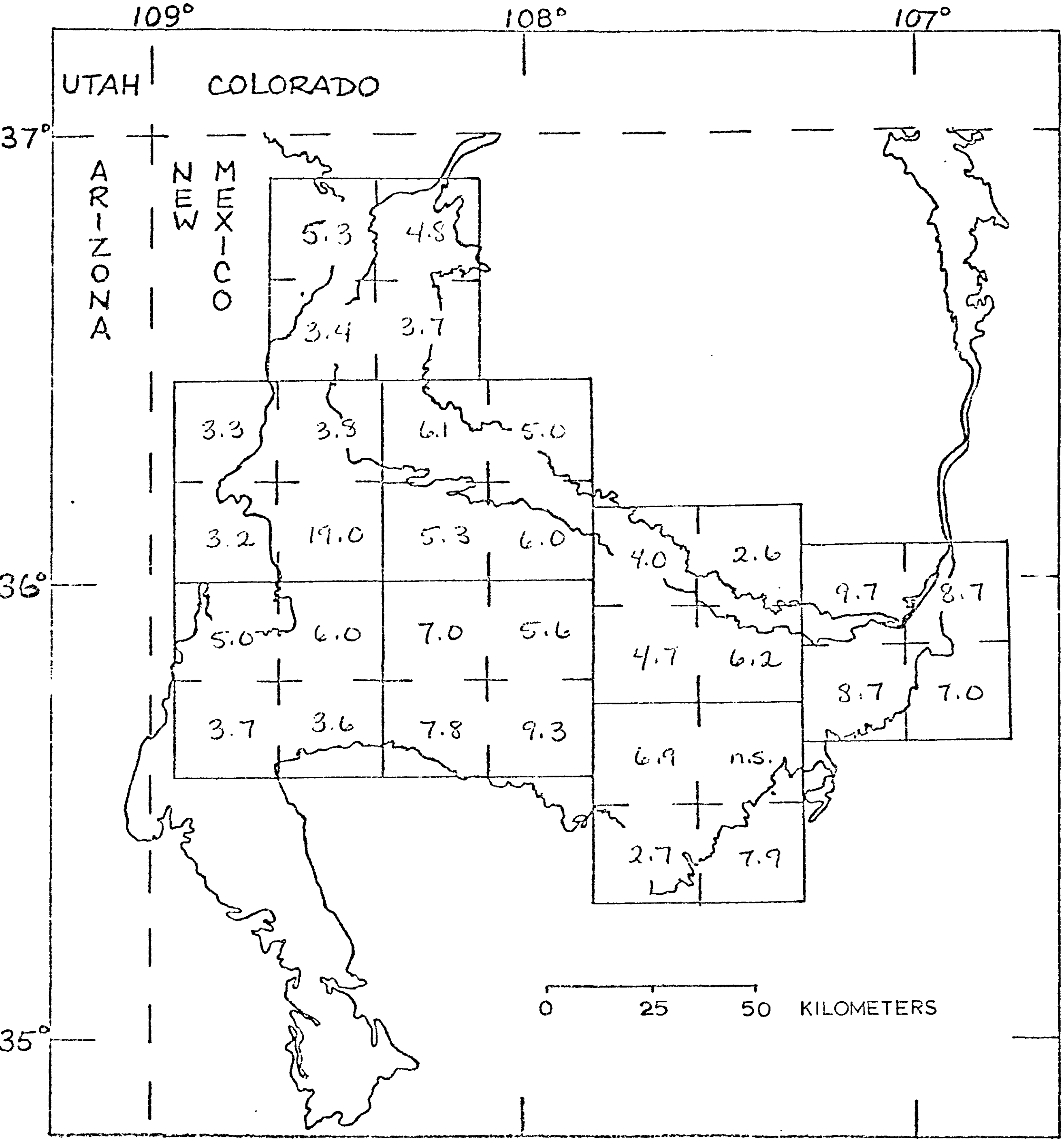


Figure 4.--Regional distribution of As in A-horizon soils. Values (ppm) are arithmetic means of 25-km cells; n.s., not sampled.

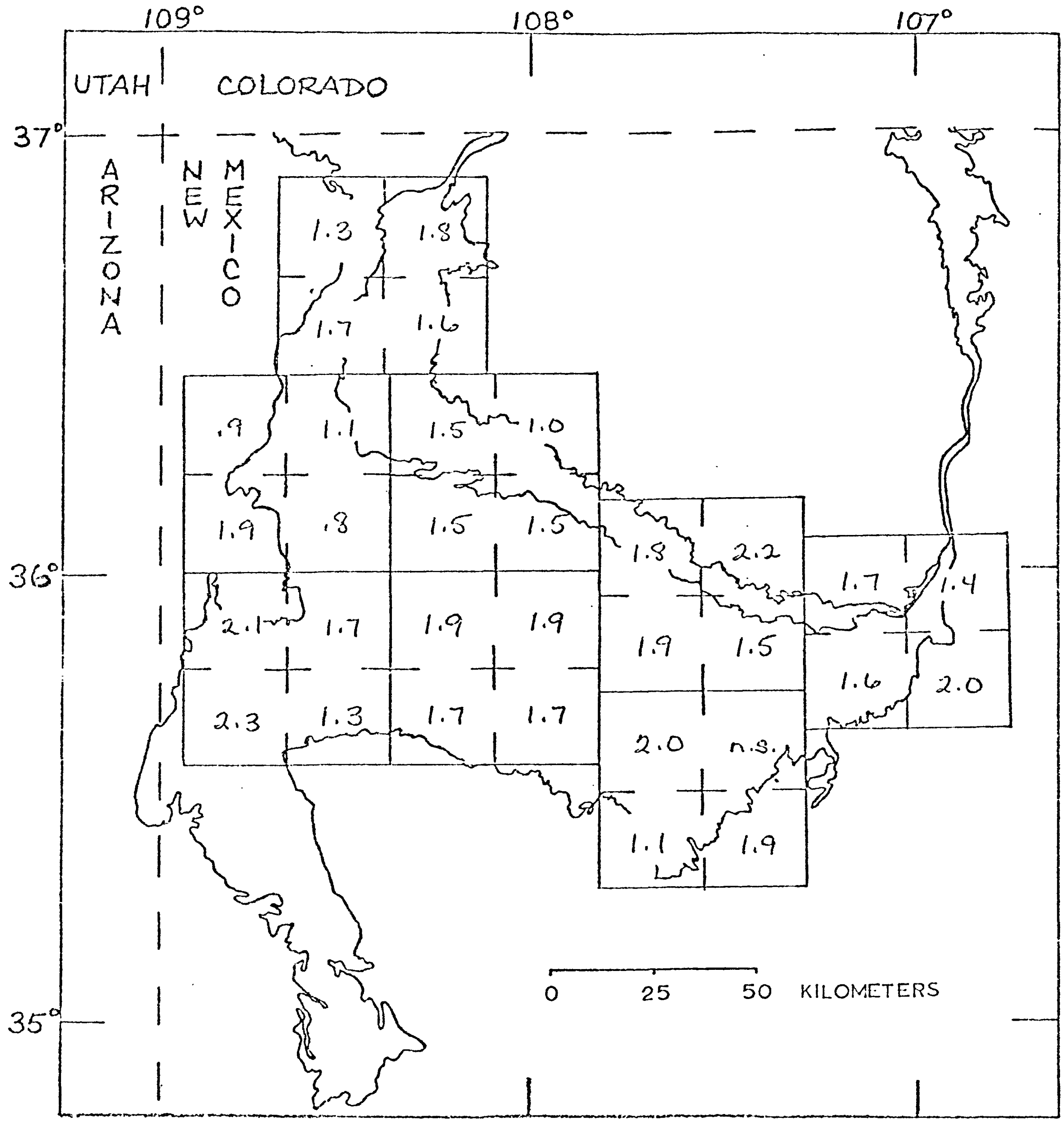


Figure 5.--Regional distribution of K in A-horizon soils. Values (%) are arithmetic means of 25-km cells.

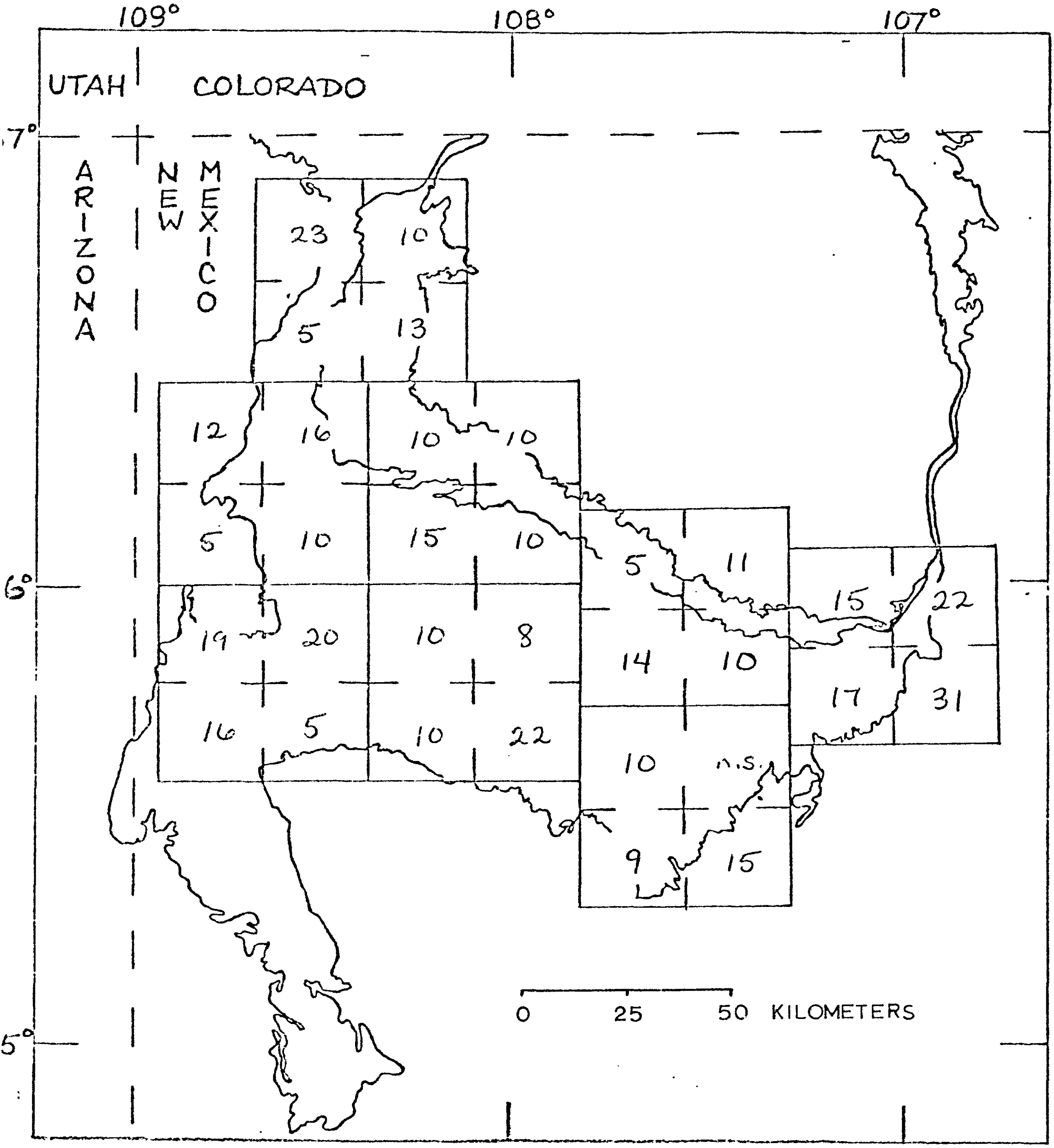


Figure 6.--Regional distribution of Li in A-horizon soils. Values (ppm) are arithmetic means of 25-km cells.

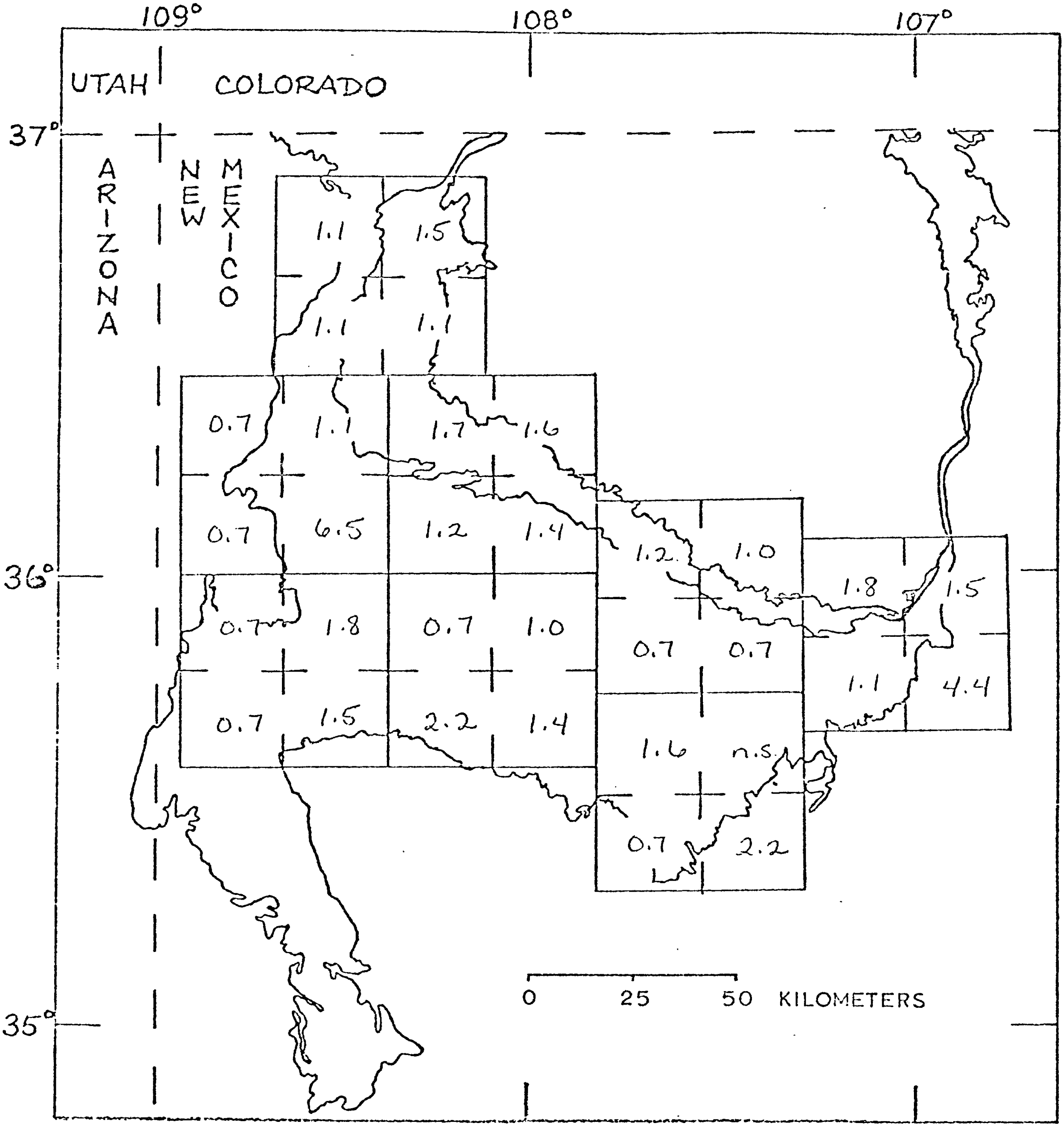


Figure 7.--Regional distribution of Mo in A-horizon soils. Values (ppm) are arithmetic means of 25-km cells.

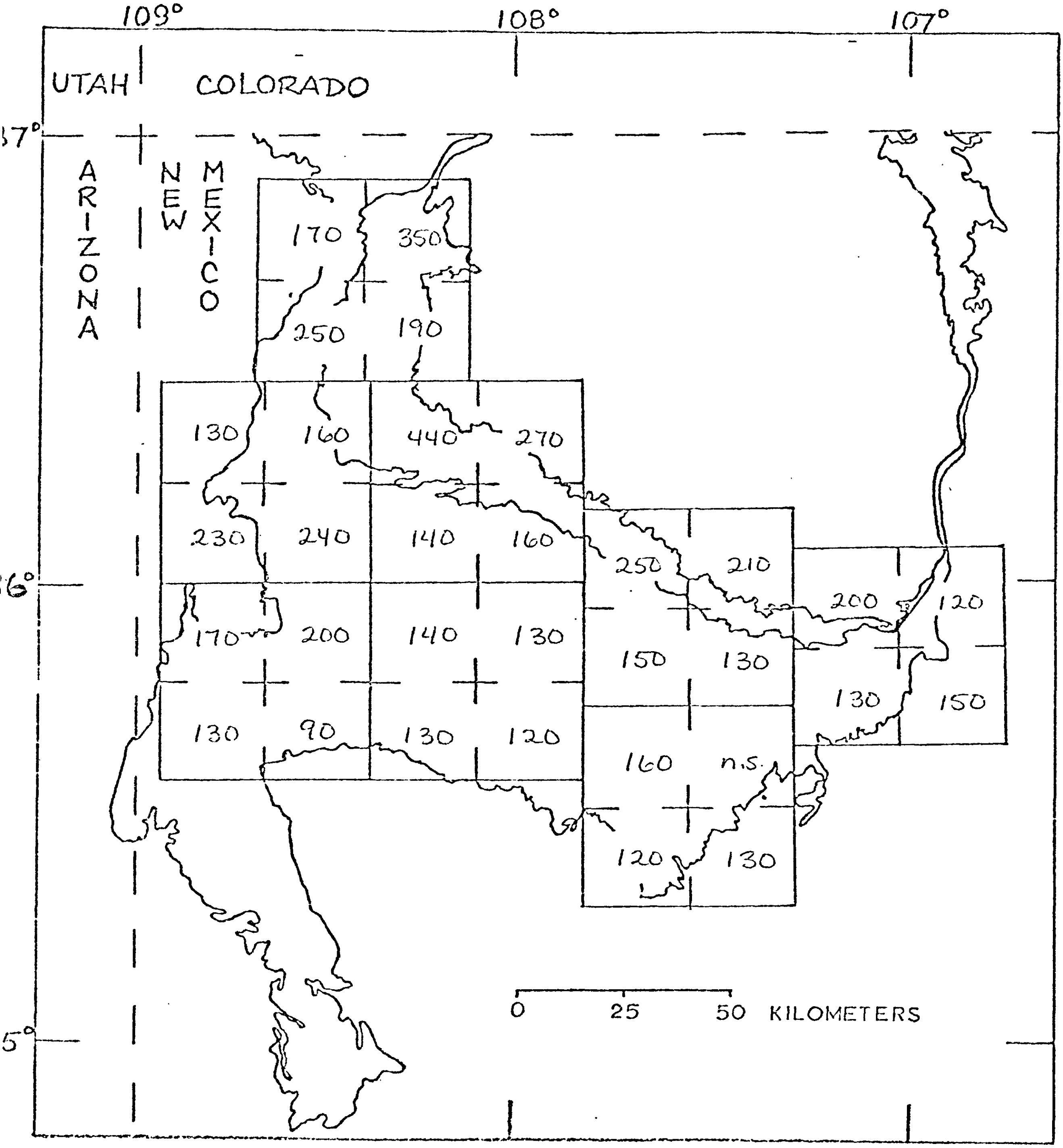


Figure 8.--Regional distribution of Sr in A-horizon soils. Values (ppm) are arithmetic means of 25-km cells.

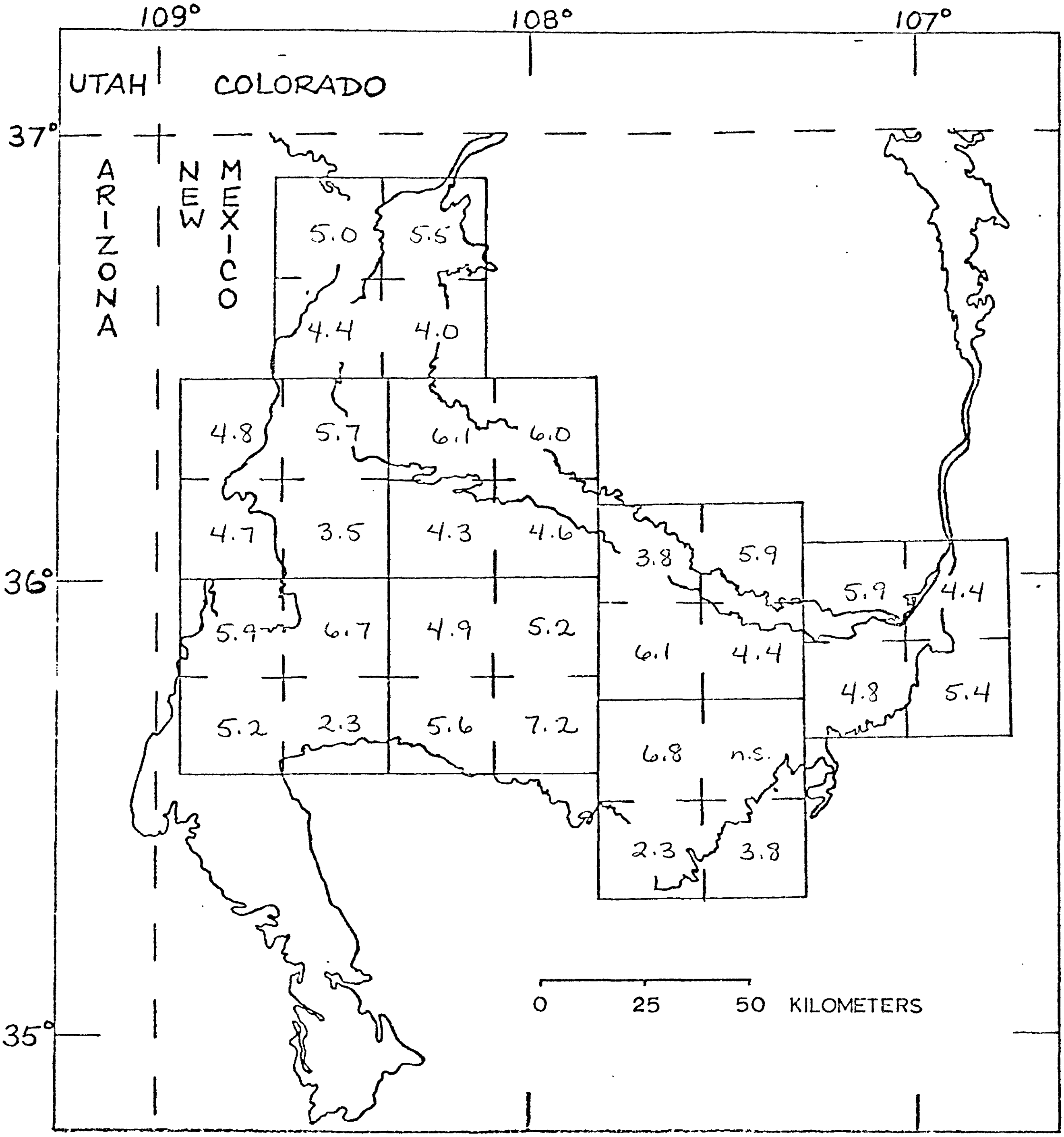


Figure 9.--Regional distribution of Al in C-horizon soils. Values (%) are arithmetic means of 25-km cells.

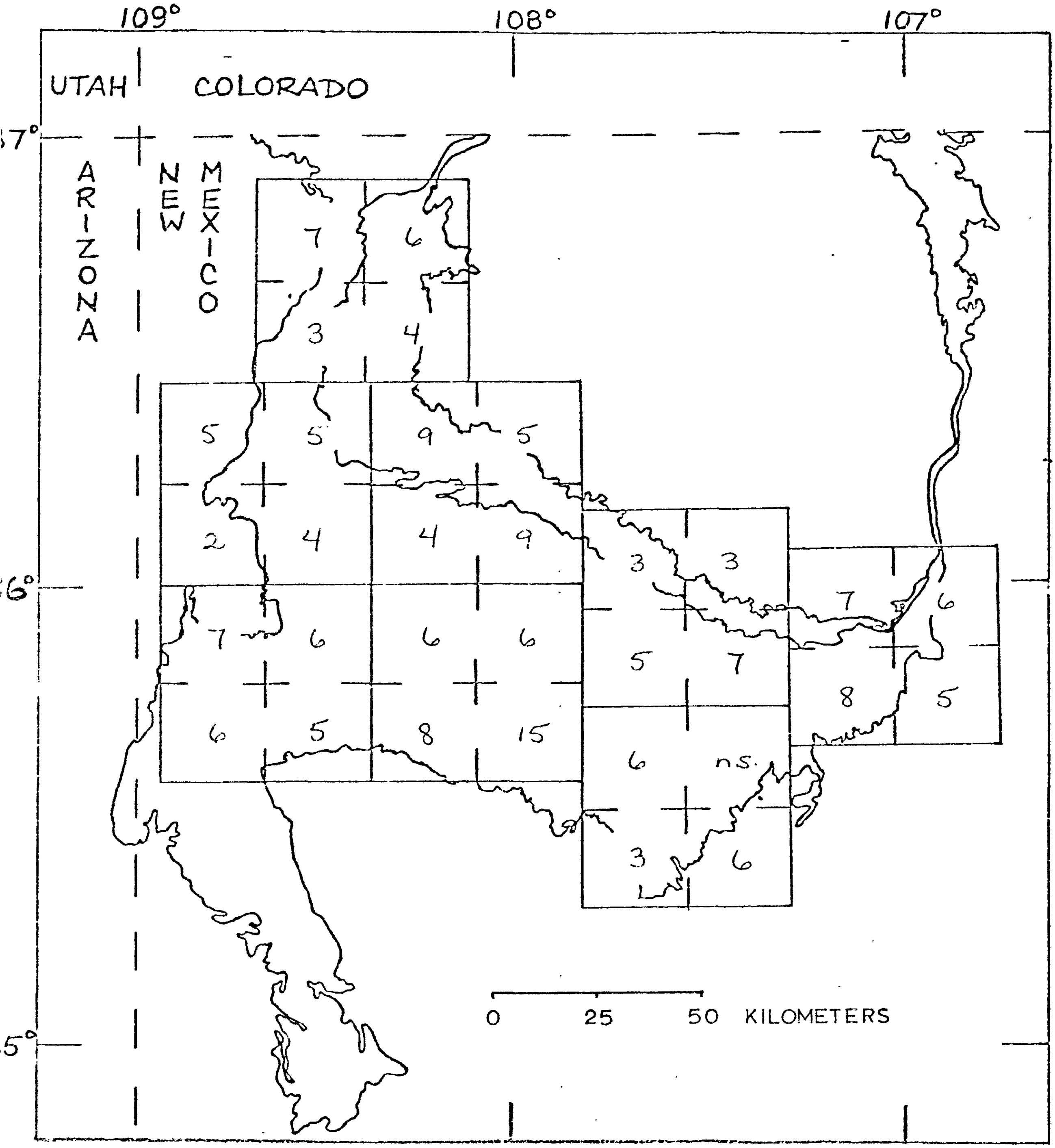


Figure 10.--Regional distribution of As in C-horizon soils. Values (ppm) are arithmetic means of 25-km cells.

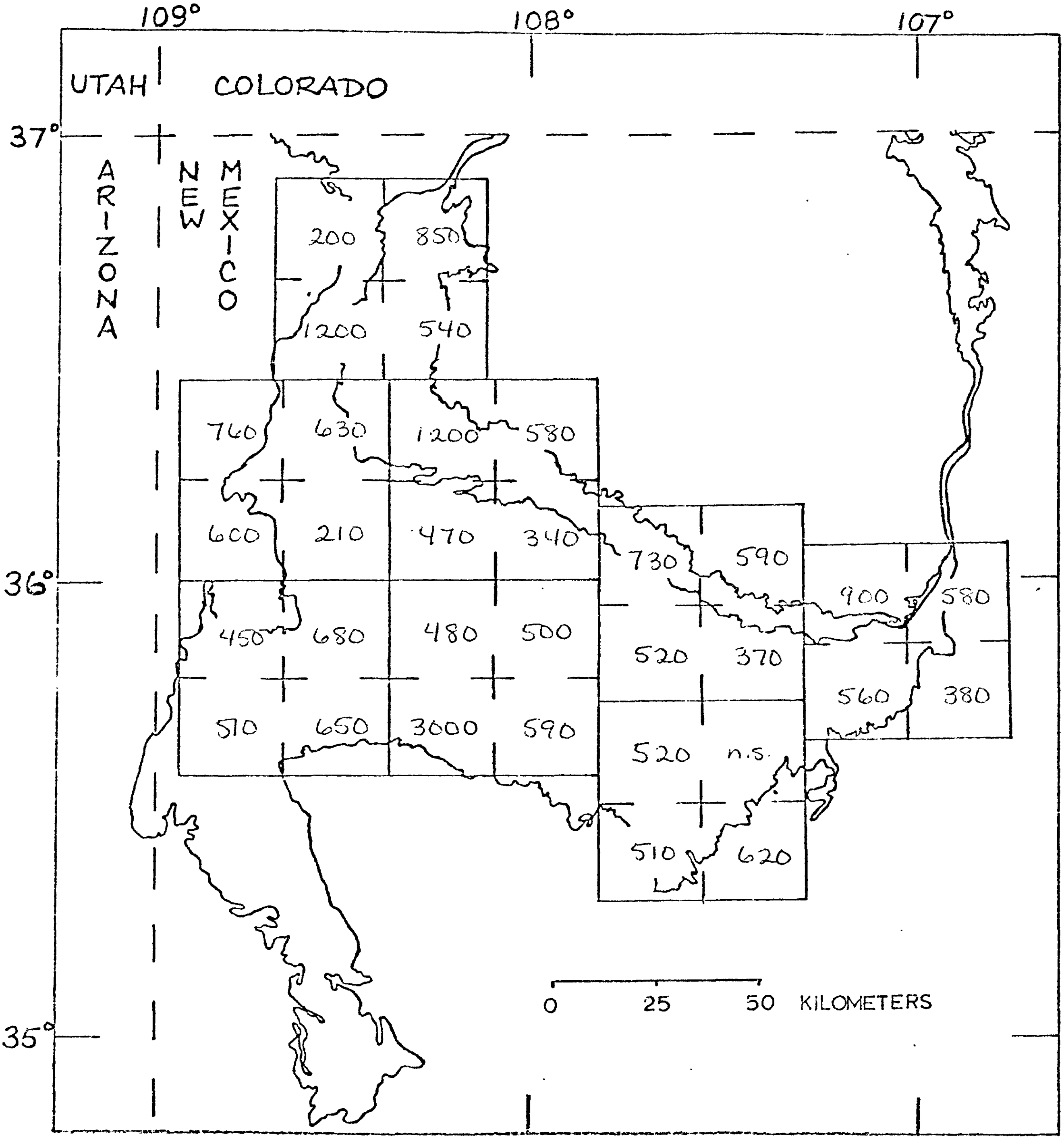


Figure 11.--Regional distribution of Ba in C-horizon soils. Values (ppm) are arithmetic means of 25-km cells.

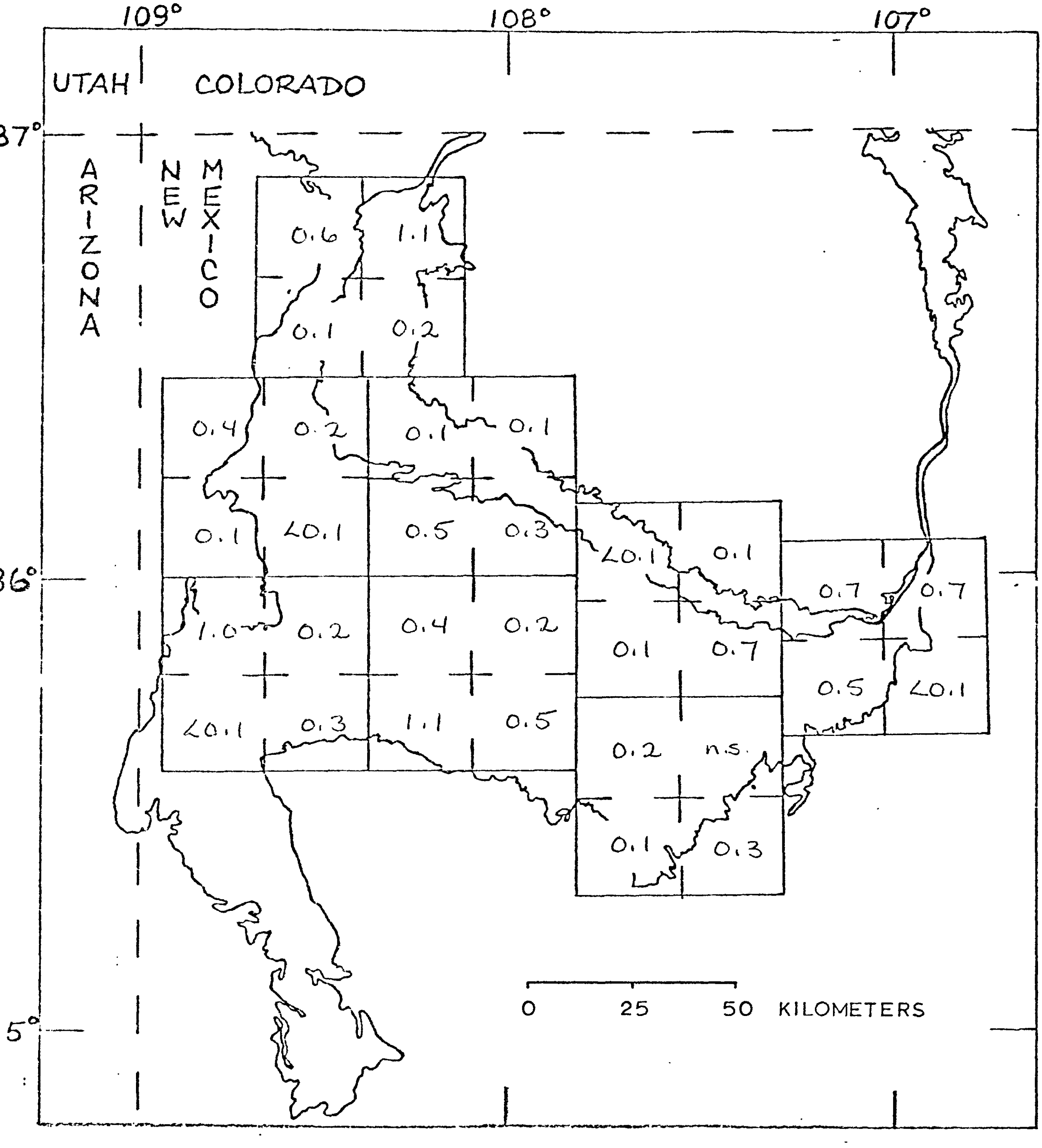


Figure 12.--Regional distribution of carbonate-C in C-horizon soils. Values (%) are arithmetic means of 25-km cells.

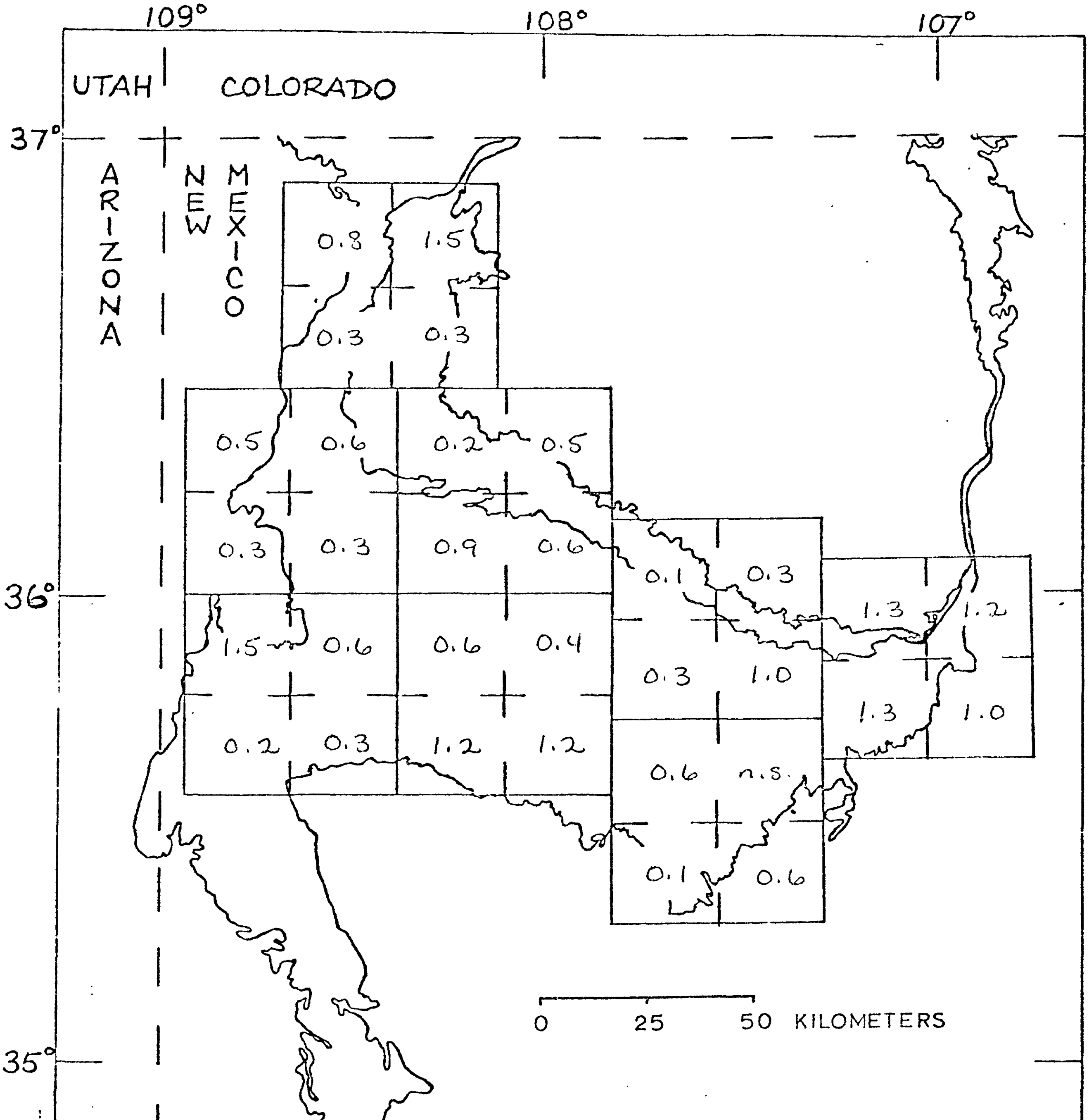


Figure 13.--Regional distribution of total-C in C-horizon soils. Values (%) are arithmetic means of 25-km cells.

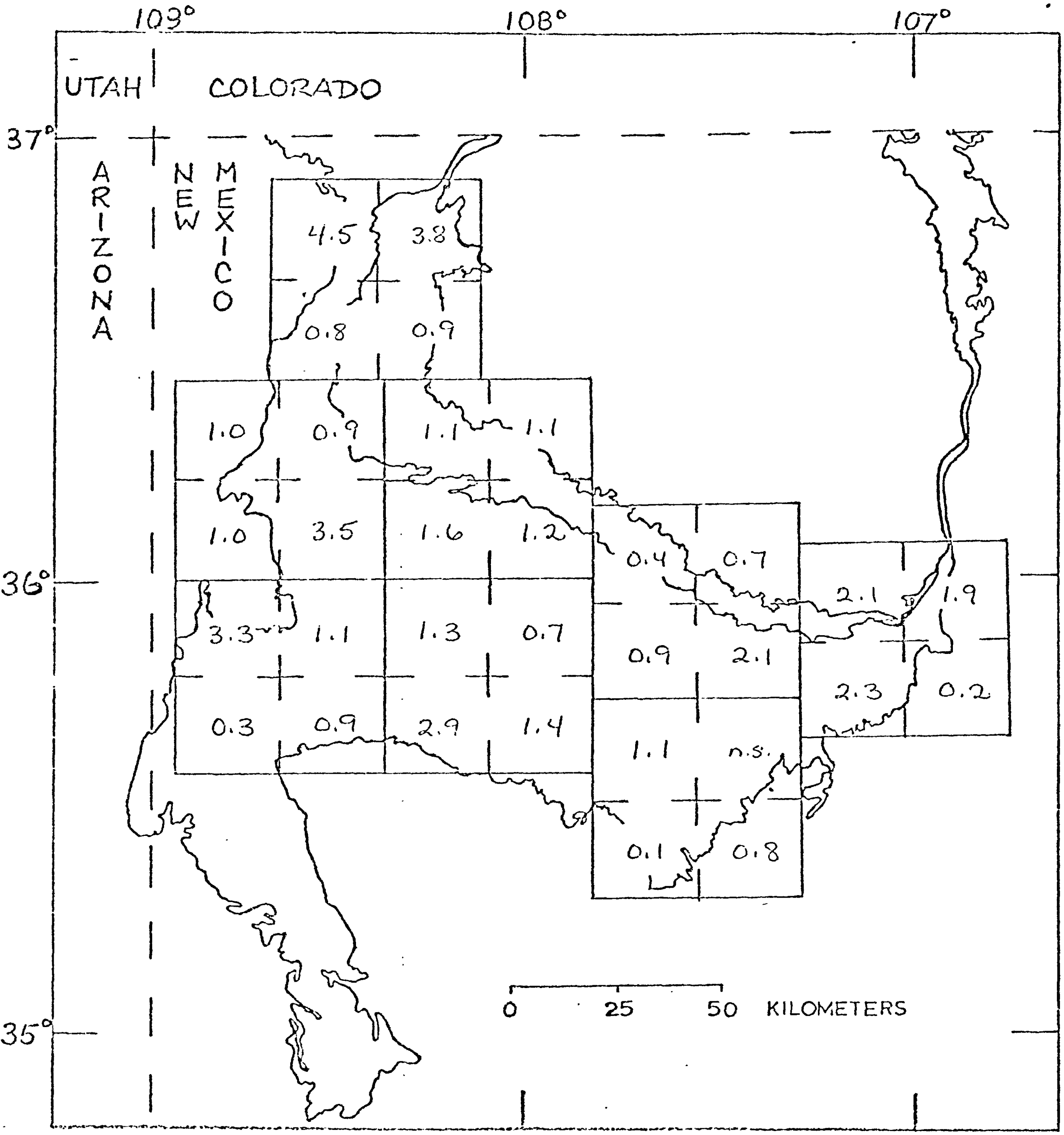


Figure 14.--Regional distribution of Ca in C-horizon soils. Values (%) are arithmetic means of 25-km cells.

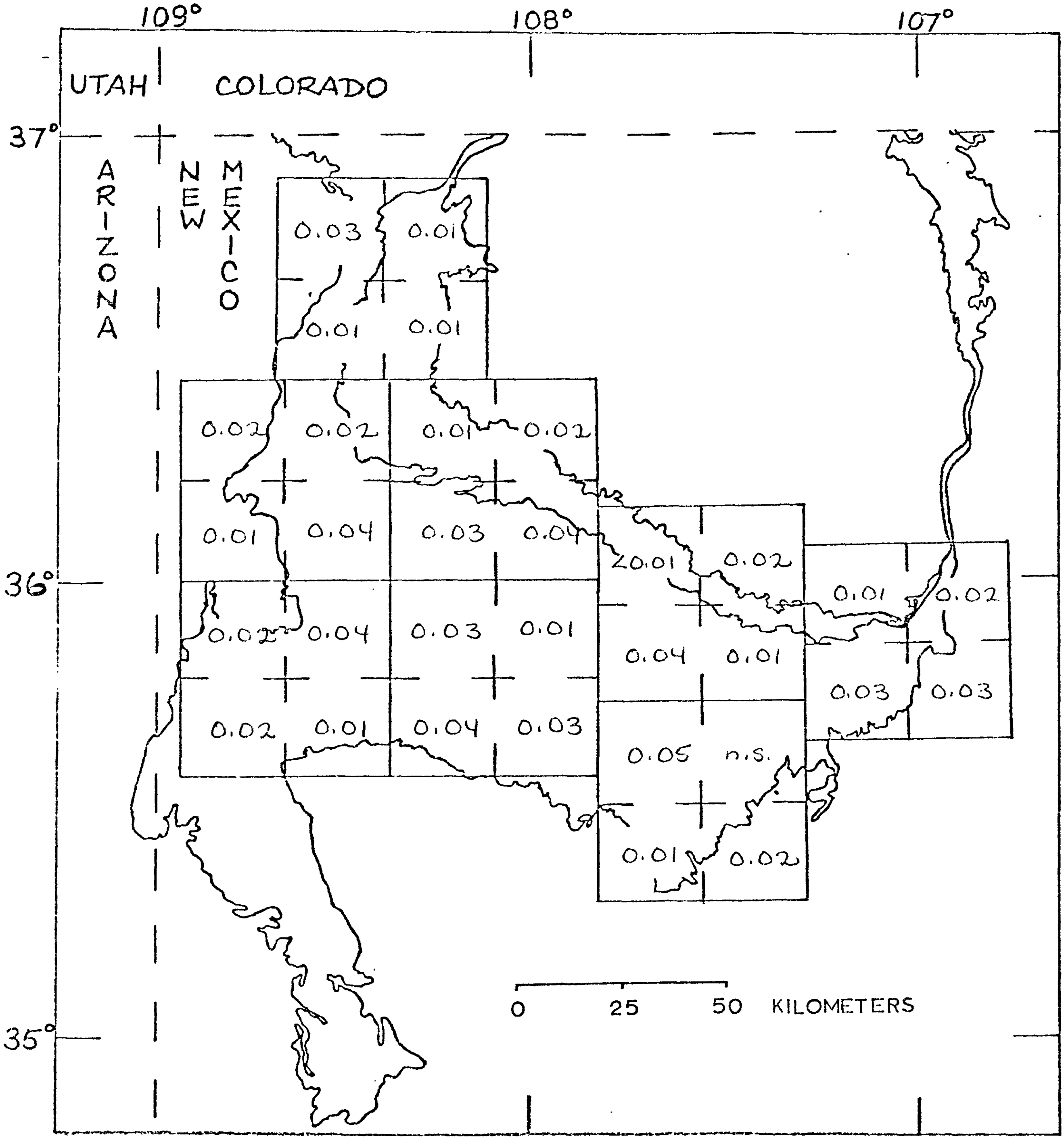


Figure 15.--Regional distribution of Hg in C-horizon soils. Values (ppm) are arithmetic means of 25-km cells.

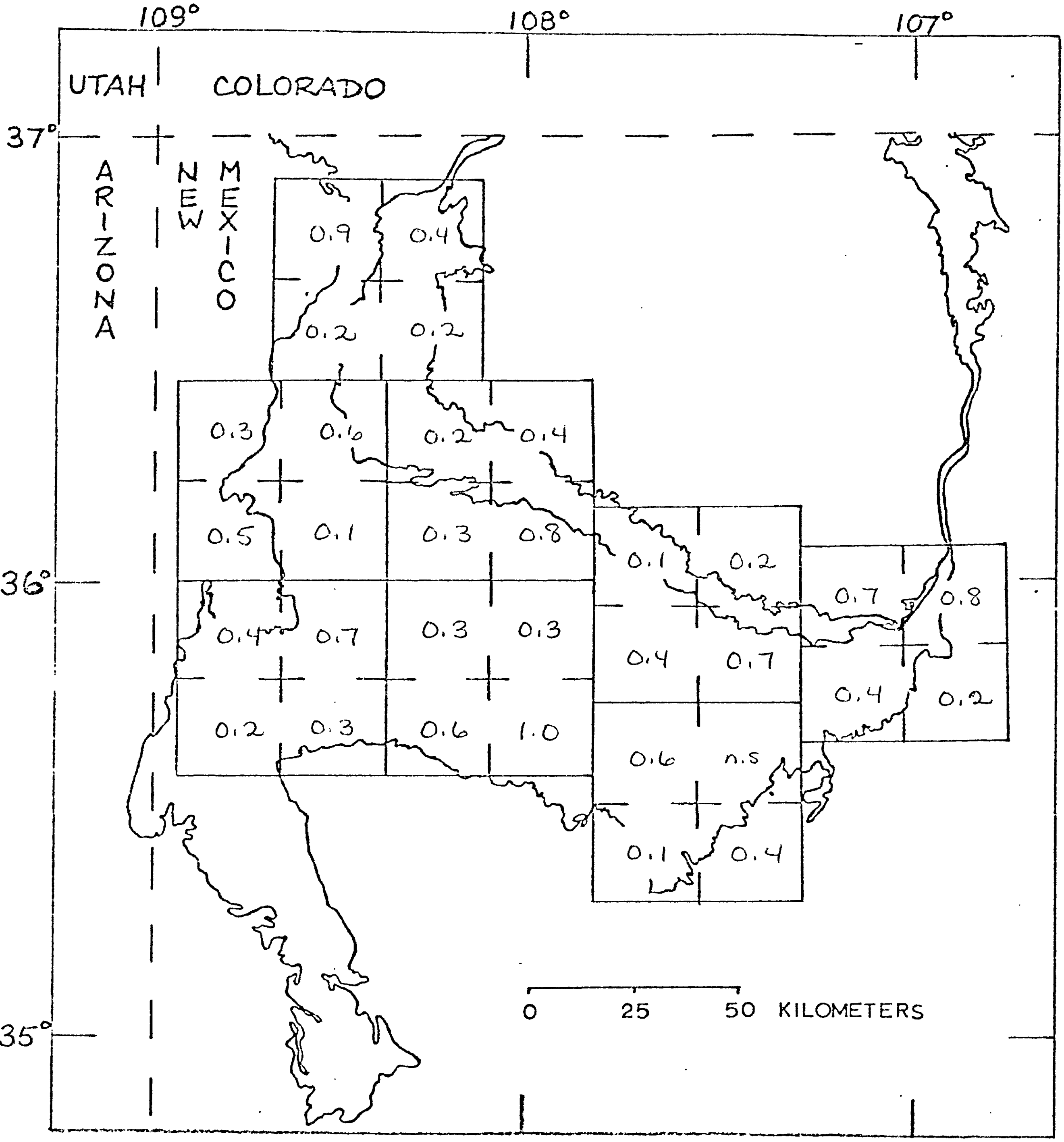


Figure 16.--Regional distribution of Mg in C-horizon soils. Values (%) are arithmetic means of 25-km cells.

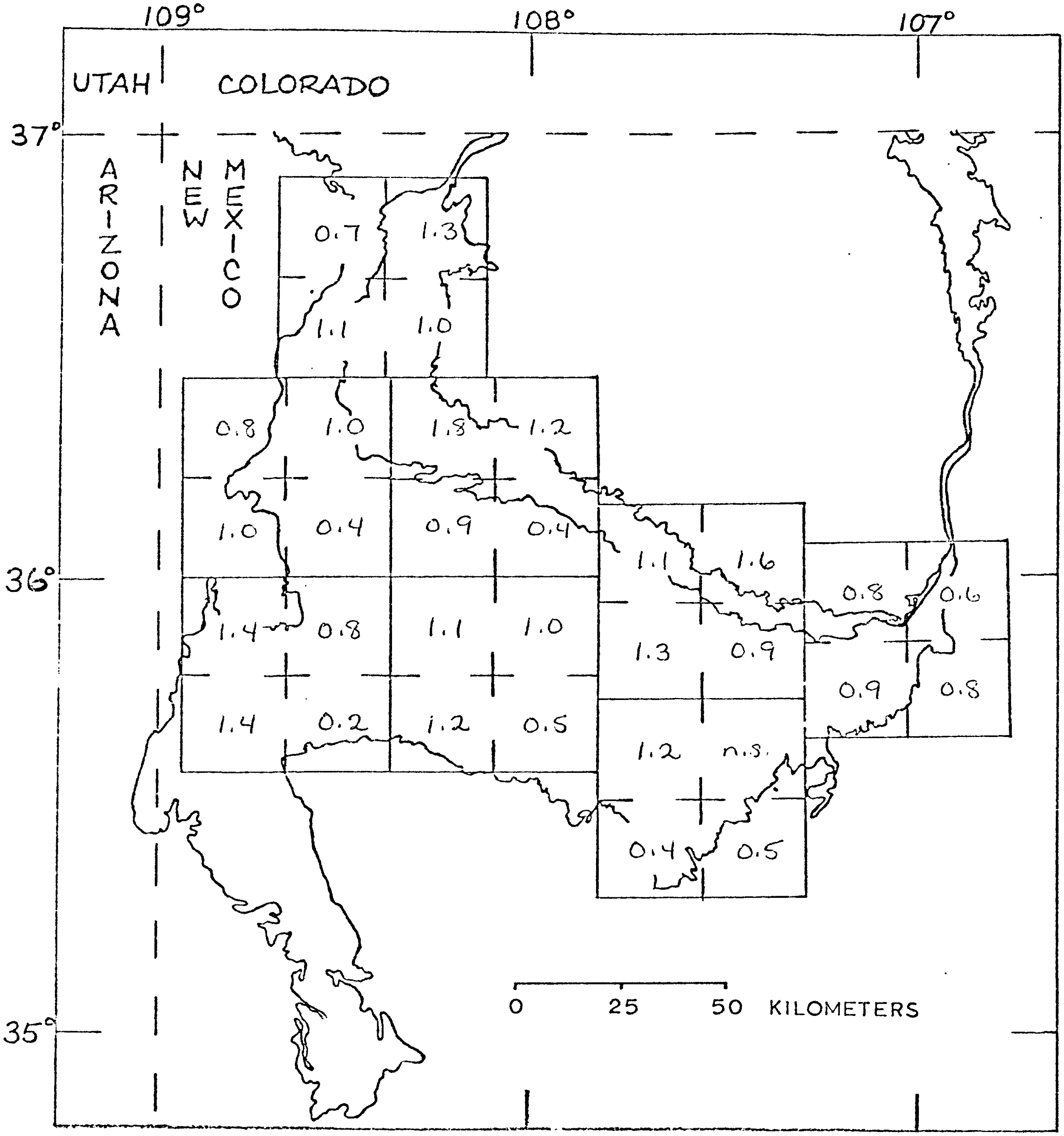


Figure 17.--Regional distribution of Na in C-horizon soils. Values (%) are arithmetic means of 25-km cells.

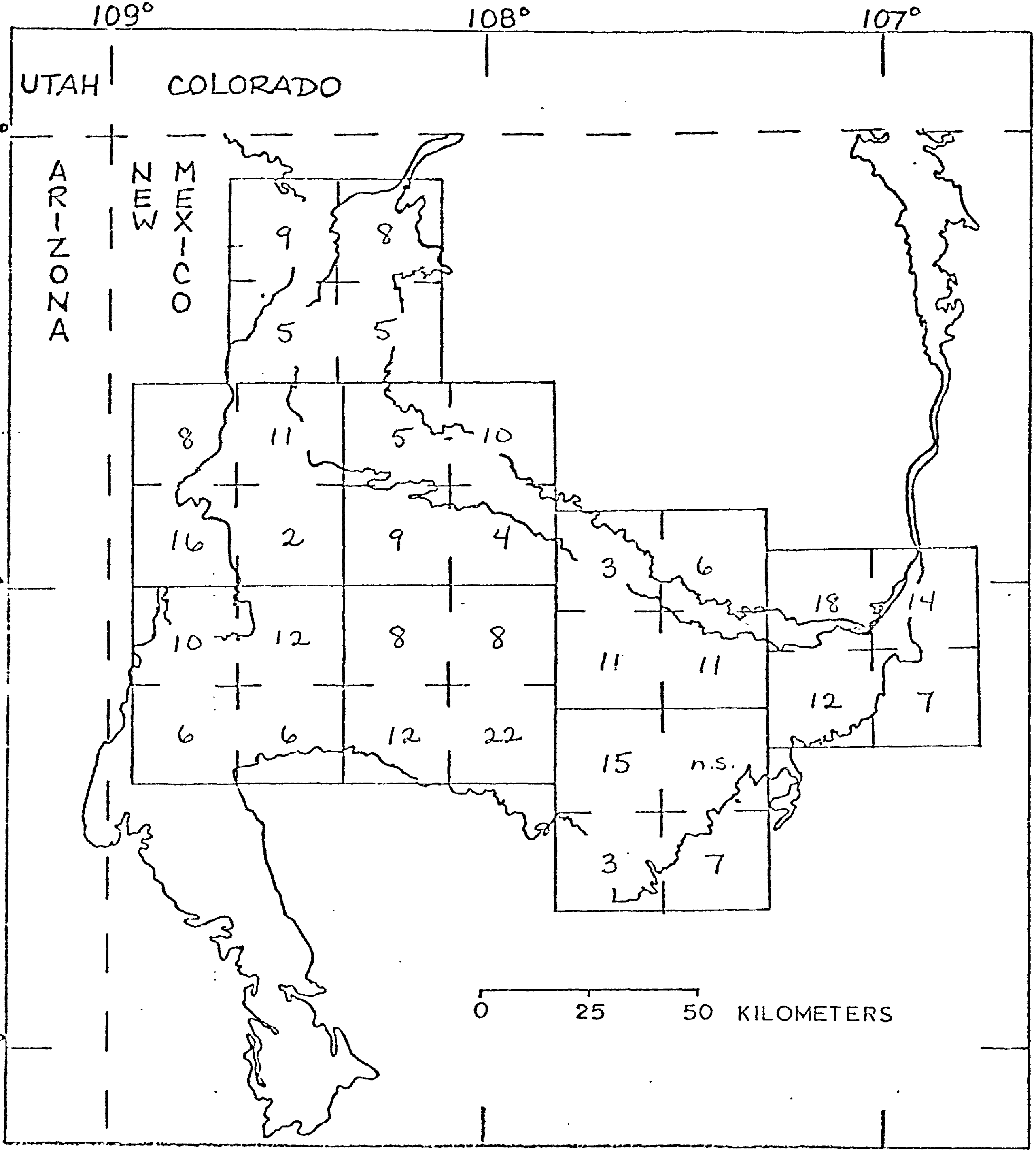


Figure 18.--Regional distribution of Ni in C-horizon soils. Values (ppm) are arithmetic means of 25-km cells.

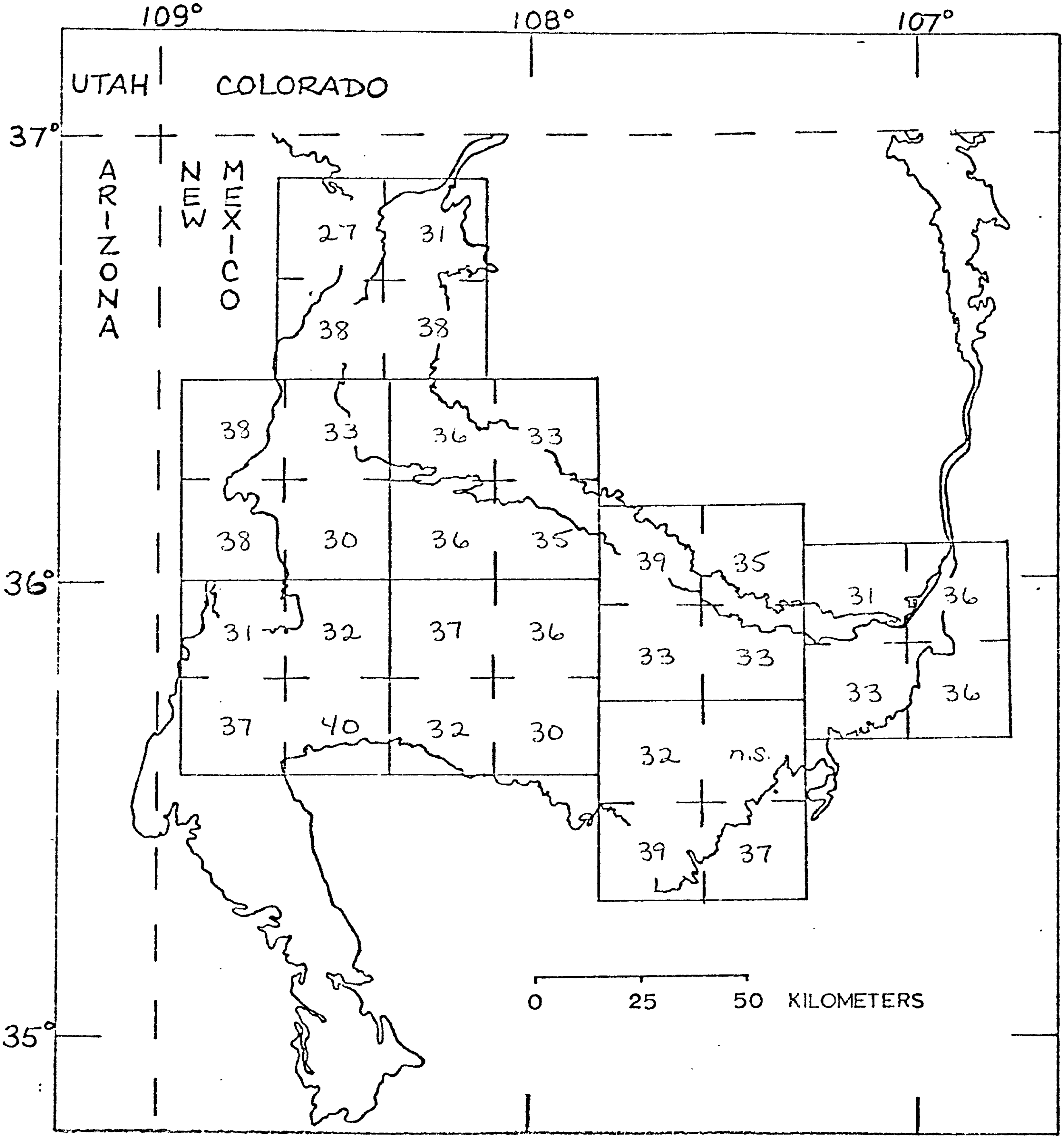


Figure 19.--Regional distribution of Si in C-horizon soils. Values (%) are arithmetic means of 25-km cells.

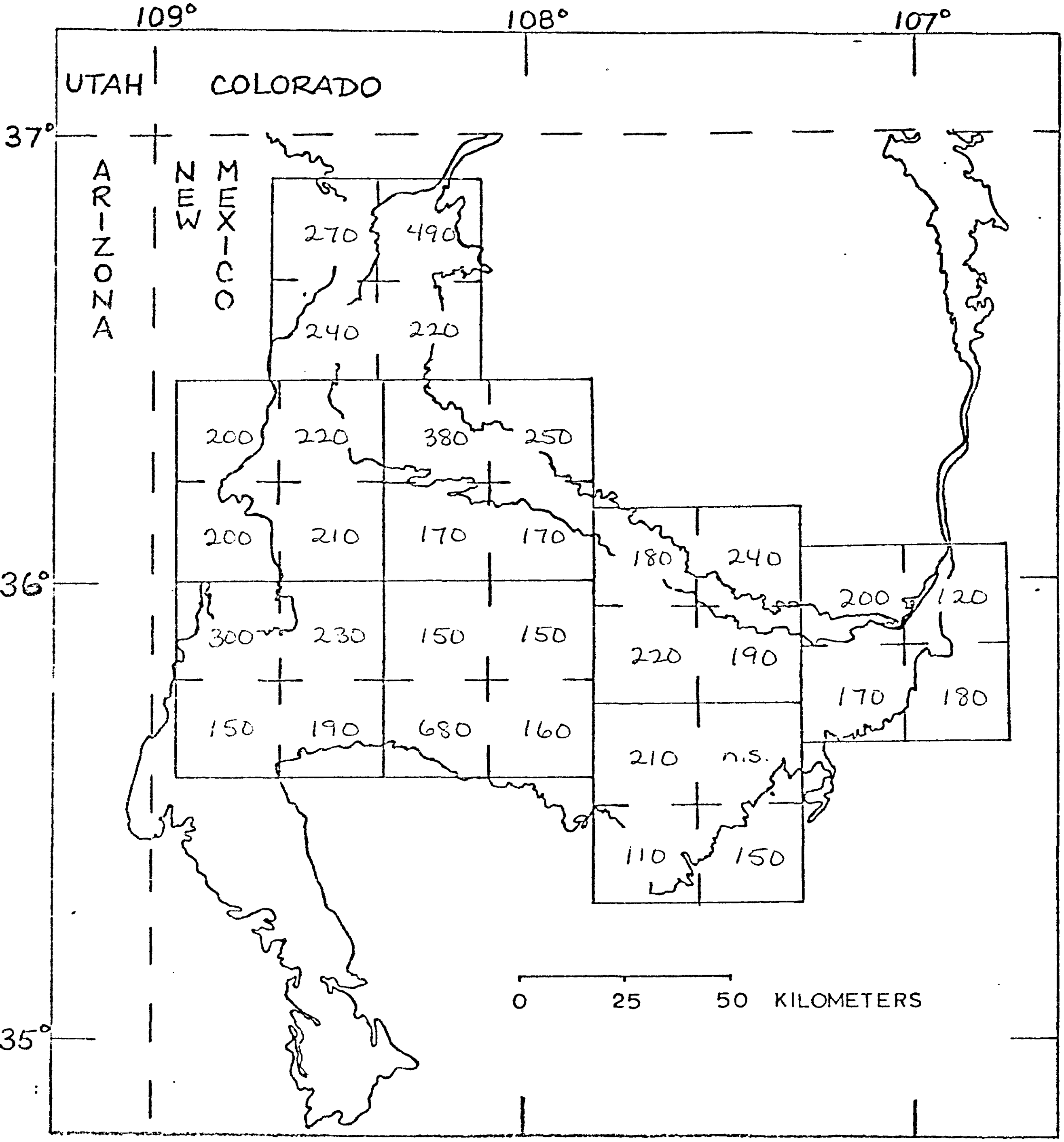


Figure 20.--Regional distribution of Sr in C-horizon soils. Values (ppm) are arithmetic means of 25-km cells.

Therefore, even though it may be possible to prepare reliable maps for a number of other elements by collecting three or four random samples per 25-km cell (n_r in tables 1 and 2), the maps thus generated would most likely exhibit only poorly developed regional patterns. Baseline values for the element composition of all soil materials in the area are summarized in tables 3 and 4, respectively. The baseline value reflects the range in concentration to be expected in samples of natural soil materials.

Soil Taxonomy

From the 47 voucher specimens, 17 soil series were recognized (table 5) and three specimens were not represented by any recognizable soil series. The 47 soils were divided into seven great groups (table 5). Six of the great groups consisted of two or more series while one great group was represented by a single soil. The arithmetic means for total content of each element were tested for significant differences using a multiple comparison test (Natrella, 1961, p. 3-40). The results of this test for A- and C-horizon soils are presented in tables 6 and 7, respectively. In addition, the data for the single sample representing the Haplustoll great group is included in those tables, but no attempt was made to statistically compare its element content with that of the other great groups, because no estimate of variance is possible for a single sample.

In general, there are significant differences between great groups for many elements. In the A horizon (table 6), 10 elements are significantly highest in content in the Natrargid great group (Si is also significantly lowest in content), 17 elements are significantly lowest in content in the Torripsamment great group (Si is also significantly highest), and only three elements show no significant differences between any of the great groups. However, only Mn and Fe in the Natrargid great group are at or above the baseline content, and only Pb, Ti, and Th in the Torrispsamment great group are at or below the baselines established for natural soils in this area (table 3).

In the C horizon (table 7), again, there are significant differences between great groups for most elements. The Calciorthid great group has the highest content of five elements, and 16 elements are significantly lowest in content in the Torripsamment great group (Si is significantly the highest). Only one element shows no significant difference in content between great groups. Only Al in the Torripsamment great group is at or below the baseline content established for natural soils in this area (table 4).

Spatial Variability and Soil Taxonomy

Taxonomy for each sampling location is shown in figure 21. From an examination of this figure, it becomes apparent that the great groups are dispersed throughout the area in a haphazard fashion. As with the maps of element content (figs. 4-20) and the variance components (tables

Table 3.--Baseline values for element content of A-horizon soils in northwest New Mexico.

[----, not determined because of low detection ratio; all measurements in parts per million unless indicated as percent]

Element, unit of measure	Geometric mean	Geometric deviation	Geometric error	Baseline value (expected 95 pct. range)	Detection ratio
Al, pct	4.7	1.27	1.04	2.9-7.6	47:47
As	5.4	1.52	1.20	2.3-12.5	47:47
B	16	2.20	1.81	3.3-77	39:47
Ba	570	1.41	1.13	290-1100	47:47
C, carbonate, pct	.04	9.37	----	<.01-3.5	30:47
C, organic, pct	.37	1.86	1.35	.11-1.3	47:47
C, total, pct	.51	1.80	1.02	.16-1.7	47:47
Ca, pct	.55	2.12	1.05	.12-2.5	47:47
Co	5.7	1.44	1.14	2.7-12	47:47
Cr	18	1.45	1.51	8.6-38	47:47
Cu	8.9	1.90	1.14	2.5-32	47:47
Er	6.1	1.21	1.28	4.2-8.9	42:47
Fe	1.1	1.62	1.03	.42-2.9	47:47
Ge	1.4	1.22	1.24	.94-2.1	47:47
Hg	.02	1.49	1.56	.01-.04	47:47
K, pct	1.7	1.21	1.02	1.2-2.5	47:47
La	27	1.38	1.28	14-51	47:47
Li	12	1.58	1.21	4.8-30	47:47
Mg	.33	1.64	1.03	.12-.89	47:47
Mn	230	1.76	1.20	74-710	47:47
Mo	1.2	1.71	1.37	.41-3.5	31:47
Na, pct	.84	1.67	1.87	.30-2.3	47:47
Nb	13	1.27	1.32	8.1-21	47:47
N	8.4	1.59	1.10	3.3-21	47:47
Pb	13	1.28	1.14	7.9-21	47:47
Rb	57	1.56	1.64	23-140	47:47
S, pct	.10	1.45	1.24	.048-.21	47:47
Sc	3.6	1.59	1.12	1.4-9.1	47:47
Si, pct	36	1.09	1.02	30-43	47:47
Sn	.43	2.68	2.04	.06-3.1	34:47
Sr	160	1.37	1.09	85-300	47:47
Th	8.2	1.35	1.18	4.5-15	47:47
Ti, pct	.21	1.38	1.06	.11-.40	47:47
U	2.5	1.30	1.06	1.5-4.2	47:47
V	41	1.49	1.09	18-91	47:47
Y	28	1.34	1.18	16-50	47:47
Yb	1.6	1.28	1.24	1.0-2.6	47:47
Zn	39	1.49	1.14	18-87	47:47
Zr	430	1.65	1.57	160-1200	46:47

Table 4.--Baseline values for element content of C-horizon soils in northwest New Mexico.

[All measurements in parts per million unless indicated as percent]

Element unit of measure	Geometric mean	Geometric deviation	Geometric error	Baseline value (expected 95 pct. range	Detection Ratio
Al, pct	5.0	1.30	1.04	3.0-8.5	47:47
As	5.4	1.46	1.14	2.5-12	47:47
B	15	2.59	2.29	2.2-100	36:47
Ba	570	1.52	1.16	250-1300	35:47
C, carbonate, pct	.18	3.71	1.37	.01-2.5	43:47
C, organic, pct	.27	2.24	1.46	.05-1.4	47:47
C, Total, pct	.54	2.01	1.01	.13-2.2	47:47
Ca, pct	1.1	2.13	1.03	.24-5.0	47:47
Co	5.7	1.62	1.09	2.2-15	47:47
Cr	18	1.51	1.32	7.9-41	47:47
Cu	8.7	1.94	1.42	2.3-33	47:47
Er	6.5	1.21	1.21	4.4-9.5	45:47
Fe, pct	1.2	1.58	1.04	.48-3.0	47:47
Ge	1.3	1.20	1.20	.90-1.9	47:47
Hg	.02	1.85	1.35	.01-.07	46:47
K, pct	1.5	1.31	1.03	.87-2.6	47:47
La	30	1.35	1.21	16-55	47:47
Li	13	1.70	1.29	4.5-38	47:47
Mg, pct	.37	1.77	1.04	.12-1.2	47:47
Mn	180	1.76	1.25	58-560	47:47
Mo	1.4	1.57	1.36	.57-3.5	47:47
Na, pct	.91	1.56	1.06	.37-2.2	47:47
Nb	12	1.32	1.18	6.9-21	47:47
Ni	8.6	1.67	1.10	3.1-24	47:47
Pb	12	1.36	1.18	6.5-22	47:47
Rb	62	1.47	1.30	29-130	47:47
S, pct	.14	2.44	1.10	.02-.83	47:47
Sc	4.0	1.61	1.15	1.5-10	47:47
Si, pct	34	1.10	1.03	28-41	47:47
Sn	.62	2.55	1.66	.10-4.0	39:47
Sr	202	1.42	1.10	100-410	47:47
Ti, pct	.22	1.41	1.05	.11-.44	47:47
Th	8.3	1.38	1.12	4.4-16	47:47
U	2.7	1.40	1.06	1.4-5.3	47:47
V	44	1.55	1.14	18-110	47:47
Y	29	1.45	1.19	14-61	47:47
Yb	1.6	1.45	1.13	.76-3.4	47:47
Zn	37	1.66	1.03	13-100	46:47
Zr	332	1.64	1.33	120-890	47:47

Table 5.--Great groups and soil series sampled in northwestern New Mexico.

[Numbers in parentheses are the number of samples in each soil series]

Great Group	Soil Series
Calciorthid	Avalon (2)
Camborthid	Kinnear (2) Koyen (1) La Fonda (1) Notal (4) unknown (1)
Haplargid	Doak (2) Mayqueen (5) Monicero (2) Shiprock (3) Shiprock varient (2) unknown (1)
Haplustoll	Manzano (1)
Natrargids	Huerfano (3)
Torriorthent	Fruitland (6) Persayo (1) Turley (7) unknown (1)
Torripsamment	Sheppard (2)

Table 6.--Multiple comparison test of arithmetic means of element composition of A horizons for taxonomic great groups.

[Values for a single element followed by the same small letter are not significantly different at the 0.05 probability level. Numbers in parentheses are numbers of samples in each great group. All measurements in parts per million unless indicated as percent]

Element	Natrargid (3)	Torriorthent (15)	Calciorthid (2)	Camborthid (9)	Haplargid (15)	Torripsamment (2)	Haplustoll (1)
Al, pct--------	4.1c	5.3a	5.2ab	5.2ab	4.5bc	3.1d	5.1
As-------------	10a	6.2b	5.1b	5.7b	5.4b	3.0c	2.6
B--------------	23a	23a	17a	18a	20a	3.5b	11
Ba-------------	910a	690b	510c	530c	530c	430	860
C, organic, pct	.39a	.48a	.44a	.53a	.36a	.41a	.56
C, total, pct--	1.1a	.70b	.67b	.61bc	.40c	.61bc	.56
Ca, pct--------	2.1a	.86c	1.3b	.52cd	.42d	.68cd	.49
Co-------------	7.5a	6.9ab	5.7bc	6.5abc	5.2c	3.1d	4.7
Cr-------------	21ab	18b	24a	19ab	20ab	13c	16
Cu-------------	15a	13ab	12ab	11ab	8.7b	3.4c	5.2
Er-------------	4.9d	6.8a	6.4ab	5.9bc	5.9bc	5.1cd	3.2
Fe, pct--------	2.9a	1.4b	1.1b	1.2b	1.1b	.59c	.65
Ge-------------	1.1d	1.6a	1.6a	1.4b	1.3bc	1.2cd	1.2
Hg-------------	.02a	.02a	.02a	.02a	.02a	.02a	.02
K, pct---------	1.2a	1.7a	1.8a	1.8a	1.7a	1.4b	2.2
La-------------	26b	31a	31a	31a	26b	12c	28
Li-------------	16a	14ab	12b	16a	11b	12b	11
Mg, pct--------	.48a	.48a	.39ab	.35b	.30b	.27b	.17
Mn-------------	790a	280bc	390a	260bc	190cd	130d	210
Mo-------------	2.8a	1.3bc	1.1bc	1.7b	1.1bc	1.0c	1.0
Na, pct--------	.64c	.89b	1.2a	.94b	.99ab	.57c	1.6
Nb-------------	11b	13ab	14a	14a	13ab	12ab	15
Ni-------------	11a	11a	8.6ab	9.2ab	8.0b	4.0c	5.4
Pb-------------	15a	15a	14a	14a	13a	7.9	17
Rb-------------	52a	63a	60a	66a	60a	58a	95
S, pct---------	.21a	.10bc	.08c	.13b	.09bc	.07c	.10
Sc-------------	4.4ab	5.0a	3.8ab	4.4ab	3.3bc	2.1c	2.3
Si, pct--------	33d	35c	35c	36c	37b	40a	36
Sn-------------	.7ab	.8a	.6ab	.6ab	.5b	.6ab	.3
Sr-------------	180b	170bc	250a	160bc	170bc	140c	210
Th-------------	10a	9.6ab	8.5bc	8.5bc	7.8c	4.5d	8.1
Ti, pct--------	.24a	.25a	.21a	.23a	.21a	.11b	.20
U--------------	3.4a	2.9b	2.8bc	2.8bc	2.4cd	1.8e	1.8
V--------------	38b	51a	45ab	46ab	41ab	22c	25
Y--------------	31a	32a	29a	30a	27a	21b	19
Yb-------------	1.5b	1.8a	1.6ab	1.6ab	1.5b	1.8a	1.2
Zn-------------	52a	48ab	46ab	46ab	34c	21d	26
Zr-------------	490b	490b	830a	400b	460b	690a	470

Table 7.--Multiple comparison test of arithmetic means of element composition of C horizons for taxonomic great groups.

[Values for a single element followed by the same small letter are not significantly different at the 0.05 probability level. Numbers in parentheses are numbers of samples in each great group. All measurements in parts per million unless indicated as percent]

Element	Caldiorthid (2)	Camborthid (9)	Torriorthent (15)	Natrargid (3)	Haplargid (15)	Torripsamment (2)	Haplustoll (1)
Al, pct	6.1ab	6.2a	5.4b	4.0c	4.6c	3.0d	5.9
As	4.8ab	6.2a	5.9a	5.9a	6.1a	3.3b	2.7
B	13cd	21ab	24ab	28a	18bc	8.8d	<5
Ba	670a	570ab	610ab	360b	770a	510ab	590
C, carbonate, pct	.61a	.33b	.30b	.39b	.31b	.23b	.07
C, organic, pct	.30bc	.48a	.39ab	.32bc	.26bc	.20c	.20
C, total, pct	.91a	.81ab	.69abc	.71ab	.57bc	.43c	.27
Ca, pct	2.7b	1.3c	1.2c	3.3a	1.2c	.63d	.69
Co	6.4bc	8.4a	6.8abc	7.0ab	5.1c	3.2d	5.8
Cr	16ab	19ab	19ab	21a	19ab	15b	20
Cu	15a	14a	14a	8.1b	6.6bc	3.5c	6.2
Er	6.7a	7.2a	6.9a	6.5ab	6.1b	4.7c	5.7
Fe, pct	1.5ab	1.6a	1.5ab	1.2bc	1.0c	.60d	.88
Ge	1.2c	1.5a	1.3bc	1.3bc	1.4abc	1.4abc	1.3
Hg	.03ab	.03ab	.02bc	.04a	.02bc	.01c	.02
K, pct	1.6a	1.6a	1.7a	.78c	1.7a	1.3b	2.3
La	46a	35b	32bc	27c	29c	17d	29
Li	10cd	18a	17ab	19a	13bc	7.0d	12
Mg, pct	.44a	.47a	.50a	.41ab	.36ab	.27b	.22
Mn	190bc	230ab	260a	68d	180bc	140c	170
Mo	2.4a	1.9b	1.5bc	1.2c	1.2c	.7d	1.8
Na, pct	1.4a	1.1b	.92bc	.75c	1.0b	.51d	1.6
Nb	12a	13a	13a	14a	12a	13a	11
Ni	8.9bc	12a	11ab	7.7c	8.1c	4.4d	6.1
Pb	12ab	14a	13ab	6.3d	11bc	9.1c	17
Rb	35c	76a	71a	50b	66a	43bc	100
S, pct	.60b	.20c	.11c	2.3a	.15c	.07c	.11
Sc	6.2a	6.5a	4.8b	3.7bc	3.4cd	2.1d	3.4
Si, pct	31d	33cd	35bc	31d	36ab	38a	35
Sn	.5cd	1.2a	.9ab	1.1a	.8bc	.1d	.5
Sr	380a	220b	190bc	240b	230b	150c	240
Th	11a	10a	9.5ab	7.9bc	7.5c	5.2d	8.9
Ti, pct	.26ab	.29a	.24b	.28ab	.19c	.12d	.20
U	2.7c	3.5b	3.0bc	4.1a	2.3d	1.7e	1.8
V	61ab	63a	50bc	37d	41cd	24e	39
Y	37a	36a	31ab	36a	27b	17c	24
Yb	1.9a	1.9a	1.7a	1.6a	1.8a	1.0b	1.2
Zn	46a	55a	49a	32b	31bc	20c	32
Zr	440b	370b	390b	620a	350b	200c	190

1 and 2), no regional map patterns are suggested.

At the 5-km cell size, only three out of every 16 sample locations result in comparisons of great groups of extreme composition (Natrargid, Torripsamment, or Caliorthid) with other great groups of average composition in adjacent 5-km cells (fig. 21). In seven cases adjacent 5-km cells contain the same great group (fig. 21). The variance components at the 5-km cell level (tables 1 and 2) are in agreement with soil taxonomy (fig. 21)--variance components suggest that not much variation is measured at the 5-km cell level when compared to the 25-km or 1-km cell levels.

At the 1-km cell level, three times out of eight, the great groups of extreme composition (Natrargid, Torripsamment, or Calciorthid) are of extreme composition adjacent to some other great group of average or intermediate composition (fig. 21)--hence, a comparison of extremes. Only two out of every eight locations have the same great group as their neighboring locations (fig. 21). Analysis of variance also suggests this by the large variance component measured at the 1-km cell level (tables s and 2).

Conclusion

Chemical content of soils in northwestern New Mexico exhibits variation largely at two geographic scales--between 25-km cells and 1-km cells. Taxonomic grouping of soils (great group level) also indicates similar patterns in variation. Within the area, neither maps of element content based on 25-km cell means nor taxonomic great groups show distinct regional patterns. An examination of published maps showing features such as soil, geology, climate, topography, and other physical characteristics of the landscape suggests no reasons for these patterns. Instead, these maps suggest that gradational-regional patterns might be present. However, it appears that, because of the general uniformity of the study area, local topographic features that affect climatic regimes, which in turn influence soil taxonomy (such as accumulating depressions--Natrargids, and sand dunes--Torripsamments), may occur at repeating intervals of about 1 km and about 25 km.

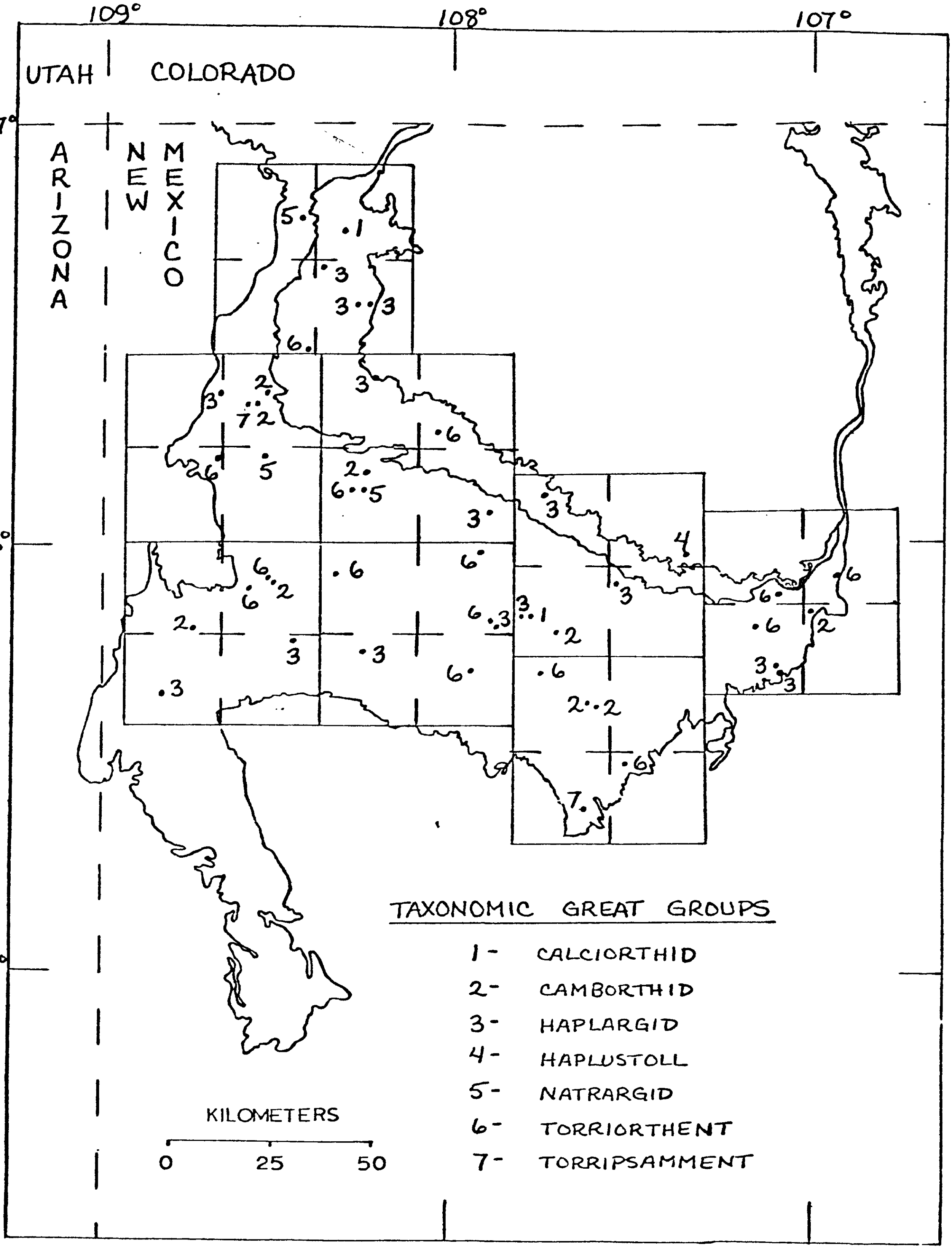


Figure 21.--Map of the study area showing the taxonomic names (great groups) at each sampling locality.

Variation in Element Content of the Doak, Shiprock, and Sheppard Soil Association in New Mexico

by

R. C. Severson

A and C horizons of soil were collected at 30 localities in northwest New Mexico. The localities were confined within the boundaries of the mapped occurrence (Dane and Bachman, 1965) of the coal-bearing Fruitland and Kirtland Formations of Cretaceous age (figure 22), and also within the boundaries of the mapped occurrence of the Doak, Shiprock, and Sheppard soil associations (Maker and others, 1973). These soils are considered to be prime materials for stockpiling and using as topsoil in mineland reclamation.

The actual sampling locations were selected randomly based on an unbalanced, nested, five-level, analysis-of-variance design of the barbell type. Three barbells were oriented in the area by selecting compass directions at random. The major axis of each barbell was 10 km long, and the sequentially smaller axes were 5 km, 1 km, and 0.1 km long. A barbell sampling design is shown in figure 23. Ten localities were sampled in each barbell (as shown by the x's in fig. 23), resulting in the collection of 30 samples each of A- and C-horizon soils. Ten of the 30 samples from each horizon were split and analyzed in duplicate. Sample preparation and analysis are detailed on pages 2 and 6 of this report.

Voucher specimens of the 30 soils sampled were classified taxonomically by J. E. Ruiz and Leroy Hacker, soil scientists with the USDA-SCS in Aztec and Albuquerque,, New Mexico, respectively. Differences in chemical content were evaluated at the family taxonomic level. Taxonomic criteria (Soil Survey Staff, 1975) at this level include particle-size classes, mineralogy classes, calcareous and reaction classes, and soil temperature classes. At the family level, the groupings consist of soil with similar chemical and physical properties which are deemed to affect their response to management for production of plants, and for engineering purposes.

This work was undertaken (1) to provide data on the element composition of soil that may be used as topsoil in mineland reclamation work, (2) to assess the spatial variability of the soil, and (3) to examine relations between soil taxonomy and spatial variability.

Variance Components

Sampling was designed to measure variation over increments of distance. Total variation was subdivided into components, each associated with a predetermined range in distance. Variance components for 36 elements, each expressed as a percentage of total variance, are shown in table 8 for A horizons and table 9 for C horizons of soils.

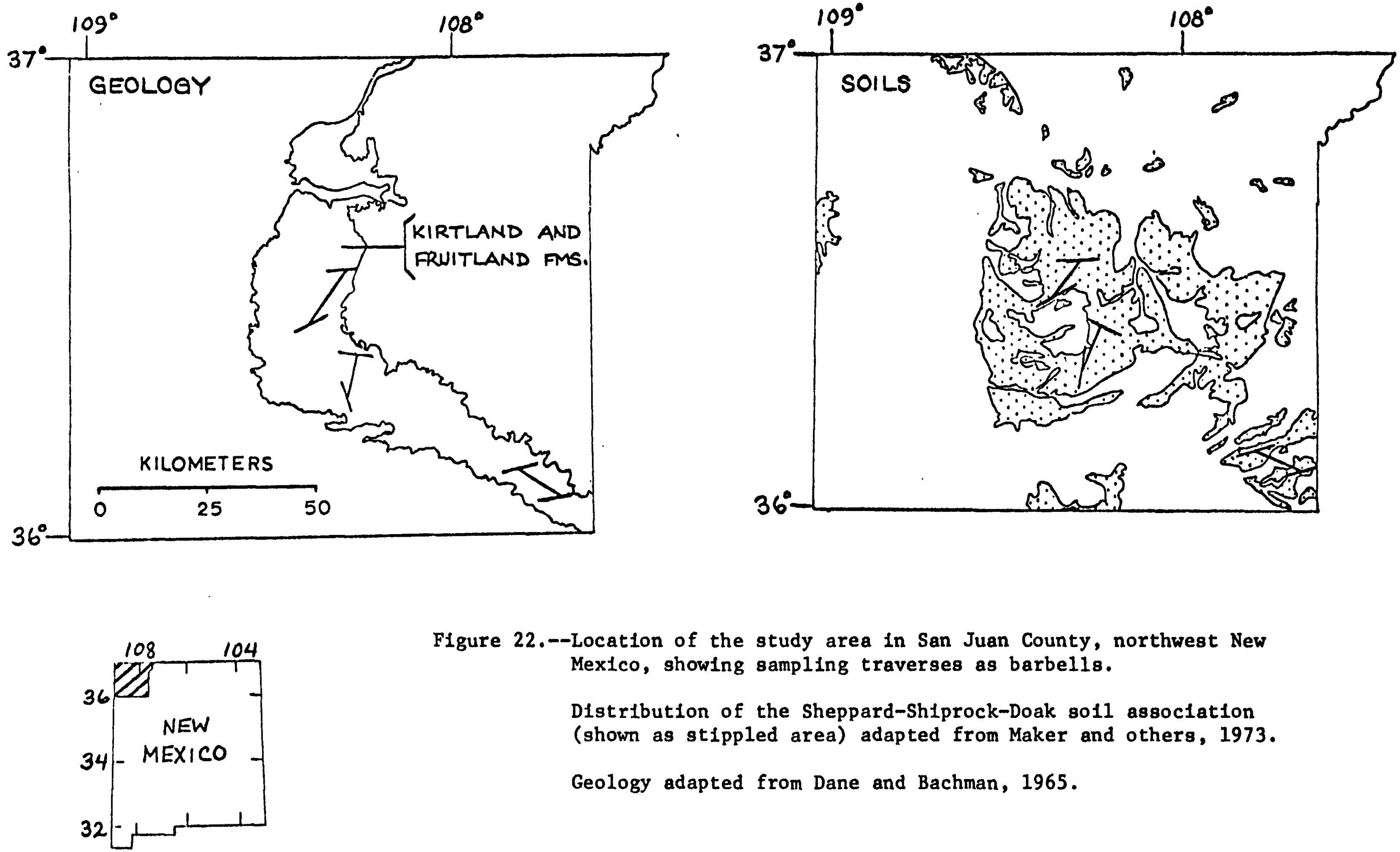


Figure 22.--Location of the study area in San Juan County, northwest New Mexico, showing sampling traverses as barbells.

Distribution of the Sheppard-Shiprock-Doak soil association (shown as stippled area) adapted from Maker and others, 1973.

Geology adapted from Dane and Bachman, 1965.

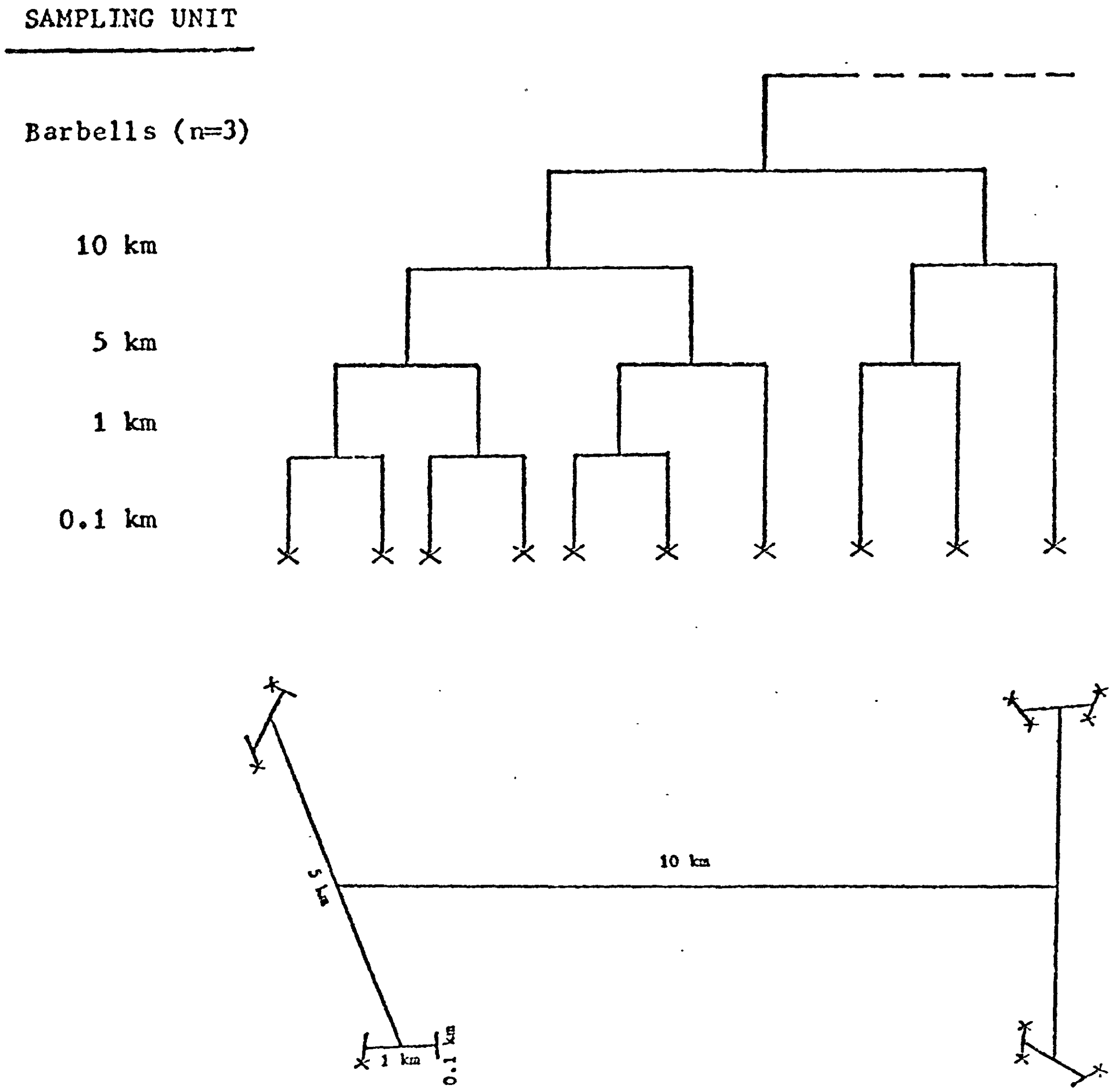


Figure 23.--Diagram of the unbalanced, nested, analysis-of-variance design. Sample site indicated by (X).

Table 8.--Variance components, for A-horizon soils, expressed as a percentage of total variance.

[An asterisk is used to denote significance of variance components at the 0.05 probability level]

Element	Total $\log_{10}$ variance	Percent of total variance					
		Between barbells	5-10 km	1-5 km	1-.1 km	.1-0 km	Analyses
Al	.0036	0	16.1	5.2	45.1*	0	33.6
As	.0111	0	0	30.1	0.5	0	69.4
B	.0327	0	10.1	10.9	0	0	79.0
Ba	.0257	0.8	0	0	54.8*	0	44.4
Be	.0040	0.6	0	8.4	6.9	0	84.1
C, organic	.0294	1.2	54.6*	0	14.6	14.1	15.5
C, total	.0225	0	61.2*	0	9.2	26.5*	3.1
Ca	.0237	0	11.7	0	32.8*	0	55.5
Co	.0133	0	9.0	0	38.8*	0	52.2
Cr	.0489	0	29.3	7.2	0	8.8	54.7
Cu	.0244	0	21.1	30.2	0	31.0*	17.7
Fe	.0085	0	.7	51.1	13.6	28.6*	6.0
Ge	.0050	2.4	0	16.7	0	52.3*	28.6
Hg	.0485	0	0	0	23.3	21.2	55.5
K	.0020	10.8*	0	3.9	9.8	0	75.6
La	.0099	0	22.9	23.6	0	7.3	46.2
Li	.0038	15.5	0	35.8	0	28.3	20.4
Mg	.0171	43.1	0	33.5*	2.2	19.0*	2.2
Mn	.0336	0	10.2	34.5	0	20.5	34.8
Na	.0055	2.1	34.2	9.3	46.1*	5.7*	2.6
Nb	.0145	1.1	0	27.9*	0	45.6*	25.4
Ni	.0124	0	6.7	28.0	23.3	0	42.0
Pb	.0071	11.2	0	19.3	6.4	0	63.1
Rb	.0042	0	0	20.8	12.8	42.1*	24.3
Sc	.0086	0	16.1	33.2	0.6	0	50.1
Si	.0009	0	6.4	4.0	27.4*	0	62.2
Sn	.2857	16.8	0	0	35.8	13.0	34.4
Sr	.0118	5.4	32.0*	0	48.5*	7.6	6.5
Th	.0129	18.9*	0	29.1	8.6	7.4	36.0
Ti	.0108	49.4	9.4	22.5*	0	12.2*	6.5
U	.0085	50.7	10.7	14.4	0	10.9	13.3
V	.0077	0	0	54.1	5.0	22.8	18.1
Y	.0205	0	6.4	21.5	0	56.6*	15.5
Yb	.0252	3.2	0	0	0	23.6	73.2
Zn	.0057	0	0	56.1	4.7	24.3*	14.9
Zr	.0389	28.8	0	0	13.3	0	57.9

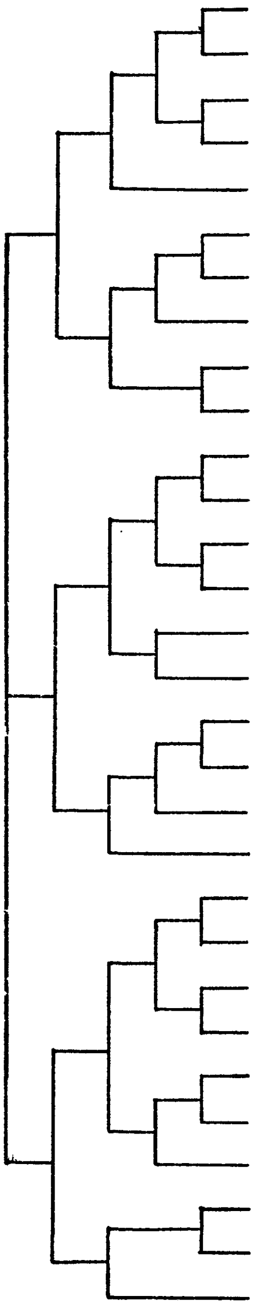
Table 9.--Variance components, for C-horizon soils, expressed as a percentage of total variance.

[An asterisk is used to denote significance of variance components at the 0.05 probability level]

Element	Total $\log_{10}$ variance	Percent of total variance					
		Between barbells	5-10 km	1-5 km	1-.1 km	.1-0 km	Analyses
Al----------	.0081	0	19.1	42.1*	6.5	0	32.3
As----------	.0239	0	0	22.6	35.7*	0	41.7
B-----------	.1013	17.4	4.7	0	0	56.5*	21.4
Ba----------	.0244	0	19.4*	0	9.4	52.3*	18.9
Be----------	.0041	0.8	6.2	0	10.9	17.4	64.7
C, carbonate	.3678	4.4	0	12.1	0	75.0*	8.5
C, organic--	.2590	25.7	0	26.0	12.6	0	35.7
C, total----	.1123	10.6	0	39.9	0	49.1*	.4
Ca----------	.1040	12.9	0	40.0*	0	43.3*	3.8
Co----------	.0204	6.7	8.5	37.3	2.6	37.9*	7.0
Cr----------	.0501	15.5	0	27.9	2.7	0	53.9
Cu----------	.0769	10.8	29.0	7.2	0	22.7	30.3
Fe----------	.0282	4.6	3.3	50.7*	0	25.5*	15.9
Ge----------	.0203	10.6	9.1	9.2	4.5	0	66.6
Hg----------	.0940	3.2	0	0	12.8	0	84.0
K-----------	.0045	3.8	35.2	32.7*	0	0.1	28.2
La----------	.0153	0	4.3	47.4	8.5	14.2	25.6
Li----------	.0213	14.2	44.0	7.0	21.9*	0.8	12.1
Mg----------	.0502	26.2	35.3	13.6	0	24.7*	.2
Mn----------	.0504	0	35.7	3.4	0	21.6	39.3
Na----------	.0105	0	0	68.9*	21.6*	3.2	6.3
Nb----------	.0378	26.3*	0	0	43.3*	3.0	27.4
Ni----------	.0400	22.6	23.3	19.1	4.1	27.0*	3.9
Pb----------	.0119	9.7	2.9	20.2	0	5.5	61.7
Rb----------	.0096	10.8	12.9	23.0	8.5	0	44.8
Sc----------	.0214	6.0	29.6	23.3	0	24.4	16.7
Si----------	.0010	0	0	34.1*	0	39.7	26.2
Sn----------	.7026	4.9	0	0	0	0	95.1
Sr----------	.0180	40.7	7.2	5.8	3.3	0	43.0
Th----------	.0202	0	42.2	24.9	0.6	14.6	17.7
Ti----------	.0163	23.3	0	21.8	0.7	18.9	35.3
U-----------	.0179	30.3	0	28.7	23.3*	14.5*	3.2
V-----------	.0266	5.5	6.7	47.8*	0	34.6*	5.4
Y-----------	.0248	0	0	39.1	9.5	2.4	49.0
Yb----------	.0779	0	11.8	7.5	0	0	80.7
Zn----------	.0204	4.1	10.5	56.4*	0	26.5*	2.5
Zr----------	.0736	33.3	6.8	1.2	10.5	13.6	34.6

Figure 24.--Soil taxonomy, at the family level, superimposed on the sampling design.

Bar-bell	Kilometers 10 5 1 0.1	Soil Taxonomy



Typic torriorthent; coarse loamy, mixed (calcareous), mesic
Typic haplargid; fine loamy, mixed, mesic
Typic torrispamment; mixed, mesic
Typic haplargid, coarse loamy, mixed, mesic
Typic calciorthid; fine loamy, mixed, mesic
Typic haplargid, fine loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic calciorthid; fine loamy, mixed, mesic
Typic haplargid, fine loamy, mixed, mesic
Typic haplargid, fine loamy, mixed, mesic
Typic haplargid, fine loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed mesic
Typic haplargid, fine loamy, mixed, mesic
Typic haplargid, fine loamy, mixed, mesic
Typic torriorthent; coarse loamy, mixed (calcareous), mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic
Typic haplargid; coarse loamy, mixed, mesic

Table 10.--Baseline values for element content of A-horizon soils of the Doak-Sheppard-Shiprock soil association in northwest New Mexico.

[All measurements in parts per million unless indicated as percent]

Element	Geometric mean	Geometric deviation	Geometric error	Baseline (expected 95 percent range)	Detection ratio
Al, pct	4.4	1.12	1.08	3.5 - 5.5	30:30
As	3.3	1.22	1.22	2.2 - 4.9	30:30
B	16	1.42	1.45	7.9 - 32	30:30
Ba	620	1.24	1.28	400 -950	30:30
Be	1.3	1.13	1.14	1.0 - 1.7	30:30
C, carbonate, pct.	<.01	53.4	1/----	2/----	3:30
C, organic, pct	.35	1.39	1.17	.18- .68	30:30
C, total, pct	.36	1.36	1.06	.20- .67	30:30
Ca, pct	.64	1.26	1.30	.40- 1.0	30:30
Co	4.9	1.28	1.21	3.0 - 8.0	30:30
Cr	20	1.54	1.46	8.4 - 47	30:30
Cu	8.8	1.41	1.16	4.4 - 17	30:30
Er	4.9	1.31	1/----	2.9 - 8.4	17:30
Fe, pct	.91	1.23	1.05	.60- 1.4	30:30
Ge	1.3	1.17	1.09	.95- 1.8	30:30
Hg	.02	1.55	1.46	.01- .05	29:30
K, pct	2.1	1.05	1.09	1.9 - 2.3	30:30
La	28	1.24	1.17	18 - 43	30:30
Li	13	1.13	1.07	10 - 17	30:30
Mg, pct	.25	1.29	1.05	.15- .42	30:30
Mn	240	1.42	1.28	120 -480	30:30
Mo	.98	1.21	1/----	.67- 1.4	13:30
Na, pct	1.12	1.17	1.03	.82- 1.5	30:30
Nb	10	1.26	1.15	6.3 - 16	30:30
Ni	6.2	1.29	1.18	3.7 - 10	30:30
Pb	11	1.20	1.17	7.6 - 16	30:30
Rb	83	1.15	1.08	63 -110	30:30
S, pct	.04	1.42		.02- .08	18:30
Sc	2.9	1.22	1.16	1.9 - 4.3	30:30
Si, pct	34	1.05	1.06	31 - 37	30:30
Sn	.76	3.33	2.06	.07- 8.4	24:30
Sr	220	1.21	1.07	150 -320	30:30
Th	7.7	1.25	1.17	4.9 - 12	30:30
Ti, pct	.22	1.23	1.06	.15- .33	30:30
U	2.2	1.22	1.08	1.5 - 3.3	30:30
V	28	1.21	1.09	19 - 41	30:30
Y	30	1.33	1.14	17 - 53	30:30
Yb	2.0	1.41	1.37	1.0 - 4.0	30:30
Zn	31	1.18	1.07	22 - 43	30:30
Zr	390	1.45	1.41	190 -820	30:30

1/ Not estimated because of low detection ratio.

2/ Not computed because the geometric mean is censored.

Table 11.--Baseline values for element content of C-horizon soils of the Doak-Sheppard-Shiprock soil association in northwest New Mexico.

[All measurements in parts per million unless indicated as percent]

Element	Geometric mean	Geometric deviation	Geometric error	Baseline (expected 95 percent range)	Detection ratio
Al, pct----------	4.4	1.21	1.12	3.0 - 6.4	30:30
As----------------	3.7	1.39	1.26	1.9 - 7.1	30:30
B-----------------	11	1.83	1.40	3.3 - 37	26:30
Ba----------------	690	1.34	1.17	380 -1200	30:30
Be----------------	1.3	1.16	1.13	.97- 1.7	30:30
C, carbonate, pct.	.10	3.91	1.50	.01- 1.5	26:30
C, organic, pct---	.10	2.65	2.02	.01- .70	29:30
C, total, pct-----	.27	1.95	1.05	.07- 1.0	30:30
Ca, pct-----------	1.02	1.77	1.16	.33- 3.2	30:30
Co----------------	4.4	1.37	1.09	2.3 - 8.3	30:30
Cr----------------	13	1.50	1.46	5.8 - 29	30:30
Cu----------------	6.3	1.73	1.42	2.1 - 19	30:30
Er----------------	4.5	1.37	[1]----	2.4 - 8.4	13:30
Fe, pct-----------	.83	1.41	1.17	.42- 1.7	30:30
Ge----------------	1.2	1.20	1.31	.83- 1.7	30:30
Hg----------------	.02	1.72	1.91	.01- .06	25:30
K, pct------------	2.1	1.17	1.09	1.5 - 2.9	30:30
La----------------	27	1.33	1.16	15 - 48	30:30
Li----------------	12	1.37	1.12	6.4 - 23	30:30
Mg, pct-----------	.23	1.58	1.02	.09- .57	30:30
Mn----------------	220	1.63	1.37	83 - 580	30:30
Mo----------------	.86	1.81	[1]----	.26- 2.8	12:30
Na, pct-----------	1.1	1.23	1.06	.73- 1.7	30:30
Nb----------------	9.2	1.43	1.26	4.5 - 19	28:30
Ni----------------	5.4	1.53	1.09	2.3 - 13	30:30
Pb----------------	9.7	1.29	1.22	5.8 - 16	30:30
Rb----------------	86	1.22	1.16	58 - 130	30:30
S, pct------------	.04	1.69	[1]----	.01- .11	18:30
Sc----------------	2.5	1.32	1.15	1.4 - 4.4	30:30
Si, pct-----------	34	1.06	1.04	30 - 38	30:30
Sn----------------	.75	4.92	6.57	.03- 18	22:30
Sr----------------	210	1.25	1.22	130 - 330	30:30
Th----------------	7.0	1.31	1.15	4.1 - 12	30:30
Ti, pct-----------	.18	1.31	1.19	.11- .31	30:30
U-----------------	1.9	1.28	1.06	1.2 - 3.1	30:30
V-----------------	28	1.40	1.09	14 - 55	30:30
Y-----------------	25	1.38	1.29	13 - 48	30:30
Yb----------------	1.6	1.48	1.78	.73- 3.5	30:30
Zn----------------	26	1.36	1.05	14 - 48	30:30
Zr----------------	270	1.82	1.44	82 - 890	29:30

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[1] Not estimated because of low detection ratio.

Table 12.--Multiple comparison test of arithmetic means of element composition of A horizons for taxonomic families.

[Values for a single element followed by the same small letter are not significantly different at the 0.05 probability level. Numbers in parentheses are numbers of samples in each family; all measurements in parts per million unless indicated as percent]

Element	Typic haplargid, fine loamy, mixed, mesic (7)	Typic torriorthent, coarse loamy, mixed (calcareous), mesic (2)	Typic calciorthid, fine loamy, mixed, mesic (2)	Typic haplargid, coarse loamy, mixed, mesic (18)	Typic torripsamment, mixed, mesic (1)
Al, pct----------	4.7 b	5.3 a	4.4 bc	4.3 c	4.3
As----------------	3.5 a	3.6 a	3.2 a	3.4 a	2.3
B-----------------	19 ab	11 c	20 a	16 b	8.4
Ba----------------	630 c	810 a	720 b	610 c	600
Be----------------	1.4 ab	1.3 c	1.5 a	1.3 c	1.4
C, carbonate, pct.	<.01b	<.01b	.03a	.01ab	<.01
C, organic, pct---	.46a	.31b	.28b	.36b	.22
C, total, pct-----	.46a	.31b	.31b	.37b	.22
Ca, pct----------	.68bc	1.1 a	.73b	.60c	.56
Co----------------	6.5 a	5.5 b	4.8 bc	4.6 c	3.1
Cr----------------	26 a	18 b	26 a	20 ab	9.8
Cu----------------	13 a	8.5 b	8.2 b	8.3 b	5.4
Er----------------	5.3 a	4.8 a	<4.6 a	4.8 a	<4.6
Fe, pct----------	1.0 a	1.0 a	.93a	.89a	.58
Ge----------------	1.4 ab	1.1 c	1.5 a	1.3 bc	1.4
Hg----------------	.02a	.02a	.03a	.02a	.02
K, pct-----------	2.1 a	1.9 b	2.0 a	2.1 a	2.0
La----------------	31 a	31 a	30 a	28 a	19
Li----------------	14 a	12 b	13 ab	12 b	11
Mg, pct----------	.27ab	.26ab	.31a	.25b	.17
Mn----------------	300 ab	210 c	330 a	250 bc	140
Mo----------------	1.0 b	1.2 a	<1.0 b	<1.0 b	<1.0
Na, pct----------	1.2 b	1.6 a	1.1 b	1.1 b	1.1
Nb----------------	11 a	8.5 b	8.9 b	10 ab	9.9
Ni----------------	8.1 a	6.1 b	6.3 b	5.9 b	3.8
Pb----------------	14 a	11 b	12 b	11 b	8.8
Rb----------------	84 ab	78 b	93 a	83 b	90
S, pct-----------	.04a	.03a	.03a	.04a	<.03
Sc----------------	3.5 a	3.1 b	2.9 b	2.7 b	2.4
Si, pct----------	34 b	33 b	33 b	35 a	36
Sn----------------	1.0 b	1.5 b	2.3 a	1.2 b	1.9
Sr----------------	240 b	340 a	220 bc	200 c	200
Th----------------	8.8 a	6.7 b	8.1 a	7.7 ab	5.6
Ti, pct----------	.27a	.27a	.21b	.21b	.15
U-----------------	2.7 a	2.5 a	2.0 b	2.2 b	1.5
V-----------------	33 a	32 ab	29 bc	28 c	20
Y-----------------	34 a	29 a	30 a	32 a	19
Yb----------------	2.4 a	2.1 a	2.5 a	2.1 a	1.6
Zn----------------	34 a	33 a	33 a	30 a	23
Zr----------------	580 a	370 b	500 a	360 b	210

Table 13.--Multiple-comparison test of arithmetic means of element composition of C horizons for taxonomic families.

[Values for a single element followed by the same small letter are not significantly different at the 0.05 probability level. Numbers in parentheses are numbers of samples in each family; all measurements in parts per million unless indicated as percent]

Element	Typic haplargid, fine loamy, mixed, mesic (7)	Typic torriorthent, coarse loamy, mixed (calcareous), mesic (2)	Typic calciorthid, fine loamy, mixed, mesic (2)	Typic haplargid, coarse loamy, mixed, mesic (18)	Typic torripsamment, mixed, mesic (1)
Al, pct----------	5.0 a	5.1 a	3.8 b	4.2 b	4.6
As---------------	4.6 a	3.7 bc	3.0 c	3.9 ab	1.7
B----------------	19 a	13 b	4.6 c	12 b	<5
Ba---------------	710 a	760 a	730 a	720 a	740
Be---------------	1.4 a	1.4 a	1.3 a	1.3 a	1.2
C, carbonate, pct.	.22a	.13a	.19a	.19a	.27
C, organic, pct---	.20a	.19ab	.03c	.12b	.16
C, total, pct-----	.42a	.32ab	.22b	.31ab	.43
Ca, pct----------	1.4 a	1.3 a	1.0 a	1.1 a	1.3
Co---------------	5.6 a	4.7 ab	3.3 c	4.3 bc	4.7
Cr---------------	19 a	12 b	14 b	12 b	14
Cu---------------	12 a	8.5 b	4.2 c	5.6 c	7.7
Er---------------	5.2 a	<4.6 a	<4.6 a	<4.6 a	<4.6
Fe, pct----------	1.2 a	.97b	.59c	.76c	1.2
Ge---------------	1.5 a	1.1 b	1.2 b	1.2 b	1.0
Hg---------------	.02a	.02a	.01a	.02a	<.01
K, pct-----------	2.0 a	2.0 a	2.2 a	2.2 a	2.1
La---------------	30 b	26 b	40 a	26 b	21
Li---------------	18 a	14 b	9.5 c	11 c	13
Mg, pct----------	.42a	.27b	.15c	.21bc	.25
Mn---------------	250 a	210 a	200 a	270 a	190
Mo---------------	1.2 a	1.0 ab	<1.0 b	1.1 ab	<1.0
Na, pct----------	1.2 b	1.4 a	1.1 b	1.1 b	1.3
Nb---------------	11 a	10 a	7.5 b	9.2 ab	9.9
Ni---------------	8.9 a	5.3 b	3.3 c	5.1 b	5.0
Pb---------------	10 ab	8.6 b	11 a	10 ab	11
Rb---------------	87 a	85 a	93 a	88 a	65
S, pct-----------	.06a	.03b	.06a	.03b	.07
Sc---------------	3.6 a	2.5 b	2.0 c	2.3 bc	2.2
Si, pct----------	33 b	34 ab	35 a	34 ab	33
Sn---------------	1.8 ab	2.5 a	1.0 b	1.7 ab	<.2
Sr---------------	250 a	220 ab	220 ab	200 b	340
Th---------------	8.7 a	5.9 b	5.9 b	7.2 b	5.3
Ti, pct----------	.24a	.18b	.14c	.16bc	.22
U----------------	2.5 a	1.9 b	1.4 c	1.9 b	2.1
V----------------	40 a	29 b	19 c	27 b	26
Y----------------	32 a	24 b	20 b	25 b	18
Yb---------------	2.1 a	1.9 a	1.3 b	1.7 ab	0.9
Zn---------------	35 a	30 b	17 d	25 c	29
Zr---------------	550 a	180 b	150 b	290 b	300

Analytical error variance greater than 50 percent is considered excessive. Any interpretations for elements with excessive analytical error must be viewed with caution--13 elements in the A horizon (table 8) and 7 elements in the C horizon (table 9) exceed this threshold.

In general, variation associated with the larger distance increments, for most elements in both A and C horizons, is non-significant (tables 8 and 9). Moreover, total variation in most elements is low, suggesting a rather uniform composition of the soil sampled within the study area. Therefore, because of this uniformity, baseline values describing element content in soil may be extrapolated to other parts of the region as the most probable concentration.

Baseline Values

Baseline values (Tidball and Ebens, 1976) are presented in tables 10 and 11 for A and C horizons of soil, respectively. The baseline is the 95 percent range in element content to be expected in samples of natural soils. For most elements, the geometric means for A and C horizons are similar. However, the expected range is greater for C horizons (table 11) than for A horizons of soils (table 10).

Soil Taxonomy

The taxonomy of the soils collected at each location of the nested sampling design is shown in figure 24. The 30 localities are represented by 5 groups at the family taxonomic level. The Shiprock soil series (typic haplargid; coarse loamy, mixed, mesic) and Doak soil series (typic haplargid; fine loamy, mixed, mesic) were dominant within the area and were represented by 18 and 7 of the samples, respectively. Only 1 or 2 samples of each of the 3 other taxonomic groups were collected. A multiple comparison test (Natrella, 1961, pg. 3-40) was used to test for significant differences between element content of each soil group. The results for the test for A and C horizons are presented in tables 12 and 13. The data for the single sample representing the typic torriorthent, mixed, mesic group is also included in those tables, but its element content was not statistically compared with that of the other taxonomic groups, because no estimate of variance is possible for a single sample. For 9 elements in the A horizon (table 12) and for 8 elements in the C-horizon (table 13), there were no significant differences between taxonomic groups. For an additional 21 elements in the A horizon and an additional 19 elements in the C horizon, only 2 significant groupings were found, and these groups tend to overlap.

Spatial Variability and Soil Taxonomy

Both the total variance measured (tables 8 and 9) and the multiple mean comparisons for taxonomic groups (tables 12 and 13) suggest uniformity in element composition of A and C horizons of soils sampled. Taxonomic names of soils superimposed on the sampling design (figure 24) show that, in most cases, comparisons involving the same or similar soil groups are being made by analysis of variance. In addition, no patterns or groupings of dissimilar taxonomic groups are observed at any specific level of the sampling design.

Summary

Variation in element content in A and C horizons of soils is small in the area of northwest New Mexico that was sampled. This area is represented by the Doak, Shiprock, Sheppard soil association, which was sampled in the area mapped as the Fruitland and Kirtland Formations of Cretaceous age. Of the 30 localities sampled at random, 18 consisted of the Shiprock soil series (typic haplargid; coarse loamy, mixed, mesic) and 7 consisted of the Doak soil series (typic haplargid; fine loamy, mixed, mesic). Three other groups at the family taxonomic level were recognized.

Differences between means in element content for the taxonomic soil groups was small based on a multiple comparison test. Content of 40 elements in A and C horizons can best be summarized by a baseline value; additional sampling and analysis required to prepare maps of element content in soil would probably be of little additional value because of the low geochemical variability exhibited by the soils sampled.

The soils sampled are considered to be prime materials for stockpiling and later use as topsoil after mining and reclamation have taken place. The data in this study can be used as baseline values for the natural, undisturbed soil before mining and reclamation. In addition they may provide helpful information on element content of soil when anticipating problems of toxicity or deficiency for the 40 elements measured. After mining and reclamation, element content in samples of minesoil can be compared to the expected contents tabulated in this report to detect changes in composition. (See p. 47, this volume, for such an application of this data.)

Spatial Variation in Total Element Content of Minesoils at the San Juan Mine in Northwest New Mexico

by

R. C. Severson

Samples of topsoil and minespoil were collected at six locations at the San Juan Mine (figure 25) from an area that had been reclaimed in 1974--graded, topsoiled, and revegetated. Sample locations were selected randomly, based on a four-level, nested, analysis-of-variance design (Leone and others, 1968). The sampling design is shown in figure 26. Within about a four hectare area, the axes of a barbell were oriented by selecting a compass direction at random. The major axis of the barbell was 100 m long, and the sequentially smaller axes were 25 m and 5 m long, respectively. Each of the six topsoil and minespoil samples were split and analyzed twice, yielding a total of 24 samples. The topsoil consisted of a uniform layer of about 20 cm of soil that had been stockpiled prior to mining and then replaced after coal mining and regrading of the spoil material was completed. This 20 cm of topsoil was sampled. The minespoil underlying the topsoil was sampled to a depth of 50 cm with a barrel-type auger. Sample preparation and analysis are described on page 2 of this report.

The material used as topsoil is represented by the Doak-Shiprock soil association (Maker and others, 1973). These soils have formed mainly in thick alluvial deposits that occupy stream terraces and alluvial fans which are now from 30 m to 100 m above present stream channels. They appear on the landscape as gently sloping tops of benches and mesas. The minespoil material consists of a mixture of lithologies, characteristic of the Kirtland and Fruitland Formations of Cretaceous age. Fragments of coal are noticeable in the minespoil material but generally make up a small percentage of the total volume.

This work was undertaken (1) to provide data on the chemical composition of topsoil and minespoil from a reclaimed area of the San Juan Mine, (2) to assess the spatial variability in composition of topsoil and minespoil, and (3) to determine the minimum number of random samples needed, within an area of specified size, to prepare a reliable map of topsoil and minespoil chemical composition.

Variance Components

Sampling was designed to measure variation over increments of distance. Total variation was subdivided into components, each associated with a predetermined range in distance. Variance components for 40 elements, each expressed as a percentage of total variance are shown in table 14 for topsoil and in table 15 for minespoil.

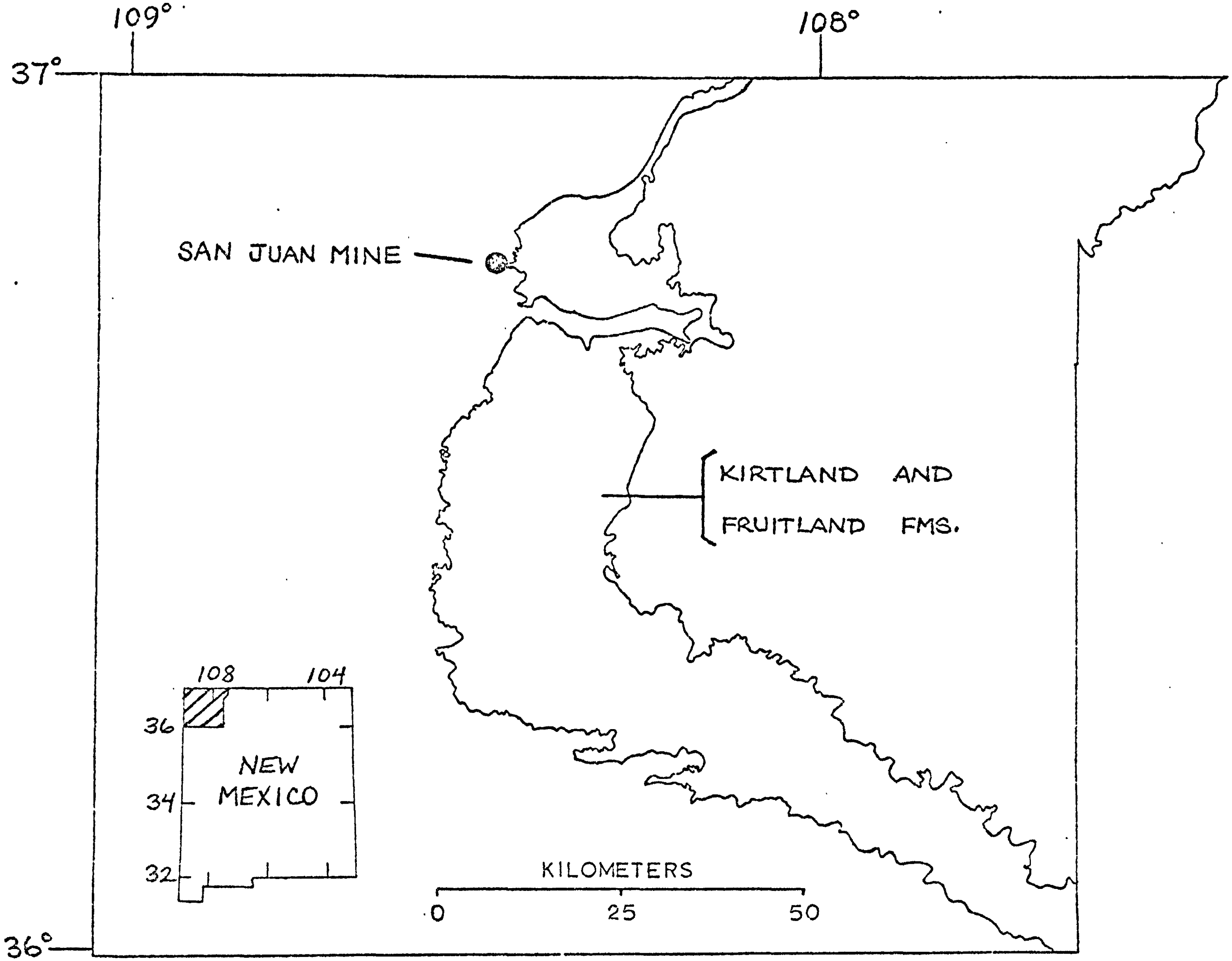

Figure 25.--Location of the San Juan Mine in San Juan County, northwest New Mexico. Geology adapted from Dane and Bachman, 1965.

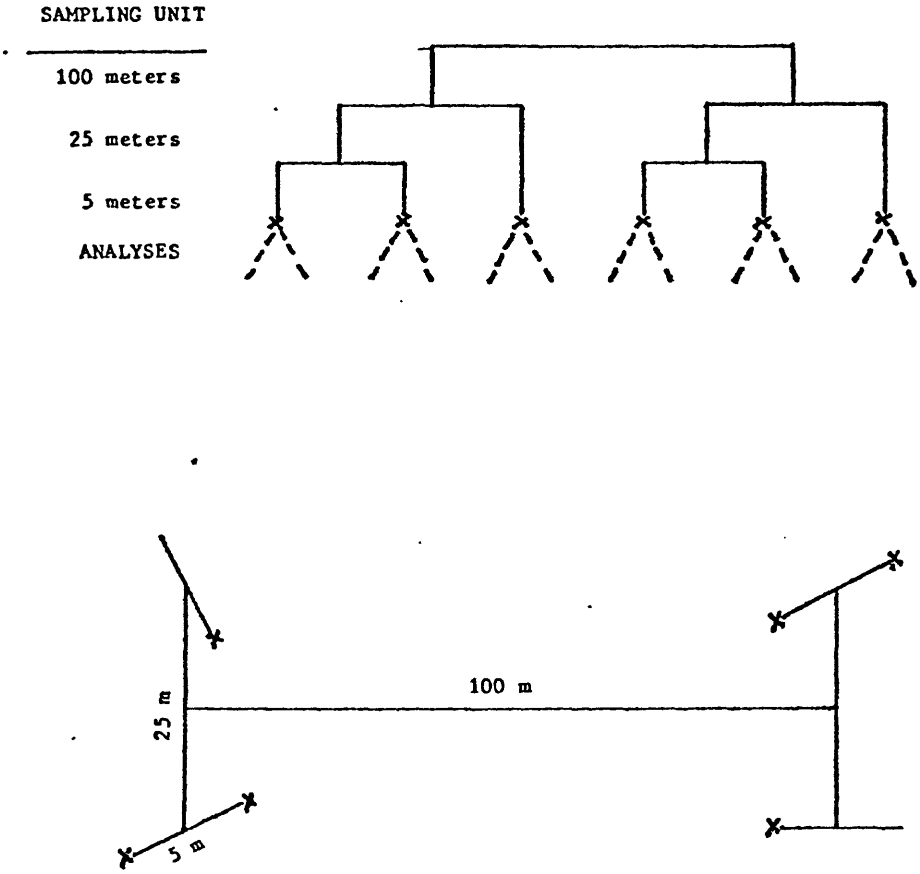

Figure 26.--Diagram of the unbalanced, nested, sampling design. X's are sampling locations.

Table 14.--Variance components, for topsoil, expressed as a percentage of total variance and minimum number of samples (n_r) needed to map patterns of element content for areas 5 m and 25 m on a side at an 80 percent confidence level.

[n.d., not determined; an asterisk is used to denote significance of variance components at the 0.05 probability level]

Element	Total $\log_{10}$ variance	Percent of total variance				n_r	
		25-100 m	5-25 m	0-5 m	Analytical	5 m	25 m
Al	.0017	13.8	0	78.9*	7.3	6	6
As	.0448	49.8	3.2	5.7	41.3	3	3
B	.1069	0	0	62.3	37.7	n.d.	n.d.
Ba	.0211	12.8	0	2.0	85.2	6	6
Be	.0028	18.5	0	40.0	41.5	5	5
C, carbonate	.0373	40.9	0	41.8*	17.3	3	3
C, organic	.2811	24.6	0	73.8*	1.6	4	4
C, total	.2296	32.7	0	67.2*	0.1	3	3
Ca	.0178	66.8	0	32.1*	1.1	2	2
Co	.0045	0	58.4	0	41.6	n.d.	2
Cr	.0369	3.3	0	36.0	60.7	>30	>30
Cu	.0316	0	0	87.9*	12.1	n.d.	n.d.
Er	.0035	2.2	0	75.0*	22.8	>30	>30
Fe	.0017	4.8	0	48.8	46.4	15	15
Ge	.0208	0	0	35.0	65.0	n.d.	n.d.
Hg	.1740	7.6	0	88.1*	4.3	10	10
K	.0007	12.4	0	83.7*	3.9	7	7
La	.0257	13.9	0	46.2	39.7	6	6
Li	.0039	9.7	0	86.5*	3.8	8	8
Mg	.0007	16.7	0	81.4*	1.9	5	5
Mn	.0219	0	27.8	27.7	44.5	n.d.	4
Mo	.0191	58.0	0	28.5*	13.5	2	2
Na	.0003	0	82.8	1.5	15.7	n.d.	2
Nb	.0123	0	0	48.4	51.6	n.d.	n.d.
Ni	.0039	0	0	84.4*	15.6	n.d.	n.d.
Pb	.0051	0	2.5	0	97.5	n.d.	>30
Rb	.0006	36.6	23.8	0	39.6	3	2
S	.0685	0	0	96.0*	4.0	n.d.	n.d.
Sc	.0040	22.3	10.4	24.5	42.8	4	3
Si	.0008	9.6	0	88.4*	2.0	8	8
Sn	.2904	12.2	0	73.3*	14.5	7	7
Sr	.0465	16.2	0	0	83.8	5	5
Th	.0063	0	0	35.4	64.6	n.d.	n.d.
Ti	.0008	0	58.4	0	41.6	n.d.	2
U	.0091	18.9	0	76.8*	4.3	5	5
V	.0018	0	25.2	0	74.8	n.d.	4
Y	.0037	32.0	0	40.7	27.3	3	3
Yb	.0026	9.1	0	19.6	71.3	8	8
Zn	.0023	0	0	97.5*	2.5	n.d.	n.d.
Zr	.0624	0	49.4*	0	50.6	n.d.	3

Table 15.--Variance components, for minespoil, expressed as a percetage of total variance and minimum number of samples (n_r) needed to map patterns of element content for areas 5 m and 25 m on a side at an 80 percent confidence level.

[n.d., not determined; an asterisk is used to denote significance of variance components at the 0.05 probability level]

Element	Total $\log_{10}$ variance	Percent of total variance				n_r	
		25-100 m	5-25 m	0-5 m	Analytical	5 m	25 m
Al----------	.0037	0	0	94.6*	5.4	n.d.	n.d.
As----------	.0110	0	36.8	49.1*	14.1	n.d.	3
B-----------	.0474	0	0	53.3	46.7	n.d.	n.d.
Ba----------	.0426	2.4	0	0	97.6	>30	>30
Be----------	.0032	7.1	0	40.8	52.1	10	10
C, carbonate	.0785	0	68.7	0	31.3	n.d.	2
C, organic--	.4214	6.4	0	94.5*	0.1	12	12
C, total----	.3629	5.7	0	99.2*	0.1	13	13
Ca----------	.0076	0	76.6	21.9*	1.5	n.d.	2
Co----------	.0105	0	30.7	52.6*	16.7	n.d.	4
Cr----------	.0207	0.8	0	83.3*	15.9	>30	>30
Cu----------	.0666	4.7	0	34.0	61.3	15	15
Er----------	.0049	0	0	64.6	35.4	n.d.	n.d.
Fe----------	.0085	0	0	88.0*	12.0	n.d.	n.d.
Ge----------	.0604	0	0	92.1*	7.9	n.d.	n.d.
Hg----------	.1416	1.5	0	95.7*	2.8	>30	>30
K-----------	.0054	5.5	0	94.1*	0.4	14	14
La----------	.0110	0	37.8	0	62.2	n.d.	3
Li----------	.0022	0	13.7	78.0*	8.3	n.d.	6
Mg----------	.0042	0	10.6	88.5*	0.9	n.d.	8
Mn----------	.0193	1.0	0	86.4*	12.6	>30	>30
Mo----------	.0044	0	0	55.2	44.8	n.d.	n.d.
Na----------	.0124	62.3	0	37.4*	0.3	2	2
Nb----------	.0271	0	36.5	26.5	37.0	n.d.	3
Ni----------	.0066	0	37.8	52.0*	10.2	n.d.	3
Pb----------	.0303	16.2	0	76.7*	7.1	5	5
Rb----------	.0046	0	0	88.0*	12.0	n.d.	n.d.
S-----------	.0997	3.5	0	83.8*	12.7	>30	>30
Sc----------	.0206	0	74.4	19.1*	6.5	n.d.	2
Si----------	.0044	13.6	0	85.5*	0.9	6	6
Sn----------	.0160	0	21.9	0	78.1	n.d.	5
Sr----------	.0053	73.9	0	18.8*	7.3	2	2
Th----------	.0039	0	0	16.5	83.5	n.d.	n.d.
Ti----------	.0042	0	0	92.5*	7.5	n.d.	n.d.
U-----------	.0067	0	18.1	79.0*	2.9	n.d.	5
V-----------	.0136	0	0	95.2*	4.8	n.d.	n.d.
Y-----------	.0105	0	30.8	51.1*	18.1	n.d.	4
Yb----------	.0139	0	56.9	15.1	28.0	n.d.	2
Zn----------	.0046	0	0	94.8*	5.2	n.d.	n.d.
Zr----------	.0294	0	37.6	0	62.4	n.d.	3

Excessive analytical error variance (>50 percent) is exhibited by 10 elements for topsoil (table 14) and for 6 elements for minespoil (table 15). In general, percent analytical error variance is greatest for elements in topsoil. However, total variance is generally less in topsoil than in minespoil for the same element. Therefore, while actual variation due to laboratory procedures may be similar for both topsoil and minespoil, it appears as a larger percentage of the total variation in topsoil because less total variation was measured in topsoil.

One use of variance components is to calculate the minimum number of samples (n_r--see p. 6 of this report) necessary to estimate the magnitude of the sampling effort that would be required to prepare a geochemical map of topsoil and minespoil. Values of n_r for areas 5 m on a side and 25 m on a side are presented in table 14 for topsoil and in table 15 for minespoil. In general, much more intensive sampling would be required to map element content in minespoil than topsoil at either 5 m or 25 m. In fact, for many elements in minespoil, it would impractical to attempt to prepare a map at these distance intervals because so little variation was measured at these intervals; most variation was measured at distances of <5 m.

Geochemical Baseline Values

Baselines in element composition of topsoil and minespoil are summarized in tables 16 and 17. The baseline estimates the 95 percent range in concentration to be expected in topsoil and minespoil (Tidball and Ebens, 1976). Minespoil is higher in content of many elements than is topsoil (carbonate-C, Cr, K, Nb, Si, and Zr being the exceptions). Only three elements exhibit similar geometric means (Pb, Rb, and Yb). Baselines for elements in minespoil are wider than for topsoil and this simply reflects the fact that minespoil is more variable than topsoil.

Baseline values for similar types of soil can be found in this volume (tables 10 and 11) and can be used to compare with element concentrations measured in individual samples of topsoil and minespoil. Those elements whose content in a large portion of the topsoil or minespoil samples collected is outside of the baseline content in natural soils are shown in table 18. For topsoil, the element content is similar to C horizons of natural soil, with only Be exceeding the baseline value and only B being below the baseline value. A few elements in topsoil exceed the baseline value for natural A horizons of soil. This can be expected because when soils are stockpiled, generally A, B, and C horizons are mixed. The natural A horizon would tend to be lower in mobile elements than B or C horizons because of the sparse vegetative cover in the area and the subsequently low rate of element cycling. In addition, leaching would tend to produce a net removal of mobile elements from the A horizon. For minespoil, the content of several elements is not similar to either natural A- or C-horizon soils. Many elements in minespoil exceed the baseline value for natural soils, while only Si is below the baseline value for natural C-horizon soils. Both S and organic C are high in minespoil, and fragments of coal were

Table 16.--Baseline values for element content of topsoil at the San Juan Mine in northwest New Mexico.

[All measurements in parts per million unless indicated as percent]

Element	Geometric mean	Geometric deviation	Geometric error	Baseline (expected 95 percent range)	Detection ratio
Al, pct	4.9	1.06	1.03	4.4 - 5.5	12:12
As	2.9	1.53	1.37	1.2 - 6.8	12:12
B	6.9	1.84	1.59	2.0 - 23	12:12
Ba	450.0	1.37	1.36	240 -840	12:12
Be	2.4	1.10	1.08	2.0 - 2.9	12:12
C, carbonate, pct.	.28	1.39	1.20	.15- .54	12:12
C, organic, pct	.44	2.91	1.17	.05- 3.7	12:12
C, total, pct	.78	2.29	1.02	.15- 4.1	12:12
Ca, pct	1.3	1.26	1.03	.82- 2.1	12:12
Co	6.0	1.14	1.11	4.6 - 7.8	12:12
Cr	22	1.41	1.41	11 - 44	12:12
Cu	10	1.48	1.15	4.6 - 22	12:12
Er	6.5	1.10	1.07	5.4 - 7.9	12:12
Fe, pct	1.4	1.09	1.07	1.2 - 1.7	12:12
Ge	1.3	1.31	1.31	.76- 2.2	12:12
Hg	.01	2.01	1.22	<.01- .04	12:12
K, pct	1.5	1.05	1.01	1.4 - 1.7	12:12
La	25	1.36	1.26	14 - 46	12:12
Li	17	1.11	1.03	14 - 21	12:12
Mg, pct	.42	1.05	1.01	.38- .46	12:12
Mn	260	1.36	1.26	140 -480	12:12
Mo	1.8	1.29	1.12	1.1 - 3.0	12:12
Na, pct	1.2	1.04	1.02	1.1 - 1.3	12:12
Nb	11	1.26	1.20	6.9 - 17	12:12
Ni	8.6	1.14	1.06	6.6 - 11	12:12
Pb	11	1.15	1.18	8.3 - 15	12:12
Rb	70	1.05	1.04	63 - 77	12:12
S, pct	.10	1.55	1.13	.04- .24	12:12
Sc	3.9	1.14	1.10	3.0 - 5.1	12:12
Si, pct	35	1.06	1.01	31 - 39	11:12
Sn	1.1	2.24	1.60	.22- 5.5	12:12
Sr	190	1.55	1.57	79 -460	12:12
Th	7.7	1.19	1.16	5.4 - 11	12:12
Ti, pct	.23	1.05	1.04	.21- .25	12:12
U	2.9	1.16	1.05	2.2 - 3.9	12:12
V	45	1.08	1.09	39 - 52	12:12
Y	27	1.11	1.08	22 - 33	12:12
Yb	1.6	1.10	1.10	1.3 - 1.9	12:12
Zn	41	1.08	1.02	35 - 48	12:12
Zr	420	1.51	1.51	180 -960	11:12

Table 17.--Baseline values for element content in minespoil at the San Juan Mine in northwest New Mexico.

[All measurements in parts per million unless indicated as percent]

Element	Geometric mean	Geometric deviation	Geometric error	Baseline (expected 95 percent range)	Detection ratio
Al, pct	6.1	1.11	1.03	5.0 - 7.5	12:12
As	4.3	1.22	1.10	2.9 - 6.4	12:12
B	13	1.52	1.41	5.6 - 30	12:12
Ba	590	1.46	1.61	280 -1300	12:12
Be	2.7	1.11	1.10	2.2 - 3.3	12:12
C, carbonate, pct.	.23	1.63	1.43	.09- .61	12:12
C, organic, pct	2.3	2.59	1.05	.34- 15	12:12
C, total, pct	2.6	2.45	1.03	.43- 16	12:12
Ca, pct	1.4	1.16	1.03	1.0 - 1.9	12:12
Co	8.5	1.22	1.10	5.7 - 13	12:12
Cr	14	1.26	1.14	8.8 - 22	12:12
Cu	18	1.58	1.50	7.2 - 45	12:12
Er	7.1	1.15	1.10	5.4 - 9.4	12:12
Fe, pct	1.7	1.17	1.08	1.2 - 2.3	12:12
Ge	1.4	1.59	1.17	.55- 3.5	12:12
Hg	.03	1.80	1.16	.01- .10	12:12
K, pct	1.4	1.12	1.01	1.1 - 1.8	12:12
La	32	1.21	1.21	22 - 47	12:12
Li	22	1.10	1.03	18 - 27	12:12
Mg, pct	.56	1.13	1.01	.44- .72	12:12
Mn	340	1.32	1.12	200 - 590	12:12
Mo	2.7	1.13	1.11	2.1 - 3.4	12:12
Na, pct	1.7	1.22	1.02	1.1 - 2.5	12:12
Nb	9.2	1.41	1.26	4.6 - 18	12:12
Ni	12	1.18	1.06	8.6 - 17	12:12
Pb	11	1.33	1.11	6.2 - 19	12:12
Rb	71	1.14	1.06	55 - 92	12:12
S, pct	.26	1.63	1.30	.10- .69	12:12
Sc	5.4	1.33	1.09	3.1 - 9.6	12:12
Si, pct	30	1.11	1.01	24 - 37	12:12
Sn	1.9	1.27	1.29	1.2 - 3.1	12:12
Sr	270	1.14	1.05	210 - 350	12:12
Th	9.8	1.14	1.14	7.5 - 13	12:12
Ti, pct	.27	1.14	1.04	.21- .35	12:12
U	4.1	1.17	1.03	3.0 - 5.6	12:12
V	56	1.26	1.06	35 - 89	12:12
Y	32	1.23	1.11	21 - 48	12:12
Yb	1.6	1.25	1.15	1.0 - 2.5	12:12
Zn	56	1.14	1.04	43 - 73	12:12
Zr	300	1.35	1.37	160 - 550	12:12

observed when sampling these minespoils. The other elements that also exceed the baseline values are probably associated with these fragments of coal.

Summary

Data for 40 elements are presented for topsoil and minespoil from the San Juan Mine in northwest New Mexico. The samples were collected from an area about four hectares in size that had been reclaimed in 1974--graded, topsoiled, and revegetated.

Topsoil tends to be less variable in its composition than does minespoil. Variation at <5 m tends to obscure variation at greater distances for many elements in minespoils, whereas variation in topsoil is also large at <5 m but does not totally obscure variation at greater distances.

Most elements were higher in content in minespoil (generally by a factor of less than 2) than in topsoil. The exceptions were carbonate C, Cr, K, Nb, Si, and Zr.

Baseline values computed for each element in both topsoil and minespoil tend to encompass a wider range in minespoil than topsoil because minespoil tends to be much more variable in composition than does topsoil.

Element composition of topsoil tends to be similar to the element composition of natural C-horizon soils. Element composition of minespoil is not similar to either natural A- or C-horizon soils. Fragments of coal in minespoil are probably responsible for the element values which exceed the baseline values for natural A- and C-horizon soils.

Table 18.--Elements in a large portion of the samples of topsoil or minespoil that are outside of the range for baseline contents in natural soils similar to those used for topsoil in mineland reclamation.

Elements exceeding baseline for;		Elements below baseline for;	
A-horizon soil	C-horizon soil	A-horizon soil	C-horizon soil
	Topsoil		
Be, total-C Ca, Fe, Li Mg, Mo, S, V	Be	Hg	B, Hg, K
	Minespoil		
Al, Be organic C total C, Ca, Co Cu, Fe, Li, Mg Mo, Na, Ni, S Sc, U, V, Zn	Be, organic C total C, Co Fe, Na, S, Sc U, V, Zn	none	Si

Geochemical Variation Within the Garden Gulch Member of the Green River Formation, USGS Core CR-2, Piceance Creek Basin, Rio Blanco County, Colorado

Walter E. Dean
and
John R. Donnell

Introduction

The Garden Gulch Member is the oldest lithologic unit of the Eocene Green River Formation in the Piceance Creek Basin of western Colorado. The Garden Gulch contains more clay, less carbonate, and generally has lower oil yields than the overlying Parachute Creek Member that forms the main body of the Green River Formation. U.S. Geological Survey oil shale core CR-2 was drilled in the northern part of the Piceance Creek Basin, in the southeast corner of T. 1 N., R. 97 W. (Fig. 27). The relationship of the oil-yield log for the Garden Gulch Member in the CR-2 core relative to the oil-yield log for the entire core is shown in figure 28.

The dominant lithology of the Garden Gulch Member in the CR-2 core is laminated, olive-gray to olive-black claystone with variable amounts of carbonate (mostly dolomite) and tuffaceous material (Fig. 29). According to Hite and Dyni (1967), Robb and Smith (1974), and Trudell and others (1970), the dominant minerals in the Garden Gulch are illite and quartz with minor albite, K-feldspar, dolomite, and calcite. Illite usually forms about two-thirds of the mineral matter in the Garden Gulch, but constitutes less than 20 percent of the organic-rich dolomitic marlstones (the typical so-called oil shale) of the overlying Parachute Creek Member (Robb and Smith, 1974; Trudell and others, 1970).

Chemical Analyses

Samples of the Garden Gulch Member in the CR-2 core were collected at approximately 0.3-meter intervals, crushed, and homogenized for oil-yield determinations and chemical analyses. Each analysis therefore represents an average for the 0.3-meter sample interval. Concentrations of Al, Fe, Mg, Ca, K, Ti, B, Cr, Cu, Ga, Mn, Mo, Ni, Pb, Sc, Sr, V, Yb, and Zr were measured by semiquantitative optical emission spectroscopy in 264 samples. Results of these analyses are plotted as functions of depth within the core in figure 30. More complete, quantitative analyses were also obtained for 32 of the samples, representing approximately every tenth 0.3-meter sample from the Garden Gulch. Concentrations of Si, Al, Ca, K, Fe, S, and Ti were determined by X-ray fluorescence. Concentrations of Mg, Na, Li, Rb, and Hg were determined by atomic absorption spectrophotometry. The concentration of fluorine was measured by specific fluoride ion electrode. Concentrations of U and Th were determined by neutron activation analysis. All analyses were performed at analytical laboratories of the U.S. Geological Survey,

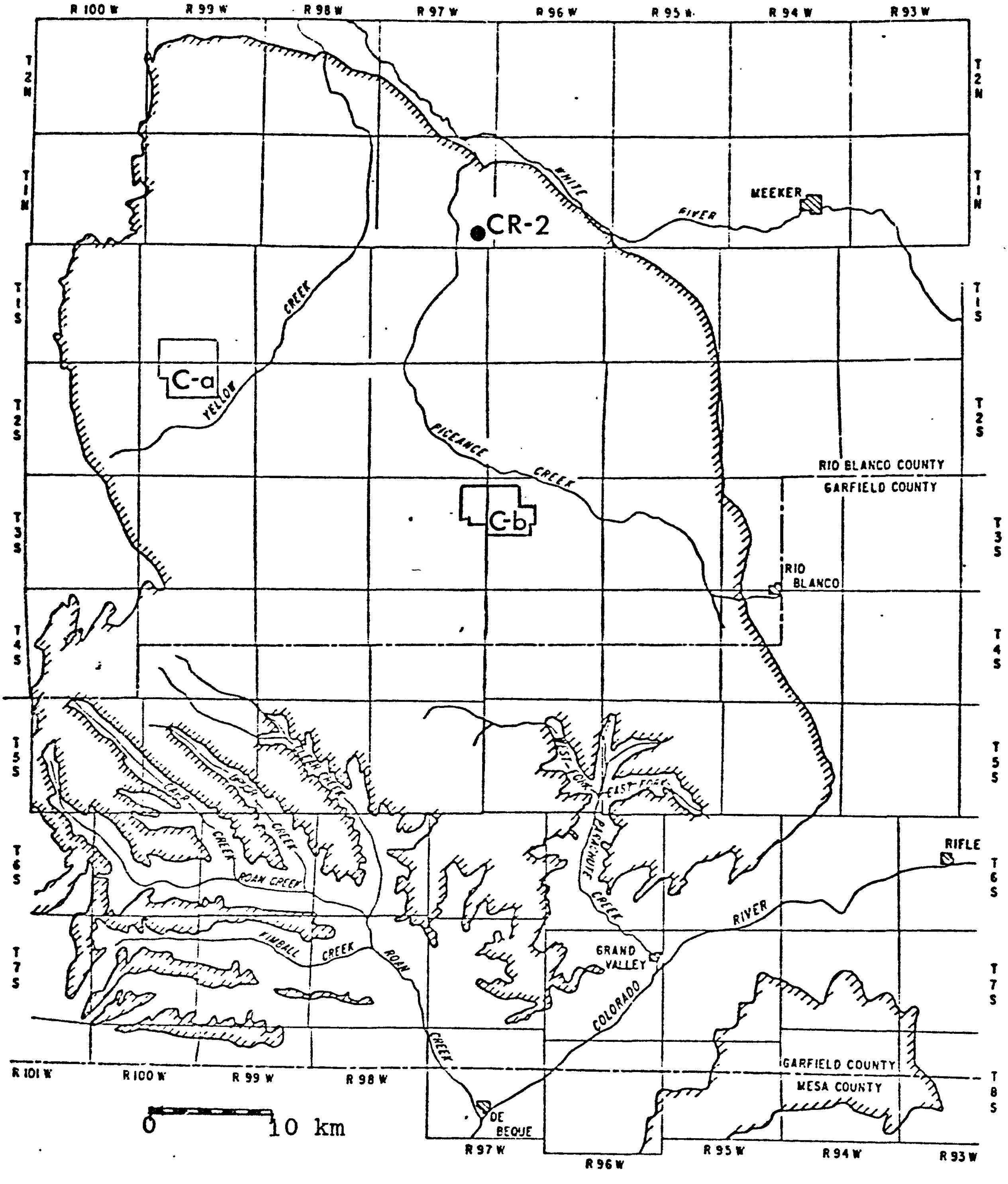

Figure 27.--Index map of the Piceance Creek Basin, Colorado showing the location of USGS oil shale corehole CR-2. The blocks labeled C-a and C-b are the two Colorado prototype oil shale development lease tracts. Hachured line encloses the Piceance Creek Basin.

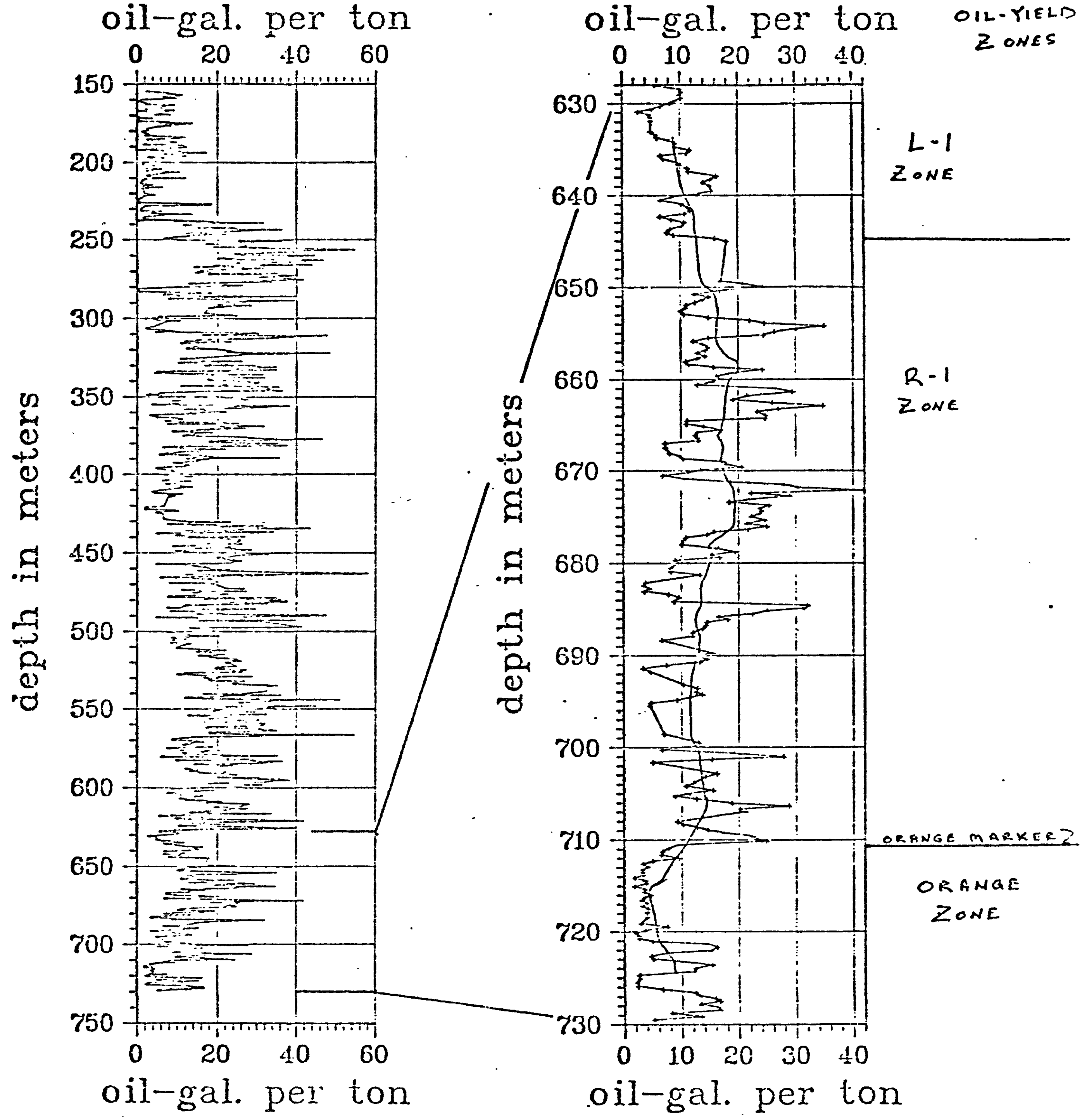

Figure 28.--Oil yield logs for the entire CR-2 core (left) and for the lower 100 meters in the Garden Gulch Member of the Green River Formation (right). The smoothed curve through the oil-yield log for the lower 100 meters was generated using a 31-sample moving average. Oil-rich (R-1) and oil-lean (orange and L-1) zones are indicated to the right of the oil-yield log for the lower 100 meters.

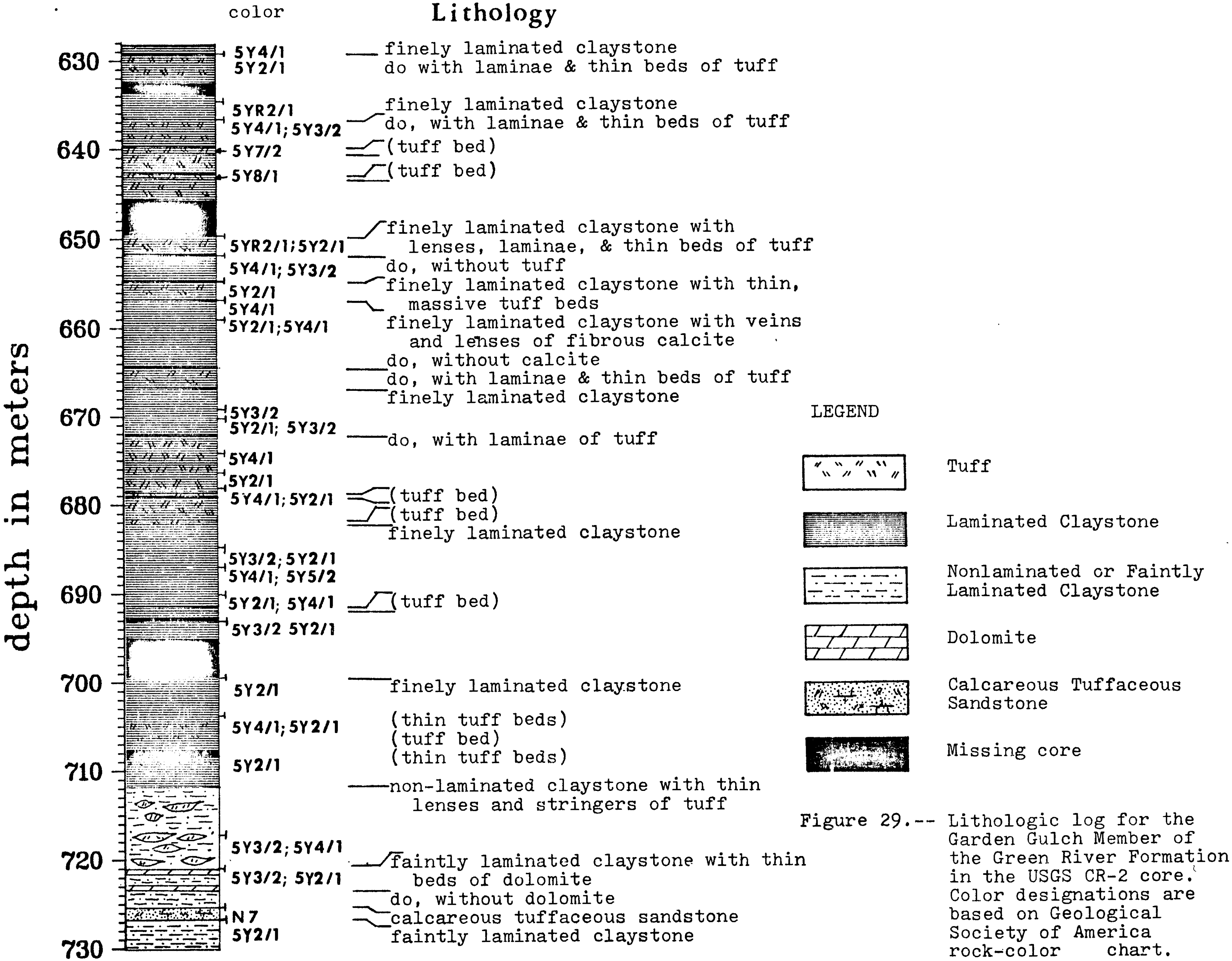

Figure 29.-- Lithologic log for the Garden Gulch Member of the Green River Formation in the USGS CR-2 core. Color designations are based on Geological Society of America rock-color chart. do-same as above.

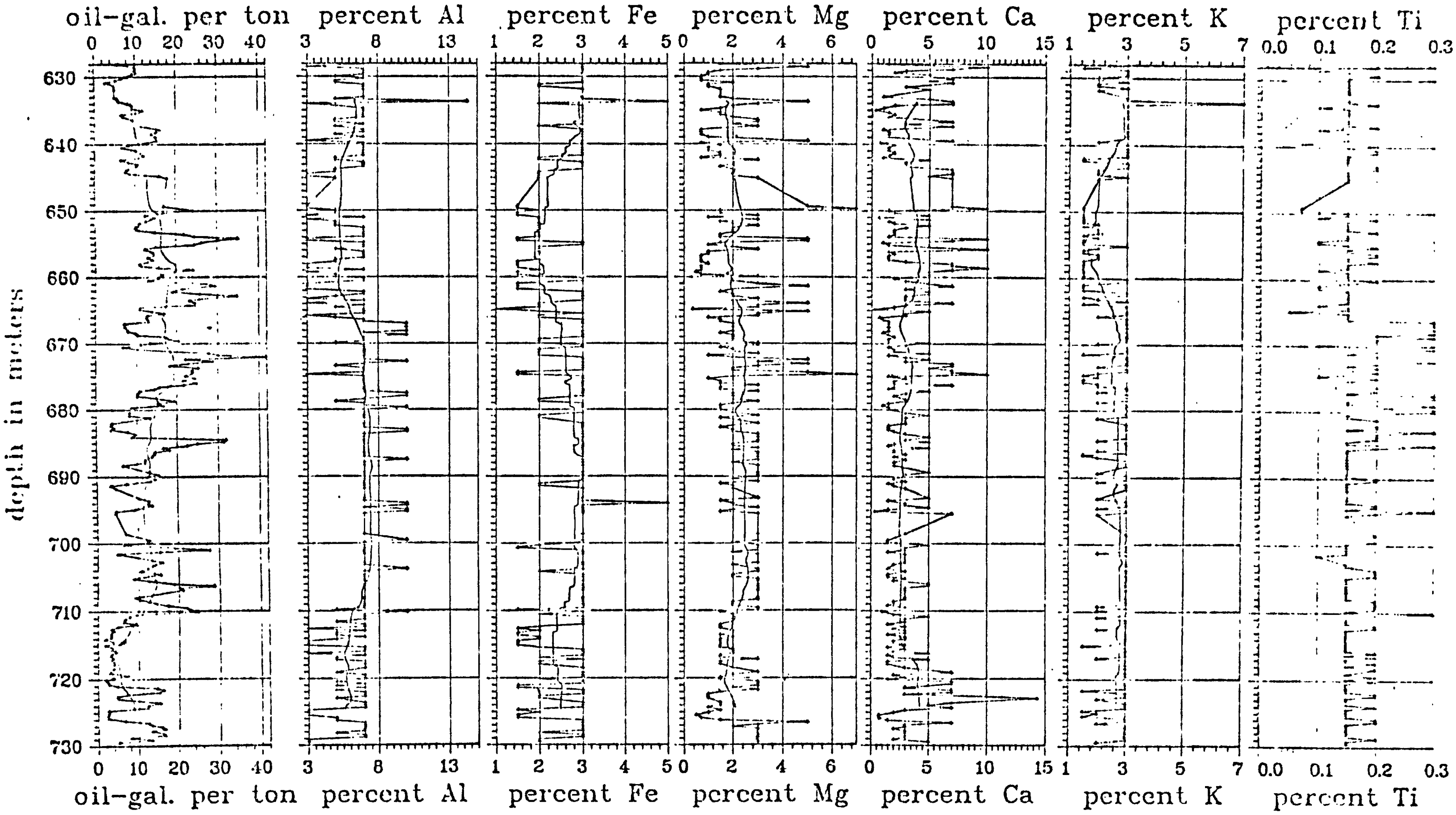

Figure 30.--Profiles of concentrations of Al, Fe, Mg, Ca, K, Ti, B, Cr, Cu, Ga, Mn, Mo, Ni, Pb, Sc, Sr, V, Yb, and Zr, determined by semiquantitative emission spectroscopy, in the Garden Gulch Member of the Green River Formation in the CR-2 core. A profile of oil yield, repeated from figure 2, is included for comparison. The smoothed curves through the raw data profiles were generated using a 31-sample moving average.

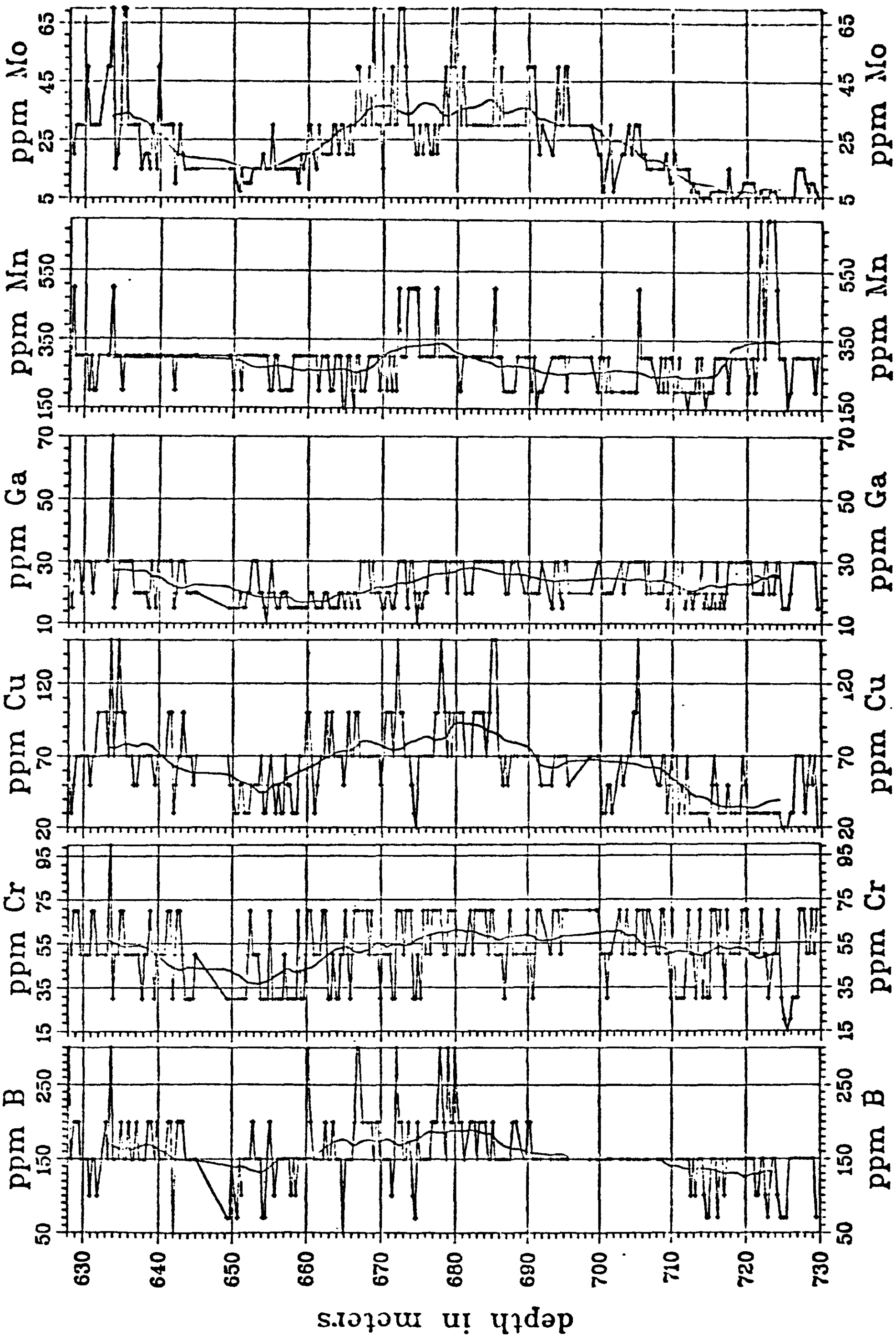

Figure 30.--(Continued)

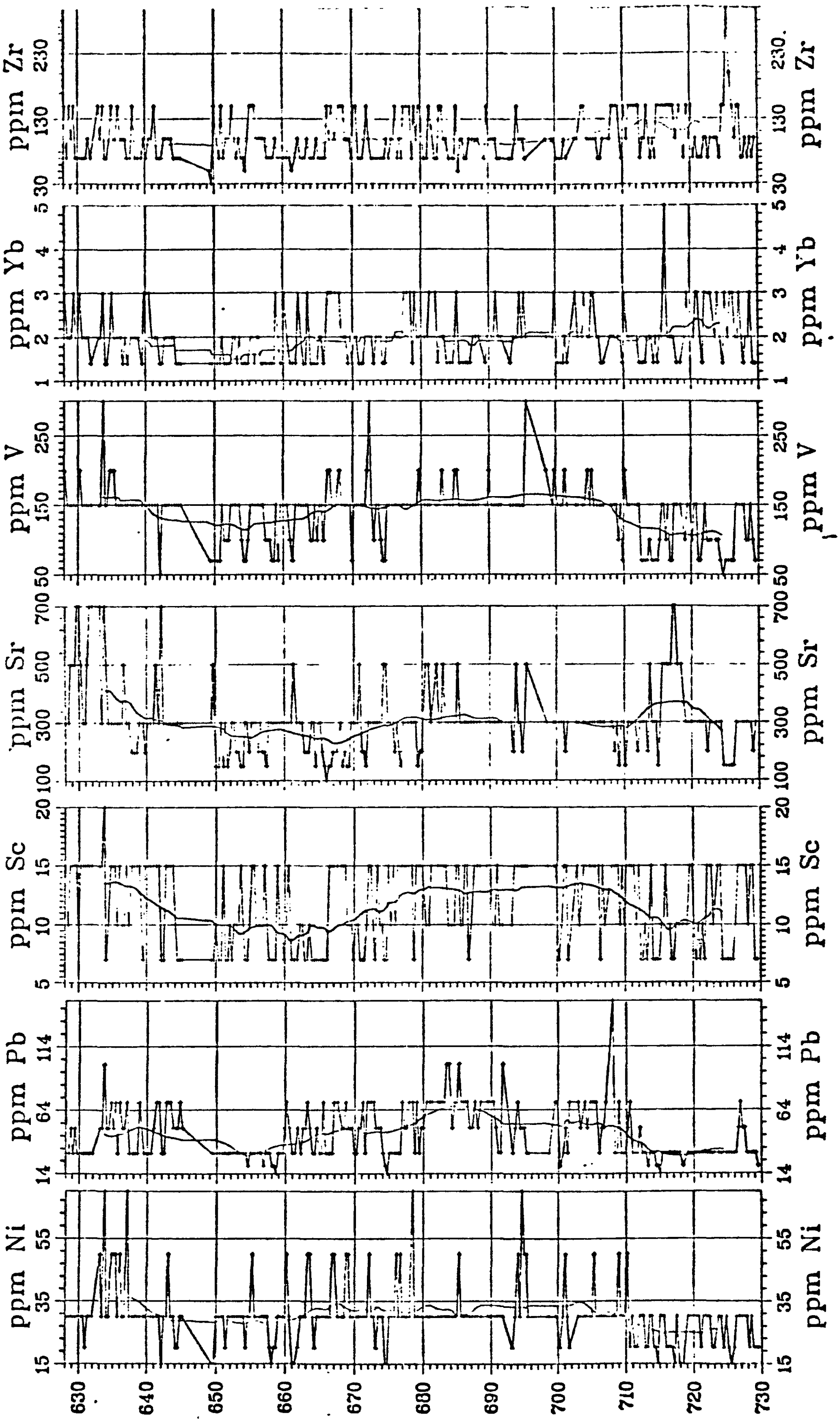

Figure 30.--(Continued)

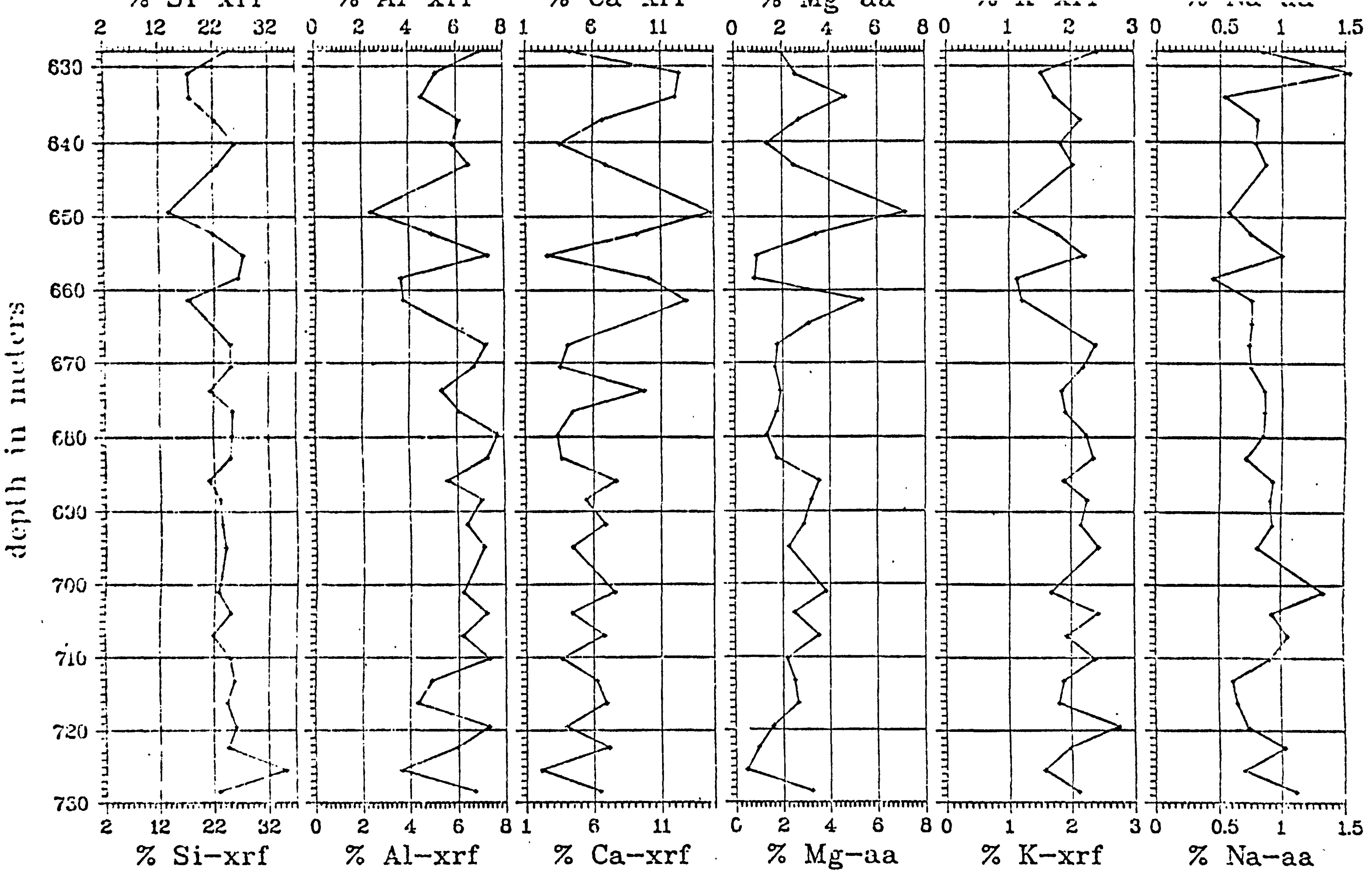

Figure 31.--Profiles of concentrations of Si, Al, Ca, Mg, K, Na, Fe, S, Ti, F, Li, Rb, U, Th, and Hg, determined by quantitative X-ray fluorescence (xrf), atomic absorption (aa), specific ion electrode (elec), and neutron activation analysis (naa), in the Garden Gulch Member of the Green River Formation in the CR-2 core.

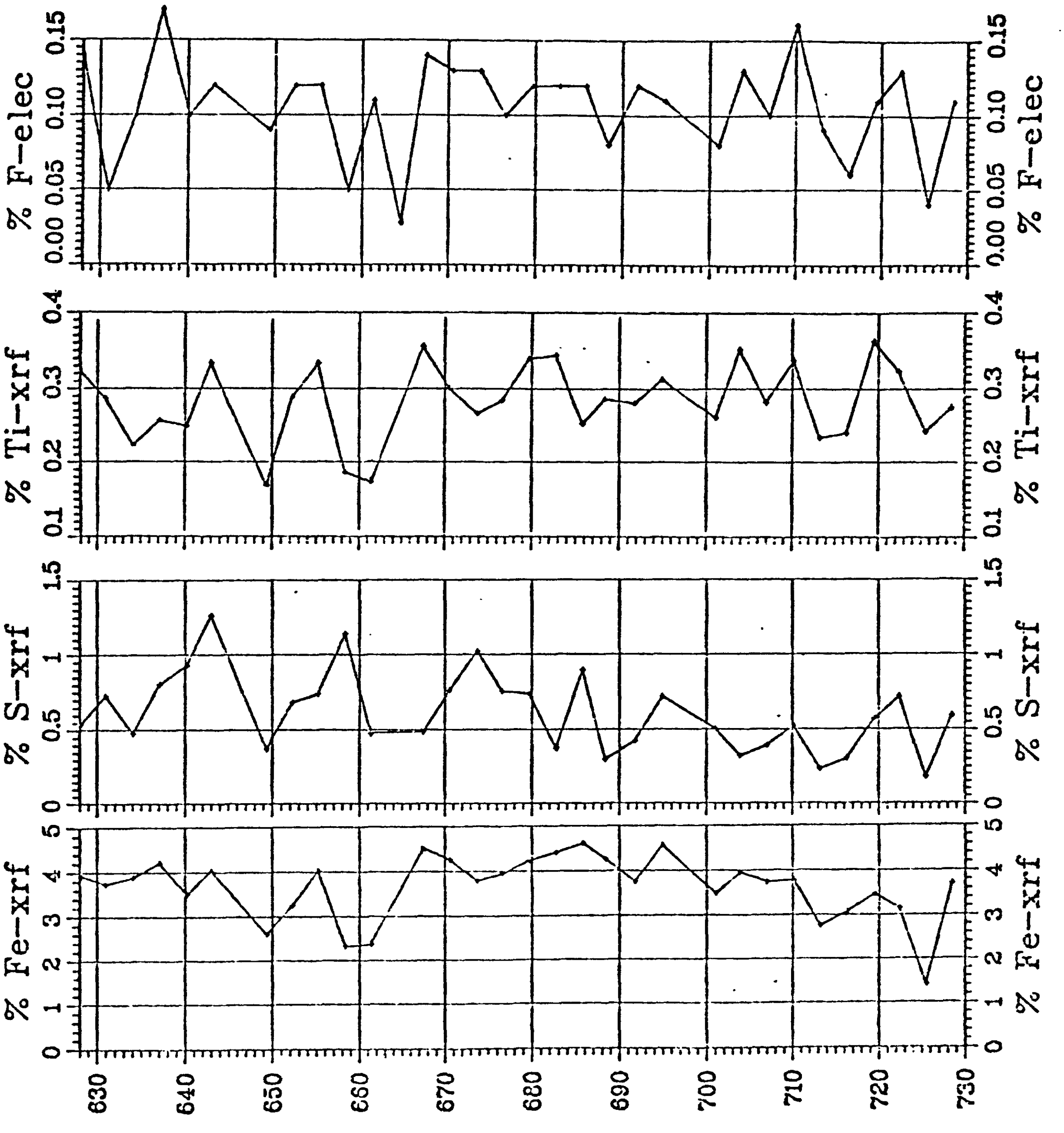

Figure 31.--(Continued)

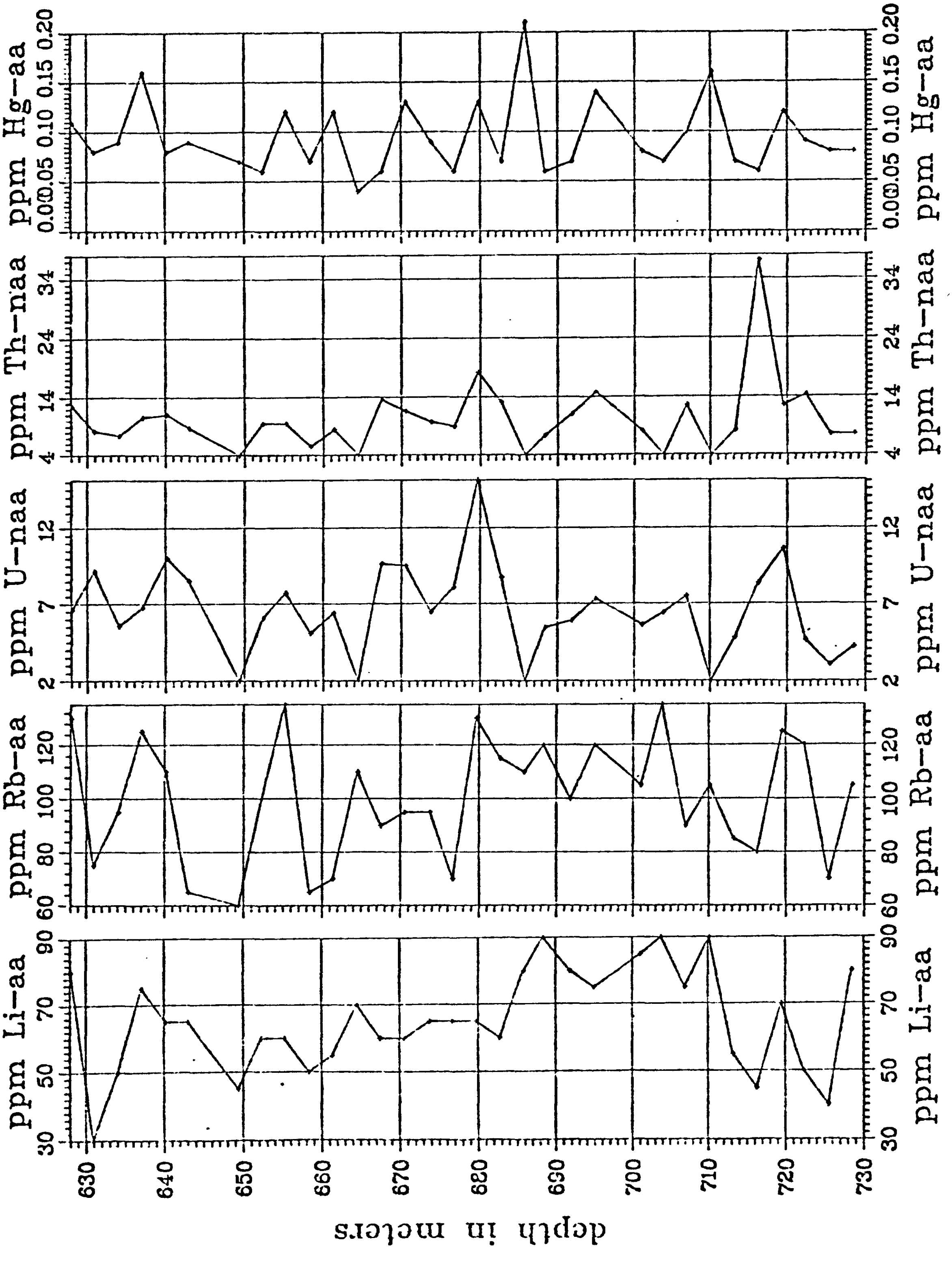

Figure 31.--(Continued)

in Denver. Details of these analytical methods are described by Wahlberg (1976), Huffman and Dinnin (1976), Neiman (1976), and U.S. Geological Survey (1976). Results of these additional analyses are plotted as functions of depth within the core in figure 31.

Results and Discussion

Element Associations

Correlation coefficients were computed among 19 elements determined by semiquantitative emission spectroscopy, plus percent ash and oil yield, in 264 samples from the Garden Gulch. The matrix of correlation coefficients is presented in table 19. In order to simplify analysis of the relationships among the 21 variables, based on correlations, the correlation coefficient matrix was used as input for R-mode factor analysis. The R-mode method examines the matrix of correlation coefficients for variables that are most highly correlated. It then computes new coefficients (factor loadings) reflecting the intervariable correlations. The variables with highest loadings for a particular factor are most closely related to each other and are most characteristic of that factor. Loadings for the first three factors from the R-mode analysis, after varimax rotation, are given in table 20. As many as 10 factors were extracted by the R-mode analysis, but we found that three factors provided the most satisfactory solution; each factor beyond three can be explained by variability in a single element and does not contribute to understanding interelement relationships.

Factor 1 is a "clay-trace-element factor" expressing interrelationships among the elements Al, Fe, K, Ti, B, Cr, Cu, Ga, Mo, Ni, Pb, Sc, and V. Most of these elements are strongly correlated, with loadings on Factor 1 greater than 0.4 (Table 19). These elements probably reside in the fine-grained, noncarbonate mineral fraction.

Factor 2 is simply an "organic-inorganic factor" expressing the expected strong negative correlation in the two-component system of total organic matter (as expressed by oil yield) and total mineral matter (as expressed by % ash).

Factor 3 is a "carbonate factor" and has highest loadings for Ca, Mg, Sr, and Mn. The association of Sr with the carbonate fraction is expected because of the well-known substitution of Sr for Ca in Ca-bearing carbonate minerals. However, it appears that most of the Mn, at least in these samples, is also incorporated in carbonate minerals.

Correlation analysis of the additional elements determined by the more complete, quantitative analyses of 32 samples shows that most (Si, F, Li, Rb, U, and Zn) are associated with the clay fraction, that is they correlate with the 13 elements with high loadings (>0.5) for R-mode factor 1 (Table 20). Apparently none of the additional elements is dominantly associated with either the organic or carbonate fractions, because none correlate highly with oil yield, total carbon, or any of

ARRAY OF CORRELATION COEFFICIENTS -

	1 Ash%	2 Al%-S	3 Fe%-S	4 Mg%-S	5 Ca%-S	6 K%-S	7 Ti%-S	8 B ppm-S	9 Cr ppm-S	10 Cu ppm-S
1 Ash%	1.0000	-0.1036	-0.1201	-0.2546	-0.0216	0.1490	-0.0396	-0.1596	0.0333	-0.3809
2 Al%-S	-0.1036	1.0000	0.5914	-0.1239	-0.3742	0.5629	0.5675	0.5149	0.6077	0.4328
3 Fe%-S	-0.1201	0.5914	1.0000	0.0213	-0.1457	0.5113	0.3679	0.4789	0.5214	0.4354
4 Mg%-S	-0.2546	-0.1239	0.0213	1.0000	0.4769	-0.0433	-0.2442	-0.0995	-0.0149	0.0092
5 Ca%-S	-0.0216	-0.3742	-0.1457	0.4769	1.0000	-0.2850	-0.4006	-0.3210	-0.1915	-0.2483
6 K%-S	0.1490	0.5629	0.5113	-0.0433	-0.2850	1.0000	0.3253	0.4534	0.5577	0.3542
7 Ti%-S	-0.0396	0.5675	0.3679	-0.2442	-0.4006	0.3253	1.0000	0.5277	0.4235	0.3494
8 B ppm-S	-0.1596	0.5149	0.4789	-0.0995	-0.3210	0.4534	0.5277	1.0000	0.5056	0.5656
9 Cr ppm-S	0.0333	0.6077	0.5214	-0.0149	-0.1915	0.5577	0.4235	0.5056	1.0000	0.4022
10 Cu ppm-S	-0.3809	0.4328	0.4354	0.0092	-0.2483	0.3542	0.3494	0.5656	0.4022	1.0000
11 Ga ppm-S	0.0510	0.6137	0.5604	-0.0271	-0.1805	0.6431	0.3400	0.4594	0.5749	0.4309
12 Mn ppm-S	-0.1398	0.0121	0.1850	0.1945	0.5250	0.0051	0.0002	0.0207	0.1156	0.0543
13 Mo ppm-S	-0.2969	0.4508	0.4334	0.0335	-0.1956	0.2874	0.4124	0.5477	0.3917	0.6608
14 Ni ppm-S	-0.2266	0.4273	0.4263	-0.0831	-0.2445	0.3046	0.3040	0.4501	0.3283	0.4594
15 Pb ppm-S	-0.2247	0.4331	0.4629	0.1187	-0.2205	0.4131	0.2626	0.4740	0.3581	0.6059
16 Sc ppm-S	-0.0300	0.6348	0.6163	-0.1962	-0.2523	0.4295	0.4160	0.4719	0.5357	0.4125
17 Sr ppm-S	0.2081	0.0619	0.1220	0.1533	0.2678	0.1581	-0.1491	-0.0436	0.1847	0.0655
18 V ppm-S	-0.1731	0.5675	0.5955	0.0144	-0.1623	0.3977	0.3948	0.5441	0.5221	0.6015
19 Yb ppm-S	0.1716	0.3508	0.3552	-0.2326	-0.1208	0.3902	0.3997	0.3057	0.3722	0.1760
20 Zr ppm-S	0.2283	0.2710	0.1591	-0.2870	-0.3628	0.2148	0.4334	0.1902	0.1528	-0.0017
25 wt % oil	-0.9290	-0.0302	-0.0256	0.2717	0.1039	-0.2612	-0.0668	0.0520	-0.1026	0.2532

	11 Ga ppm-S	12 Mn ppm-S	13 Mo ppm-S	14 Ni ppm-S	15 Pb ppm-S	16 Sc ppm-S	17 Sr ppm-S	18 V ppm-S	19 Yb ppm-S	20 Zr ppm-S	25 wt % oil
1 Ash%	0.0510	-0.1398	-0.2969	-0.2266	-0.2247	-0.0300	0.2081	-0.1731	0.1716	0.2283	-0.9290
2 Al%-S	0.6137	0.0121	0.4508	0.4273	0.4331	0.6348	0.0619	0.5675	0.3508	0.2710	-0.0302
3 Fe%-S	0.5604	0.1850	0.4334	0.4263	0.4629	0.6163	0.1220	0.5955	0.3552	0.1591	-0.0256
4 Mg%-S	-0.0271	0.1945	0.0335	-0.0831	0.1187	-0.1962	0.1533	0.0144	-0.2326	-0.2870	0.2717
5 Ca%-S	-0.1805	0.5250	-0.1956	-0.2445	-0.2205	-0.2523	0.2678	-0.1623	-0.1208	-0.3628	0.1039
6 K%-S	0.6431	0.0051	0.2874	0.3046	0.4131	0.4295	0.1581	0.3977	0.3902	0.2148	-0.2612
7 Ti%-S	0.3400	0.0002	0.4124	0.3040	0.2626	0.4160	-0.1491	0.3948	0.3997	0.4334	-0.0668
8 B ppm-S	0.4594	0.0207	0.5477	0.4501	0.4740	0.4719	-0.0436	0.5441	0.3057	0.1902	0.0520
9 Cr ppm-S	0.5749	0.1156	0.3917	0.3283	0.3581	0.5357	0.1847	0.5221	0.3722	0.1528	-0.1026
10 Cu ppm-S	0.4309	0.0543	0.6608	0.4594	0.6059	0.4125	0.0655	0.6015	0.1760	-0.0017	0.2532
11 Ga ppm-S	1.0000	0.1338	0.3943	0.3082	0.4377	0.5954	0.2096	0.4658	0.3228	0.1797	-0.1780
12 Mn ppm-S	0.1338	1.0000	0.0418	0.0654	-0.0152	0.1225	0.1547	0.0328	0.1359	-0.1332	0.1370
13 Mo ppm-S	0.3943	0.0418	1.0000	0.4830	0.4861	0.3963	0.0603	0.5794	0.1725	0.0625	0.2054
14 Ni ppm-S	0.3082	0.0654	0.4830	1.0000	0.3875	0.4260	-0.0841	0.4525	0.2620	0.1572	0.1348
15 Pb ppm-S	0.4377	-0.0152	0.4861	0.3875	1.0000	0.3665	0.0329	0.4680	0.1390	0.0693	0.0815
16 Sc ppm-S	0.5954	0.1225	0.3963	0.4260	0.3665	1.0000	0.0667	0.5754	0.4895	0.3024	-0.1019
17 Sr ppm-S	0.2096	0.1547	0.0603	-0.0841	0.0329	0.0667	1.0000	0.0879	0.0318	-0.0495	-0.2295
18 V ppm-S	0.4658	0.0328	0.5794	0.4525	0.4680	0.5754	0.0879	1.0000	0.2608	0.1080	0.0343
19 Yb ppm-S	0.3228	0.1359	0.1725	0.2620	0.1390	0.4895	0.0318	0.2608	1.0000	0.3844	-0.2247
20 Zr ppm-S	0.1797	-0.1332	0.0625	0.1572	0.0693	0.3024	-0.0495	0.1080	0.3844	1.0000	-0.2845
25 wt % oil	-0.1780	0.1370	0.2054	0.1348	0.0815	-0.1019	-0.2295	0.0343	-0.2247	-0.2845	1.0000

Table 19.--Matrix of correlation coefficients for 21 compositional variables in 264 samples from the Garden Gulch Member of the Green River Formation, Piceance Creek Basin, Colorado.

Table 20.--Loadings for three rotated factors of R-mode factor analysis of 21 compositional variables in 264 samples from the Garden Gulch Member of the Green River Formation, Piceance Creek Basin, Colorado.

Variable	Factor 1	Factor 2	Factor 3
1 Ash%	-0.18701	0.88907	-0.07350
2 Al%-S	0.79104	0.09672	-0.15843
3 Fe%-S	0.77173	0.07202	0.11901
4 Mg%-S	-0.02701	-0.29064	0.64353
5 Ca%-S	-0.28898	-0.02111	0.80895
6 K%-S	0.66976	0.34699	-0.00068
7 Ti%-S	0.58182	0.07007	-0.42675
8 B ppm-S	0.76631	-0.10448	-0.19159
9 Cr ppm-S	0.76336	0.21306	0.07926
10 Cu ppm-S	0.72102	-0.36577	-0.01730
11 Ga ppm-S	0.74480	0.26663	0.12201
12 Mn ppm-S	0.16236	-0.01052	0.61899
13 Mo ppm-S	0.69462	-0.31537	-0.03275
14 Ni ppm-S	0.60352	-0.21098	0.15735
15 Pb ppm-S	0.65294	-0.20618	0.01064
16 Sc ppm-S	0.75089	0.18706	-0.08192
17 Sr ppm-S	0.16569	0.36159	0.54892
18 V ppm-S	0.77213	-0.09519	0.02544
19 Yb ppm-S	0.46758	0.39371	-0.12809
20 Zr ppm-S	0.23822	0.38164	-0.48667
21 OIL GPT	0.02358	-0.89538	0.09962

the carbonate variables.

Stratigraphic Variations in Element Concentration

Keeping in mind the interelement relationships discussed above, it is possible to examine the plots of element concentrations in figures 30 and 31 for variations within the Garden Gulch Member and for chemical zones based on these variations. Most of the elements plotted in figure 30 exhibit considerable local variability ("noise") that makes it difficult to discern stratigraphic trends. These trends are best observed in the curves of smoothed data that are plotted over the curves of raw data in figure 30.

Most of the elements that were found to be associated under factor 1 of the R-mode analysis exhibit two zones of relatively high concentration and two zones of relatively low concentration within the Garden Gulch Member in the CR-2 core. We emphasize that the terms "high" and "low" concentrations are relative only to these samples. These chemical zones can also be related, in a general way, to the rich and lean oil-yield zones (as defined by Donnell and Blair, 1970 and Cashion and Donnell, 1972). The four zones based on element variability are most clearly visible in the smoothed profiles for Al, Fe, B, Cu, Mo, Pb, Sc, and V in figure 30. The two zones of high concentrations of the factor 1 elements occur between 628 and 645 meters, and between about 660 and 710 meters. The two zones of low concentrations occur between 645 and 660 meters, and about 710 and 730 meters.

The lowest zone of low concentration of factor 1 elements (710 to 730 meters) corresponds to one of the lowest zones of low oil yield in the Green River Formation in the Piceance Creek Basin (the so-called orange zone; figure 28). Ostracods are common in this zone, as are lenses and stringers of tuffaceous material (Fig. 29). This zone also contains more carbonate than most of the Garden Gulch, as evidenced by common thin beds of dolomite (Fig. 29) and relatively high concentrations of factor 3 (carbonate) elements, especially Ca, Mn, and Sr. This zone may represent a less saline, early lacustrine phase of Lake Uinta in northwestern Colorado (Roehler, 1974).

The oil-lean orange zone is overlain by an oil-rich zone referred to as the R-1 zone, which extends from 645 to 710 meters in the CR-2 core (Fig. 28). The organic-rich strata of this zone were apparently deposited at the beginning of more saline conditions in Lake Uinta (Roehler, 1974). The R-1 zone can be subdivided into two chemical zones based on the geochemical profiles in figures 30 and 31. The zone between 660-670 and 710 meters contains relatively high concentrations of the factor 1 (clay) elements. This is particularly noticeable in the plots of Al, Fe, B, Cu, Mo, Pb, Sc, V, Li, and Rb (Figs. 30 and 31). In contrast, the upper chemical zone of the R-1 oil-yield zone (between 645 and about 660 meters) contains relatively low concentrations of the same factor 1) elements, and relatively high concentrations of the carbonate-related variables Ca and Mg (Fig. 30). This zone also contains relatively high concentrations of sulfur (Fig. 31).

The upper chemical zone in the Garden Gulch (between 628 and about 645 meters) roughly corresponds to an oil-lean zone called the L-1 zone (Fig. 28). Unlike the lower oil-lean zone (orange zone), the L-1 zone contains relatively high concentrations of the factor 1 elements Fe, K, Cr, Cu, Mo, Ni, Pb, Sc, and V (Fig. 30). The behavior of Sr in this zone is in marked contrast to the other carbonate-related elements. The concentration of Sr is highest in both of the oil-lean zones (orange and L-1), whereas Ca and Mn are present in high concentrations in the orange zone and low concentrations in the L-1 zone.

Element Content of Lichens and Soils Near a New Powerplant, Colstrip, Montana--Preoperational Levels

by

Larry P. Gough and James A. Erdman

Introduction

The Colstrip Powerplant is located in Rosebud County 150 km east of Billings and 40 km south of Forsyth, Montana, (fig. 32). According to a company brochure (Montana Power and Puget Sound Power and Light Companies, no date), two units, each with approximately 330 MW(e) gross generating capacity, currently burn subbituminous coal, which is supplied by a strip mine at the site. In order to conform with current emissions regulations, the 154-m stack associated with each unit is equipped with three wet scrubbers. Although original company plans called for at least two more units capable of supplying 700 MW(e) additional power, The Environmental Protection Agency recently ruled that the powerplant which went "on line" in late 1975 is responsible for the deterioration of the Class I (near-pristine) air quality of the nearby Northern Cheyenne Indian Reservation. This ruling makes the prospect of additional units questionable.

In July 1975, we sampled the foliose soil lichen _Parmelia chlorochroa_ Tuck., surface soil, and ponderosa pine needles and stems along upwind and downwind transects at the Colstrip Powerplant. This study was prompted by our early results from a similar sampling design at the Dave Johnston Powerplant in Wyoming, which indicated that element emissions from the Dave Johnston coal-fired plant were influencing the element content of plant materials nearby. Results from the Dave Johnston studies, which involved collections of _P. chlorochroa_, silver sagebrush, and big sagebrush, are now available (Gough and Erdman, 1977; Anderson and Keith, 1977; Connor and others, 1976). A second impetus for the Colstrip study was the prospect of being able to sample plants and soils before and after the powerplant became operational. This report gives our data from the preoperational 1975 collection of lichen and soil; the ponderosa pine data are still being evaluated and will not be reported here. The postoperational collections were completed in July, 1978; however, the element analyses of the samples are not yet available.

Methods

Lichen sample collections and preparation

Composite samples of the foliose soil lichen _Parmelia chlorochroa_ were collected at sites spaced at geometric intervals along north and southeast transects (fig. 32). Each sample was composed of numerous

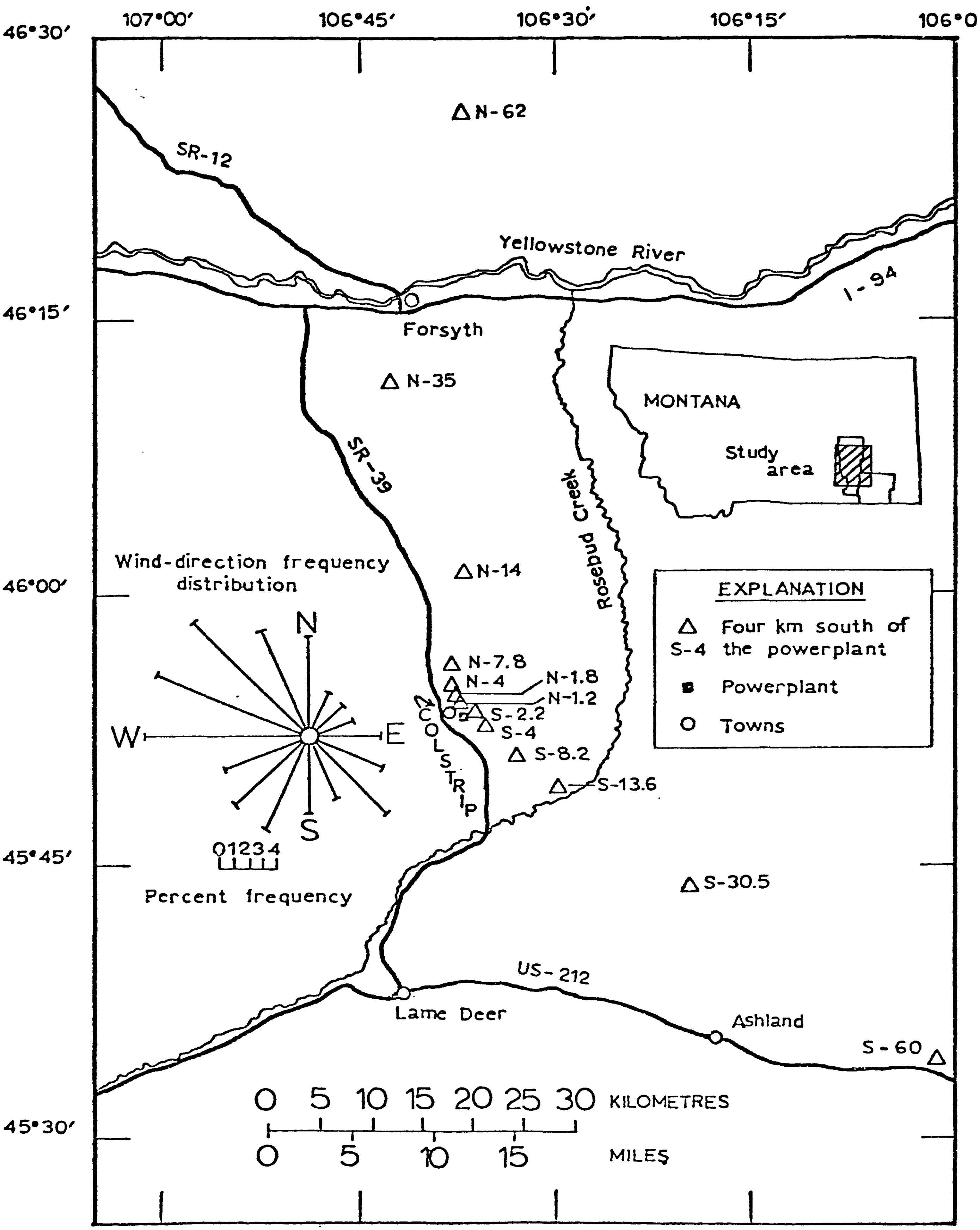

Figure 32.--Approximate locations of sampling sites along two transects near Colstrip, Montana. The wind-rose diagram (U.S. Geological Survey 1973) is from data obtained 94 m above ground level at Colstrip for the period between 12 November, 1971, and 11 November, 1972.

thalli (that is, the simple vegetative plant body) collected within two small areas of about 50 m^2 at each site. These two areas were generally separated by at least 25 m. This lichen was so uncommon at the 32 km southeast location that we were able to collect only one sample.

The lichen varied greatly in its general abundance; however, even at those sites where thalli were extremely sparse, enough material was obtained for all of the chemical analyses. Habitat preference for individual thalli varied from site to site. In general, thalli were either free or tangled among plant debris and around the bases of grasses. The thalli were quite often found attached to sandstone or clinker fragments when these fragments were abundant on the soil surface. The thalli occurred in localized patches several square meters in extent and were most commonly associated with the short grasses *Bouteloua gracilis* (bluegrama) and *Koeleria macrantha* (Junegrass).

We are aware of the taxonomic uncertainty associated with this particular lichen (Hale, 1974; S. Shushan, Univ. of Colorado, oral commun., 1978), but for this study we prefer to recognize the morphological variants as simply forms of *P. chlorochroa* and do not attempt to distinguish these forms as separate species.

Since soil contamination may confound any effects due to powerplant stack effluents on subsequent sampling, all samples were cleaned prior to analysis (see Gough and Erdman, 1977). After ultrasonic washing, the samples were dried, ground (<2 mm mesh), and burned to ash (Harms, 1976). The ashed material was analyzed using emission spectroscopy (Neiman, 1976) and atomic absorption spectrometry. Some of the dried *unashed* material was analyzed for volatile elements by various techniques (Harms, 1976). For those elements analyzed in ash, the dry-weight-equivalent concentrations were calculated for the lichen material using the formula:

$$Cd = Ca\ A/100,$$

where Cd is the concentration in the dry material, Ca is the concentration in ash, and A is the percent ash yield.

Soil sample collection and preparation

Since elements associated with powerplant activity were expected to be found in greatest abundance near the soil surface, samples of the surface veneer were taken. These were collected at each site (except at one location, 32 km southeast) using a drywall knife 25 cm wide made of stainless steel. The knife was pushed along the soil surface at a depth that did not exceed 1 cm. Each sample was composited over several square meters.

All samples were dried in the laboratory using forced air at ambient temperature. The samples were then disaggregated and passed through a 10-mesh (2 mm) sieve. Chemical analyses were performed on this material by emission spectroscopy (Neiman, 1976) and by X-ray fluorescence, atomic absorption spectrometry, neutron activation and various other techniques (Huffman and Dinnin, 1976).

Data analysis

Prior to chemical analysis, splits of the dried and ground plant material and of the <2 mm soil material were made of about 25% of the samples. These splits were added to the original lot of plant and soil samples, and all samples were analyzed in a random order. The analysis of splits of a proportion of the total number of samples gave us an estimation of the precision of our analytical methods for each element. All analyses were performed in laboratories of the U.S. Geological Survey in Denver by the following individuals: Jim Baker, Ardith Bartel, L. A. Bradley, E. Brandt, P. H. Briggs, N. M. Conklin, J. G. Crock, I. C. Frost, Johnnie Gardner, Patricia Guest, J. C. Hamilton, T. F. Harms, R. J. Knight, H. T. Millard, Wayne Mountjoy, C. S. E. Papp, G. O. Riddle, J. A. Thomas, Michelle Tuttle, J. S. Wahlberg, Bill Walz.

Of 72 elements analyzed for in a total of 32 samples (including splits) of lichen material, 39 elements were not detectable by the methods used. The only censoring in the remaining 33 elements consisted of a single "not detected" value for Ga; in addition, Sb was not analyzed for in another sample. Since the analysis of variance requires completely numeric data sets, the Ga "hole" was substituted with a value equal to 0.7 times the Ga lower limit of determination, whereas the Sb "hole" was substituted with a value equal to the Sb concentration of its companion sample. For those concentrations determined on an ash basis, the values were substituted with dry weight equivalents using the formula given above.

Of 70 elements analyzed for in a total of 40 samples (including splits) of soil material, 32 elements were not detectable by the methods used. Of the remaining 38 elements, three (F, I, and Se) had 1, 19, and 21 concentration values, respectively, that were detected but were below the lower limit of determination. A value equal to 0.7 times the lower limit of determination was substituted for these censored values in the analysis of variance.

The relation between the concentration of an element in the material sampled and distance (on a geometric scale) from the powerplant was evaluated using linear regression analysis. Prediction equations were calculated using the form:

$$\log_{10} \underline{X} = \underline{a} + \underline{b} \log_{10} \underline{D},$$

where $\underline{X}$ is an estimate of the concentration of the element (in parts per million or percent), $\underline{a}$ and $\underline{b}$ are, respectively, the intercept and slope of the regression line, and $\underline{D}$ is the distance from the powerplant in kilometers.

Using analysis of variance for regression (see, for example, Rickmers and Todd, 1967, p. 254) F-ratios were tested to evaluate (1) whether or not the linear (or first degree) curve adequately described the relation between the response variable Y log (element concentration) and the predictor variable X log (distance from powerplant), and (2) whether or not the slope of the regression line was significantly different from zero. Assuming the first test resulted in a fit of the linear model to the data, then the second test assessed whether or not a true relationship existed between X and Y.

RESULTS AND DISCUSSION

Colstrip Unit 1 did not begin commercial operation until November 1975, and Unit 2 until August 1976. We assumed, therefore, that the element composition of the vegetation and soils that were collected in July 1975 would not be influenced by stack emissions. Also, because all sites were located on the Fort Union Formation of Tertiary age, we assumed that any geochemical influence of the substrate on the vegetation would be fairly uniform throughout the extent of the traverses. However, because there has been some limited vehicular, construction, and mining activity in the area since 1924 (Schafer and others, 1976), and this sort of activity accelerated about 1971, we recognize a potential for a point-source "dust factor."

Table 21 represents regression and analytical data on thirteen elements in the dry material of soil lichens that showed significant regression trends (slopes significantly different from zero at the 0.05 probability level). Most of these trends (eleven) were along the north or upwind transect. These trends were all negative (negative b), indicating that the element concentration in the plant material decreased with increasing distance from the powerplant. An inspection of the significance-of-model column shows that for all eleven northerly trends, the linear model was adequate in explaining the relation between element concentration and distance. This fact, that there is no significant lack of fit of the data to the model, would indicate that relations with significance of slope values $\leq$ 0.05 were, in fact, depicting real relations between X and Y. Only three of these elements (Cr, Fe, and Ga), however, showed coefficient of determination values that were 0.50 or greater, which indicates that the relation between X and Y (log distance and log concentration) for these three elements explained $\geq$ 50% of the total variability in the data.

A 0.50 coefficient of determination is a threshold established in previous studies of point-source effects (Gough and Erdman, 1977; Severson and Gough, 1978). It is an arbitrary value but one which indicates that there exists a possible relationship between powerplant operations and the element concentration in samples close to the facility. The very narrow range in the observed Ga concentrations may be enough to make mere chance important in its negative regression trend; however, the trends for Cr and Fe appear to be related to the operations of the powerplant. When compared to the coefficient of

Table 21.--Element concentration in the dry material of Parmelia chlorochroa as a function of distance from the Colstrip Powerplant, Colstrip, Montana.

[a is the intercept and b is the slope of the regression equation; significance of the slope is the probability level at which the slope is different from zero; significance of model is the probability level at which the linear regression model adequately describes the relation; coefficient of determination is an expression of the proportion of the total variation in the dependent variable that is accounted for by the linear model; percent laboratory error is the variance due to analytical error expressed as a percent of the total variance.]

Element	Regression statistics					Percent laboratory error	Observed range
	a	b	Significance of		Coefficient of determination		
			slope	model			
			North (upwind) transect[1]				
Ba, ppm-	1.8	-0.15	0.02	0.29	0.36	42	30 -100
Cr, ppm-	1.1	- .20	.001	.93	.64	20	4.5 - 14
F, ppm--	1.7	- .06	.02	.20	.39	14	35 - 55
Fe, pct.	- .39	- .25	.004	.46	.51	20	.10- .60
Ga, ppm-	.45	- .15	.006	.57	.50	11	1.0 - 3.0
K, pct.	- .63	- .08	.03	.07	.32	8	.15- .27
Na, ppm-	2.1	- .07	.006	.71	.47	16	90 -160
Ni, ppm-	.70	- .14	.03	.90	.33	21	2.2 - 6.0
S, ppm--[2]	2.9	- .06	.01	.10	.40	31	500 -750
Sb, ppm-	- .89	- .11	.006	.36	.48	55	.08- .15
Zn, ppm-	1.6	- .08	.03	.75	.33	11	28 - 62
			Southeast (downwind) transect[3]				
Ni, ppm-	.38	.22	.01	.05	.53	21	2.5 - 6.0
Sr, ppm-	1.7	- .17	.02	.87	.48	11	27 - 60

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[1] Statistics based on 14 samples.

[2] Total sulfur.

[3] Statistics based on 11 samples.

determination for elements related to the Dave Johnston Powerplant (Gough and Erdman, 1977), however, the values in Table 21 are small. Certainly the strong influence that the Dave Johnston Powerplant has on the element content of nearby P. chlorochroa was not evident at Colstrip in 1975. An examination of Table 22 will show that the Cr and Fe trends were also greatly influenced by the high concentration of these elements in samples collected at $\leq$ 2 km from the powerplant.

For the southeast (downwind) transect Sr was the only element in lichen that showed a significant negatively sloping trend and a relatively high coefficient of determination (0.48, table 21). Other studies (Gough and Erdman, 1977; Connor and others, 1976; Klein and others, 1975) have shown Sr to be related to the overall powerplant operations, and not necessarily to emissions only.

The element content (geometric means and observed ranges) of 25 elements in lichen ash at Colsrip was compared with the element content of lichen ash for 22 samples from the Powder River Basin, Wyoming (Erdman and Gough, 1977). In general, the geometric means and ranges for most elements compared very favorably. The only exceptions were the geometric means for Co, F, Hg, and Ni, which were about twice as great in the Colstrip samples as in the Basin samples, and the geometric mean of U in the Basin samples, which was three times greater than in the Colstrip samples.

Numerous significant regression trends were noted for elements in soils (Table 23). All trends except K on the north transect, however, were positive and are therefore unlikely to be related to the operations of the powerplant. The coefficient of determination for K was low (0.30), and the trend appeared to be dominated by two small concentration values at 64 km (Table 24). Along the southeast transect all but one of the eight trends was negative, and several trends (K, Rb, and U) had coefficients of determination $\geq$0.50. For K and Rb there is a significant lack of fit of the data to the linear mode, raising the question as to whether or not the relation between X and Y has any real or interpretable meaning. The coefficient of determination for the U trend was 0.50. Two features of the trend, however, make it questionable as being related to the powerplant: (1) there is significant lack of fit of the data to the linear model at the 0.10 probability level, and (2) there is only a 1-ppm spread in the data. It would appear, therefore, that none of the soil element trends are directly related to the operations of the powerplant.

A major purpose of this preoperational study was to establish, using regression analysis, whether or not uniform background concentrations existed for a given element in lichen and soil. For those element trends resulting in significant positive or negative slopes, a uniform background was demonstrated. With the analysis of the post-operational data, not only will the appearance of new significant regression trends be important, but also useful changes may occur in the models in Tables 21 and 23 for those elements not showing uniform concentration backgrounds.

Table 22.--*Parmelia chlorochroa* element content (dry weight) and ash yield, Colstrip Powerplant, Colstrip, Montana

[S indicates Semiquantitative Spectrographic analyses; A indicates atomic absorption analyses]

Sample	Latitude			Longitude			Kilometers	Ash%	Al%-S	As ppm	B ppm-S	Ba ppm-S	Ca/A%	Cd/A ppm
	D	M	S	D	M	S								
							North (upwind) of the powerplant							
C5N01L1	45	53	37N	106	37	07W	1.2	20	1.40	1.2	30.0	100	2.4	0.7
C5N01L2	45	53	37N	106	37	07W	1.2	17	1.19	1.2	25.5	85	2.6	0.7
C5N02L1	45	53	10N	106	37	10W	1.8	17	0.51	0.9	11.9	51	3.9	0.5
C5N02L2	45	53	54N	106	37	10W	1.8	18	0.54	0.8	9.0	54	4.5	0.6
C5N04L1	45	55	06N	106	37	04W	4.0	12	0.60	1.0	18.0	36	2.0	0.3
C5N04L2	45	55	06N	106	37	04W	4.0	12	0.36	0.9	18.0	36	2.4	0.4
C5N08L1	45	57	05N	106	37	43W	7.8	20	0.60	0.7	14.0	60	4.6	0.6
C5N08L2	45	57	05N	106	37	43W	7.8	19	0.57	0.8	13.3	57	4.6	0.8
C5N16L1	46	00	35N	106	36	28W	14.0	16	1.12	1.2	24.0	48	2.7	0.6
C5N16L2	46	00	35N	106	36	28W	14.0	16	0.80	1.2	11.2	48	3.2	0.4
C5N32L1	46	11	55N	106	41	15W	35.0	18	0.54	1.0	12.6	54	4.7	0.8
C5N32L2	46	11	55N	106	41	15W	35.0	15	0.30	0.8	10.5	30	4.5	0.8
C5N64L1	46	26	15N	106	37	25W	62.0	16	0.48	0.7	11.2	48	4.2	0.5
C5N64L2	46	26	15N	106	37	25W	62.0	15	0.45	0.8	10.5	30	4.1	0.6
							Southeast (downwind) of the powerplant							
C5S02L1	45	52	55N	106	35	20W	2.2	20	0.60	1.2	14.0	60	4.2	0.6
C5S02L2	45	52	55N	106	35	20W	2.2	20	0.60	1.2	14.0	60	4.0	0.5
C5S04L1	45	51	58N	106	34	11W	4.0	18	0.54	0.9	12.6	54	4.3	0.5
C5S04L2	45	51	58N	106	34	11W	4.0	17	0.51	0.9	11.9	34	5.1	0.5
C5S08L1	45	50	38N	106	31	34W	8.2	17	0.85	1.6	25.5	119	2.9	0.5
C5S08L2	45	50	38N	106	31	34W	8.2	20	1.40	1.0	30.0	140	2.8	0.7
C5S16L1	45	48	50N	106	28	15W	13.6	19	0.57	1.0	13.3	38	4.6	0.5
C5S16L2	45	48	50N	106	28	15W	13.6	19	0.57	1.0	13.3	38	4.6	0.5
C5S32L1	45	43	18N	106	17	55W	30.5	19	1.33	1.4	13.3	57	3.6	0.6
C5S64L1	45	34	10N	105	59	50W	60.0	20	0.60	0.8	14.0	60	3.4	0.5
C5S64L2	45	34	10N	105	59	50W	60.0	18	1.26	0.9	12.6	126	2.5	0.6

Table 22.--*Parmelia chlorochroa* element content (dry weight) and ash yield, Colstrip Powerplant, Colstrip, Montana-continued

Sample	Co/A ppm	Cr ppm-S	Cu ppm-S	F ppm	Fe%-S	Ga ppm-S	Hg ppm	K/A%	Li/A ppm	Mg%-S
North (upwind) of the powerplant-continued										
C5N01L1	1.40	14.0	14.0	55	0.60	3.0	0.15	0.26	1.60	0.30
C5N01L2	1.02	11.9	11.9	55	0.51	2.5	0.20	0.27	1.02	0.25
C5N02L1	1.36	8.5	11.9	45	0.25	2.6	0.15	0.19	0.51	0.12
C5N02L2	1.08	12.6	12.6	50	0.27	2.7	0.15	0.17	1.26	0.13
C5N04L1	0.96	8.4	18.0	45	0.24	1.8	0.40	0.24	0.60	0.18
C5N04L2	0.84	8.4	8.4	40	0.18	1.8	0.15	0.20	0.96	0.08
C5N08L1	1.20	10.0	14.0	45	0.30	3.0	0.35	0.17	1.20	0.14
C5N08L2	1.14	5.7	5.7	50	0.29	1.9	0.15	0.18	0.95	0.13
C5N16L1	1.44	8.0	11.2	50	0.32	2.4	0.20	0.24	1.12	0.24
C5N16L2	1.28	8.0	11.2	50	0.24	2.4	0.10	0.24	0.96	0.16
C5N32L1	1.08	5.4	12.6	40	0.18	1.8	0.30	0.15	0.90	0.13
C5N32L2	0.60	4.5	10.5	35	0.11	1.1	0.15	0.15	0.60	0.11
C5N64L1	0.96	8.0	11.2	45	0.24	1.6	0.15	0.19	0.80	0.11
C5N64L2	1.05	4.5	10.5	40	0.11	1.5	0.15	0.15	0.75	0.11
Southeast (downwind) of the powerplant-continued										
C5S02L1	1.40	10.0	14.0	60	0.30	3.0	0.15	0.24	1.20	0.14
C5S02L2	1.60	6.0	14.0	50	0.30	3.0	0.25	0.24	0.80	0.30
C5S04L1	1.08	9.0	12.6	45	0.27	1.8	0.30	0.15	1.08	0.13
C5S04L2	0.85	5.1	11.9	40	0.17	1.2	0.25	0.16	0.68	0.12
C5S08L1	1.02	11.9	25.5	55	0.34	2.6	0.45	0.22	1.53	0.25
C5S08L2	1.60	14.0	14.0	45	0.60	3.0	0.25	0.24	1.80	0.30
C5S16L1	1.14	5.7	13.3	45	0.29	1.9	0.15	0.19	1.14	0.13
C5S16L2	0.95	5.7	13.3	55	0.29	1.9	0.15	0.21	0.95	0.13
C5S32L1	1.52	13.3	13.3	50	0.57	2.8	0.15	0.23	1.33	0.29
C5S64L1	1.60	6.0	10.0	45	0.30	3.0	0.40	0.24	0.60	0.14
C5S64L2	1.26	12.6	12.6	50	0.27	2.7	0.15	0.20	1.26	0.27

Table 22.--*Parmelia chlorochroa* element content (dry weight) and ash yield, Colstrip Powerplant, Colstrip, Montana-continued

Sample	Mn ppm-S	Mo/A ppm	Na/A ppm	Ni ppm-S	P/A ppm	Pb ppm-S	Tot. S ppm	Sb ppm	Se ppm	Sr ppm-S
North (upwind) of the powerplant-continued										
C5N01L1	100	0.80	160	6.0	600	20	650	0.15	0.30	40
C5N01L2	51	0.68	119	5.1	510	12	750	0.15	0.25	34
C5N02L1	51	0.68	119	2.6	510	26	750	0.10	0.30	26
C5N02L2	54	0.72	108	5.4	540	18	750	0.10	0.30	27
C5N04L1	60	0.48	108	3.6	720	18	650	0.10	0.30	24
C5N04L2	36	0.48	108	3.6	360	18	650	0.10	0.30	18
C5N08L1	60	0.80	100	6.0	600	20	650	0.10	0.25	30
C5N08L2	57	0.76	114	3.8	570	13	650	0.15	0.25	29
C5N16L1	80	0.64	128	3.2	480	11	650	0.10	0.30	24
C5N16L2	48	0.64	112	4.8	480	11	650	0.10	0.30	24
C5N32L1	54	0.72	90	3.6	540	18	500	0.10	0.25	54
C5N32L2	45	0.60	105	2.3	450	23	500	0.08	0.25	45
C5N64L1	48	0.64	96	3.2	480	16	700	0.08	0.30	32
C5N64L2	45	0.60	90	2.3	450	11	600	0.08	0.25	45
Southeast (downwind) of the powerplant-continued										
C5S02L1	60	0.80	140	3.0	600	14	800	0.15	0.30	60
C5S02L2	60	0.80	120	3.0	600	14	800	0.10	0.25	30
C5S04L1	54	0.72	108	2.7	288	13	600	0.15	0.25	54
C5S04L2	51	0.68	102	2.6	272	17	650	0.10	0.25	51
C5S08L1	51	0.68	136	5.1	510	26	800	0.20	0.35	34
C5S08L2	100	0.80	200	6.0	600	30	550	0.25	0.30	40
C5S16L1	57	0.76	114	3.8	570	13	750	0.10	0.25	38
C5S16L2	57	0.76	133	2.8	570	13	700	0.10	0.30	29
C5S32L1	95	0.76	95	5.7	570	29	850	0.15	0.25	29
C5S64L1	40	0.80	80	6.0	600	14	800	0.10	0.25	30
C5S64L2	54	0.72	90	5.4	540	13	650	0.10	0.25	27

Table 22.--*Parmelia chlorochroa* element content (dry weight) and ash yield, Colstrip Powerplant, Colstrip, Montana-continued

Sample	Ti ppm-S	U/A ppm	V ppm-S	Y ppm-S	Zn/A ppm	Zr ppm-S
North (upwind) of the powerplant-continued						
C5N01L1	600	0.080	14.0	6.0	62	40.0
C5N01L2	510	0.068	11.9	5.1	41	25.5
C5N02L1	255	0.068	5.1	5.1	37	17.0
C5N02L2	270	0.072	12.6	5.4	38	12.6
C5N04L1	180	0.096	8.4	3.6	42	8.4
C5N04L2	180	0.096	6.0	2.4	32	18.0
C5N08L1	300	0.080	10.0	4.0	30	14.0
C5N08L2	285	0.076	9.5	3.8	40	13.3
C5N16L1	240	0.128	11.2	4.8	45	24.0
C5N16L2	240	0.064	11.2	4.8	36	24.0
C5N32L1	270	0.072	9.0	3.6	31	12.6
C5N32L2	225	0.060	4.5	3.0	29	7.5
C5N64L1	240	0.064	8.0	3.2	34	11.2
C5N64L2	225	0.060	4.5	4.5	35	15.0
Southeast (downwind) of the powerplant-continued						
C5S02L1	300	0.160	14.0	4.0	31	14.0
C5S02L2	300	0.160	6.0	3.0	32	10.0
C5S04L1	270	0.072	5.4	2.7	24	9.0
C5S04L2	255	0.068	5.1	2.6	28	8.5
C5S08L1	340	0.136	11.9	3.4	34	25.5
C5S08L2	600	0.160	14.0	6.0	40	30.0
C5S16L1	285	0.076	5.7	3.8	38	13.3
C5S16L2	285	0.076	9.5	2.8	29	13.3
C5S32L1	570	0.076	13.3	5.7	29	28.5
C5S64L1	300	0.080	10.0	3.0	35	10.0
C5S64L2	270	0.072	12.6	5.4	36	27.0

Table 23.--Element concentration in the surface soil (<1 cm in depth) as a function of distance from the Colstrip Powerplant, Colstrip, Montana.

[*a* is the intercept and *b* is the slope of the regression equation; significance of the slope is the probability level at which the slope is different from zero; significance of model is the probability level at which the linear regression model adequately describes the relation; coefficient of determination is an expression of the proportion of the total variation in the dependent variable that is accounted for by the linear model; percent laboratory error is the variance due to analytical error expressed as a percent of the total variance]

Element	Regression Statistics					Percent laboratory error	Observed range
	a	*b*	Significance of		Coefficient of determination		
			slope	model			
North (upwind) transect[1]							
As, ppm-	0.78	0.09	0.05	0.22	0.29	28	4.7 - 11
Ba, ppm-	2.6	.13	.01	.80	.42	30	300 -1000
K, pct.	.25	- .03	.04	.37	.30	12	1.4 - 1.9
Na, pct.	- .23	.09	.01	.002	.43	1	.55- 1.1
Sr, ppm-	1.9	.21	.001	.92	.59	58	70 - 200
V, ppm--	1.8	.08	.004	.55	.51	58	70 - 100
Southeast (downwind) transect[2]							
Be, ppm-	.44	- .15	.02	.20	.47	23	1.5 - 3
F, ppm--	-1.2	- .13	.04	.16	.40	31	.04- .07
K, pct.	.04	- .08	.003	.03	.65	12	1.5 - 2.3
Mg, pct.	.14	- .14	.04	.22	.37	3	.61- 1.7
Na, pct.	- .30	.14	.02	.01	.48	1	.54- 1.1
Rb, ppm-	2.0	- .14	.002	.03	.68	12	55 - 100
Th, ppm-	1.1	- .09	.02	.07	.45	73	7.0 - 12
U, ppm--	.52	- .06	.01	.10	.50	24	2.3 - 3.3

[1] Statistics based on 14 samples.
[2] Statistics based on 11 samples.

Table 24.--Soil (1 cm surface veneer) element content, Colstrip Powerplant, Colstrip, Montana.

[S indicates semiquantitative spectrographic analyses; A indicates atomic absorption analyses]

Sample	Latitude			Longitude			Kilometers	Al %	As ppm	B ppm-S	Ba ppm-S	Be ppm-S	Ca %	T-C%	Co ppm-S	Cr ppm-S	Cu ppm-S
	D	M	S	D	M	S											
								North (upwind) of the powerplant									
C5N01S1	45	53	36	106	37	6	1.2	4.6	6.7	30	700	1.5	.38	1.12	7	50	15
C5N01S2	45	53	36	106	37	6	1.2	4.6	6.9	30	500	2.0	.46	1.39	7	30	15
C5N02S1	45	53	53	106	37	9	1.8	4.0	6.9	50	500	2.0	2.75	1.95	7	70	15
C5N02S2	45	53	53	106	37	9	1.8	3.7	4.7	30	300	1.5	3.60	2.24	7	70	15
C5N04S1	45	55	5	106	37	4	4.0	4.5	8.2	50	500	2.0	1.35	1.48	7	70	20
C5N04S2	45	55	5	106	37	4	4.0	3.9	8.5	50	500	1.5	2.66	2.39	7	30	20
C5N08S1	45	57	5	106	37	42	7.8	3.9	5.7	50	700	2.0	.81	1.05	7	30	15
C5N08S2	45	57	5	106	37	42	7.8	3.9	5.2	50	500	1.5	2.11	1.87	5	50	10
C5N16S1	46	0	34	106	36	28	14.0	4.3	8.9	50	700	2.0	.47	1.39	7	50	15
C5N16S2	46	0	34	106	36	28	14.0	4.3	7.3	50	500	2.0	.53	1.47	7	70	15
C5N32S1	46	11	54	106	41	15	35.0	3.9	9.7	30	700	1.5	2.42	1.73	7	50	15
C5N32S2	46	11	54	106	41	15	35.0	4.9	11.1	30	700	1.5	.98	1.54	7	70	20
C5N64S1	46	26	15	106	37	24	62.0	4.8	9.2	30	1,000	2.0	1.31	1.36	7	70	15
C5N64S2	46	26	15	106	37	24	62.0	5.2	7.0	30	700	2.0	1.48	1.56	7	50	15
								Southeast (downwind) of the powerplant									
C5S02S1	45	52	54	106	35	20	2.2	5.4	7.3	30	700	3.0	.55	1.16	7	50	20
C5S02S2	45	52	54	106	35	20	2.2	5.0	7.0	50	500	3.0	.66	2.31	7	50	20
C5S04S1	45	51	57	106	34	10	4.0	4.0	9.2	70	500	2.0	1.27	1.87	7	30	15
C5S04S2	45	51	57	106	34	10	4.0	4.2	12.1	30	300	1.5	4.35	2.88	7	30	20
C5S08S1	45	50	38	106	31	33	8.2	5.0	9.8	50	700	2.0	1.15	2.79	7	70	30
C5S08S2	45	50	38	106	31	33	8.2	5.2	7.8	30	1,000	2.0	1.38	2.84	10	70	30
C5S16S1	45	48	50	106	28	14	13.6	4.4	6.0	30	700	2.0	1.13	2.01	7	50	15
C5S16S2	45	48	50	106	28	14	13.6	4.2	6.4	30	500	1.5	.93	1.91	7	70	15
C5S32S1	45	43	18	106	17	54	30.5	4.5	9.5	30	700	2.0	2.99	2.16	10	70	20
C5S64S1	45	34	9	105	59	49	60.0	4.2	4.8	20	700	1.5	.80	1.52	7	30	10
C5S64S2	45	34	9	105	59	49	60.0	4.7	6.0	30	700	1.5	.52	1.19	7	30	10

Table 24.--Soil (1 cm surface veneer) element content, Colstrip Powerplant, Colstrip, Montana.

Sample	F%	Fe %	Ga ppm-S	Ge ppm	Hg ppm	I ppm	K %	Li ppm	Mg %	Mn ppm-S	Na %	Nb ppm-S	Ni ppm-S	Pb ppm-S
North (upwind) of the powerplant														
C5N01S1	.04	2.1	15	1.8	.02	.64	1.9	19	.60	300	.67	15	15	15
C5N01S2	.04	2.2	15	1.7	.02	<.50	1.8	18	.71	300	.62	15	15	15
C5N02S1	.04	2.1	20	1.5	.04	<.50	1.7	16	1.16	300	.68	15	15	15
C5N02S2	.04	1.7	20	1.3	.02	1.17	1.6	15	1.12	300	.67	15	15	15
C5N04S1	.06	2.1	20	1.5	.03	.91	1.9	20	.83	300	.58	15	15	20
C5N04S2	.05	2.1	15	1.3	.03	.98	1.7	17	1.05	300	.56	15	15	15
C5N08S1	.04	1.6	15	1.5	.02	.54	1.7	17	.87	300	.73	15	15	15
C5N08S2	.05	1.6	15	1.4	.02	.98	1.7	15	1.44	200	.68	15	10	15
C5N16S1	.05	2.1	15	1.6	.03	.51	1.8	17	.72	300	.73	20	15	15
C5N16S2	.05	2.1	15	1.8	.02	<.50	1.7	16	.70	300	.74	15	15	15
C5N32S1	.04	1.9	15	3.2	.02	.65	1.4	16	1.08	300	.65	15	15	15
C5N32S2	<.04	2.2	20	1.4	.03	.77	1.7	19	1.10	200	.67	15	15	15
C5N64S1	.05	2.2	20	1.8	.02	<.50	1.6	18	1.13	300	1.05	15	20	15
C5N64S2	.05	2.2	20	1.5	.03	<.50	1.6	18	1.12	300	1.08	15	15	15
Southeast (downwind) of the powerplant														
C5S02S1	.07	2.7	20	1.8	.02	.59	2.2	23	.95	300	.68	20	15	15
C5S02S2	.07	2.4	20	1.9	.03	.57	2.3	23	.99	300	.63	15	15	20
C5S04S1	.05	1.8	15	1.4	.02	<.50	1.8	17	1.12	300	.67	15	15	20
C5S04S2	.06	2.0	15	1.5	.03	.84	1.7	16	1.66	200	.57	15	15	15
C5S08S1	.04	2.3	30	2.2	.03	<.50	1.8	22	1.12	300	.59	15	15	30
C5S08S2	.04	2.4	20	2.8	.04	<.50	1.8	20	1.17	300	.63	15	15	30
C5S16S1	.07	2.1	20	1.5	.02	.93	1.7	19	1.21	300	.56	15	15	30
C5S16S2	.05	1.7	15	1.8	.03	<.50	1.7	18	.97	300	.55	15	15	20
C5S32S1	.05	2.1	20	1.5	.04	.70	1.8	17	1.06	300	.74	15	20	30
C5S64S1	.04	1.8	20	2.1	.02	<.50	1.5	13	.71	300	1.10	15	15	15
C5S64S2	.04	2.0	15	2.6	.02	<.50	1.6	13	.61	300	1.11	15	15	15

Table 24.--Soil (1 cm surface veneer) element content, Colstrip Powerplant, Colstrip, Montana.

Sample	Rb ppm	Sc ppm-S	Se ppm	Si %	Sn ppm	Sr ppm-S	Th ppm	Ti %	U ppm	V ppm-S	Y ppm-S	Yb ppm-S	Zn ppm	Zr ppm-S
					North (upwind) of the powerplant									
C5N01S1	75	7	<.10	31	1.64	100	9.5	.27	2.7	70	30	3	73	150
C5N01S2	75	5	.10	29	1.83	70	8.3	.27	2.9	70	30	3	65	150
C5N02S1	60	7	<.10	30	3.45	100	8.8	.27	2.6	70	20	3	54	150
C5N02S2	60	5	.14	30	1.46	70	9.2	.23	2.3	70	30	3	47	150
C5N04S1	75	7	.26	30	.89	70	9.3	.27	2.9	70	30	3	61	150
C5N04S2	65	5	.24	29	1.29	150	9.3	.26	2.6	70	30	3	59	200
C5N08S1	65	7	<.10	28	1.42	100	7.3	.25	2.7	70	30	3	54	200
C5N08S2	60	5	<.10	29	1.51	70	7.8	.26	2.5	70	30	3	53	150
C5N16S1	70	7	<.10	30	1.19	150	11.5	.31	3.3	70	50	5	63	300
C5N16S2	65	5	.23	30	1.39	100	9.6	.29	3.4	70	30	3	64	200
C5N32S1	60	5	<.10	29	1.28	150	8.2	.23	2.5	70	30	3	59	150
C5N32S2	70	7	.18	30	.95	150	9.8	.30	3.1	100	30	3	64	200
C5N64S1	65	7	<.10	28	1.42	200	10.4	.27	2.5	100	30	3	74	200
C5N64S2	65	7	<.10	29	1.36	200	7.5	.27	2.7	100	30	3	74	200
					Southeast (downwind) of the powerplant									
C5S02S1	100	7	<.10	30	1.81	70	11.5	.31	3.0	70	30	3	128	150
C5S02S2	100	7	.13	28	1.67	100	10.5	.30	3.0	70	30	3	70	150
C5S04S1	70	5	<.10	31	.88	70	8.9	.26	2.9	70	30	3	59	200
C5S04S2	65	5	.12	26	1.76	150	9.4	.22	2.8	70	20	3	59	150
C5S08S1	80	7	.11	27	1.71	150	11.1	.30	3.3	100	30	3	81	200
C5S08S2	80	10	.17	28	2.00	150	11.6	.33	3.2	70	30	3	82	200
C5S16S1	70	7	<.10	29	1.33	150	10.3	.29	3.0	70	30	3	73	150
C5S16S2	65	5	.17	29	1.84	70	10.6	.27	2.7	50	50	7	62	150
C5S32S1	60	7	.12	29	.88	200	9.4	.27	2.7	100	30	3	63	200
C5S64S1	55	7	<.10	28	1.05	150	7.1	.24	2.3	70	20	3	54	150
C5S64S2	60	5	<.10	30	1.51	150	8.1	.28	2.5	70	15	3	66	150

Total and Extractable Element Composition of Some Northern Great Plains Soils

by

R. C. Severson, J. M. McNeal, and L. P. Gough

ABSTRACT

Samples of A and C horizons were collected from geochemically diverse soils at 21 locations in the unglaciated portion of the northern Great Plains. Samples were extracted with DTPA (diethylenetriaminepentaacetic acid), $MgNO_3$ (magnesium nitrate), $NH_4C_2O_4$ (ammonium oxalate), and $C_6H_6O_2$ (hydroquinone), and the concentrations of Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn were determined. Total content of all these elements, except Cd, was also determined. Ca, K, and Na exhibit significant correlations between all extracts tested, but do not exhibit significant correlations between concentration in extracts and total content. Cu, Fe, Mg, and Mn exhibit significant correlations between total content and concentration in several extracts. Ni and Zn do not exhibit significant correlations between extracts and total content, nor do they exhibit significant correlations among extracts. Percent analytical error was high for Cd, Co, and Pb, because their abundance in soils was close to the detection limit, and consequently few significant correlations were seen for these elements. The correlations and observed patterns between extractable concentration and total content indicate that no single extraction agent solubilized a constant portion of an element in all soil types. However, for an individual soil sample, many extraction agents tend to solubilize similar relative portions of the total content for several of the elements.

INTRODUCTION

Meaningful measures of the plant-available fraction of an element in soil are becoming increasingly important because new legislation concerning toxic levels of certain elements in soils is being drafted by State and Federal legislatures. This legislation deals mainly with reclaiming areas that have been disturbed by surface mining for mineral and energy resources. It is being written, in part, to minimize the potential hazard of toxic effects of trace elements in soil as they may affect plants, waters, and animals.

Much success has been attained in agronomic situations (Coffman and Miller, 1973; Halstead, Finn, and MacLean, 1969; Haq and Miller, 1972; and Randall, Schulte, and Corey, 1976) in predicting availability of various trace elements to plants by using an extract of soil. Only limited success has been obtained for natural soil-plant systems using these same extracts (Gough, Severson, and McNeal, 1978; and Severson, Gough, and McNeal, 1977). Similar work on soil-plant systems is just beginning in the western United States on mine-reclaimed soils, but the indication is that little success is being obtained using the extracts that have been proven successful in agronomic situations (Safaya, 1978).

Much has been learned about the occurrence of elements in geochemically diverse soil reservoirs (Gatehouse, Russell, and Van Moort, 1977; Jenne and Luoma, 1977; Le Riche and Weir, 1963; Mitchell, 1972; and Viets, 1962). However, much more work is needed on the mechanisms by which elements in various soil reservoirs are made available to plants, and the search for extracts that will selectively mimic these mechanisms should continue. This report discusses the use of selected chemical-solution extracts in assessing element solubilization in geochemically diverse soils.

Methods

Soil Sampling

Samples of A- and C-horizon soils, as defined by their morphologic features, were collected at 21 locations in the unglaciated portion of the northern Great Plains coal region (Fig. 33). The sampling locations were selected for their chemical diversity (U.S. Geological Survey, 1976, p. 57-81; Severson, Gough, and McNeal, 1977, p. 4-8) and consisted only of natural, uncultivated soil profiles. At each of the 21 sites and for each soil horizon, the sample consisted of a composite of material from three randomly selected locations within a 50-square-meter area. The composite sample was mixed in the field and passed through a sieve with 1-cm openings to remove plant debris and rocks. More than 95 percent of the soil material passed the sieve at all 21 sites.

All soil samples were dried in the laboratory at ambient temperature with forced air. The samples were disaggregated in a mechanical mortar and pestle and passed through a 10-mesh sieve. In all cases, more than 95 percent of the material passed the 10-mesh sieve. Ten of the 21 samples from each soil horizon were randomly chosen and used as duplicate samples to estimate error in sample preparation and analysis. All 62 samples were placed in a random order and analyzed in this sequence to convert any systematic bias to random error.

Total Chemical Analyses

A split of each disaggregated minus-2-mm sample was further ground to minus-100 mesh in a ceramic mill. Total Ca, Cu, Fe, K, Mg, Mn, Na, and Zn were determined by atomic absorption spectroscopy following complete dissolution of the sample (Miesch, 1976, p. 12-14). A semi-quantitative emission spectrograph was used for the determination of total Co, Ni, and Pb (Myers, Havens, and Dunton, 1961). Samples were prepared and analyzed in the laboratories of the U.S. Geological Survey in Denver, Colorado, by P. H. Briggs, J. G. Crock, Carol Gent, Mollie Jane Malcolm, R. E. McGregor, and G. O. Riddle.

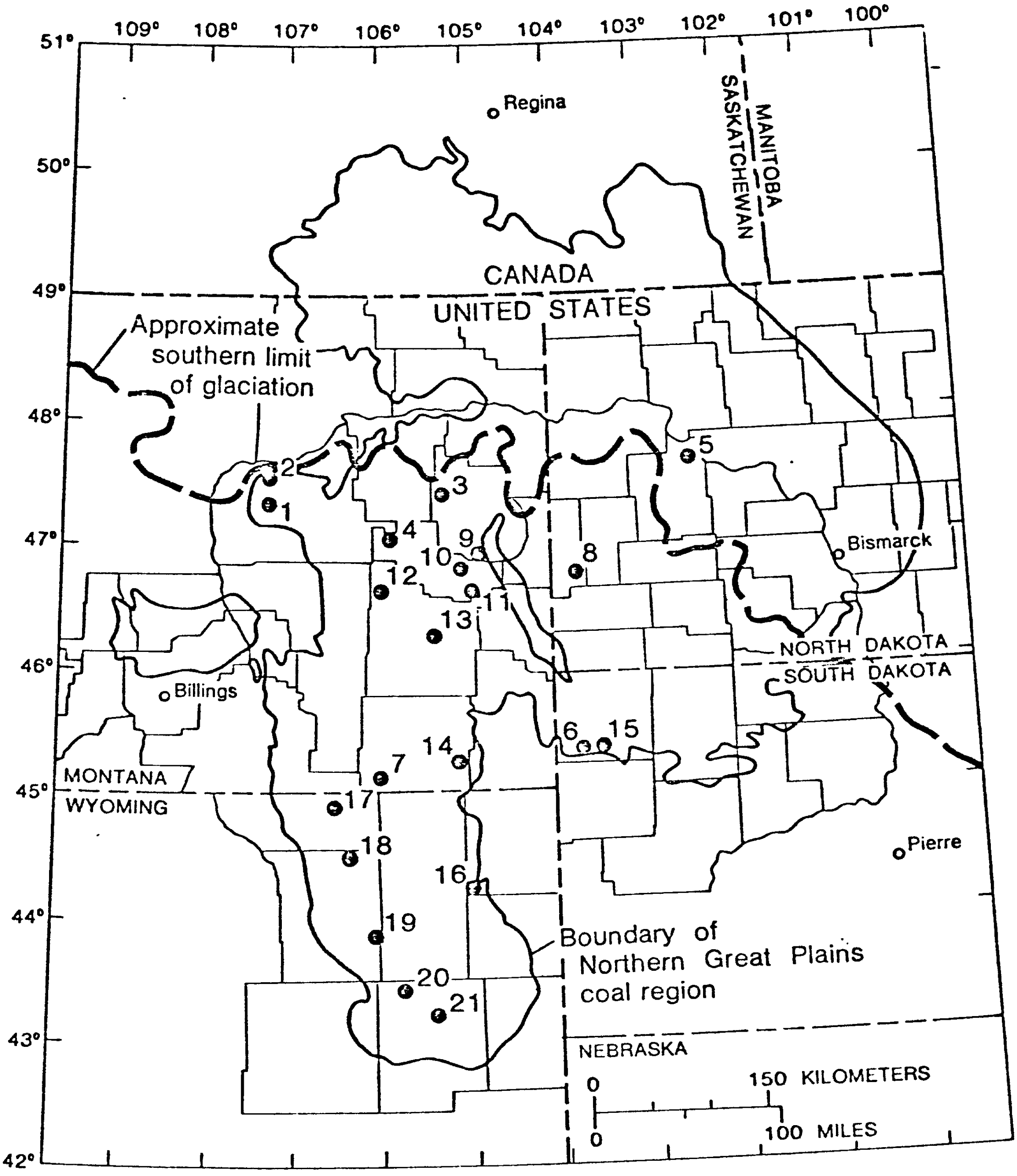

Figure 33.--Map showing locations of sampling sites (solid dots) in the Northern Great Plains coal region.

Extraction and Analyses

All extractions were performed using the following method: 1--15.0 g of soil plus 30.0 ml of the extraction solution was placed in a 125-ml erlenmeyer flask, and the flask was stoppered and mixed on a reciprocal shaker for two hours. 2--The solution was decanted into a 50-ml test tube and centrifuged at about 2000 rpm for 30 minutes. 3--The coarse organic material remaining in suspension was removed by filtering through coarse acid-washed filter paper, and the solution was collected in acid-washed polyethylene bottles. 4--The solutions were acidified to about pH 3 with five drops of concentrated nitric acid.

The extracts were analyzed for Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn by atomic absorption spectroscopy. Electrodeless discharge lamps provided improved sensitivity for Cd and Pb. Calcium, Mg, and sometimes K or Na were determined on a 1:50 dilution which contained 1 percent La. All other elements were determined on the stock extract solution.

Extraction Solutions

Splits of each sample were extracted independently with five different solutions. In addition, splits of the A-horizon soils were extracted with HCl. The extraction solutions have been reported in the literature as being acceptable, each for certain elements, for relating soil and plant composition or as measures of soil element availability to certain plants. The six extraction solutions are:

DTPA (diethylenetriaminepentaacetic acid)--consists of a solution of 0.005 $\underline{M}$ DTPA, 0.1 $\underline{M}$ triethanolamine, and 0.01 $\underline{M}$ calcium chloride at pH 7.3. This extract is described by Lindsay and Norvell (1969). Because Ca was included in the extraction solution to prevent the dissolution of calcium carbonate, it was not determined in the soil extract.

EDTA (ethlenediaminetetraacetic acid)--consists of 0.01 $\underline{M}$ EDTA in a 1.0 $\underline{M}$ ammonium acetate solution at pH 7.0. Because the Na salt of EDTA was used to prepare the solution, Na was not determined in the soil extract. This extraction solution was reported by Randall, Schulte, and Corey (1976) as being useful for relating soil Mn to plant Mn.

$MgNO_3$ (magnesium nitrate)--consists of a 1.0 $\underline{M}$ magnesium nitrate solution. This extraction solution was reported by Randall, Schulte, and Corey (1976) as having limited usefulness in predicting plant-available Mn. Because of the Mg content of the extractant, Mg was not determined in the soil extract.

$NH_4C_2O_4$ (ammonium oxalate)--consists of a 0.2 $\underline{M}$ ammonium oxalate solution at pH 3.0. This extraction is light sensitive and was performed in darkness so that only the more amorphous Fe and Mn oxides would be dissolved. This extraction procedure is described by McKeague and Day (1966).

HCl (hydrochloric acid)--consists of a 0.1 M hydrochloric acid solution. Sorenson, Oelsligle, and Knudsen (1971) review the rationale and applicability of this extraction solution for predicting the status of available Zn, Fe, and Mn in soils.

$C_6H_6O_2$ (hydroquinone)--consists of 0.2 percent hydroquinone in a 1.0 M ammonium acetate solution at pH 7.0. This extraction solution was reported by Shuman and Anderson (1974) as having limited use in predicting soil Mn available for utilization by field crops.

Statistical Analyses

Simple correlation coefficients were computed for each of the 12 elements between each of the six extracts, and between each extract and total content. Arithmetic means, standard deviations, and observed ranges are also reported for each element. Simple linear regression equations can be computed relating the same element measured between different extractions, or relating extractable and total content by using the correlation coefficients and standard deviation. The observed range gives the approximate limit in which the regression equation is considered to be valid. However, caution should be used if the equations generated are used for predictive purposes. Even though an equation may be deemed highly significant at the 0.001 probability level, the equation may explain only a small portion of the observed variation. Relations that are correlated at the 0.001 probability level are labeled "highly significant", and those correlated at the 0.01 probability level are labeled "significant."

RESULTS AND DISCUSSION

Simple correlations between element concentrations in the various soil extracts and between the extracts and total content are presented for the 12 elements in Tables 25-36. The upper triangle of each correlation matrix contains coefficients for A-horizon soil, and the lower triangle contains the coefficients for C-horizon soil. Summary statistics (arithmetic mean, standard deviation, observed range, and detection ratio) are presented for total content and for each extraction method in Tables 37-43. The HCl extract was determined only on the A-horizon soil samples because, in general, the A-horizon samples were void of carbonates, and the C-horizon samples contained appreciable carbonates. It was felt that the dissolution of carbonates and associated constituents was not an appropriate means of assessing the concentration of elements in soil that are readily utilized by plants. Calcium in the DTPA extraction, Na in the EDTA extraction, and Mg in the $MgNO_3$ extraction were not determined because these elements were constituents of the extracting solution.

In several cases, a specific element was below the detection limit in an extraction solution. Therefore, the tables of correlation coefficients are not complete or symmetrical. Where only a few

Table 25.--Correlations between Ca in various extracts of A- and C-horizon soils and between various extracts and total content for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level. The upper triangle of the correlation matrix contains coeffficients for A horizons and the lower triangle contains coefficients for C horizons. DTPA extract is excluded because Ca was a constituent part of the solution. Ca in the $NH_4C_2O_4$ extract was below the detection limit. HCl extraction was not performed on the C horizon]

	Total	EDTA	$MgNO_3$	$C_6H_6O_2$	HCl
Total		0.47	0.42	0.50	0.41
EDTA	-0.29		.99**	.98**	.86**
$MgNO_3$	- .34	.97**		.93**	.86**
$C_6H_6O_2$	- .21	.95**	.91**		.87**

Table 26.--Correlations between Cd in various extracts of A- and C-horizon soils for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level, and a single asterisk (*) is used at the 0.01 level. The upper triangle of correlation matrix contains coefficients for A horizons and the lower triangle contains coefficients for C horizons. Total content of Cd was not determined. HCl extraction was not performed on the C horizon]

	DTPA	EDTA	$MgNO_3$	$NH_4C_2O_4$	C6H602	HCl
DTPA		0.82**	0.36	0.04	0.15	0.39
EDTA	0.77**		.59*	.20	.17	.46
$MgNO_3$	.33	.44		.28	.03	.40
$NH_4C_2O_4$	.23	.31	.18		.06	- .07
$C_6H_6O_2$	.56*	.32	- .22	.08		- .05

Table 27.--Correlations between Co in various extracts of A- and C-horizon soils for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level, and a single asterisk (*) is used at the 0.01 level. The upper triangle of the correlation matrix contains coefficients for A horizons and lower triangle contains coefficients for C horizons. Total content of Co and its content in the $C_6H_6O_6$ extract were below the detection limit for both A and C horizons. HCl extraction was not performed on the C horizon]

	DTPA	EDTA	$MgNO_3$	$NH_4C_2O_4$	HCl
DTPA		0.39	0.15	0.57*	0.46
EDTA	-0.05		.75**	.37	- .21
$MgNO_3$	.04	.17		.17	- .44
$NH_4C_2O_4$	.43	- .07	- .02		.29

Table 28.--Correlations between Cu in various extracts of A- and C-horizon soils and between various extracts and total content for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level, and a single asterisk (*) is used at the 0.01 level. The upper triangle of the correlation matrix contains coefficients for A horizons and the lower triangle contains coefficients for C horizons. Cu in the $C_6H_6O_2$ extract was below the detection limit for both the A and C horizons. HCl extraction was not performed on the C horizon]

	Total	DTPA	EDTA	$MgNO_3$	$NH_4C_2O_4$	HCl
Total		0.81**	0.75**	0.79**	0.76**	-0.40
DTPA	0.69**		.94**	.60*	.77**	- .08
EDTA	.59*	.91**		.43	.84**	.04
$MgNO_3$	.55*	.33	.12		.44	-.54
$NH_4C_2O_4$	- .06	.07	.07	- .01		.18

Table 29.--Correlations between Fe in various extracts of A- and C-horizon soils and between various extracts and total content for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level, and a single asterisk (*) is used at the 0.01 level. The upper triangle of the correlation matrix contains coefficients for A horizons and the lower triangle contains coefficients for C horizons. Fe in the $C_6H_6O_2$ extract was below the detection limit in both A and C horizons. HCl extraction was not performed on the C horizon]

	Total	DTPA	EDTA	$MgNO_3$	$NH_4C_2O_4$	HCl
Total		-0.45	-0.51	0.45	0.51	-0.61*
DTPA	0.10		.95**	- .05	.22	.63*
EDTA	- .26	.85**		.01	.21	.66*
$MgNO_3$	.14	- .09	- .28		.26	- .34
$NH_4C_2O_4$	- .10	.82**	.85**	.26		- .04

Table 30.--Correlations between K in various extracts of A- and C-horizon soils and between various extracts and total content for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level, and a single asterisk (*) is used at the 0.01 level. The upper triangle of the correlation matrix contains coefficients for A horizons and the lower triangle contains coefficients for C horizons. HCl extraction was not performed on the C horizon]

	Total	DTPA	EDTA	$MgNO_3$	$NH_4C_2O_4$	$C_6H_6O_2$	HCl
Total		-0.11	-0.09	<0.01	-0.09	-0.11	-0.15
DTPA	-0.07		.99**	.97**	.99**	.99**	.96**
EDTA	- .22	.79**		.98**	.99**	.99**	.95**
$MgNO_3$	- .11	.82**	.65*		.97**	.98**	.91**
$NH_4C_2O_4$	- .02	.88**	.74**	.69**		.99**	.96**
$C_6H_6O_2$	- .04	.95**	.85**	.79**	.89**		.95**

Table 31.--Correlations between Mg in various extracts of A- and C-horizon soils and between various extracts and total content for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level, and a single asterisk (*) is used at the 0.01 level. The upper triangle of the correlation matrix contains coefficients for A horizons and the lower triangle contains coefficients for C horizons. $MgNO_3$ extract is excluded because Mg was a constituent part of the solution. HCl extraction was not performed on the C horizon]

	Total	DTPA	EDTA	$NH_4C_2O_4$	$C_6H_6O_2$	HCl
Total		-0.12	0.62*	0.81**	0.65*	0.88**
DTPA	<0.01		.01	- .04	- .01	- .11
EDTA	.65*	.29		.70**	.99**	.47
$NH_4C_2O_4$	.55*	.19	.58*		.71**	.62*
$C_6H_6O_2$	.59*	.29	.84**	.43		.53

Table 32.--Correlations between Mn in various extracts of A- and C-horizon soils and between various extracts and total content for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level, and a single asterisk (*) is used at the 0.01 level. The upper triangle of the correlation matrix contains coefficients for A horizons and the lower triangle contains coefficients for C horizons. Mn in the $MgNO_3$ extract of the C horizon was below the detection limit. HCl extract was not performed on the C horizon]

	Total	DTPA	EDTA	$NH_4C_2O_2$	$C_6H_6O_2$	$MgNO_3$	HCl
Total		0.58*	0.18	0.72**	0.86**	-0.09	0.07
DTPA	0.27		.33	.79**	.76**	.44	.67**
EDTA	- .18	.73**		.38	.12	.73**	.48
$NH_4C_2O_4$	- .15	.31	.65*		.85**	.41	.55*
$C_6H_6O_2$	.43	.71**	.51	.53		.13	.36
$MgNO_3$	--	--	--	--	--		.75**

Table 33.--Correlations between Na in various extracts of A- and C-horizon soils and between various extracts and total content for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level. The upper triangle of the correlation matrix contains coefficients for A horizons and the lower triangle contains coefficients for C horizons. EDTA extract is not included because Na was a constituent part of the solution. Na in the $C_6H_6O_2$ extract for both A and C horizons was below the detection limit. HCl extract was not performed on the C horizon]

	Total	DTPA	$MgNO_3$	$NH_4C_2O_4$	HCl
Total		-0.27	-0.30	-0.30	-0.26
DTPA	.14		.97**	.71**	.99**
$MgNO_3$	.14	1.0**		.71**	.96**
$NH_4C_2O_4$	.19	.98**	.98**		.76**
$C_6H_6O_2$	.15	1.0 **	1.0 **	.99**	

Table 34.--Correlations between Ni in various extracts of A- and C-horizon soils and between various extracts and total content for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level, and a single asterisk (*) is used at the 0.01 level. The upper triangle of the correlation matrix contains coefficients for A horizons and the lower triangle contains coefficients for C horizons. Ni in the $C_6H_6O_2$ extract of both A and C horizons and in the $MgNO_3$ extract of the C horizon was below the detection limit. HCl extraction was not performed on the C horizon]

	Total	DTPA	EDTA	$NH_4C_2O_4$	$MgNO_3$	HCl
Total		0.53	0.46	0.53	0.18	0.39
DTPA	0.20		.93**	.91**	.02	.68**
EDTA	.02	.87**		.87**	.01	.72**
$NH_4C_2O_4$	.28	.63*	.74**		.06	.54
$MgNO_3$	--	--	--			.03

Table 35.--Correlations between Pb in various extracts of A- and C-horizon soils for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level, and a single asterisk (*) is used at the 0.01 level. The upper triangle of the correlation matrix contains coefficients for A horizons and the lower triangle contains coefficients for C horizons. Total content of Pb was below the detection limit for A and C horizons. HCl extraction was not performed on the C horizon]

	DTPA	EDTA	$MgNO_3$	$NH_4C_2O_4$	$C_6H_6O_2$	HCl
DTPA		0.93**	0.46	-0.17	0.65*	-0.15
EDTA	0.70**		.54	- .04	.66*	- .27
$MgNO_3$	.04	.60*		- .26	.55*	- .40
$NH_4C_2O_4$	- .22	- .15	- .26		- .14	- .07
$C_6H_6O_2$	.05	.26	- .05	- .13		- .34

Table 36.--Correlations between Zn in various extracts of A- and C-horizon soils and between various extracts and total content for some Northern Great Plains soils.

[A double asterisk (**) is used to denote significance at the 0.001 probability level. The upper triangle of the correlation matrix contains coefficients for A horizons and the lower triangle contains coefficients for C horizons. Zn in the $MgNO_3$ extract was below the detection limit for the C horizon. HCl extraction was not performed on the C horizon]

	Total	DTPA	EDTA	$NH_4C_2O_4$	$C_6H_6O_2$	$MgNO_3$	HCl
Total		0.33	0.31	0.50	0.52	-0.19	-0.25
DTPA	0.39		.69**	.88**	.29	.52	.47
EDTA	.35	.88**		.87**	.28	.53	.47
$NH_4C_2O_4$	- .32	.52	.45		.37	.07	.51
$C_6H_6O_2$	.25	- .22	- .12	- .11		.07	.06
$MgNO_3$	--	--	--	--	--		.87**

Table 37.--Summary statistics for total element content of some Northern Great Plains soils.

[Detection ratio, number of samples in which the element was found in measurable concentrations relative to the number of samples analyzed; ---, not computed because of low detection ratio]

Element, unit of measure	Arithmetic Mean	Standard Deviation	Observed range	Detection ratio
		A horizon		
Ca, pct.	1.1	0.52	0.42- 2.0	21:21
Co, ppm	---	---	<5 - 7	12:21
Cu, ppm	14	7.3	5 - 30	21:21
Fe, pct.	2.8	0.81	1.5 - 4.6	21:21
K, pct	2.3	0.26	2.0 - 3.0	21:21
Mg, pct.	1.1	0.45	0.46- 1.8	21:21
Mn, ppm	400	120	220 -670	21:21
Na, pct.	1.1	0.58	.09- 2.4	21:21
Ni, ppm	7.0	3.5	<5 - 15	18:21
Pb, ppm	---	---	<10 - 10	10:21
Zn, ppm	60	17	25 - 86	21:21
		C horizon		
Ca, pct.	4.7	3.8	0.52- 12.2	21:21
Co, ppm	---	---	<5 - 10	12:21
Cu, ppm	15	7.0	6 - 36	21:21
Fe, pct.	3.2	0.86	1.9 - 5.1	21:21
K, pct	2.2	0.31	1.8 - 2.9	21:21
Mg, pct.	1.9	1.2	0.59- 4.3	21:21
Mn, ppm	410	170	230 -890	21:21
Na, pct.	1.0	0.59	0.22- 2.4	21:21
Ni, ppm	8.3	3.9	<5 - 15	20:21
Pb, ppm	---	---	<10 - 15	7:21
Zn, ppm	55	13	28 - 89	21:21

Table 38.--Summary statistics for DTPA extractable element concentrations, in parts per million, and the percent of the total content that was extracted from some Northern Great Plains soils.

[Elements that have single entries are reporting concentrations in the soil extract; for elements with double entries, the value without parentheses is the concentration in the soil extract and the value enclosed in parentheses is the percent of the total content in soil extracted; detection ratio, number of samples in which the element was found in measurable concentrations relative to the number of samples analyzed]

Element	Arithmetic mean		Standard deviation		Observed range		Detection ratio
			A horizon				
Cd-----	0.1		0.064		0.04- 0.3		21:21
Co-----	.2		.10		.06- .4		21:21
Cu-----	.5	(3.4)	.27	(1.4)	.1 - 1.2	(1.7 - 7.0)	21:21
Fe-----	14	(.06)	10	(.061)	2 - 49	(.009- .3)	21:21
K------	210		130		110 - 720	(.5 - 3.6)	21:21
Mg-----	420	(5.0)	470	(8.6)	190 -2400	(1.5 -42)	21:21
Mn-----	10	(2.5)	3.4	(.79)	4 - 15	(1.0 - 3.9)	21:21
Na-----	11	(.2)	21	(.38)	2 - 83	(.01 - 1.6)	21:21
Ni-----	.8	(11)	.59	(6.9)	.2 - 2.6	(2.0 -27)	21:21
Pb-----	.6		.28		.3 - 1.4		21:21
Zn-----	.9	(1.4)	1.1	(1.5)	.2 - 5.3	(.3 - 6.7)	21:21
			C horizon				
Cd-----	.03		.029		<.01- .1		19:21
Co-----	.2		.11		<.05- .4		21:21
Cu-----	.5	(3.1)	.20	(.95)	.1 - .8	(1.6 - 4.8)	21:21
Fe-----	7	(.02)	3.7	(.017)	3 - 19	(.01 - .09)	21:21
K------	88	(.4)	17	(.094)	59 - 120	(.2 - .6)	21:21
Mg-----	1100	(7.5)	1600	(16)	260 -7800	(2.1 -79)	21:21
Mn-----	4	(1.1)	3.3	(.87)	1 - 14	(.4 - 4.4)	21:21
Na-----	220	(2.5)	340	(3.4)	4 -1400	(.05 - 1.0)	21:21
Ni-----	.6	(8.1)	.48	(6.3)	.1 - 2.1	(2.2 -30)	21:21
Pb-----	.3		.11		.2 - .6		21:21
Zn-----	.06	(.1)	.040	(.069)	.01- .2	(.02 - .3)	21:21

Table 39.--Summary statistics for EDTA extractable element concentrations, in parts per million, and the percent of the total content that was extracted from some Northern Great Plains soils.

[Elements that have single entries are reporting concentrations in the soil extract; for elements with double entries, the value without parentheses is the concentration in the soil extract and the value enclosed in parentheses is the percent of the total content in soil extracted; detection ratio, number of samples in which the element was found in measurable concentrations relative to the number of samples analyzed]

Element	Arithmetic mean	Standard deviation	Observed range	Detection ratio
		A horizon		
Ca-----	2200 (23)	1100 (9.4)	990 -5100 (6.4 -40)	21:21
Cd-----	.2	.084	.06- .4	21:21
Co-----	.3	.17	.2 - .7	21:21
Cu-----	1.0 (7.4)	.47 (3.0)	.3 - 15 (3.5 -15)	21:21
Fe-----	10 (.05)	11 (.057)	.5 - 42 (.002- .2)	21:21
K------	370 (1.6)	230 (1.1)	170 -1300 (.8 - 6.3)	21:21
Mg-----	380 (3.7)	190 (1.3)	180 - 970 (1.7 - 6.6)	21:21
Mn-----	14 (3.6)	8.0 (2.0)	5 - 44 (1.3 -10)	21:21
Ni-----	.8 (13)	.47 (6.1)	.2 - 25 (5.1 -25)	21:21
Pb-----	2.3	1.0	1.0 - 4.7	21:21
Zn-----	2.3 (3.8)	2.9 (3.8)	.5 - 14 (.8 -18)	21:21
		C horizon		
Ca-----	2000 (10)	700 (11)	920 -3500 (1.1 -45)	21:21
Cd-----	.04	.030	<.01- .1	21:21
Co-----	.3	.12	.1 - .5	21:21
Cu-----	1.0 (6.8)	.41 (2.3)	.08- 1.7 (.7 -10)	21:21
Fe-----	2.9 (.01)	2.5 (.012)	.8 - 11 (.003- .05)	21:21
K------	140 (.7)	43 (.24)	60 - 250 (.3 - 1.3)	21:21
Mg-----	790 (4.6)	430 (2.3)	260 -1500 (2.0 -12)	21:21
Mn-----	2.5 (.7)	2.0 (.68)	.8 - 10 (.1 - 3.2)	21:21
Ni-----	.7 (11)	.44 (7.8)	.4 - 2.1 (3.7 -37)	21:21
Pb-----	1.1	.30	.7 - 1.7	21:21
Zn-----	.3 (.5)	.10 (.20)	.2 - .5 (.3 - 1.0)	21:21

Table 40.--Summary statistics for HCl extractable element concentrations, in parts per million, and the percent of the total content that was extracted from some Northern Great Plains soils.

[Elements that have single entries are reporting concentrations in the soil extract; for elements with double entries, the value without parentheses is the concentration in the soil extract and the value enclosed in parentheses is the percent of the total content in soil extracted; detection ratio, number of samples in which the elements was found in measurable concentrations relative to the number of samples analyzed. HCl extraction was not performed on the C horizon]

Element	Arithmetic mean	Standard deviation	Observed range	Detection ratio
		A horizon		
Ca-----	2200 (23)	720 (10)	940 -3400 (8 -42)	21:21
Cd-----	.2	.088	.04- .3	21:21
Co-----	.6	.36	.2 - 1.6	21:21
Cu-----	.1 (1.4)	.12 (1.7)	.03- .6 (.2 - 6.3)	21:21
Fe-----	3.5 (.02)	4.2 (.021)	.2 - 13 (.0005- .07)	21:21
K------	230 (1.0)	130 (.65)	100 - 730 (.5 - 3.7)	21:21
Mg-----	500 (4.7)	240 (.95)	210 -1000 (3.1 - 6.5)	21:21
Mn-----	50 (13)	25 (7.2)	8 - 94 (1.9 -24)	21:21
Na-----	14 (.2)	21 (.40)	4 - 84 (.03 - 1.7)	21:21
Ni-----	1.0 (15)	.60 (8.2)	.1 - 2.2 (2.9 -30)	21:21
Pb-----	.8	.29	.2 - 1.3	21:21
Zn-----	1.4 (2.6)	1.4 (2.7)	.05- 5.4 (.08 -10)	21:21

Table 41.--Summary statistics for MgNO$_3$ extractable element concentrations, in parts per million, and the percent of the total content that was extracted from some Northern Great Plains soils.

[Elements that have single entries are reporting concentrations in soil extract; for elements with double entries, the value without parentheses is the concentration in the soil extract and the value enclosed in parentheses is the percent of the total content in soil extracted; detection ratio, number of samples in which the element was found in measurable concentrations relative to the number of samples analyzed]

Element	Arithmetic mean		Standard deviation		Observed range		Detection ratio
				A horizon			
Ca-----	2400	(24.)	1300	(11)	870 -5300	(6 -46)	21:21
Cd-----	.1		.037		.06- .2		21:21
Co-----	.3		.17		.03- .7		21:21
Cu-----	.05	(.3)	.054	(.25)	<.01- .17	(.006 - .7)	18:21
Fe-----	2.0	(.007)	1.8	(.0054)	.1 - 7.0	(.0005- .02)	21:21
K------	280	(1.2)	130	(.67)	140 - 770	(.7 - 3.9)	21:21
Mn-----	11	(3.0)	6.6	(2.1)	1 - 24	(.2 - 6.8)	21:21
Na-----	18	(.3)	27	(.56)	2 - .01	(.01 - 1.9)	21:21
Ni-----	.2	(2.8)	.17	(2.8)	<.05- .6	(.07 - 8.9)	17:21
Pb-----	.3		.21		<.05- .7		19:21
Zn-----	.2	(.4)	.36	(.72)	<.01- 1.5	(.01 - 2.8)	20:21
				C horizon			
Ca-----	1900	(9.4)	760	(10)	850 -3200	(.7 -38)	21:21
Cd-----	.08		.027		.02- .1		21:21
Co-----	.2		.15		<.05- .6		19:21
Cu-----	.04	(.2)	.024	(.15)	<.01- .08	(.008 - .5)	19:21
Fe-----	.5	(.002)	.33	(.0010)	.2 - 1.4	(.0005- .005)	21:21
K------	94	(.4)	25	(.14)	53 - 140	(.2 - .7)	21:21
Mn-----	----		----		<.1 - 11		5:21
Na-----	270	(3.1)	430	(4.2)	8 -1800	(.07 -13)	21:21
Ni-----	----		----		<.05- .4		13:21
Pb-----	.2		.18		.02- .7		21:21
Zn-----	----		----		<.01- .01		21:21

Table 42.--Summary statistics for $NH_4C_2O_4$ extractable element concentrations, in parts per million, and the percent of the total content that was extracted from some Northern Great Plains soils.

[Elements that have single entries are reporting concentrations in the soil extract; for elements with double entries, the value without parentheses is the concentration in the soil extract and the value enclosed in parentheses is the percent of the total content in soil extracted; detection ratio, number of samples in which the element was found in measurable concentrations relative to the number of samples analyzed]

Element	Arithmetic mean		Standard deviation		Observed range		Detection ratio
				A horizon			
Ca-----	---		---		<0.5 - 57		14:21
Cd-----	.04		.017		<.01- .07		20:21
Co-----	2.6		1.2		.2 - 5.3		21:21
Cu-----	2.6	(20)	1.6	(9.0)	.1 - 6.8	(1.4 - 36)	21:21
Fe-----	530	(1.9)	230	(.73)	150 -1100	(.7 - 3.0)	21:21
K------	300	(1.3)	160	(.82)	150 - 940	(.7 - 4.7)	21:21
Mg-----	630	(5.7)	430	(2.0)	230 -1700	(2.9 - 11)	21:21
Mn-----	170	(40)	95	(18)	.5 - 330	(.2 - 63)	21:21
Na-----	24	(.4)	23	(.43)	3 - 81	(.02 - 1.4)	21:21
Ni-----	2.4	(33)	2.1	(21)	.05- 9.8	(1.0 - 98)	21:21
Pb-----	.4		.20		<.05- .9		19:21
Zn-----	3.3	(5.4)	2.4	(3.3)	.02- 11	(.04 - 14)	21:21
				C horizon			
Ca-----	---		---		<.5 - 370		7:21
Cd-----	.02		.014		<.01- .05		20:21
Co-----	1.5		1.9		<.05- 5.8		20:21
Cu-----	1.1	(8.5)	1.3	(10)	.05- 3.8	(.4 - 32)	21:21
Fe-----	240	(.9)	350	(1.5)	.3 -1300	(.001- 5.8)	21:21
K------	99	(.5)	36	(.18)	44 - 180	(.2 - .9)	21:21
Mg-----	910	(5.6)	370	(2.6)	350 -1600	(2.3 - 11)	21:21
Mn-----	42	(13)	63	(20)	<.1 - 190	(.01 - 60)	20:21
Na-----	210	(2.3)	400	(3.2)	2 -1800	(.03 - 12)	21:21
Ni-----	1.5	(18)	1.9	(23)	<.05- 6.1	(.3 - 83)	18:21
Pb-----	.2		.22		<.05- .8		19:21
Zn-----	.5	(1.0)	.58	(1.2)	<.01- 1.9	(.02 - 3.6)	20:21

Table 43.--Summary statistics for $C_6H_6O_2$ extractable element concentrations, in parts per million, and the percent of the total content that was extracted from some Northern Great Plains soils.

[Elements that have single entries are reporting concentrations in the soil extract; for elements with double entries, the value without parentheses is the concentration in the soil extract and the value enclosed in parentheses is the percent of the total content in soil extracted; detection ratio, number of samples in which the element was found in measurable concentrations relative to the number of samples analyzed]

Element	Arithmetic mean	Standard deviation	Observed range	Detection ratio
A horizon				
Ca-----	2000 (21)	1200 (8.8)	710 -5300 (5.3 -37)	21:21
Cd-----	.6	.30	.2- 1.6)	21:21
K------	370 (1.7)	260 (1.3)	160 -1400 (.8 - 7.2)	21:21
Mg-----	450 (4.4)	200 (1.4)	220 -1000 (2.2 - 7.9)	21:21
Mn-----	130 (31)	51 (6.2)	49 - 240 (20 -49)	21:21
Na-----	---	---	<.5- 97)	8:21
Pb-----	.9	.20	.5- 1.3)	21:21
Zn-----	.7 (1.2)	.063 (.40)	.6- .8 (.9- 2.6)	21:21
C horizon				
Ca-----	2300 (11)	780 (13)	720 -3800 (1.3 -49)	21:21
Cd-----	.7	.72	.2- 3.6)	21:21
K------	130 (.6)	40 (.21)	64 - 220 (.3 - 1.1)	21:21
Mg-----	800 (4.8)	450 (2.5)	120 -1600 (.5 -12)	21:21
Mn-----	77 (20)	39 (11)	17 - 150 (6.2 -49)	21:21
Na-----	270 (3.1)	450 (4.3)	<.5-1900 (.07-13)	20:21
Pb-----	.8	.20	.4- 1.2)	21:21
Zn-----	.7 (1.2)	.81 (.34)	.6- 1.0 (.7 - 2.4)	21:21

determinations resulted in censored values, the values were replaced with small, arbitrary concentrations (see detection ratios in Tables 37-43). The small number of replaced values were included in the computation of correlation coefficients because they do not materially alter the interpretation of the results. The correlations between each soil extract and total content are presented and discussed by groups of elements that exhibit similar patterns.

Calcium, Potassium, and Sodium

Total content of Ca (Table 25), K (Table 30), and Na (Table 33) in soil exhibits no significant correlations with concentrations of these elements in the extraction solutions tested. However, the correlations between the extracts tested for both A and C soil horizons are all highly significant, with one exception noted.

Even though no significant correlations were observed between total element content and concentration of an element in extracts, it is interesting to note the portion of the total content which was solubilized by the various extracts. In the A horizon, an average of about 20 percent of the total Ca (Tables 39-41, and 43), 1-2 percent of the total K (Tables 38-43), and 0.3 percent of the total Na (Tables 38 and 40-42) was extracted regardless of the extraction solution used. In the C horizon, an average of about 10 percent of the total Ca (Tables 39, 41, and 43), 0.5 percent of the total K (Tables 38, 39, and 41-43), and 2.5 percent of the total Na (Tables 38 and 41-43) was extracted, again, regardless of the extraction solution used. Even though all extraction solutions give similar "ballpark" values for an element solubilized when all 21 samples are considered collectively, the data for individual samples do not indicate that similar amounts are being extracted from each sample. The raw data (see Table 44 for an example, and Severson, Gough, and McNeal, 1977, p. 83-89) indicate that individual samples highest in total Ca, K, or Na tend to be highest in extractable Ca, K, or Na; however, many exceptions are noted. This trend is also indicated by the few significant correlations (Table 25, 30, and 33) between the total amount of an element and the extractable amount for these diverse soils. In addition, in Tables 38-43 the observed range in percent-of-total extracted is shown to span one or two orders of magnitude. These data possibly indicate that the total content of an element consists of several different element reservoirs that may or may not be solubilized by the various extracting solutions. However, the strong correlations between the element concentrations in various extraction solutions would indicate a tentative conclusion to be that within a single soil sample, all extraction agents are apparently solubilizing similar relative portions of the total content.

For the remaining nine elements, the relations are not as consistent either among extraction solutions or between total content and extractable concentration.

Copper, Iron, Magnesium, and Managanese

Table 44.--Total amount, in percent, and extractable amounts, in parts per million, of Ca, K, and Na in selected A- and C-horizon samples of soil from the Northern Great Plains which show extremes in their total content of these elements.

[---, HCl extraction was not performed on the C horizon]

Method of Analysis	Calcium					
	Soil horizon, and sample location in figure 33					
	A-13	A-15	A-12	C-16	C-11	C-3
Total	0.42	1.0	2.0	0.52	6.5	1.2
EDTA	1300	1500	5100	2300	1500	3000
HCl	1500	1400	3100	---	---	---
$MgNO_3$	1300	1100	5300	2000	1000	2900
$NH_4C_2O_4$	1.0	1.0	39	330	<.5	<.5
$C_6H_6O_2$	1100	900	5300	2600	1600	3200

	Potassium					
	Soil horizon, and sample location in figure 33					
	A-14	A-11	A-2	C-17	C-11	C-2
Total	2.1	2.5	3.0	1.9	2.4	2.9
DTPA	130	240	170	81	110	56
EDTA	250	390	280	170	150	100
HCl	170	280	200	---	---	---
$MgNO_3$	180	310	240	96	99	78
$NH_4C_2O_4$	210	350	240	76	110	67
$C_6H_6O_2$	240	410	250	130	160	96

	Sodium					
	Soil horizon, and sample location in figure 33					
	A-17	A-11	A-2	C-17	C-11	C-2
Total	0.09	1.2	2.4	0.38	1.0	2.4
DTPA	3.5	2.1	4.8	8.9	6.5	52
HCl	5.8	4.4	8.8	---	---	---
$MgNO_3$	14	1.5	9.5	17	7.5	68
$NH_4C_2O_4$	12	3.3	23	6.9	4.6	26
$C_6H_6O_2$	3.1	5.1	18	9.1	7.0	93

Cu (Table 28), Fe (Table 29), Mg (Table 31), and Mn (Table 32) are grouped together because they show significant or highly significant correlations between their concentration in one or more of the extraction solutions and total content. In the A horizon, Cu extracted in relation to total content was as follows: $NH_4C_2O_4$ extract--20 percent (Table 42); EDTA extract--7 percent (Table 39); DTPA extract--3 percent (Table 38); and $MgNO_3$ extract--0.3 percent (Table 41). All of the above relations between extractable Cu and total Cu are highly significant. In the C horizon, extractable Cu and total Cu are significantly correlated, and the amount extracted is as follows: EDTA extract--7 percent (Table 39); DTPA extract--3 percent (Table 38); and $MgNO_3$ extract--0.2 percent (Table 41). No significant correlations between HCl extractable Cu and total were observed, but the extractable fraction ranged from 0.2 to 0.6 percent of total content (Table 40). Copper was below the detection limit for too many samples in the $C_6H_6O_2$ extract (Table 43) to justify its inclusion in the correlation matrix. Copper in the $NH_4C_2O_4$ extract of C-horizon soil was not significantly related to total content, but the extractable fraction ranged from 0.4 to 32 percent (Table 42).

From the percent of total Cu solubilized by the various extracts (Tables 38-43), it appears that Cu extracted at a neutral pH ($C_6H_6O_2$ extract) makes up the smallest fraction. The next largest fraction was extracted by $MgNO_3$ and HCl extracts. Slightly more Cu was extracted at a neutral pH (EDTA extract) than was extracted at a slightly alkaline pH (DTPA extract). The largest portion of the Cu extracted was at an acid pH ($NH_4C_2O_4$ extract). The selective action of the various extractants appears to be a determining factor in Cu solubilization. The significant correlations among the extracting agents themselves and with total content suggest that Cu is distributed among several reservoirs in soil in proportion to its total content.

The HCl extraction of Fe (Table 29) has a significant negative correlation with total content and a positive correlation with DTPA and EDTA extracts in the A horizon. The positive relations (DTPA, EDTA, and HCl extractions) are all highly significant or nearly so. In the C horizon, DTPA, EDTA, and $NH_4C_2O_4$ correlations are all highly significant. The extractable Fe fraction represents a very small portion of total content in the A horizon: $NH_4C_2O_4$--2 percent (Table 42); DTPA extract--0.06 percent (Table 38); and EDTA extract--0.05 percent (Table 39).

Extraction methods that are correlated in the A horizon are not the same methods that are correlated in the C horizon. This suggests that extractable Fe occurs in different reservoirs in each horizon. Iron extracted by $MgNO_3$ is a very small portion of total Fe (0.01 percent in the A horizon, and 0.002 percent of total in the C horizon, Table 41). The lack of significant correlation between extractable and total content implies that Fe is not distributed among reservoirs in proportion to its total content. It is not possible to interpret the implication of the negative relation between total Fe and HCl extractable Fe from the present data.

In both A and C horizons, about 5 percent of the total Mg was solubilized (Tables 37-43) regardless of the extracting solution. Total content and all of the extract concentrations, except DTPA extract, are correlated (Table 31) at least at the 0.05 probability level (correlation coefficient of 0.43). Magnesium in the DTPA extract is not significantly correlated with total content or with any of the other extract concentrations (Table 31). DTPA extractable Mg ranged from 2 to 42 percent of total Mg in the A horizon and ranged from 2 to 79 percent of total Mg in the C horizon.

Magnesium exhibits patterns similar to those discussed previously for Ca, K, and Na. The important exceptions are that Mg in the DTPA extract is not related to any other extract or to total content, and that all other extracting agents are significantly correlated with total content. The slight differences noted in Mg concentration in the various extracting solutions may be related to the extracting solution pH. The differences are probably not due to the specific action of the various extracting agents. The more acid extractants solubilized the most Mg and the more basic extractants solubilized the least Mg (DTPA being an exception).

In the A horizon, correlations between the total content of Mn, and Mn in DTPA, $NH_4C_2O_4$, and $C_6H_6O_2$ extracts are highly significant or nearly so (Table 32). The extractable portion of the total Mn content exhibits a large range among extracting agents. The $NH_4C_2O_4$ extract solubilizes about 40 percent of the total content (Table 42), whereas $C_6H_6O_2$ extracts about 30 percent (Table 43), and DTPA extracts about 2 percent (Table 14). Manganese in EDTA, $MgNO_3$, and HCl extracts is not significantly related to total Mn content. The approximate amount of Mn solubilized by these extracting agents is as follows: EDTA extract--4 percent (Table 39); $MgNO_3$ extract--3 percent (Table 41); and HCl extract--13 percent (Table 40).

In the C horizon, the Mn concentration in any of the extracting agents is not significantly correlated with total content. The approximate portion of the total Mn solubilized by the extracting agents is as follows: DTPA extract--1 percent (Table 38); EDTA extract--0.7 percent (Table 39); $NH_4C_2O_4$ extract--13 percent (Table 42); and $C_6H_6O_2$ extract--20 percent (Table 43).

In general, about one-third to two-thirds of the amount of Mn extracted in the A horizon was extracted from the C horizon. However, the total content of Mn is about equal in the A and C horizons. Therefore, Mn probably exists in different reservoirs in the two horizons.

Nickel and Zinc

Nickel (Table 34) and zinc (Table 36) exhibit some similar patterns when extracted from soil by various extracting agents. In both the A and C horizons, Ni and Zn each exhibit no significant correlations between total content and any of the extracting agents.

Correlations between A-horizon DTPA, EDTA, HCl, and $NH_4C_2O_4$ extracts for both Ni and Zn (in addition, $MgNO_3$ extract for Zn) are significant or nearly so. In the C horizon, for both Ni and Zn, DTPA, EDTA, and $NH_4C_2O_4$ extracts are significantly correlated or nearly so.

In both soil horizons, about 2 to 3 times the Ni is solubilized by the $NH_4C_2O_4$ extract as is solubilized by the other extracting agents. For Zn, again $NH_4C_2O_4$ solubilizes the maximum amount in both soil horizons. The other extracting agents (DTPA, EDTA, and HCl) do not solubilize similar amounts.

The data for Ni implies that two major reservoirs occur: one that is extracted by DTPA, EDTA, and HCl; and any other that is extracted by $NH_4C_2O_4$. The data for Zn implies that it may be present in several sources in each soil horizon. From the data it is not possible to suggest the relative portions occurring in these various sources.

The extracts solubilized about 10 to 30 percent of the total Ni in the A horizon and about 10 to 20 percent of the total in the C horizon. About 1 to 5 percent of the total Zn is solubilized in the A horizon and about 0.1 to 1 percent of the total Zn is solubilized in the C horizon.

Cadmium, Cobalt, and Lead

Cd (Table 26), Co (Table 27), and Pb (Table 35) correlations between their concentrations in the various extracting agents or with total content exhibit no consistent patterns either between extracting agents or between soil horizons. The low abundance of Cd, Co, and Pb is near the detection limit of the analytical method used (Severson, Gough, and McNeal, 1977, p. 56-69), probably accounting for the lack of consistent relations. The correlations and summary statistics for these elements are presented to provide some indication as to their abundance in Northern Great Plains soils.

SUMMARY

Samples of A- and C-horizon soils that were known to be geochemically diverse were collected at 21 locations in the unglaciated portion of the Northern Great Plains. The samples were disaggregated, and the minus-2-mm fraction was saved for analysis. Extractable concentrations of Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn were determined on each sample. Total content of all these elements, except Cd, was also determined. Splits of each sample were extracted with six different agents--DTPA, EDTA, HCl, $MgNO_3$, $NH_4C_2O_4$, and $C_6H_6O_2$. Each of these extracting agents has been reported in the literature as being useful for relating, under agronomic conditions, concentration of one or more elements in soils to that in plants.

Correlations between an element's concentration in an extract and its total content provide an array of relations that suggest there are many inconsistencies in assessing element solubilization when soils that are geochemically different are analyzed by chemical-solution extracts.

Correlations for a single element between the various extracting solutions are significant. Correlations between extractable concentration and total content, in general, are not significant. Percent of total element concentration solubilized by the various extractants ranges greatly from sample to sample. This trend, for many but not all elements, suggests that the various extracting agents are not solubilizing elements in proportion to total content when all samples are considered as a group, but that within a single sample, many extracting solutions are apparently solubilizing similar relative portions of the total content.

Potential Toxicologic Problems Associated with Strip Mining

by

James A. Erdman

Introduction

Surface coal production in the Northern Great Plains is expected to exceed that of the Eastern or Appalachian Region. This projection has stimulated a great interest in the effects of strip mining on the agriculture of this area. The Surface Mining Control and Reclamation Act of 1977 requires mine operators to prove they can restore the land to its original productivity. Much of the region is prime farmland, and ultimately the agricultural productivity of these lands must be as good as or better than it was before (Waldrop, 1977). The science of land reclamation--basically spoil stabilization and revegetation--is still in its infancy. Geochemical problems recognized to date are those that relate to toxicities or deficiencies with regard to establishing a vegetative cover, such as effects of sodium-rich materials or inadequate levels of phosphorus.

To date, there has been little recognition that reclaimed mine lands may pose a nutritional problem at higher levels in the food chain, principally to livestock and wildlife, despite the awareness and documentation by veterinarians and toxicologists of element deficiencies or toxicities in both natural settings and disturbed environments. Only a handful of researchers appears to be looking at changes in the biogeochemical system beyond revegetation. A recent study calls attention to the potential for molybdenosis on certain mined lands in the West (Erdman and others, 1978).

The types of deleterious effects will probably be those of subtle, chronic chemical imbalance rather than frank intoxication. Thornton (1974) elaborated on this idea as follows:

> The use of contaminated land for agriculture is a controversial topic and must depend on such factors as the form and distribution of the contaminant metals, their solubility, availability and potential toxicity, coupled with local factors, such as soil type, drainage, pH, farm management and proposed cropping sequence. In addition to the well established soil-plant-animal relationship, recent investigations have demonstrated a parallel soil-animal situation in that cattle, for instance, have been shown to involuntarily ingest up to 10% of their dry matter intake as soil under farming conditions in southwest England. On contaminated land this may represent an intake of ten times the amount of copper, lead or arsenic in the form of soil to that in herbage. It is evident, however, that under certain

conditions both crops and livestock can survive apparently quite happily on land containing well above normal amounts of potentially toxic metals. We need to find out far more on the potential sub-lethal, sub-clinical and marginal effects of these elements on both health and production. In addition, we must assess in some detail the effects, if any, of these metals on food quality.

One of the many energy-related investigations of the U.S. Geological Survey over the past several years has been regional geochemical and biogeochemical surveys in the western energy regions in order to establish norms (baselines) for a large suite of elements in various natural media. Such norms are being used to assess the impact of resource--mainly coal--development in the West. More local, topical studies were conducted simultaneously on the effects of power-plant emissions on the surrounding countryside, and the effects of reclaimed mined lands on the mineral composition of forage and small grains. For some of these studies, the regional baselines are utilized.

Emphasis in this paper will be on just one potential problem associated with strip mining--molybdenosis, a copper-deficiency disease that occurs especially in cattle and sheep (Dye and O'Harra, 1959). From my experience, the incidence of molybdenosis-like symptoms appears to be frequent and widespread in the West. It is probably far more prevalent in natural systems (Kubota, 1975) than in those altered by man's activities (Christianson and Jacobson, 1971; Dollahite and others, 1972).

My interest in the geochemistry of mine spoils in the Northern Great Plains grew out of an earlier study in central Missouri (Ebens and others, 1973), the results of which implicated a clay-mining operation in the weight loss and reproductive failure of a herd of black angus cattle. Such symptoms led Dr. Arthur Case, veterinary toxicologist with the University of Missouri, to suspect molybdenosis as the possible cause, even though this nutritional disease is rarely encountered in eastern environments. Results of our survey of the geochemical system demonstrated certain trace-metal anomalies, which included molybdenum, and simply confirmed Dr. Case's diagnosis.

Methods

Samples of sweetclover (<u>Melilotus</u> sp.) and associated soil and/or spoil material were collected during late summer of 1974 from 10 randomly selected sites at each of eight surface mines scattered throughout the Northern Great Plains (fig. 34). Sweetclover was selected because of its abundance on many of the coal mine spoils in the region, its extensive use in spoil rehabilitation, and its palatability to livestock. The sampling design and analytical methods are detailed elsewhere (Erdman and others, 1978). Smaller studies of other agriculturally important plants were conducted at the same time. One

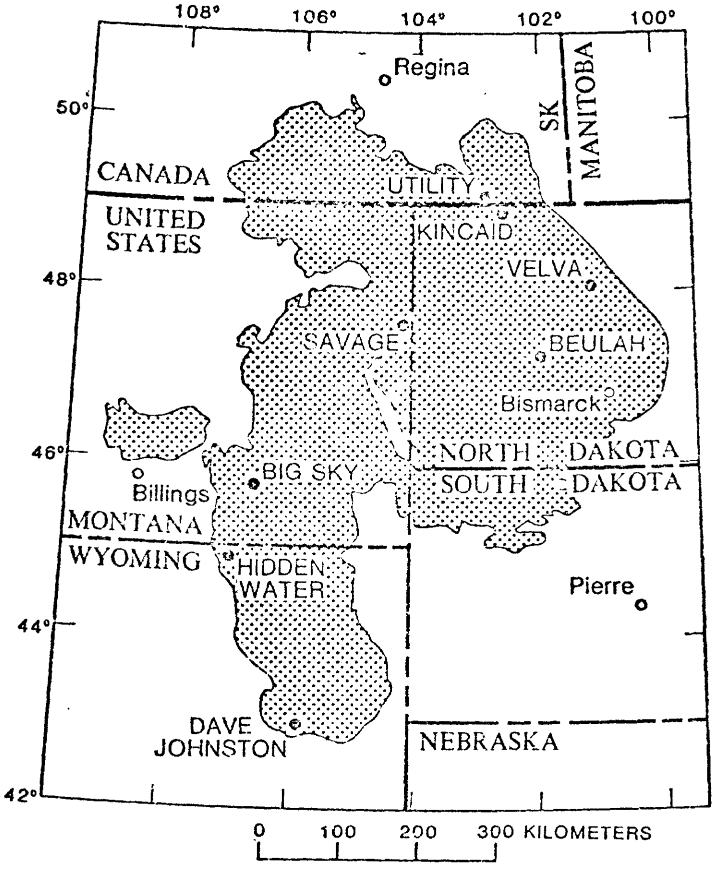

Figure 34.--The Northern Great Plains coal province, showing locations of the eight surface mines sampled for sweetclover and associated spoil material. (From Erdman and others, 1978.)

such study assessed the effects of spoils at the Dave Johnston Mine in southern Wyoming on the element composition of Fairway crested wheatgrass (Erdman and Ebens, 1978). Background data on the composition of small grains were obtained from a broad-scaled study (Erdman and Gough, 1978). The details of this study need not be repeated here, but samples were collected from 17 farms scattered across the southwest portion of the Northern Great Plains (fig. 35).

Results and Discussion

Average concentrations for copper (Cu) and molybdenum (Mo), Cu:Mo ratios in sweetclover, and pH values of spoils from the eight mines sampled are given in fig. 36. It is difficult to arrive at a consensus from the literature for critical levels of Mo and Cu:Mo ratios, but 5 ppm for Mo and a ratio of 2:1 are reasonable as being critical for cattle. It thus seems that at least five of the mines could present some management problems with regard to cattle operations. The pH of the spoils appears to exert a significant control on the Mo contents of the sweetclover, a factor that has been well documented in the literature. The total Mo content in the spoils materials (unpublished data) shows no relationship whatsoever to the Mo in the plants.

A number of elements were judged unusually high in wheat grains sampled from the Big Sky Mine. The most anomalous, however, was Mo; the Mo content of one of the three samples from there exceeded the typical concentration established for winter wheat by a factor of five (fig. 37). This abnormally high concentration of Mo in the grain of wheat is compatible with the large Mo concentrations in sweetclover from this mine (fig. 36). The native soils in the vicinity of the Big Sky Mine seem also to contain high amounts of available Mo; samples of wheat from the two farms nearest this mine contained the largest concentrations of Mo of any of the 17 samples analyzed.

Mo in crested wheatgrass (Agropyron cristatum) at the Dave Johnston Mine (Table 45) is of less concern. Grasses generally are not Mo accumulators as are sweetclover and many other legumes. Moreover, the availability of Mo is decidedly lower owing to the acidity of the spoils. Some essential elements, such as copper, magnesium, and phosphorus, are present in nutritionally deficient or marginal amounts. Uranium (U), in grass samples from the spoils occurs, however, in concentrations three times as large as those in wheatgrass growing on undisturbed ground. The Dave Johnston Mine occurs on the edge of the southern Powder River Basin uranium district, and so uraniferous overburden might be expected. No critical levels of U in forage are available, but U is radioactive and can be highly toxic. Larger than normal concentrations of U were also found in the sweetclover from these spoils.

In conclusion, the importance of documenting these effects of mine spoils on the mineral composition of forage and crops is that we should

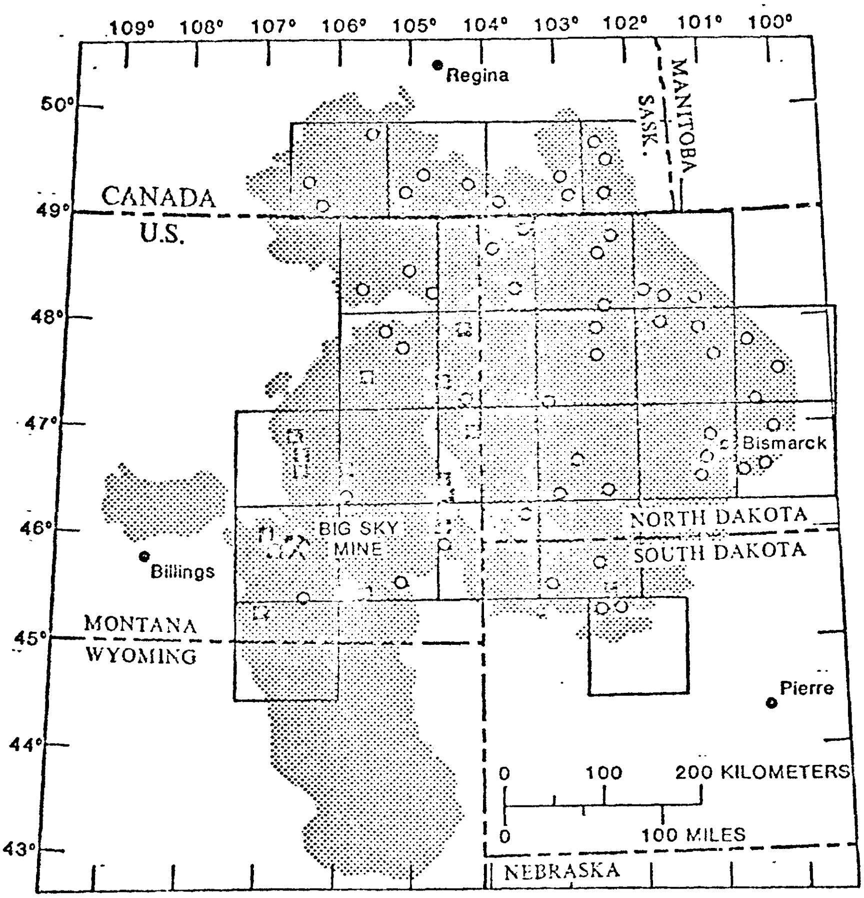

Figure 35.--Grain sampling localities (farms) in the Northern Great Plains coal province (shaded). Solid quares indicate winter-wheat sample localities described in this report. Open circles indicate spring-wheat sample localities. The grid cells are 100 km on a side. The Wyoming portion of the province was excluded from the sampling design because of sparse wheat production.

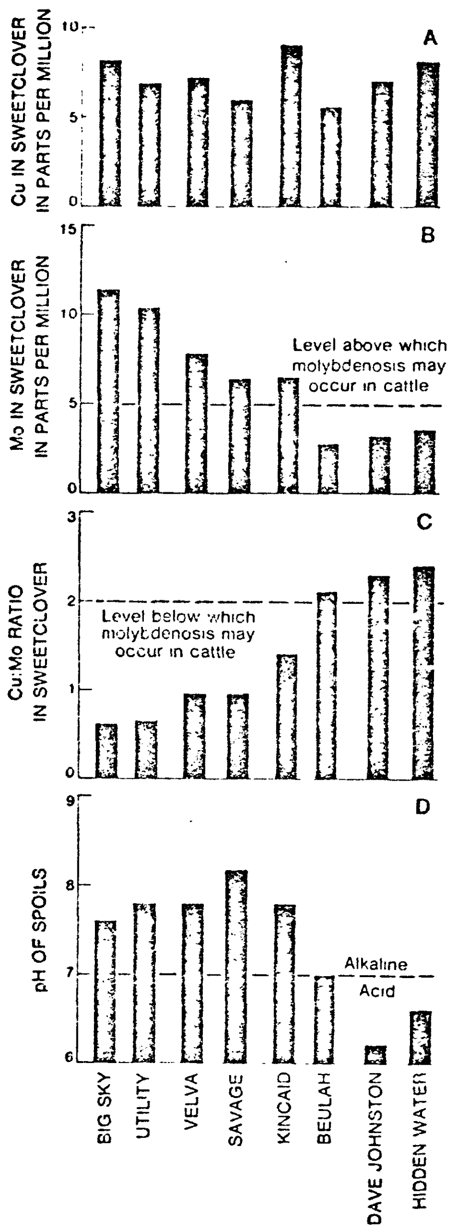

Figure 36.--Mean copper (A) and molybdenum (B) concentration in sweetclover. Cu:Mo ratios in sweetclover (C), and pH values of associated spoil materials (D) at eight surface coal mines in the Northern Great Plains. Each mean is based on 10 randomly selected samples. (From Erdman and others, 1978.)

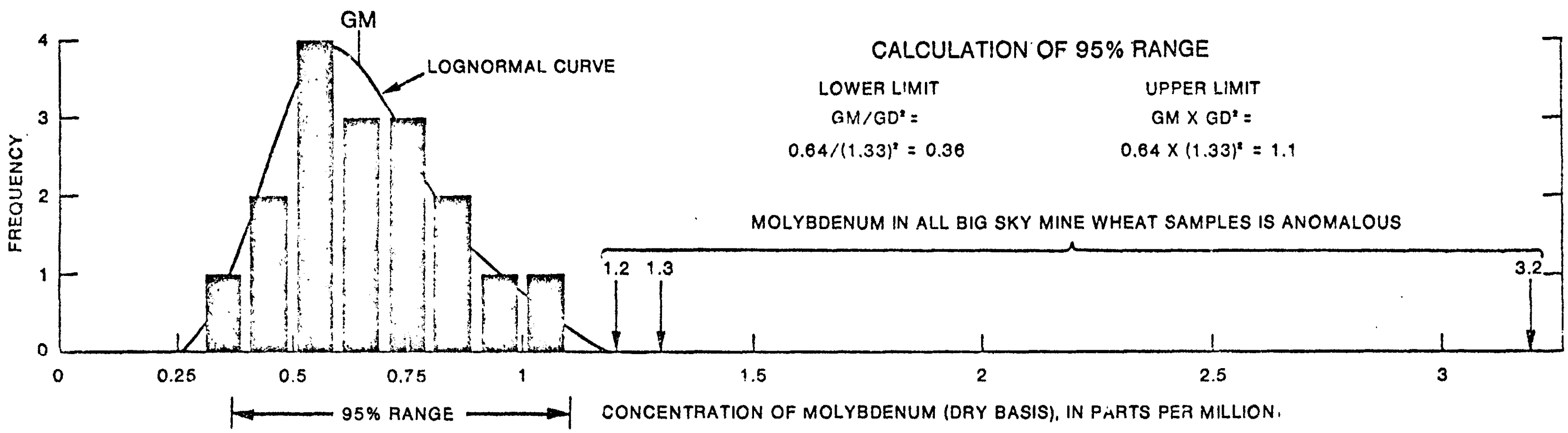

Figure 37.--Molybdenum concentrations in samples of winter wheat from the Big Sky Mine, Montana (arrows), compared to the distribution of molybdenum in 17 samples from farms in the Northern Great Plains (histogram). (From Erdman and Gough, 1978.)

Table 45.--Geometric mean concentrations and the observed ranges of elements in crested wheatgrass from topsoil borrow areas and from reclaimed spoil areas at the Dave Johnston Mine, Wyoming.[1]

Element	Topsoil borrow areas		Reclaimed spoil areas	
	Mean	Range	Mean	Range
Al, % -------	0.069	0.030-.27	0.11	0.041-.37
B, ppm ------	15	11-28	17	11-48
Ba, ppm -----	12	6-22	10	6-22
Ca, % -------	.26	.22-.30	.23	.16-.35
[2]Cd, ppm -----	.054	.016-.15	.082	.034-.15
[3]Co, ppm -----	.069	<.054-.13	.099	<.058-.44
Cr, ppm -----	.27	.11-.60	.40	.16-1.1
Cu, ppm -----	2.8	1.6-6.0	3.2	1.6-5.9
[2]F, ppm ------	4.5	3-6	6.2	3-10
Fe, ppm -----	190	81-350	270	120-740
Hg, ppm------	.011	.01-.02	.011	.01-.02
K, % --------	1.1	.90-1.4	1.2	.72-1.6
Li, ppm -----	.82	.29-1.8	1.3	.58-4.0
Mg, % -------	.12	.08-.17	.11	.08-.17
[3]Mn, ppm -----	16	5.6-36	39	23-140
Mo, ppm -----	.39	<.38-.58	.43	<.39-.84
Na, ppm -----	8.4	3.6-22	11	3.5-21
[3]P, % --------	.13	.09-.19	.084	.041-.17
S, total, % -	.17	.10-.27	.18	.09-.33
Se, ppm -----	.23	.10-.60	.27	.10-.70
Si, % -------	1.2	.7-1.9	.98	.44-1.9
Sr, ppm -----	25	16-39	25	14-41
Ti, ppm -----	16	3-50	26	11-74
[2]U, ppm ------	.021	<.021-.067	.062	<.028-.55
[2]V, ppm ------	.63	<.54-.98	.82	<.69-1.5
[3]Zn, ppm -----	20	13-28	26	18-32

[1] Data are based on 10 samples and their analytical duplicates from each area; concentrations are expressed on a dry basis.

[2] Means are significantly different at the $\underline{P} < 0.05$ level.

[3] Means are significantly different at the $\underline{P} < 0.01$ level.

be able to anticipate problems that may ensue after the rehabilitated lands have been released for agricultural use. To my mind, very little attention has been directed towards this area of mine-land reclamation.

Summary

Reclaimed surface-mined lands in the Northern Great Plains region may cause significant departures from normal in the element composition of agriculturally important plants. The potential of a copper-deficiency disease (molybdenosis) in cattle is of particular concern with regard to both legumes, in which copper-to-molybdenum ratios of 2:1 are commonplace, and grasses to a limited extent. Vegetation growing on spoils material has enhanced concentrations of many other essential trace elements, although concentrations of the major nutrient, phosphorus, eppear to be lower.

Availability of Elements in Soils to Native Plants, Northern Great Plains--Assessment of New Data

by

Larry P. Gough, James M. McNeal, and Ronald C. Severson

Last year's report (Severson and others, 1977) detailed the progress of our availability work with uncultivated soils and native plants in the Northern Great Plains from its inception in the summer of 1976 until about September of 1977. Because that report, and a more recent manuscript dealing with the plant biogeochemistry of the project (Gough and others, 1978), detail our literature review, overall objectives, sample site locations, and methodology (both field and laboratory), we will not repeat such information here.

At the time of the completion of the two manuscripts mentioned above, we had analyzed the data relating the element content of washed western wheatgrass, silver sagebrush, and above-ground biomass to the element content of three extracts of soil (DTPA, EDTA, and ammonium oxalate) and also total soil. This report summarizes our interpretations of the soil-plant relations involving these three extractants and total soil as well as element data from soil extracts using magnesium nitrate, hydrochloric acid, and hydroquinone. This brings to a total of six the extractants utilized. The methodology of the three new extractants is given on pages 90-91 of this report. The following list gives the six extractants and their generalized mode of extraction:

Extractant	Mode of extraction
DTPA	chelation
EDTA	chelation
Ammonium oxalate	reduction
HCl	dilute acid hydrolysis
Hydroquinone	reduction
Magnesium nitrate	ion exchange

RESULTS AND DISCUSSION

Correlation analysis

Table 46 presents simple correlation coefficients for relations between elements in plants (dry weight base) or plant ash and thirteen soil physical and chemical properties. Correlations are given at the 0.10, 0.05, and 0.01 probability levels for each plant species. None of the correlations (r) exceeds 0.7, and therefore no coefficient of determination (r^2) is greater than 0.50. This indicates that less than 50% of the total variability in the soil-plant comparison data is explained by any relation.

Table 46.--Correlation coefficients between the amounts of elements (and ash yield) in plant material and soil physical and chemical properties.

[Tests of significance for wheatgrass and biomass use 19 degrees of freedom (d.f.), for sagebrush 17 d.f.; $\underline{p}$ ($r_{19\ d.f.} \geq 0.55$) = 0.01, $\underline{p}$ ($r_{19\ d.f.} \geq 0.43$) = 0.05, $\underline{p}$ ($r_{19\ d.f.} \geq 0.37$) = 0.10; $\underline{p}$ ($r_{17\ d.f.} \geq 0.57$) = 0.01, $\underline{p}$ ($r_{17\ d.f.} \geq 0.46$) = 0.05, $\underline{p}$ ($r_{17\ d.f.} \geq 0.39$) = 0.10]

	Soil physical and chemical properties, soil horizon																								
Elements in plants or plant ash	Clay minerals		Dolomite		Potassium feldspar		Plagioclase		Quartz		Calcite	pH		Organic carbon		CEC		Sand		Silt		Clay		Water	
	A	C	A	C	A	C	A	C	A	C	C	A	C	A	C	A	C	A	C	A	C	A	C	A	C
WESTERN WHEATGRASS (n = 21)																									
Ash			-0.52																						
Ca											0.37	0.61													
Cd										-0.44	.43								-0.45				0.47		
Co																									
Cu												.54													
Fe												.47													
K			- .47						0.37		- .49	- .63		0.41											
Mg														.37											
Mn	0.57			0.42	-0.40		-0.37					.48	0.38	.46	0.46	0.41		-0.62		0.60	0.45	0.55		0.47	-0.41
Na	.44											.62			.38			- .41			.37	.41			
Ni						0.40						.41		- .39											
Pb										- .39	.49	.40						- .39		.39	.44				
Zn	.61				- .50		- .40					.61				.43		- .58		.56		.52		.53	
BIOMASS (n = 21)																									
Ash													.45	- .50											
Ca									.53																
Cd	- .47	-0.56										.43				- .45		.37	.42		- .37		- .39	- .41	
Co														- .41											
Cu	- .65				.41	.44			.58					- .55	- .41	- .56		.60		- .51		- .61		- .58	
Fe												.44													
K	- .51			- .55	. .39				.51		- .53	- .52	- .48				.39	.47		- .43	- .48	- .44			.42
Mg									.51																.41
Mn							- .44																		
Na			.45																						
Ni				- .48										- .42					.43				- .43		
Pb				.67						- .44	.63	.41	.65				- .41				.44				- .44
Zn																									
SILVER SAGEBRUSH (n = 19)																									
Ash					- .53							.49													
Ca																									
Cd			- .39									- .47					.39								
Co			.40																						
Cu	.44															.53		- .41				.41		.44	
Fe			.39						- .40			.66					- .53								- .45
K					- .64				- .39																- .44
Mg														.37					- .39						
Mn										- .39	.44		.60												
Na																	- .44								
Ni	.44								- .50							.51						.42		.53	
Pb											.41														
Zn					- .50																				

Few consistent patterns are noted either between plants for a given horizon and soil feature or between horizons for a given plant and soil feature. Significant relations between pH and elements in plants, however, were more numerous than those between the elements and any of the other properties. Of the three plant materials, wheatgrass showed the most significant (≤ 0.05) correlations between pH and elements in the A horizon (no significant relations were noted for the C horizon). This may be because wheatgrass is generally shallow-rooted. Potassium concentrations in wheatgrass decreased with increasing soil pH, while Ca, Cu, Fe, Mn, Na, and Zn concentrations increased. The linear regression equations relating element concentrations in wheatgrass to soil pH are:

$$
\begin{aligned}
\text{Log Ca} &= -1.36 + 0.10\,\text{pH} \quad (r^2 = 0.37)\\
\text{Log Cu} &= -1.35 + .16\,\text{pH} \quad (r^2 = .29)\\
\text{Log Fe} &= .45 + .20\,\text{pH} \quad (r^2 = .21)\\
\text{Log K} &= .58 - .15\,\text{pH} \quad (r^2 = .40)\\
\text{Log Mn} &= .41 + .12\,\text{pH} \quad (r^2 = .22)\\
\text{Log Na} &= -.26 + .23\,\text{pH} \quad (r^2 = .39)\\
\text{Log Zn} &= -.001 + .17\,\text{pH} \quad (r^2 = .37)
\end{aligned}
$$

In the above equations, except for Ca and K, which are expressed in percent, the element concentrations in wheatgrass are expressed in parts per million (ppm) of the plant dry matter.

These data indicate that, for the A-horizon soils sampled, Ca, Cu, Fe, Mn, Na, and Zn become more available to wheatgrass with increasing soil pH (over a range of pH from 6.2 to 8.2). These trends are, of course, contrary to the general notion of the relation of pH to the availability of these elements to plants in general (Hodgson, 1963) and to grasses in particular (Bohn and Aba-Husayn, 1971). Because there is no other soil feature in the A horizon which is commonly related to many of these elements (with the exception of the association of Mn, Na, and Zn with soil clay minerals, table 46), the pH relations are considered worth noting. It is possible that some other soil feature not measured (such as microbial activity or Eh) may be more important than pH in determining the availability of these six elements. Other positive relations between soil pH and plant element content (table 46) were: biomass Pb and C-horizon pH ($r^2 = 0.42$), sagebrush Fe and A horizon pH ($r^2 = 0.44$), and sagebrush Mn and C horizon pH ($r^2 = 0.36$).

Simple correlation analysis was used to assess the relation between element concentration in three plant materials and the concentration of soil-extracted elements using the six extractants mentioned above. Table 47 presents correlation coefficients for those relations found to be significant at the 0.10, 0.05, and 0.01 probability levels. Even though many of the relations qualified as being highly significant ($p \le 0.01$), none of the coefficients of determination exceeded 0.50.

Using the information in table 47, several general conclusions are

Table 47.--Correlation coefficients between the amounts of elements in plant material and the amounts of those same elements in extracts of A- and C-horizons of soil and total soil.

[HCl extracts on the C-horizon soils were not performed; all extractions were on the unground <2mm soil fraction except for "DTPA (ground)," which was on the <2mm fraction ground further to pass a 100-mesh (150µm) sieve, and for "DTPA (sieved)," which was on the <150µm fraction that was separated from the <2mm fraction by dry sieving; tests of significance for wheatgrass and biomass use 19 degrees of freedom (d.f.), for sagebrush 17 d.f.; $p\ (r_{19\ d.f.} \geq 0.55) = 0.01$, $p\ (r_{19\ d.f.} \geq 0.43) = 0.05$, $p\ (r_{19\ d.f.} \geq 0.37) = 0.10$; $p\ (r_{17\ d.f.} \geq 0.57) = 0.01$, $p\ (r_{17\ d.f.} \geq 0.46) = 0.05$, $p\ (r_{17\ d.f.} \geq 0.39) = 0.10$; leaders (--) mean correlation tests could not be performed (see text)]

Elements in plants	Soil extract or total soil, soil horizon																
	DTPA (ground)		DTPA (sieved)		DTPA (unground)		EDTA		Ammonium oxalate ($NH_4C_2O_4$)		Magnesium nitrate ($MgNO_3$)		Hydro-quinone		HCl	Total soil	
	A	C	A	C	A	C	A	C	A	C	A	C	A	C	A	A	C
WESTERN WHEATGRASS (n = 21)																	
Ca	--	--	--	--	--	--	0.47				0.42		0.52		0.49		
Cd		-0.56														--	--
Co	0.39												--	--		--	--
Cu													--	--			
Fe													--	--			
K															.40		
Mg											--	--					
Mn										-0.56	-.45		.40			0.56	
Na	.59				0.48		--	--	0.64		.49		.54		.55		
Ni		-.47											--	--		--	--
Pb																--	--
Zn											-.38				-.53	.57	
BIOMASS (n = 21)																	
Ca	--	--	--	--	--	--											
Cd											-.43					--	--
Co													--	--		--	--
Cu	-.54	-.49		-0.53	-.53	-0.45	-.45	-0.38	-.59		-.57		--	--	.38	-.68	-0.46
Fe													--	--			
K																	
Mg											--	--					
Mn																	
Na	.66				.38		--	--			.37				.37		
Ni										.43		0.51	--	--		--	--
Pb								-.38		-.43		.55				--	--
Zn									-.53								
SILVER SAGEBRUSH (n = 19)																	
Ca	--	--	--	--	--	--											
Cd									.43						.45	--	--
Co	.63											-.39	--	--		--	--
Cu	.41		.42		.47		.45						--	--		.45	
Fe			-.45		-.41		-.47						--	--	-.43		
K		.51		.39													
Mg											--	--					
Mn										-.56		-.48	.60			.41	.39
Na				.40			--	--									
Ni	.61		.49		.47	.46	.63	.39	.57				--	--		--	--
Pb										-.47						--	--
Zn						.64							.42			.42	

made: (1) If both A and C horizon relations are considered, no one extract emerges as generally superior as a measure of element availability for the plant materials studied; however, the chelates (DTPA and EDTA) appear more successful as extractants for sagebrush than any of the other extractants. (2) Although there are isolated instances where an element in an individual soil extract related well with a particular plant material, in general, if an element in plant material relates well with the element content in one extract, that same element in plant material will also relate well with the element content of several extracts. This is evident in A-horizon soils for such relations as wheatgrass Na to extracted Na and sagebrush Ni to extracted Ni. (3) Considering all extracts (except HCl, where only A-horizon data is available) and total soil, many more important relations were determined for the A horizon than for the C horizon. (4) Many more elements in sagebrush expressed relations with the various extracts than were expressed by wheatgrass or biomass. (5) Species differences are great, as there were no obvious similarities among species based on either elements or extracts.

One explanation for the lack of either element or extract similarity between species (mentioned above) is suggested by the data in table 48. The table presents correlation coefficients between the element content of the three plant materials. Except for a few elements (most notably Fe and Pb) the element contents in the various plant materials are independent. In general these data suggest that relations between elements in plants and extracted elements would not be similar for the different plant materials.

Linear regression analysis

Prediction equations for all significant (≤ 0.05) positive relations in table 47 were calculated using the form:

$$\log_{10} \underline{X} = \underline{a} + \underline{b} \ \log_{10} \underline{Y},$$

where X is an estimate of the concentration of the element in the plant material (in ppm), a and b are, respectively, the intercept and slope of the regression line, and Y is the concentration of the element in the soil extract. The regression equations are presented in table 49.

These equations are considered to have potential for predicting the uptake by selected plants of certain elements from soil extracts; however, additional verification is needed to substantiate the utility of these equations. At least in those instances where extract concentrations fall within the ranges of those found in this study (see table 49), the following predictive situations occur:

Table 48.--Correlation coefficients between the amounts of elements (and ash yield) in various plant materials.

[*, significant ($p \le 0.05$); **, highly significant ($p \le 0.01$)]

	Correlation coefficients between:		
Property	Sagebrush and biomass (n=19)	Wheatgrass and biomass (n=21)	Wheatgrass and sagebrush (n=19)
Ash	0.66**	0.33	0.43
Cadmium	.49*	-.05	.24
Calcium	.22	-.04	.29
Cobalt	-.35	.46*	.22
Copper	-.26	.28	.35
Iron	.84**	.89**	.80**
Lead	.02	.67**	.49*
Magnesium	.34	.38	.55*
Manganese	.49*	.32	.31
Nickel	.23	.43	.36
Potassium	-.09	.37	-.22
Sodium	.38	.64**	.27
Zinc	.01	.20	.21

Table 49.--Element content of plants as a function of the element content of extracts of A- and C-horizon soils or total soil.

[Except where noted, all element concentrations are in parts per million; only independent variables significant at the <0.05 probability level are included in the prediction equation; all extractions were on the unground <2mm soil fraction except for "DTPA (ground)", which was on the <2mm fraction ground further to pass a 100-mesh (150μm) sieve, and for "DTPA (sieved)", which was on the <150μm fraction that was separated from the <2mm fraction by dry sieving]

Soil horizon	Regression equation	Percent of variance explained
	Wheatgrass (n = 21)	
A	Log Ca[1] = -0.46 + 0.26 log EDTA Ca[1]	22
	Log Ca[1] = -1.5 + 0.25 log hydroquinone Ca	27
	Log Ca[1] = -0.41 + 0.33 log HCl Ca[1]	24
	Log Na = 1.0 + 0.36 log DTPA (ground) Na	35
	Log Na = 1.2 + 0.26 log DTPA Na	23
	Log Na = 1.0 + 0.36 log ammonium oxalate Na	41
	Log Na = 1.1 + 0.28 log magnesium nitrate Na	24
	Log Na = 1.1 + 0.29 log hydroquinone Na	29
	Log Na = 1.0 + 0.38 log HCl Na	30
	Log Mn = -0.65 + 0.74 log total soil Mn	31
	Log Zn = -0.20 + 0.78 log total soil Zn	32
	Biomass (n = 21)	
A	Log Na = 1.5 + 0.24 log DTPA (ground) Na	44
C	Log Ni = -0.27 + 0.14 log magnesium nitrate Ni	38
	Sagebrush (n = 19)	
A	Log Cu = 0.85 + 0.20 log DTPA Cu	22
	Log Mn = 0.38 + 0.57 log hydroquinone Mn	36
	Log Ni = 0.07 + 0.35 log DTPA (ground) Ni	37
	Log Ni = 0.08 + 0.23 log DTPA Ni	22
	Log Ni = 0.09 + 0.23 log DTPA (sieved) Ni	24
	Log Ni = 0.09 + 0.48 log EDTA Ni	40
	Log Ni = -0.01 + 0.17 log ammonium oxalate Ni	32
C	Log K = -0.27 + 0.18 log DTPA (ground) K	26
	Log Ni = 0.14 + 0.32 log DTPA Ni	26
	Log Zn = 1.9 + 0.29 log DTPA Zn	41

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[1] Concentrations are in percent.

Plant Material	Element	Soil Horizon
Wheatgrass	Ca, Na, Mn, Zn	A
Biomass	Na	A
	Ni	C
Sagebrush	Cu, Mn, Ni	A
	K, Ni, Zn	C

Linear multiple regression analysis

Multivariate relations were investigated between elements in plants (dependent variables) and independent variables such as extracted elements and additional physical and chemical properties of soil (for a complete listing of the independent variables utilized, see table 50). This was done to improve the prediction of plant-available elements in soils (that is, explain a greater proportion of the total variance between plant and soil relations).

Although only independent variables significant at the 0.05 probability level were included in the equations, about one-third of the multivariate equations explained less than 50% of the total variance. We arbitrarily present here only those multiple regression equations (for wheatgrass, biomass, and sagebrush) that explain $\geq$ 50% of the total variation (tables 51, 52, 53). The prediction equations are, of course, useful only when the same independent variables, as are presented in these equations, are measured. Therefore equations in tables 51, 52, and 53 which include commonly measured independent variables such as pH, CEC, particle size distribution, and extractable element concentration, have the greatest potential utility.

The independent variables in the equations in tables 51, 52, and 53 do not necessarily appear in order of relative importance, nor do the magnitude of the regression coefficients indicate relative importance. An attempt was made, however, to quantify the relative importance of the independent variables, regardless of sign, and these are presented in table 54. This quantification was accomplished as follows: (1) From the generated multiple regression equations, the individual standard partial regression coefficients (or regression weights) were normalized so that their sum equaled one. (2) The normalized standard partial regression coefficient were then multiplied by the number of times that the individual independent variable occurred in separate regression equations in an extract within a soil horizon.

From table 54 the following generalizations can be made concerning the relative importance of the independent variables that occurred in the regression equations presented in tables 51, 52, and 53: (1) The greatest number of independent variables associated with wheatgrass were in the A horizon relations. Of these variables, pH was nearly always the most important (by factors of as much as 3 to 8) followed by the presence in the soil of minerals such as plagioclase and quartz. (2)

Table 50.--Independent variables utilized in linear multiple regression analysis.

[All extractions were on the unground <2mm soil fraction except for "DTPA (ground)", which was on the <2mm fraction ground further to pass a 100-mesh (150μm) sieve, and for "DTPA (sieved)", which was on the <150μm fraction that was separated from the <2mm fraction by dry sieving]

Element, or soil property	Soil extract or total soil, soil horizon																	
	DTPA (ground)		DTPA (unground)		DTPA (sieved)		EDTA		Ammonium oxalate ($NH_4C_2O_4$)		Magnesium nitrate ($MgNO_3$)		Hydroquinone ($C_6H_6O_2$)		HCl		Total soil	
	A	C	A	C	A	C	A	C	A	C	A	C	A	C	A	C	A	C
Ca							x	x	x	x	x	x	x	x	x		x	x
Cd	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			
Co	x	x	x	x	x	x	x	x	x	x	x	x			x			
Cu	x	x	x	x	x	x	x	x	x	x	x	x			x		x	x
Fe	x	x	x	x	x	x	x	x	x	x	x	x			x		x	x
K	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Mg	x	x	x	x	x	x	x	x	x	x			x	x	x		x	x
Mn	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Na	x	x	x	x	x	x			x	x	x	x	x	x	x		x	x
Ni	x	x	x	x	x	x	x	x	x	x	x	x			x			
Pb	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			
Zn	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
pH	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Calcite	x	x	x	x	x	x	x	x	x	x		x		x				x
Clay-m[1]	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Dolomite	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
K-spar[2]	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Plagioclase	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Quartz	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Siderite	x	x	x	x			x	x	x	x								
Clay[3]	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Sand	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Silt	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Water	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
CEC[4]	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Tot.-C[5]					x	x					x	x	x	x	x		x	x
CO_3-C[6]					x	x					x	x	x	x	x		x	x
C-wb[7]	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
C-550[8]	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Org.-C[9]					x	x					x	x	x	x	x		x	x
C-om[10]	x	x	x	x			x	x	x	x								

[1] Determined by X-ray diffraction.

[2] Potassium feldspar

[3] Determined by particle size distribution.

[4] Cation-exchange-capacity.

[5] Total carbon.

[6] Carbonate carbon.

[7] Carbon by Walkley-Black method.

[8] Carbon by ignition at 550°C.

[9] Organic carbon.

[10] Organic matter calculated from organic carbon.

Table 51.--Linear multiple regression equations relating concentrations of elements in wheatgrass to concentrations of elements in soil extracts or total soil plus additional soil physical and chemical properties of both the A and C horizon

[Percentage of the total variance explained by the regression equation is given in the first column; only independent variables significant at the 0.05 probability level are included; for a detailed explanation of the independent variables utilized in the calculation of the regression equation, see table 50; dependent variable (element in wheatgrass) concentrations are all in ppm except for Ca, K, and Mg; independent variable (element in soil extract) concentrations are all in ppm; all extractions were on the unground <2mm soil fraction except for "DTPA (ground)," which was on the <2mm fraction ground further to pass a 100-mesh (150μm) sieve, and for "DTPA (sieved)," which was on the <150μm fraction that was separated from the <2mm fraction by dry sieving]

Percent of total variance explained	Soil horizon	Linear multiple regression equation
		DTPA
51	A	Log Na = -2.5 + 0.46 pH + 0.55 log Fe
52	A	Log Cu = -3.7 + 0.40 pH + 0.58 log Fe
58	A	Log Fe = 1.8 - 0.016 plagioclase + 1.4 siderite + 0.30 log Na
59	A	Log Mg = 0.29 - 0.007 plagioclase - 0.57 log K + 0.35 log Zn
60	A	Log K = 0.74 - 0.16 pH - 0.009 plagioclase
62	C	Log Cd = -2.3 + 0.02 CEC + 0.02 calcite - 0.44 log Ni
73	A	Log Ni = -0.87 + 2.3 siderite + 0.79 log Cu + 0.22 log Na - 0.75 log Ni
		DTPA (ground)
52	C	Log Cu = 0.55 - 0.24 C-wb - 0.26 log Fe
57	A	Log Fe = 0.50 + 0.26 water - 0.96 log Cd
59	C	Log Pb = -0.19 + 0.04 dolomite - 0.28 log Ni
60	A	Log K = 0.74 - 0.16 pH - 0.009 plagioclase
61	A	Log Na = -0.33 + 0.19 pH + 0.30 log Na
72	A	Log Cu = -1.2 + 0.10 pH - 0.007 plagioclase + 9.93 siderite + 0.21 log Na
72	A	Log Zn - 1.4 - 0.008 plagioclsse + 0.01 clay-m - 0.34 log Mn
80	C	Log K = 0.66 - 0.05 dolomite - 0.68 log Mn + 0.50 log Ni + 0.74 log Pb
		DTPA (sieved)
52	A	Log Mn = 1.3 - 0.39 log Co - 0.007 sand
60	A	Log Zn = 1.3 - 0.39 log Mn + 0.01 clay-m
61	A	Log Cu = -6.9 + 1.0 log Fe + 0.02 quartz + 0.63 pH
65	A	Log K = 0.73 - 0.27 log Mn + 0.26 log An - 0.13 pH
		EDTA
55	A	Log Pb = -0.76 + 0.02 silt + 1.8 siderite
60	A	Log Cu = -4.3 + 0.52 pH - 0.01 plagioclase + 0.53 log Fe
60	A	Log Zn = 0.08 + 0.01 quartz + 0.02 clay-m
70	A	Log Ca = -1.2 + 0.08 pH - 0.006 plagioclase + 0.52 siderite
74	A	Log K = -1.5 + 0.10 water + 0.02 quartz + 0.37 log Zn

Table 51.--Linear multiple regression equations relating concentrations of elements in wheatgrass to concentrations of elements in soil extracts or total soil plus additional soil physical and chemical properties of both the A and C horizon--continued.

Percent of total variance explained	Soil horizon	Linear multiple regression equation
		Ammonium oxalate ($NH_4C_2O_4$)
60	A	Log K = 0.74 - 0.16 pH - 0.009 plagioclase
60	A	Log Zn = 0.08 + 0.01 quartz + 0.02 clay-m
70	A	Log Ca = -1.2 + 0.08 pH - 0.006 plagioclase + 0.52 siderite
78	C	Log Mn = 1.2 + 0.36 C-wb - 0.13 water - 0.16 log Co
		Magnesium nitrate ($MgNO_3$)
50	A	Log Zn = 1.1 - 0.18 log Mn + 0.008 clay-m
53	A	Log Na = -0.27 + 0.22 log Na + 0.20 pH
65	A	Log K = -0.21 + 0.18 log Zn - 0.009 plagioclase
		Hydroguinine ($C_6H_6O_2$)
52	A	Log K = 0.43 - 0.16 pH + 0.27 C-550
53	A	Log Na = -0.15 + 0.21 log Na + 0.19 pH
63	C	Log Ni = -1.6 - 0.56 log Co + 0.21 log Na + 0.04 K-spar
64	A	Log Mn = 0.74 + 0.42 log Mn - 0.003 sand + 0.12 CO_3-C
		HCL
58	A	Log K = 0.93 - 0.25 log Ni - 0.20 pH
81	A	Log Mn = 1.5 - 0.37 log Fe + 0.26 log Zn + 0.10 CO_3-C
		Total soil
60	A	Log Mn = 1.3 - 0.41 log Ca[1/] + 0.86 log Mg[1/]
64	A	Log K = 1.6 - 0.15 pH + 0.44 C-550 - 0.51 log Mn
68	C	Log Mn = 1.2 + 0.03 K-spar + 1.0 Tot.-C - 0.41 log Ca[1/]

[1/] Concentrations are in percent.

Table 52.--Linear multiple regression equations relating concentrations of elements in biomass to concentrations of elements in soil extracts or total soil plus additional soil physical and chemical properties of both the A and C horizon

[Percentage of the total variance explained by the regression equation is given in the first column; only independent variables significant at the 0.05 probability level are included; for a detailed explanation of the independent variables utilized in the calculation of the regression equation see table 50; dependent variable (element in biomass) concentrations are all in ppm except for Ca, K, and Mg; independent variable (element in soil extract) concentrations are all in ppm; all extractions were on the unground <2mm soil fraction except for "DTPA (ground)," which was on the <2mm fraction ground further to pass a 100-mesh (150μm) sieve, and for "DTPA (sieved)," which was on the <150μm fraction that was separated from the <2mm fraction by dry sieving]

Percent of total variance explained	Soil horizon	Linear multiple regression equation
		DTPA
52	C	Log Ni = -0.30 - 0.10 C-550 + 0.16 log Na
53	A	Log Na = 2.4 - 0.13 pH + 0.15 dolomite + 0.22 log Na
62	A	Log K = 1.7 - 0.23 pH - 0.71 log Mn
		DTPA (ground)
50	C	Log Ni = -0.34 - 0.09 C-550 + 0.16 log Na
52	C	Log Cu = 0.55 - 0.24 C-wb - 0.26 log Fe
55	A	Log Cu = -0.44 + 0.007 quartz - 0.19 log Cd
59	C	Log Pb - -0.19 + 0.04 dolomite - 0.28 log Ni
63	A	Log Ni = -2.0 - 0.66 log Cd + 0.43 log Fe + 0.20 log Na
68	A	Log Na - 1.4 + 0.08 dolomite + 0.28 log Na + 0.18 log Zn
80	C	Log K = 0.66 - 0.05 dolomite - 0.68 log Mn + 0.50 log Ni + 0.74 log Pb
		DTPA (sieved)
52	C	Log Ni - -0.62 + 0.14 log Na - 0.51 Tot.-C
59	A	Log K = 1.2 - 0.22 log Ni + 0.08 dolomite - 0.26 pH
		EDTA
50	A	Log Cu = -0.24 - 0.42 log Cd
63	A	Log Ni = -1.2 + 0.72 calcite - 0.73 log Cd + 0.17 log Fe
74	C	Log Pb = 2.3 + 0.02 dolomite - 0.76 log Ca - 0.62 log Ni
		Ammonium oxalate ($NH_4C_2O_4$)
63	A	Log Cu = -0.23 + 0.008 quartz - 0.13 log Cu
82	A	Log Ni = -0.17 + 0.89 calcite + 0.62 siderite - 0.18 log Ca - 0.25 log Ni + 0.31 log Pb

Table 52.--Linear multiple regression equations relating concentrations of elements in biomass to concentrations of elements in soil extracts or total soil plus additional soil physical and chemical properties of both the A and C horizon--continued

Percent of total variance explained	Soil horizon	Linear multiple regression equation
		Magnesium nitrate ($MgNO_3$)
50	C	Log Ni = -0.58 + 0.12 log Na - 0.53 Tot.-C
52	C	Log K = -0.21 + 0.21 log Co + 0.13 log Ni
55	A	Log K = 0.28 + 0.11 dolomite + 0.009 quartz - 0.20 pH
65	A	Log Ni = -1.3 - 0.27 log Cu + 0.30 log Na + 0.11 dolomite
81	A	Log Na = 0.72 - 0.52 log Cd - 0.20 log Co + 0.23 log Fe + 0.25 log Na + 0.08 dolomite
88	C	Log Pb = 4.2 - 1.1 log Ca + 0.50 log Cd - 0.26 log Mn + 0.13 CO_3-C
		Hydroquinine ($C_5H_5O_2$)
51	C	Log Ni = -0.57 + 0.12 log Na - 0.52 Tot.-C
61	C	Log Cd = -0.82 + 0.58 log Mg + 4.1 log Zn - 0.04 clay-m
69	A	Log Fe = -4.6 + 1.9 log Mg + 0.36 log Na - 5.7 log Zn + 0.01 sand
		HCL
60	A	Log Cu = 0.20 - 0.21 log Cd - 0.009 clay-m
62	A	Log Ni = 3.6 - 1.3 log Ca + 0.47 log Na
		Total soil
50	C	Log Co = -6.7 - 1.2 C-wb + 3.1 log Zn
52	A	Log Cu = 1.2 - 0.64 log Zn
62	A	Log K = -0.03 + 0.01 clay - 1.9 log Fe[1/]
67	C	Log Cd = -0.52 + 0.06 calcite - 0.02 clay-m - 0.98 log Ca[1/]

[1/] Concentrations are in percent.

Table 53.--Linear multiple regression equations relating concentrations of elements in sagebrush to concentrations of elements in soil extracts or total soil plus additional soil physical and chemical properties of both the A and C horizon

[Percentage of the total variance explained by the regression equation is given in the first column; only independent variables significant at the 0.05 probability level are included; for a detailed explanation of the independent variables utilized in the calculation of the regression equation see table 50; dependent variable (element in sagebrush) concentrations are all in ppm except for Ca, K, and Mg; independent variable (element in soil extract) concentrations are all in ppm; all extractions were on the unground <2mm soil fraction except for "DTPA (ground)," which was on the <2mm fraction ground further to pass a 100-mesh (150µm) sieve, and for "DTPA (sieved)," which was on the <150µm fraction that was separated from the <2mm fraction by dry sieving]

Percent of total variance explained	Soil horizon	Linear multiple regression equation
		DTPA
51	C	Log Cu = 1.1 + 0.25 log Zn
51	C	Log Zn = 1.8 + 0.69 log Pb
52	C	Log Fe - 3.2 - 0.03 CEC + 0.39 log Co
57	A	Log Fe = 0.38 + 0.24 pH + 0.60 calcite
57	A	Log Ni = 0.46 + 0.62 log Co
59	A	Log Na = -1.2 - 0.03 K-spar + 1.2 log Mg
72	C	Log Ni = -0.28 - 0.01 clay-m + 0.84 log Fe
75	C	Log Mn = -0.70 + 0.30 pH - 0.64 siderite + 0.41 log Pb
78	A	Log Mg = 0.01 - 0.26 calcite + 0.50 log Cd - 0.30 log K + 0.21 log Mg
83	C	Log Pb = 0.27 - 0.07 water + 0.02 calcite + 0.17 log Co - 0.23 log Cu + 0.12 log Zn
		DTPA (ground)
57	A	Log Fe = 0.38 + 0.24 pH + 0.60 calcite
66	C	Log K = -0.64 - 0.20 log Cd + 0.13 log Fe + 0.14 log K
68	C	Log Fe = 2.2 - 0.02 CEC + 0.61 log K + 0.61 log Zn
77	C	Log Cu = 0.19 - 0.38 siderite + 0.22 log Fe + 0.30 log Mn - 0.25 log Ni
99	C	Log Mn = -2.4 + 0.007 clay - 0.36 C-wb + 0.54 pH - 0.02 dolomite - 0.66 siderite + 0.03 C-om - 0.04 log Na + 0.30 log Ni
		DTPA (sieved)
50	C	Log Cd = -0.39 + 0.76 log Cu - 0.74 Tot.-C
54	A	Log Cu = 0.50 + 0.01 CEC - 0.27 C-wb
55	C	Log Ni = -0.96 + 0.76 log Fe - 0.39 C-wb
56	C	Log Mn = -0.95 + 0.18 log Cd + 0.33 pH
70	C	Log Cu = 0.01 + 0.31 log Fe + 0.29 log Mn - 0.22 log Ni

Table 53.--Linear multiple regression equations relating concentrations of elements in sagebrush to concentrations of elements in soil extracts or total soil plus additional soil physical and chemical properties of both the A and C horizon--continued

Percent of total variance explained	Soil horizon	Linear multiple regression equation
		EDTA
57	A	Log Fe = 0.38 + 0.24 pH + 0.60 calcite
78	C	Log Ni = 0.14 - 0.41 C-550 + 0.38 log Cu + 0.26 log Fe
95	C	Log Mn = -0.01 + 0.17 water + 0.32 pH - 1.4 siderite + 0.59 log Co - 0.43 log K - 0.37 log Pb
		Ammonium oxalate ($NH_4C_2O_4$)
57	A	Log Fe = 0.38 + 0.24 pH + 0.60 calcite
59	A	Log Ni = -1.7 + 0.64 log Fe
60	A	Log Cd = -0.87 + 1.6 log Co - 0.77 log Ni
61	C	Log K = -0.78 + 0.02 log Ca + 0.27 log Mg
66	C	Log Mn = -0.85 + 0.29 pH - 0.97 siderite
		Magnesium nitrate ($MgNO_3$)
51	A	Log Cu = 0.94 + 0.30 log Cd + 0.13 log Na
56	A	Log Fe = -1.8 + 0.43 log Mn + 0.48 pH
57	A	Log Ni = -0.37 + 0.14 water - 0.14 CO_3-C
64	C	Log Cd = -1.2 - 0.39 log Pb + 0.02 CEC - 0.42 Tot.-C
64	C	Log K = -1.7 + 0.04 log Na - 0.79 log Zn + 0.12 Org-C
		Hydroquinine ($C_6H_6O_2$)
57	A	Log Ni = -0.37 + 0.14 water - 0.14 CO_3-C
65	A	Log Mn = 0.65 - 0.59 log K + 0.44 log Mg + 0.60 log Mn
		HCL
67	A	Log Ni = 0.50 - 0.44 log K + 0.19 water - 0.19 CO_3-C
78	A	Log Cu = 0.42 - 0.26 log Pb + 0.01 CEC - 0.04 CO_3-C - 0.30 C-wb
		Total soil
68	C	Log Mn = -0.89 + 0.23 pH + 0.49 log Cu
69	A	Log Ni = 0.16 + 0.15 water - 0.10 CO_3-C - 1.4 log K[1]

[1] Concentrations are in percent.

Table 54.--Relative importance of independent variables used in linear multiple regression analysis

[Importance values incorporate both the weighted impact of a particular independent variable on the regression equation and the frequency of occurrence of that variable in a given extract within a given soil horizon; importance values were calculated by multiplying the normalized standard partial regression coefficient for a variable by the number of times the variable occurred in separate equations in an extract within a soil horizon; for a detailed explanation of the independent variables used, see table ; all extractions were on the unground <2mm soil fraction except for "DTPA (ground)", which was on the <2mm fraction ground further to pass a 100-mesh (150µm) sieve, and for "DTPA (sieved)", which was on the <150µm fraction that was separated from the <2mm fraction by dry sieving]

Soil extract, or total soil	Importance ranking of independent variables, by soil horizon				Soil extract, or total soil	Importance ranking of independent variables, by soil horizon			
	A horizon		C horizon			A horizon		C horizon	
				Wheatgrass					
DTPA (ground)	pH	4.71	dolomite	1.76	DTPA	pH	5.46	CEC	0.38
	plagioclase	2.49	Ni	1.32		plagioclase	2.97	Ni	.34
	Na	1.54	C-wb	.57		Fe	1.56	calcite	.28
	water	.52	Fe	.43		siderite	1.36		
	Cd	.48	Mn	.30		Na	.92		
	clay	.47	Pb	.16		Zn	.45		
	Mn	.28				K	.36		
	siderite	.18				Ni	.32		
						Cu	.24		
DTPA (sieved)	pH	1.74	(no important variables)		EDTA	siderite	1.70	(no important variables)	
	Mn	1.34				pH	1.68		
	sand	.65				quartz	1.46		
	clay	.58				plagioclase	.86		
	Zn	.38				clay	.68		
	Fe	.36				silt	.49		
	Co	.35				Fe	.39		
	quartz	.14				Zn	.36		
						water	.22		
Ammonium oxalate	pH	1.88	C-wb	.38	Magnesium nitrate	Zn	.71	(no important variables)	
	plagioclase	1.44	Co	.35		pH	.59		
	clay	.68	water	.26		clay-m	.54		
	siderite	.34				Mn	.46		
	quartz	.32				Na	.41		
						plagioclase	.29		
Hydroquinone	pH	2.42	Na	.39	HCl	pH	.64	(no data)	
	Na	.43	Cd	.37		Fe	.49		
	CO_3-C	.40	K-spar	.24		Ni	.36		
	C-550	.36				Zn	.36		
	Mn	.32				CO_3-C	.15		
	sand	.28							
Total soil	Mg	.66	tot-C	.54					
	pH	.38	Ca	.31					
	C-550	.37	K-spar	.15					
	Ca	.34							
	Mn	.25							
				Biomass					
DTPA (ground)	Cd	1.72	dolomite	1.76	DTPA	pH	1.58	C-550	0.58
	Na	1.58	Ni	1.32		Mn	.45	Na	.42
	quartz	.57	C-wb	.57		dolomite	.43		
	Fe	.35	Fe	.43		Na	.30		
	dolomite	.29	Mn	.30					
	Zn	.24	Pb	.16					
DTPA (sieved)	pH	.52	tot.-C	.63	EDTA	Cd	.41	Cd	.39
	dolomite	.25	Na	.38		CO_3-C	.34	Ni	.37
	Ni	.23				Fe	.25	dolomite	.26

Table 54.--Relative importance of independent variables used in linear multiple regression analysis--continued.

Soil extract, or total soil	Importance ranking of independent variables, by soil horizon: A horizon		C horizon		Soil extract, or total soil	Importance ranking of independent variables, by soil horizon: A horizon		C horizon	
Biomass (cont.)									
Ammonium oxalate	quartz	0.55	(no important variables)		Magnesium nitrate	dolomite	2.31	tot.-C	0.65
	Cu	.45				Na	1.06	Co	.55
	Ca	.25				Cu	.48	Ni	.45
	CO_3-C	.25				pH	.42	Ca	.42
	Ni	.23				quartz	.23	Na	.35
	Pb	.16				Fe	.22	Cd	.20
	siderite	.11				Cd	.18	CO_3-C	.20
						Co	.15	Mn	.18
Hydroquinone	Mg	.36	tot.-C	0.63	HCl	clay-m	.64	(no data)	
	Zn	.24	clay-m	.40		Ca	.56		
	sand	.22	Zn	.39		Na	.44		
	Na	.18	Na	.37		Cd	.36		
			K	.21					
Total soil	Zn	1.0	Zn	.56					
	Fe	.64	Ca	.47					
	clay	.36	C-wb	.44					
			calcite	.39					
			clay-m	.14					
Sagebrush									
DTPA (ground)	pH	.60	Fe	.96	DTPA	Mg	1.66	Pb	4.50
	CO_3-C	.40	siderite	.44		CO_3-C	1.14	Cu	2.46
			Cd	.42		Co	1.0	Fe	.62
			Cu	.35		Zn	.60	CEC	.58
			Mn	.32		Cd	.41	pH	.50
			K	.29		K-spar	.37	Co	.42
			pH	.27		K	.22	clay	.38
			C-wb	.14				siderite	.25
			Ni	.13				calcite	.24
			Pb	.11				Zn	.15
			clay	.10				water	.13
DTPA (sieved)	CEC	.59	Fe	1.74	EDTA	Fe	.60	Cu	.45
	C-wb	.41	pH	.62		CO_3-C	.40	C-550	.28
			Ni	.43				Fe	.27
			Cd	.38				pH	.24
			C-wb	.38				siderite	.24
			Mn	.32				Co	.20
								water	.14
								K	.11
								Pb	.07
Ammonium oxalate	Fe	1.0	Mg	.65	Magnesium nitrate	Fe	.65	Zn	.51
	pH	.60	pH	.56		Na	.56	Pb	.40
	Co	.58	siderite	.44		water	.53	CEC	.30
	Ni	.42	Ca	.35		CO_3-C	.47	tot.-C	.30
	calcite	.40				Cd	.44	Na	.26
						Mn	.35	org.-C	.23
Hydroquinone	water	.53	(no important variables)		HCl	water	.41	(no data)	
	CO_3-C	.47				CO_3-C	.38		
	K	.40				K	.21		
	Mn	.34							
	Mg	.26							
Total soil	water	.46	Cu	.51					
	CO_3-C	.29	pH	.49					
	K	.25							

Depending on the extract, just about as many important variables were found for the biomass relations in the A- as in the C-horizon soils. No one variable demonstrated dominance across all extracts except that, as with wheatgrass, pH and soil mineralogy occurred quite often. Within a given extract no one variable occurred with any great degree of frequency, thus the relative importance values are small. (3) The greatest number of variables associated with sagebrush were in the C-horizon relations. The presence of pH and extractable Fe and Pb, as well as a variety of other extractable metals, occurred most frequently in the equations. (4) In general, for all plant materials, the greatest number and variety of independent variables were associated with the relations involving the chelates DTPA and EDTA.

Concerning tables 51, 52, and 53 several observations are made: (1) the more mild extractants (the chelates DTPA and EDTA and the neutral salt magnesium nitrate--see table 47) gave the greatest number of significant multiple regression relations. (2) In general, the equations for a given dependent variable were nearly the same between extracts. For example, in the equations involving wheatgrass, the prediction equations for Na were almost identical between extracts. Also in the wheatgrass equations, every time plagioclase occurred in the equation its regression coefficient was nearly the same and its relation to the dependent variable was always negative.

RECOMMENDATIONS AND SUMMARY

This study utilized six soil extracts (one of which, DTPA, was used to extract three different soil preparations), two soil horizons, three native plant materials, and a broad range of uncultivated soils with different chemistries and physical properties in order to evaluate the usefulness of soil extracts in predicting soil-plant element transfers. Prediction equations utilizing both simple linear regression and multiple linear regression are presented for significant relations involving all extracts. The equations have not, however, been verified by an independent sampling program. Further, the multiple regression equations contain some independent variables that are not routinely determined in soils; therefore, in addition to the linear regression equations, those multiple regression equations with extracted elements and commonly analyzed chemical and physical soil properties will be most useful. The prediction equations should be used only for washed western wheatgrass, biomass, and silver sagebrush and only if the same methods of soil sample preparation and analysis are employed. These methods, however, are common in the literature and are referenced in Severson and others, 1977, and on pages 88-91 of this report.

Mineralogy of Shale in the Fort Union Formation in outcrop in the Northern Great Plain Coal Province

by James M. McNeal and Richard J. Ebens

Introduction

The Northern Great Plains coal Province extends from central North Dakota and northwestern South Dakota westward to east central Montana, and southward to the Powder River Basin of northwestern Wyoming, and southeastern Montana (fig. 39). This province contains very substantial quantities of low-sulfur, thick-bedded lignite in Montana and North and South Dakota, and extremely thick-bedded subbituminous to bituminous coal in the Powder River Basin. The coals occur in the Paleocene Fort Union Formation, which consists largely of interbedded fine sandstone, siltstone, and claystones deposited in a delta-floodplain-floodbasin-environment. As the bulk of the coals are strippable, information on the mineralogy of the rocks would be useful in determining potential hazardous effects of the overburden in spoil piles.

A suite of shale samples was collected from outcrops of the Fort Union Formation throughout the Northern Great Plains Coal Province. The sample design is described in U.S. Geological Survey (1976, p. 94-100) and the summary of geochemistry is given in U.S. Geological Survey (1977, p. 185-197). This report gives the results of a mineralogical examination of the shales.

Sample Design and Analytical Procedures

The samples were collected according to an unbalanced, nested analysis of variance design (Fig. 38). The design consists of seven levels, five of which are geographic, one of which is stratigraphic and one of which is analytical. The geographic levels examine variability at 200, 100, 50, 25, and 5 km intervals. The stratigraphic level represents variation between two samples collected at a sample site. A sampling site consists of a randomly selected outcrop within a 5-km cell (Fig. 39). Analytical error was estimated by randomly selecting 20 of the 60 samples for duplicate analysis. To circumvent systematic error, all 80 samples were placed in a randomized sequence prior to preparation and analysis.

The samples were prepared by crushing in a jaw crusher and were ground to less than 100 mesh by a ceramic plate grinder. Well-mixed portions of the sample were then hand-ground in a ceramic mortar and pestle for three minutes after no coarse material remained. The samples were packed into an aluminum holder and cover. The cover placed a grid texture on the surface of the sample. This preparation procedure was devised by L. Schultz (1977, personal communication). The samples were X-rayed on a standard X-ray diffraction unit with the data being put on chart-paper and magnetic tape. A computer program written by J. Hathaway (1974, personal communication to Schultz) and revised by

Schultz was used to analyze the data.

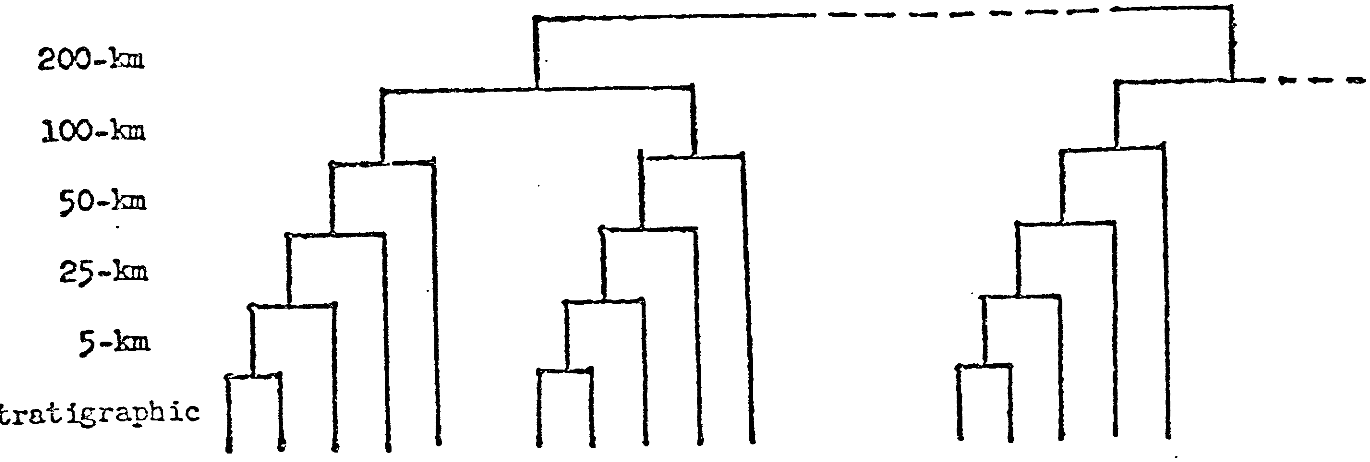
Results

The results of the analysis of variance design and summary statistics are given in Table 55. All data were logarithmically transformed prior to any computational analysis. For the analysis of variance computations, values below the detection limit of 0.1 were changed to 0.07. The geometric mean of the summary statistics was calculated by the method of Cohen (1959) for censored data.

The analysis of variance shows that only plagioclase and pyrite exhibit significant variation among the 200-km cells. The large components for plagioclase (56.0% of the total) at this level clearly reflects the extremely low concentration in the southernmost cell (Fig. 40). This result may be related to the distance from the source area of the plagioclase. Sodium is also very low in this same cell (Ebens and McNeal in USGS, 1977, Fig. 28, p. 92), suggesting that most of the Na in these rocks occurs in plagioclase. In addition, plagioclase and dolomite exhibit a relatively large percentage of their total variance at (>40%) at scales of 100 km or larger, and quartz and microcline exhibit greater than 60% of their total variances at scales of 50-100 km. Thus, four of the common rock-forming minerals--quartz, microcline, plagioclase, and dolomite--vary substantially over large-scale (>50 km) distances in these rocks.

The large analytical error in pyrite, and gypsum (and perhaps siderite) is probably due to low detection ratios for these minerals. The analytical error is relatively small for dolomite, calcite, quartz, clay, microcline, and plagioclase.

The variance components for the local levels (25-km and 5-km cells and stratigraphic level) tend to be moderately small and indicate that the clay, calcite, and dolomite content of these rocks is largely influenced by local effects. In particular, variation in calcite and dolomite may reflect the degree of weathering. None of the variance components at the stratigraphic level is particularly high, even though five minerals had variance components of greater than 10%.



Level	Source of variation	Number of units at each level	Degrees of freedom
1	Between 200-km cells	6	5
2	Between 100-km cells	12	6
3	Between 50-km cells	24	12
4	Between 25-km cells	36	12
5	Between 5-km cells	48	12
6	Stratigraphic	60	12
7	Laboratory	80	20

Figure 38.--Analysis of variance scheme for sampling shale and sandstone of the Fort Union Formation in outcrop.

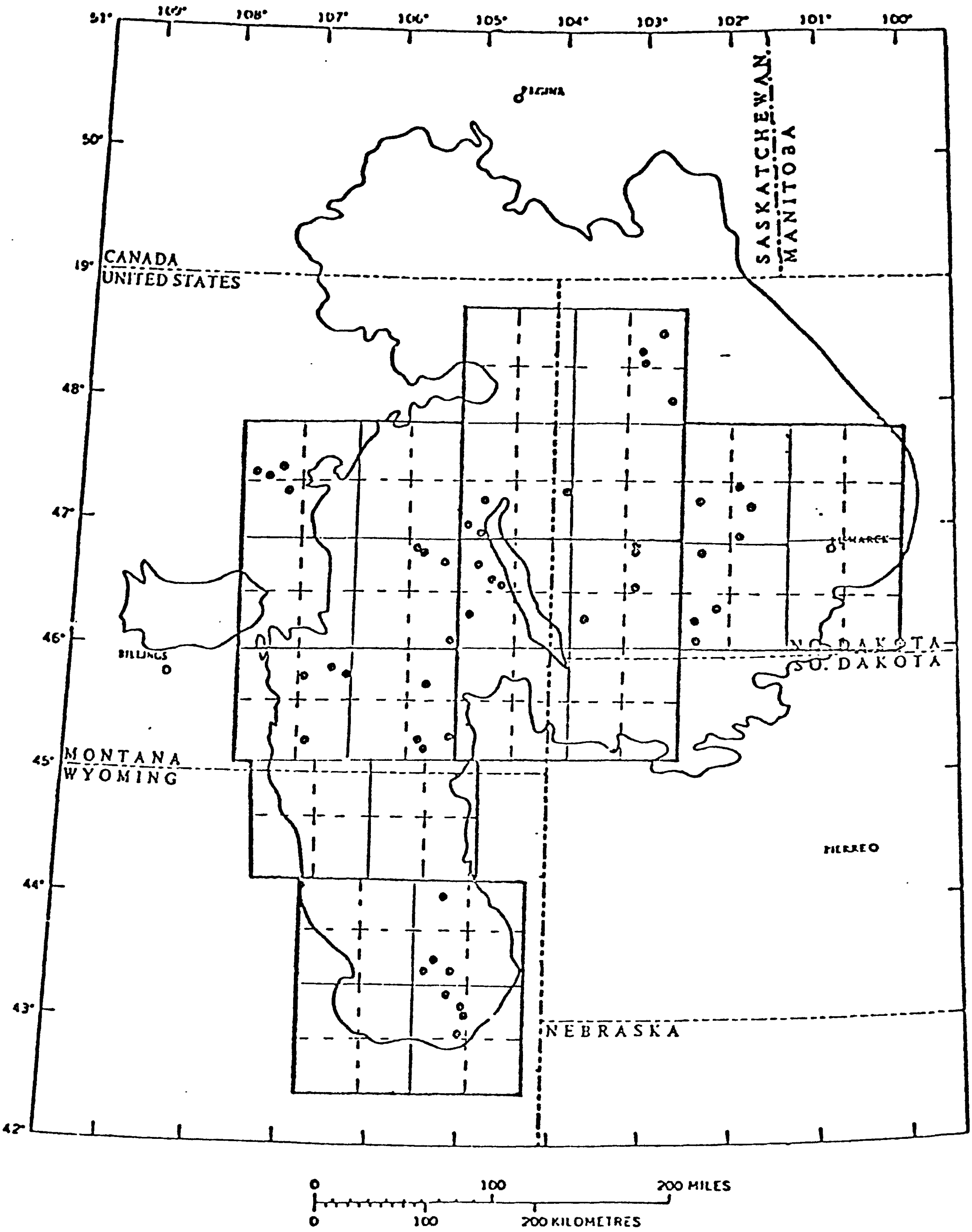


Figure 39.--Sampling localities of shale and sandstone of the Fort Union Formation in the Northern Great Plains Coal Province. Large squares are 200 km on a side; intermediate squares, 100 km; and small squares, 50 km. Dots indicate sampling localities. Map adapted from U.S. Geological Survey (1974a) and Whitaker and Pearson (1972).

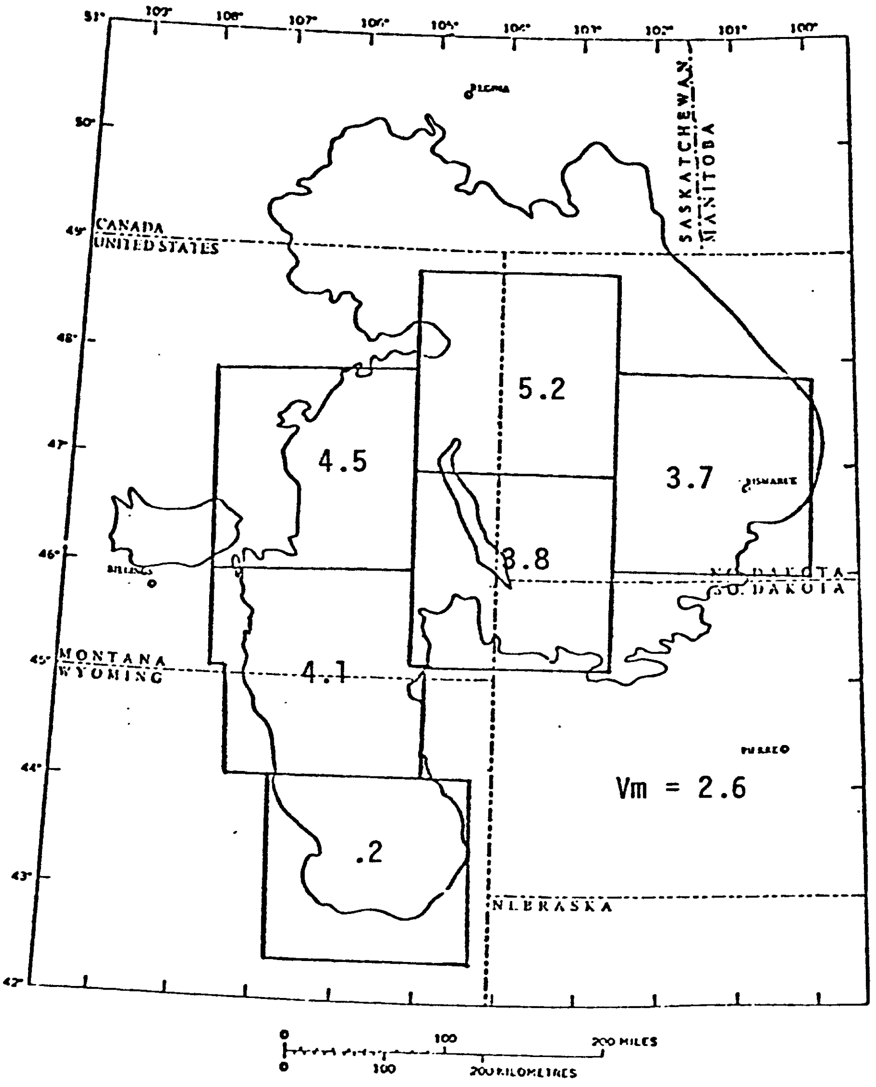


Figure 40.--Regional distribution of plagioclase in shale of the Fort Union Formation. Values are geometric means of 200-km cells and are given in percent.

Table 55.--Statistical analysis of the mineralogy of outcrop shale of the Fort Union Formation, Northern Great Plains Coal Province.

n.d., not determined; data are given in percent; an asterisk (*) indicates variance component is significantly different from zero at the 0.05 probability level

Mineral	Analysis of logarithmic variance									Summary Statistics				
	Total $\log_{10}$ variance	Variance components as percent of the total variance							Detection ratio	Geometric mean	Geometric deviation	Observed Range		Detection ratio
		Between 200-km cells	Between 100-km cells	Between 50-km cells	Between 25-km cells	Between 5-km cells	Strati- graphic	Analytical error				Minimum	Maximum	
Quartz-----	.0207	.0	.0	6.48*	2.5	2.7	27.8*	2.2	80:80	29.9	1.30	14.4	56.9	60:60
Clay-------	.0222	.0	16.5*	11.1	38.6*	17.4	14.0*	2.3	80:80	49.5	16.7	16.7	76.4	60:60
Plagioclase	.6679	56.0*	.0	3.2	.0	24.7*	4.4	11.7	67:80	4.2	1.96	0	10.8	52:60
Microcline-	.4762	.2	.0	74.1*	.0	19.7*	.5	5.6	76:80	3.2	1.57	0	9.8	56:60
Calcite----	1.0831	.0	17.3	.0	33.9*	22.3	24.9*	1.7	34:80	3.6	2.83	0	28.0	28:60
Dolomite---	1.2921	10.4	33.1*	3.2	.0	40.1*	12.0*	1.2	49:80	5.2	3.70	0	23.7	40:60
Siderite---	.3093	21.1	2.7	.0	21.1	6.8	27.6*	20.8	46:80	.6	1.60	0	1.3	36:60
Gypsum-----	.4630	.0	10.0*	7.3	10.0	21.0	5.6	46.2	18:80	2.0	2.21	0	7.3	11:60
Pyrite-----	.6827	7.0*	.0	5.0	.0	22.3	.0	65.8	20:80	1.9	1.39	0	3.0	18:60

Overburden Chemistry and Mineralogy at Hanging Woman Creek, Big Horn County, Montana, and Recommendations for Sampling at Similar Sites

by

Todd K. Hinkley, Richard J. Ebens, and Josephine G. Boerngen

Introduction

At potential coal mine sites in the Fort Union Formation which underlies a coal region of western North America, it is unknown whether there may be significant quantities of materials in the overburden rock which, after disturbance and replacement, could release toxic elements to plants, grazing animals, ground water or surface drainage. This study has two goals: first, to characterize the chemical and mineralogical composition of the various types of rocks which overlie the coal at the Hanging Woman Creek site (Montana) to determine whether potentially harmful materials are present; and second, to predict the intensity of sampling needed at this or other similar coal mine sites to estimate with acceptable confidence the likelihood of encountering rocks that contain these potentially harmful materials.

The overburden rocks in the Hanging Woman Creek site rocks are characterized by a very abrupt and complete changeability of lithic types over very short vertical distances in some portions of the section, in contrast to thick, nearly homogeneous layers of both sandstone and finer-grained rocks present in other parts of the section. The strata at the site, except for the coal itself and its immediately overlying fine-grained units, do not have great lateral continuity; there is considerable lateral thinning, interfingering, and termination of units of various lithic types. Based on stratigraphic correlation among five drill cores, the units may have greater lateral continuity north and south than in other directions. For a complete discussion of areal geology, structure, and stratigraphy in the Creek site, the reader is referred to Culbertson and others (1978).

SAMPLING AND ANALYSIS

Cores (size "nx") from five holes, drilled through all overburden and the thick Anderson coal (one hole drilled deeper, through the lower Dietz coal), ranged in length from 40 to 80 meters. Holes were spaced so that the minimum and maximum distances between holes were about 1 km, and 4 km, respectively. Four samples of each of three rock types were taken from four of the holes, and some "special" samples were taken from all five holes. The following rock types were sampled:

(1) sandstone
(2) siltstone and shale
(3) very dark colored or black shale

This classification was chosen because the three groups were expected to be chemically and mineralogically distinct. Furthermore, the chemical and mineralogical data would allow an assessment of the ability of geologists to assign correct rock names by hand specimen examination of rocks from what is, overall, a very fine grained, interstratified rock sequence. We assigned names on the basis of visual inspection of the hand specimens, often in consultation with other geologists familiar with these sedimentary rocks. Footage locations for sampling the three rock types were chosen randomly. The "special" samples were taken subjectively.

Samples were analyzed in the analytical laboratories of the U.S. Geological Survey in Lakewood, Colorado. The rocks were ground to finer than 100 mesh in a ceramic mill by R. E. McGregor. Samples were analyzed by emission spectrography for Ag, As, B, Ba, Be, Cd, Ce, Co, Cr, Cu, Ga, La, Mo, Ni, Pb, Sc, Sn, Sr, V, Y, Yb, Zn, and Zr by K. E. Horan; by atomic absorption for Mg and Na by V. M. Merritt and for Li and Zn by J. G. Crock; by delayed neutron activation for U and Th by H. T. Millard, Jr., C. L. Shields, C. M. Ellis, R. L. Nelms, and C. A. Ramsey; by X-ray fluorescence for Al, S, Ca, Si, Fe, K, Mn, and Ti, and for Sn, Ge, As, and Se (sulfide method), by J. S. Wahlberg, W. J. Walz, J. W. Baker, and M. L. Tuttle; by gravimetry for ash content (525 degrees C) by G. D. Shipley; by combustion-thermal-conductivity detection for total C, by gasometry for carbonate C, and by difference for organic C by P. H. Briggs; by wet oxidation plus atomic absorption for Hg by J. A. Thomas; and by meter for pH by G. O. Riddle. For X-ray determination, the samples were further hand-ground in an agate mortar, and the mineral composition was quantitatively determined by M. P. Pantea, using a load-packing technique and a computer method developed by L. G. Schultz to convert peak area to mineral concentration. All samples were analyzed in a random order to neutralize effects of any systematic changes in the analytical methods.

RESULTS

Chemical and mineralogical data are presented in a summarized graphical form in figures 41 and 42, respectively. In these logarithmically scaled plots an average value (geometric mean for chemistry and arithmetic mean for mineralogy) is shown for each parameter for each of the three rock types. For the chemical data (Fig. 41) bars extend to higher and lower values from the central average to show the range of concentration within which 19 of 20 samples from the same rock type could be expected to fall; this range was calculated from the variance of the geochemical data. For the mineral data, the bars represent observed ranges.

A full tabulation of the chemical and mineralogical data for each of the 108 samples (24 sandstone, 24 siltstone or shale, 23 dark shale, 37 special samples) is given in the appendix of Hinkley, Ebens and Boerngen, 1978).

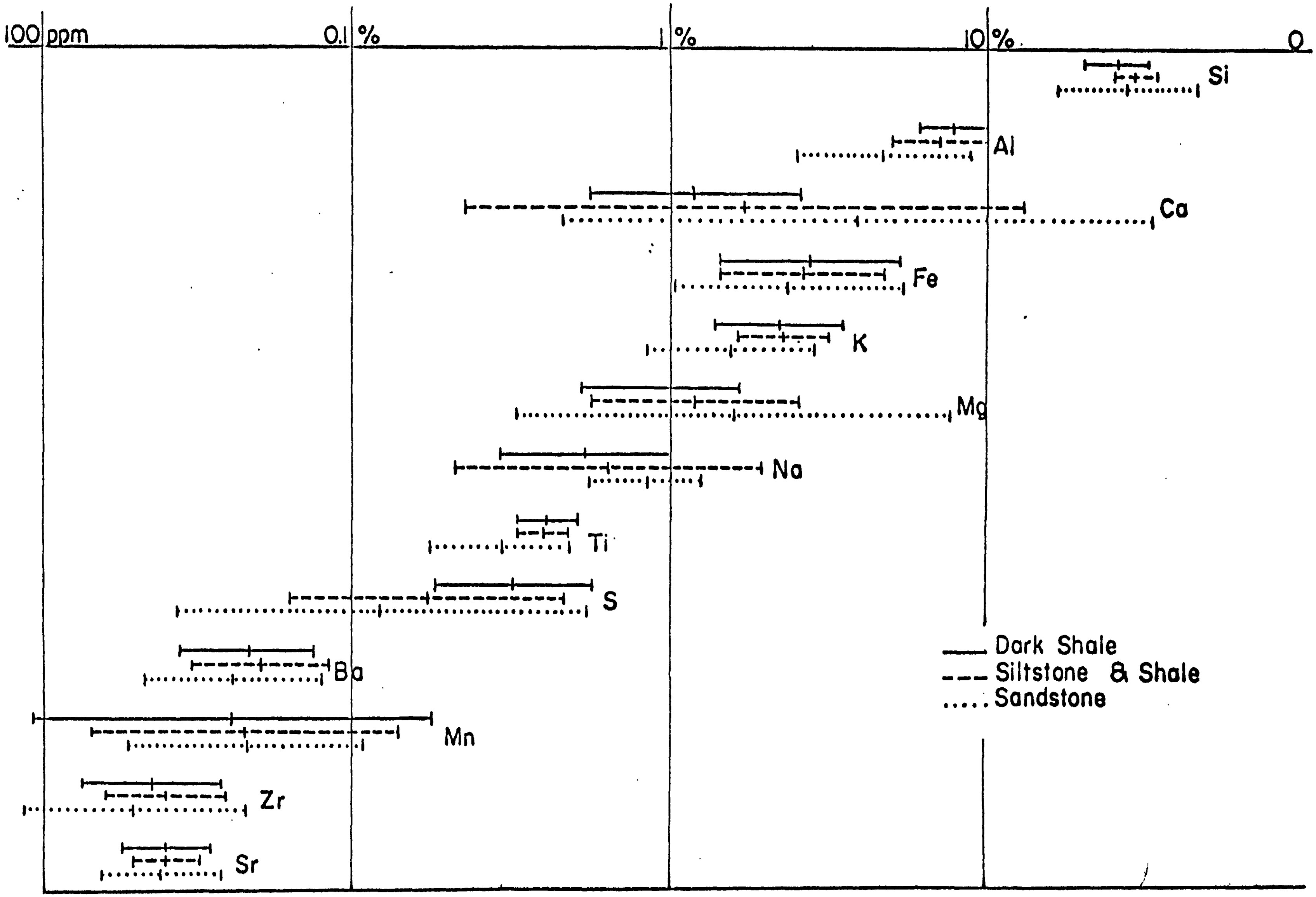


Figure 41.--Averages and expected ranges of elements by rock types, Hanging Woman Creek Site overburden rocks.

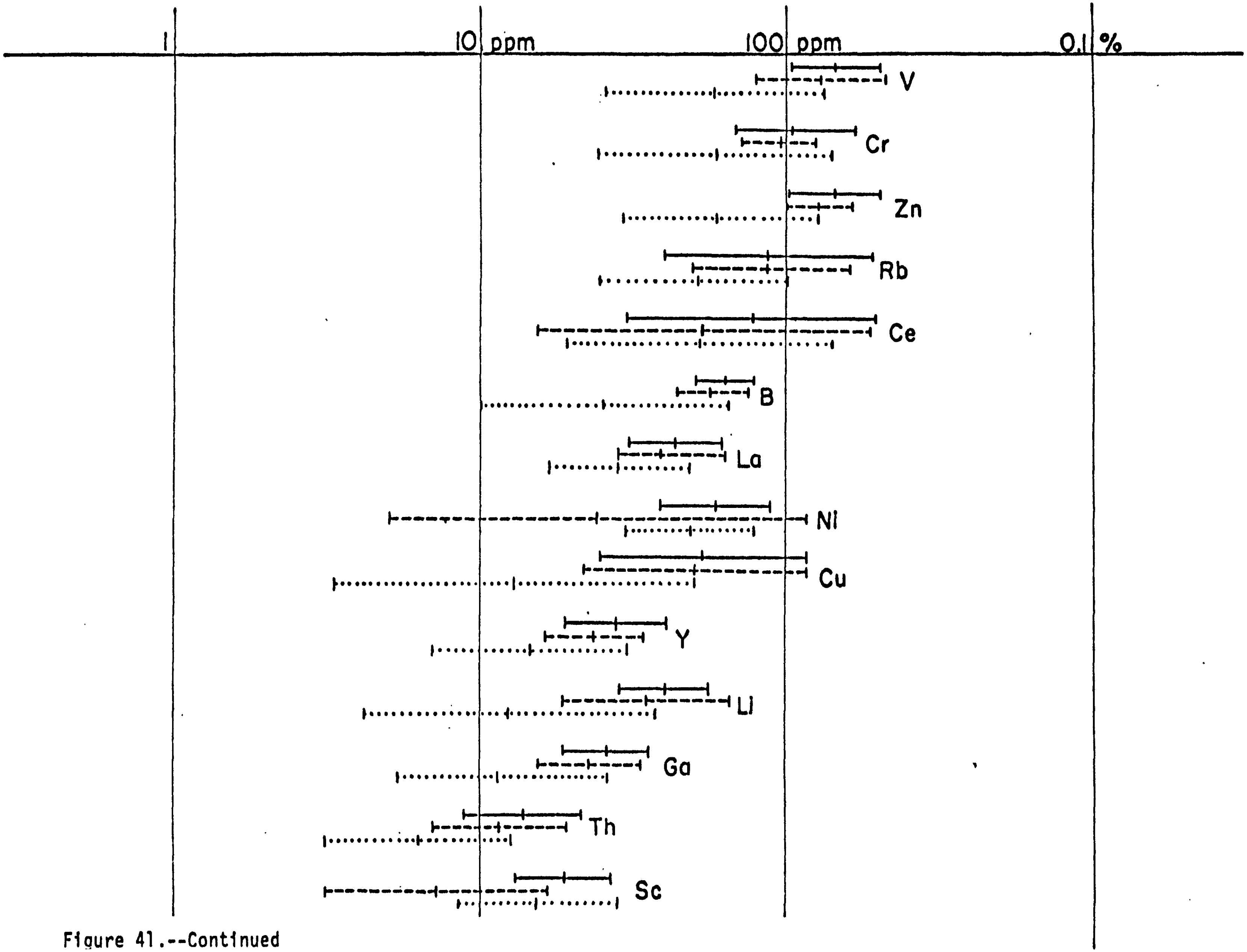


Figure 41.--Continued

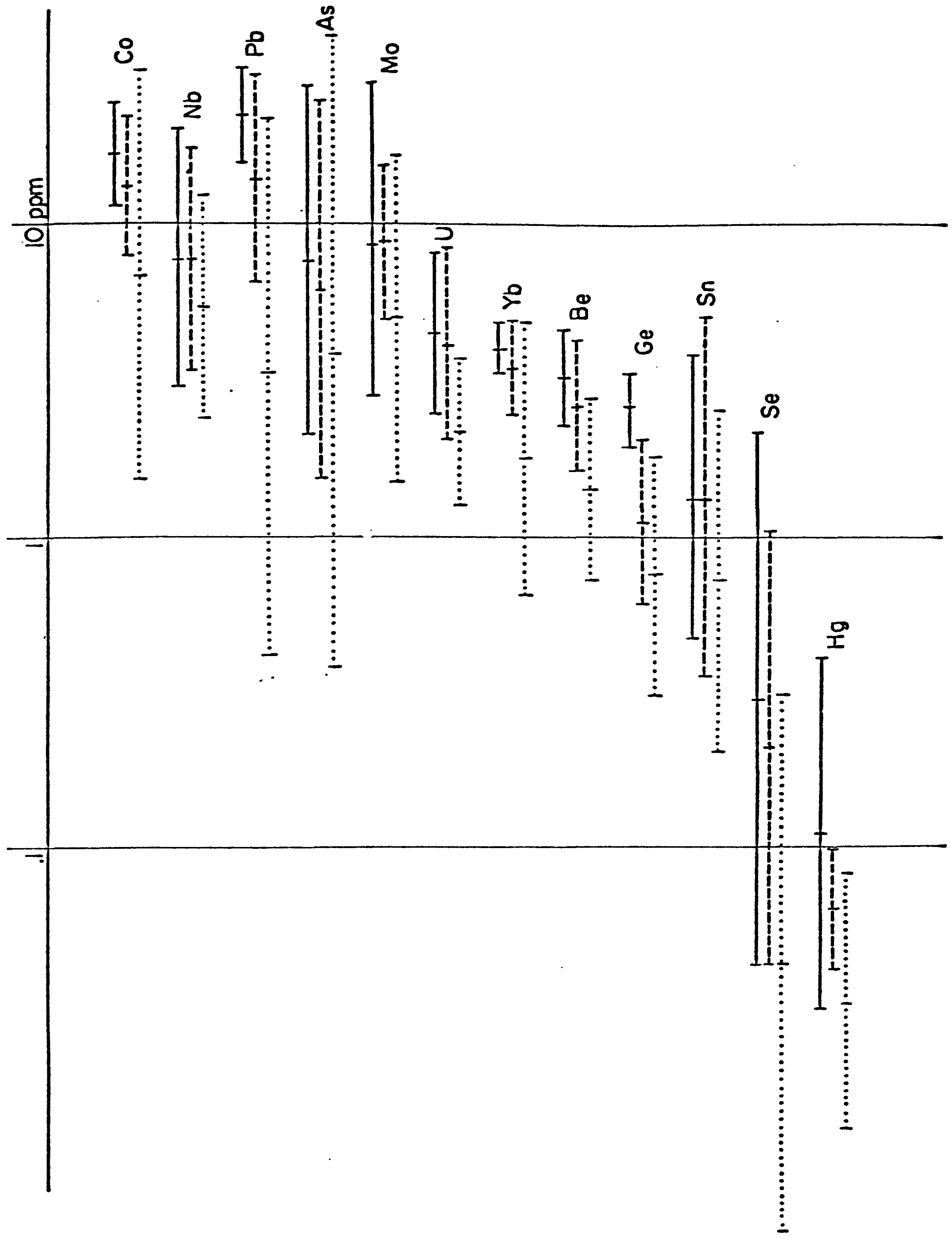
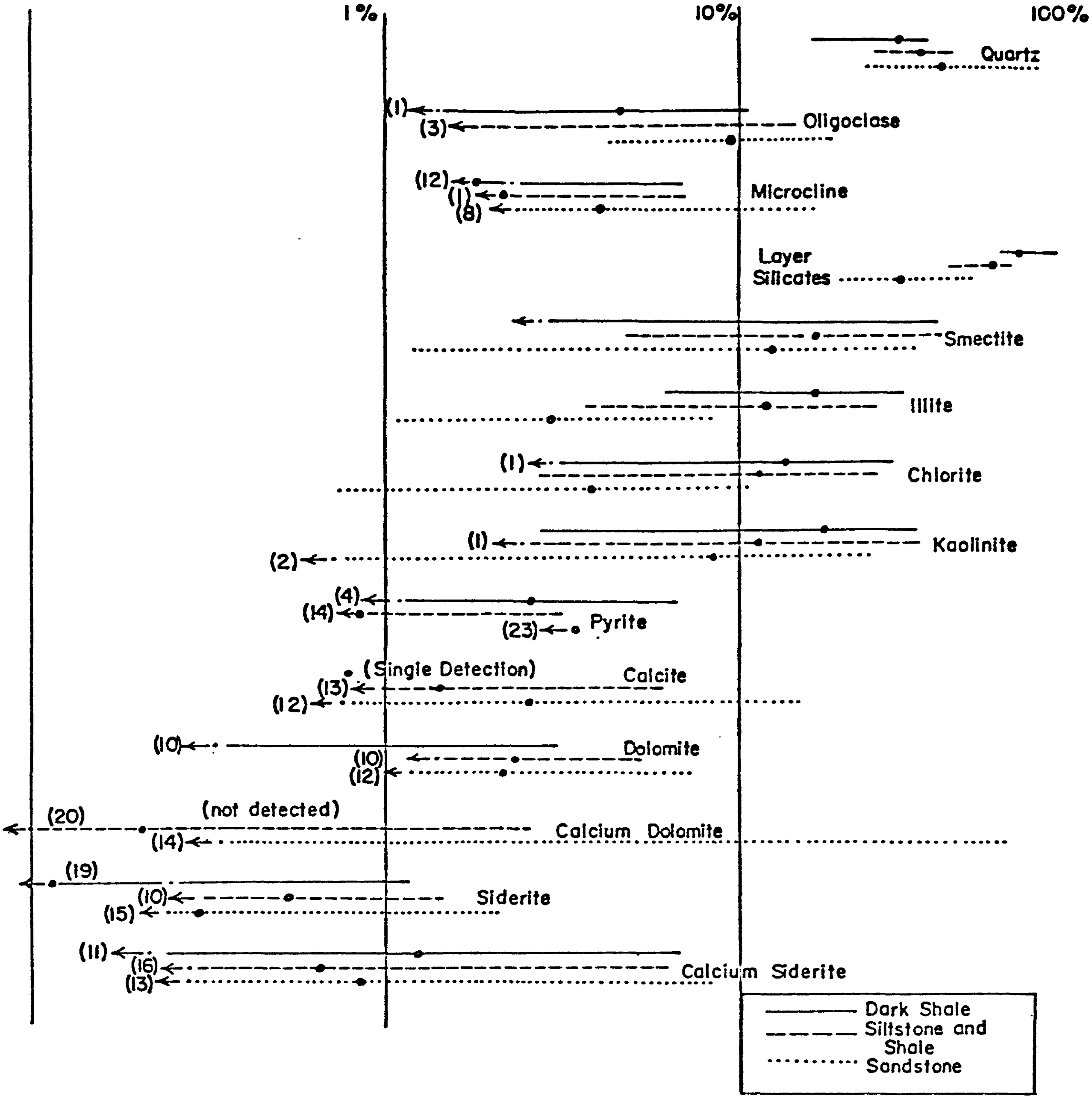


Figure 41.--Continued



(Central value on each bar is arithmetic average, extremes represent observed range. The number of samples in which the mineral was not detected (if any) is shown in parentheses at the left end of each plotted line; in such instances, the lowest detected value is marked as a small dot interrupting the line.)

Figure 42.--Averages and ranges of minerals by rock types, Hanging Woman Creek EMRIA site.

The chemical and mineral data were subjected to analysis of variance in order to determine whether the largest part of the variation in the data is due to 1) the distance between the drill holes from which the samples were taken, 2) distance between samples within the drill holes, or 3) analytical error in the laboratory. This analysis of variance was done, most importantly, to estimate how many drill holes and samples for analysis would be necessary for similar studies in the future. For example, if only a small amount of the total variance in the data reflects variation among the five cored holes from which the samples are taken (that is, if all holes tend to be chemically equivalent), then fewer drill holes may be needed in future studies of areas where the subsurface geology can be reasonably well predicted. As another example, if a large share of the total variance is attributable to differences among rock types and there is only small variance among all samples within that rock type, it may be possible to predict the chemistry of a rock type with acceptable confidence by visually classifying a hand specimen.

Discussion

The first question in this study is the following: Could an assessment of the Hanging Woman Creek site overburden rock have been made with less sampling and fewer analyses? The answer is yes if:

(A) the chemical and mineralogical data, by rock types, is constant across the study area (between the drilled holes).
(B) the rocks in a single name type (sandstone; siltstone-plus-shale; dark shale) are distinct in their composition.

Further on, we will discuss whether it is possible to extrapolate the sampling needs determined at this site to other sites in the Fort Union coal region.

The second question in this study is: Does the overburden rock contain significant volumes of chemically or mineralogically undesirable material which should not be used as soil material on the reclaimed site? Because of the general absence of widely accepted guidelines on what constitutes "undesirable" material, a tentative answer to this question can come only from a chemical and mineralogical comparison of the rock material of this study with soil material which successfully supports the native vegetation both at this site and at other places in the region.

Analysis of variance and spatial scale of chemical variation.--Table 56 presents the components of variation estimated for each rock type. The magnitude of the data in the left-hand column ("total log 10 variance") roughly correlates with the length of the bars in Figure 41 that represent the spread of concentration values for an element. The three data columns to the right of that--showing variation between holes, within holes, and between analytical duplicates (laboratory errors)--list the percentage of the total variance which is attributable to each of these three sources.

The largest share of variation in most elements is between the samples taken within a single hole. The small values in the "between holes" column for most elements indicate that the total spread of values was increased only very little by sampling from multiple holes compared to what it would have been if samples had been taken from only one of the holes. In fact, only copper and cerium in the siltstone-plus-shale, and silicon, calcium, and germanium in the sandstone showed significant variation between holes or, in other words, significant differences across the study site. A large share of the variance for some elements that are present in low concentrations or that are difficult to measure appears in the "between analytical duplicates" (laboratory error) column and represents the differences in reported values of samples which were physically divided in half and submitted to the laboratory as two splits in random sequence, with all of the other samples.

The distribution of the three components of total variance discussed above shows clearly that very nearly as much information about the range in composition of the Hanging Woman Creek rocks could have been obtained if only a single hole had been sampled; or, to put it another way, there would have been only a very slight risk of missing rocks of unusual geochemistry by sampling only one hole.

Chemical distinctiveness of the three rock types.--The ternary plot of Figure 43 shows that there is a general chemical separation of the three rock types, but with considerable overlap (see also Table 56 and Figure 41). The eight trace elements (top corner of the plot) tend to be more abundant in dark shale and siltstone-plus-shale than they are in sandstone, but the dark shale is only somewhat higher in these elements than the siltstone-plus-shale.

Sandstone and siltstone-plus-shale samples have compositions indicating that both rock types contain a mixture of quartz and feldspar grains. In a sedimentation environment where greater amounts of energy had been available, it might be expected that the two minerals would be separated by mechanical winnowing and segregated into characteristic size ranges. However, in the relatively low-energy environment of the deposition of sediments of the Fort Union Formation, both quartz and feldspar grains of all sizes were dumped in the basin, and neither sufficient mechanical energy nor time for extensive weathering were available to alter the original, mixed compositional relationships. It may be tentatively assumed that the feldspar-rich sandstone of the Fort Union, if used as soil material, would be better able to provide minor and trace elements necessary to plants than would more quartz-rich sandstone common in other regions.

The overlap in chemical composition between dark shale and siltstone-plus-shale is consistent with the fact that the two types of shale exist in continuous variation in the cores, commonly changing over small vertical distance. Mineralogical data for the three rock types

Table 56.--Statistical summary of the chemical composition of each of three rock types of overburden rock (Fort Union Formation) at Hanging Woman Creek EMRIA site.

		Variance component as percent of total				Summary statistics					
	Total $\log_{10}$ variance	Between holes	Between samples within holes	Between analytical duplicates	Detection Ratio	Geometric mean (ppm except as noted)	Geometric deviation	Observed range Minimum (ppm except as noted)	Observed range Maximum (ppm except as noted)	Expected range of 95 percent of samples Minimum	Expected range of 95 percent of samples Maximum
Part A: Sandstone											
Si, percent----	0.0112	39*	60*	1	24:24	27.0	1.28	17.1	39.4	16.5	44.2
Al, percent----	.0181	0	82*	18	24:24	4.64	1.36	2.79	8.22	2.51	8.58
Ca, percent----	.213	36*	57*	7	24:24	3.87	2.89	.456	14.2	.463	32.3
Mg, percent----	.115	33	67*	<1	24:24	1.59	2.19	.294	5.08	.332	7.63
Na, percent----	.00799	18	81*	1	24:24	.84	1.23	.549	1.08	.555	1.27
K, percent-----	.0167	30	55*	15	24:24	1.55	1.35	.909	2.31	.850	2.82
Fe, percent----	.0321	0	98*	2	24:24	2.36	1.51	1.16	7.14	1.04	5.38
Ti, percent----	.0123	0	90*	10	24:24	.29	1.29	.187	.453	.174	.483
Mn, percent----	.0355	0	36	64	17:24	.0448	1.54	.0259	.100	.0189	.106
Ag-------------	.0286	16	13	71	14:24	.22	1.48	.142	.490	.100	.482
As-------------	.253	0	29	71	23:24	3.84	3.19	<.1	48.71	.38	39
B--------------	.0410	0	94*	6	24:24	25.9	1.59	11.1	48.6	10.2	65.5
Ba-------------	.0206	5	75*	20	24:24	409	1.39	256	826	211	790
Be-------------	.0210	0	89*	11	24:24	1.42	1.40	.797	2.60	.724	2.78
Ce-------------	.0467	7	0	93	24:24	52.3	1.64	22.3	101	19.4	141
Co-------------	.108	13	84*	2	24:24	6.89	2.13	1.51	15.9	1.52	31.3
Cr-------------	.0361	8	78*	14	24:24	59.4	1.55	26.9	114	24.7	143
Cu-------------	.0852	0	98*	2	24:24	13.2	1.96	5.78	62.0	3.44	50.8
F--------------	.020	0	53	47	21:24	480	1.39	<400	900	90	930
Ga-------------	.0313	0	81*	19	24:24	11.7	1.50	6.08	21.9	5.22	26.4
Ge-------------	.0361	42*	40*	18	24:24	.76	1.55	.35	1.98	.31	1.83
Hg-------------	.0436	0	58	42	24:24	.031	1.62	.02	.1	.012	.081
La-------------	.0128	0	67*	33	24:24	28.9	1.30	17.3	43.5	17.0	48.8
Li-------------	.0562	0	75*	25	23:24	12.7	1.73	3.43	2.32	4.24	38.0
Mo-------------	.0678	0	74*	26	24:24	5.02	1.82	1.98	12.5	1.52	16.6
Nb-------------	.0317	20	16	64	24:24	5.41	1.51	2.16	10.5	2.37	12.3
Ni-------------	.117	6	91*	3	24:24	24.6	2.20	5.87	70.0	5.07	119
Pb-------------	.203	1	91*	8	17:24	3.3	2.82	.793	14.8	.413	26.1
Rb-------------	.0235	26	52*	22	24:24	52.3	1.42	24.6	83.6	25.0	102
Total S, percent	.108	7	59*	34	16:24	.12	2.13	.0530	.819	.0266	.547
Sc-------------	.0329	0	78*	22	24:24	7.37	1.52	3.33	14.5	3.19	17.0
Se-------------	-	-	-	-	7:24	.042	2.74	<.1	.29	.0056	.315
Sn-------------	.0770	0	32	68	24:24	.72	1.89	.1	1.6	.202	2.57
Sr-------------	.0096	18	57*	25	24:24	240	1.25	133	389	154	374
Th-------------	.0231	0	49	51	24:24	6.33	1.42	3.38	12.58	3.14	12.8
U--------------	.0129	8	82*	10	24:24	2.17	1.30	1.55	3.41	1.28	3.7
V--------------	.0307	0	95*	5	24:24	59.0	1.50	32.7	106	26.2	133
Y--------------	.0254	19	35	46	24:24	14.7	1.44	8.03	28.0	7.07	30.4
Yb-------------	.0485	12	15	73	24:24	1.79	1.66	.68	3.4	.65	4.9
Zn-------------	.0236	0	100*	<1	24:24	59.7	1.42	31	101	29.9	128
Zr-------------	.0324	11	27	62	24:24	196	1.51	84.7	428	85.8	446
Total C, percent	.117	15	85*	<.1	24:24	2.11	2.19	.38	6.35	.44	10.1
Organic C, percent------	.189	12	2	87	24:24	.41	2.72	.03	2.4	.055	3.03
Carbonate C, percent------	.246	29	69*	1	24:24	1.26	3.13	.13	6.05	.129	12.3
Ash, percent---	2.847[1]	0	61	39	24:24	96.4[2]	1.69[3]	92.3	98.4		
pH-------------	.442[1]	0	95*	5	24:24	8.95[2]	.66[3]	7	10		

[1] Total variance.

[2] Arithmetic mean.

[3] Standard deviation.

Table 56.--Continued

	Variance component as percent of total					Summary statistics					
	Total $\log_{10}$ variance	Between holes	Between samples within holes	Between analytical duplicates	Detection Ratio	Geometric mean (ppm except as noted)	Geometric deviation	Observed range Minimum (ppm except as noted)	Observed range Maximum (ppm except as noted)	Expected range of 95 percent of samples Minimum	Expected range of 95 percent of samples Maximum
Part B: Siltstone and Shale											
Si, percent------	0.00117	0	91*	9	24:24	28.8	1.08	25.2	31.5	24.6	33.5
Al, percent------	.00559	0	96*	4	24:24	7.01	1.19	5.14	8.81	4.95	9.93
Ca, percent------	.192	0	>99*	<1	24:24	1.71	2.75	.437	5.83	.226	12.9
Mg, percent------	.0272	0	>99*	<1	24:24	1.20	1.46	.671	1.75	.563	2.56
Na, percent------	.0595	3	96*	1	24:24	.64	1.75	.124	.978	.209	1.96
K, percent-------	.00491	0	96*	4	24:24	2.28	1.18	1.50	3.00	1.64	3.17
Fe, percent------	.0164	0	99*	1	24:24	2.62	1.34	1.96	5.36	1.46	4.71
Ti, percent------	.0017	0	94*	6	24:24	.40	1.10	.318	.447	.331	.484
Mn, percent------	.0606	0	92*	8	15:24	.0446	1.76	.0254	.125	.0144	.138
Ag---------------	.0234	0	65*	35	23:24	.38	1.42	.148	.802	.188	.766
As---------------	.0888	0	80*	20	24:24	6.10	1.99	2.67	62.2	1.54	24.2
B----------------	.0034	0	81*	19	24:24	57.8	1.14	43.9	69.8	44.5	75.1
Ba---------------	.012	<1	71*	29	24:24	503	1.29	336	880	302	837
Be---------------	.0111	0	86*	14	24:24	2.61	1.27	1.70	3.55	1.62	4.21
Ce---------------	.0730	23*	0	77	22:23	54.2	1.86	14.2	115	15.7	187
Co---------------	.0121	0	86*	14	24:24	13.0	1.29	7.43	18.9	7.83	21.7
Cr---------------	.00372	11	53	36	24:24	96.1	1.15	68.1	126	72.6	127
Cu---------------	.0335	52*	23	25	24:24	51.3	1.52	18.7	80.4	22.2	118
F----------------	.0159	0	0	100	23:24	.077	1.34	<.04	.1	.0429	.138
Ga---------------	.00704	0	77*	23	24:24	23.2	1.21	16.5	33.9	15.8	34.0
Ge---------------	.0181	0	57	43	24:24	1.12	1.36	.576	1.74	.606	2.07
Hg---------------	.00915	0	60	40	24:24	.063	1.25	.04	.09	.0403	.0984
La---------------	.00440	19	17	64	24:24	39	1.17	28.9	55.6	28.5	53.4
Li---------------	.0186	0	91*	9	24:24	35.3	1.37	20.1	56.3	18.8	66.3
Mo---------------	.0147	10	0	90	24:24	8.67	1.32	5.20	14.0	4.98	15.1
Nb---------------	.0308	0	45	55	24:24	7.66	1.50	4.21	17.9	3.40	17.2
Ni---------------	.0110	1	88*	12	24:24	49.0	1.27	33.1	67.6	30.4	79.1
Pb---------------	.0266	8	75*	18	24:24	13.9	1.46	6.00	24.7	6.52	29.6
Rb---------------	.0164	0	35	65	24:24	89.6	1.34	51.1	129	49.9	161
Total S, percent-	.0480	1	68*	31	23:24	.17	1.66	.0538	.402	.0617	.468
Sc---------------	.0159	5	71*	24	24:24	15.7	1.34	9.18	26.5	8.76	28.2
Se---------------	.123	6	0	94	19:24	.21	2.24	<.1	.790	.0419	1.05
Sn---------------	.0826	0	44	56	24:24	1.33	1.94	.15	2.32	.353	5.01
Sr---------------	.00276	1	48	55	24:24	249	1.13	189	330	195.1	318
Th---------------	.0119	5	28	68	24:24	11.7	1.29	7.19	21.7	7.03	19.5
U----------------	.0235	0	72*	28	24:24	4.14	1.42	2.91	7.75	2.05	8.35
V----------------	.0117	0	72*	28	24:24	131	1.28	85.4	186	79.9	215
Y----------------	.00621	2	43	56	24:24	23.8	1.20	16.8	32.7	76.5	34.2
Yb---------------	.00570	0	65*	35	24:24	3.45	1.19	2.45	4.52	2.44	4.89
Zn---------------	.00413	0	90*	10	24:24	110.	1.16	86.2	146	81.8	148
Zr---------------	.00926	2	45	53	24:24	248	1.25	140	327	159	388
Total C, percent-	.0416	1	98*	<1	24:24	1.39	1.60	.68	2.48	.543	3.56
Organic C, percent	.0129	0	64*	36	24:24	.85	1.30	.55	1.39	.503	1.44
Carbonate C, percent--------	1.16	0	78*	22	17:24	.11	12	<.01	1.58	.000707	1.57
Ash, percent-----	1.35[1]	9	13	77	24:24	95.2[2]	1.16[3]	93.1	98.1		
pH---------------	1.09[1]	2	94*	4	24:24	8.08[2]	1.04[3]	5.1	9.1		

[1] Total variance.

[2] Arithmetic mean.

[3] Standard deviation.

Table 56.--Continued

	Total $\log_{10}$ variance	Variance component as percent of total: Between holes	Variance component as percent of total: Between samples within holes	Variance component as percent of total: Between analytical duplicates	Detection Ratio	Summary statistics: Geometric mean (ppm except as noted)	Summary statistics: Geometric deviation	Observed range (ppm except as noted): Minimum	Observed range (ppm except as noted): Maximum	Expected range of 95 percent of samples: Minimum	Expected range of 95 percent of samples: Maximum
					Part C: Dark Shale						
i, percent--------	0.00224	0	98*	2	23:23	25.1	1.12	18.2	27.7	20.0	31.4
l, percent--------	.00302	0	79*	21	23:23	7.79	1.13	6.08	9.73	6.10	9.93
a, percent--------	.0279	6	0	94	23:23	1.19	1.47	.70	4.37	.55	2.57
Mg, percent--------	.0152	7	92*	<1	23:23	.94	1.33	.48	1.29	.53	1.66
Na, percent--------	.0182	22	77*	1	23:23	.54	1.36	.18	.79	.29	1.00
K, percent---------	.0101	0	91*	9	23:23	2.21	1.26	1.09	2.71	1.39	3 50
Fe, percent--------	.0192	0	98*	2	23:23	2.75	1.38	1.44	4.99	1.45	5.24
Ti, percent--------	.00191	0	87*	13	23:23	.41	1.11	.34	.46	.33	.51
Mn, percent--------	.104	18	71*	12	11:23	.0402	2.10	.0165	.168	.00912	.177
Ag----------------	.0545	0	0	100	20:23	.35	1.71	.12	.56	.12	1.02
As----------------	.0768	0	4	96	23:23	7.58	1.89	1.71	27.43	2.12	27.1
B-----------------	.00219	22	20	58	23:23	63.9	1.11	50.0	76.5	51.9	78.7
Ba----------------	.011	7	46	46	23:23	453	1.28	240	655	276	741
Be----------------	.00635	0	49	51	23:23	3.21	1.20	2.11	5.05	2.23	4.62
Ce----------------	.0397	0	65*	35	22:22	78.6	1.58	43.8	167	31.5	196
Co----------------	.00640	0	91*	9	23:23	16.4	1.20	11.8	20.9	11.4	23.7
Cr----------------	.00967	5	87*	8	23:23	109	1.25	66.2	252	69.8	170
Cu----------------	.0286	0	22	78	22:22	54.0	1.48	18.2	93.6	24.7	118
F-----------------	.00937	0	53	47	23:23	.08	1.26	.05	.11	.050	.127
Ga----------------	.00471	3	68*	29	23:23	26.2	1.17	17.4	35.9	19.1	35.9
Ge----------------	.0319	0	35	65	23:23	1.30	1.51	.531	2.49	.570	2.96
Hg----------------	.0797	0	98*	2	23:23	.11	1.92	.04	.44	.0298	.406
La----------------	.00546	0	53	47	23:23	43.6	1.19	28.7	59.5	30.8	61.7
Li----------------	.00501	0	0	100	23:23	40.8	1.18	31.8	51.0	29.3	56.8
Mo----------------	.0618	0	0	100	23:23	8.54	1.77	1.13	19.4	2.82	27.7
Nb----------------	.0641	0	21	79	23:23	7.54	1.62	3.22	18.3	2.87	19.8
Ni----------------	.00821	0	85*	15	23:23	58.5	1.23	37.1	77.8	38.7	88.6
Pb----------------	.00563	<1	78*	21	23:23	21.9	1.19	16.6	36.6	15.5	31.0
Rb----------------	.0283	18	70*	12	23:23	88.3	1.47	33.0	135	40.6	191
Total S, percent---	.0155	0	23	77	23:23	.32	1.33	.17	.52	.18	.57
Sc----------------	.00626	0	76*	24	23:23	19.1	1.20	12.8	24.4	13.3	27.6
Se----------------	.186	0	0	100	20:23	.30	2.70	<.1	.994	.0412	2.19
Sn----------------	.0517	10	<1	89	23:23	1.34	1.69	.424	2.40	.469	3.83
Sr----------------	.00531	0	81*	19	23:23	24.6	1.18	184	315	179	342
Th----------------	.00958	4	75*	22	23:23	14.1	1.25	9.63	23.1	9.00	22.0
U-----------------	.0160	10	87*	3	23:23	4.47	1.34	3.49	11.4	2.49	8.03
V-----------------	.00647	0	75*	25	23:23	148	1.17	105	192	107	202
Y-----------------	.00793	9	0	91	23:23	28.2	1.23	22.1	40.7	18.6	42.6
Yb----------------	.00175	0	28	72	23:23	4.00	1.10	3.39	4.77	3.31	4.84
Zn----------------	.00453	0	99*	1	23:23	125	1.17	79.5	143	91.6	172
Zr----------------	.0132	0	68*	32	23:23	221	1.30	142	352	131	383
Total C, percent---	.0846	1	99*	<1	23:23	5.60	1.95	2.54	24.89	1.47	21.3
Organic C, percent-	.219	0	37	63	23:23	4.60	2.94	.18	24.89	.332	39.8
Carbonate C, percent	.622	0	37	63	17:23	.07	6.15	<.01	.77	.00185	2.65
Ash, percent-------	75.5[1]	0	100*	<1	23:23	85.4[2]	8.69[3]	60.7	91.9		
pH----------------	.641[1]	21	76*	3	23:23	7.66[2]	.8[3]	5.4	8.4		

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[1] Total variance.

[2] Arithmetic mean.

[3] Standard deviation.

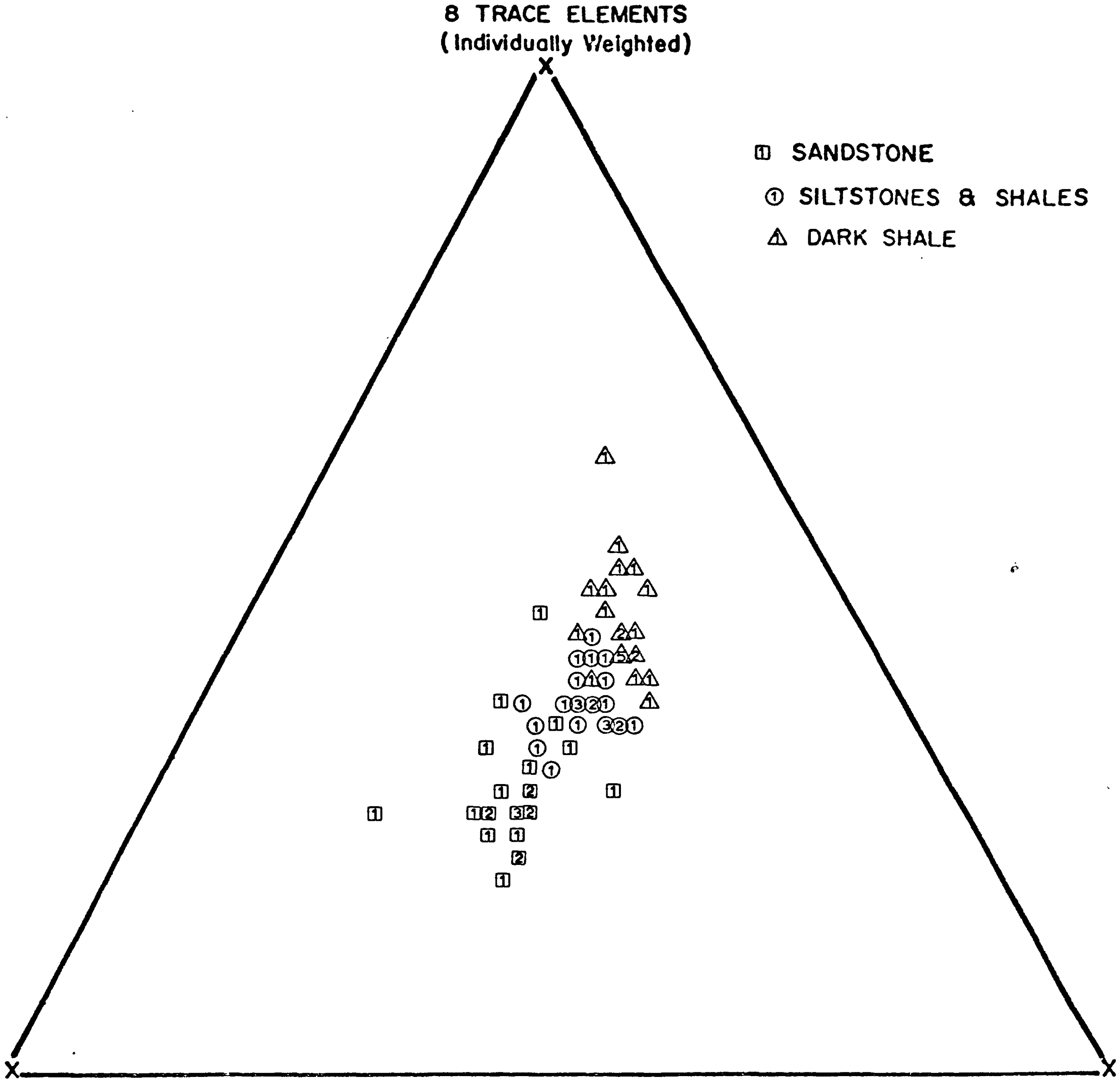

Figure 43.--Compositional relationships of the samples of the three rock types with respect to silicon, aluminum and a suite of 8 trace elements.

are presented in Table 57.

"Special" samples.--The samples not classified as members of any of the three rock-type groups were chosen subjectively, because they looked interesting or different, or in many cases because they represented a type of rock seen repeatedly up and down the section, though not commonly in great abundance. Many of these "special" samples, despite somewhat anomalous appearance, fit with good chemical and mineralogical conformity into one of the three main rock type classes of this study. On the other hand, some of the special samples have the highest concentrations of certain suites of elements, and commonly have distinctive mineralogy, which sets them apart from the three rock types.

Some significant features of the special samples are the following:

(1) The samples with the highest concentrations of minor and trace elements are dark in color and similar to dark shale. Of the three rock types, such dark shale is the most undesirable reclamation material.
(2) These dark samples commonly are close to the coal beds.
(3) Other types of special samples, distinct by their chemistry, mineralogy, or texture are rare and for this reason do not generally represent a clear chemical threat in reclamation work. The strata in which they occur are most commonly too thin to be handled separately during excavation procedures.

Of the special samples the dark, shaly or coaly rocks with high trace-element and pyrite concentrations, which promote acidity and element mobilization during weathering, may be close to either major coal beds or thinner coaly zones. A general recommendation may be made that entire strata (coal bed boundary zones and thin, low-gade coaly layers) containing such rocks be segregated for reburial away from soil and ground-water zones, wherever practical or where sufficient volumes exist to preclude acceptable dilution by larger volumes of sandy rocks.

Conspicuous rocks of other types that deserve mention constitute thin, hard strata interrupting thicker zones of soft gray or tan mudstones or sandstone. These rocks are largely mixed carbonates of two types: a hard tan rock appearing as siltstone, which is 45-60 percent calcian siderite ($[\mathrm{Fe, Ca}]\mathrm{CO}^3$); and a hard, gray or blue rock appearing as siltstone or sandstone, which is 25-60 percent magnesian calcite. Such rocks do not in general have high concentrations of minor or trace elements.

Similarity of rocks at Hanging Woman Creek study site to rocks elsewhere in the Fort Union coal region.--Table 58 presents concentrations of selected elements in the three types of rocks at the Hanging Woman Creek site (3 left-hand columns) for comparison with sandstone and fine-grained rocks of the Fort Union Formation of the

Table 57.--Statistical summary of mineral composition of the three rock types in the Fort Union Formation.

Mineral	Sandstone				Siltstones plus shale				Dark shale			
	Ratio	Arithmetic mean	Standard deviation	Observed range	Ratio	Arithmetic mean	Standard deviation	Observed range	Ratio	Arithmetic mean	Standard deviation	Observed range
Quartz	24:24	37.2	11.9	22.5-70.9	24:24	32.6	4.50	24.0-39.6	23:23	27.5	3.29	16.1-31.7
Oligoclase	24:24	9.59	3.01	4.30-17.6	21:24	7.37	4.36	0-14.1	22:23	4.58	2.81	0-10.2
Microcline	16:24	4.08	4.29	0-16.0	13:24	2.19	2.32	0-6.97	11:23	1.85	2.08	0-6.87
Layer silicates	24:24	28.0	10.2	10.9-44.1	24:24	51.7	7.29	38.3-65.5	23:23	60.7	5.46	53.7-78.4
Calcite	12:24	2.53	4.86	0-19.1	11:24	1.46	1.80	0-5.54	1:23	.0325	.159	0-0.78
Mg-calcite	1:24	.0363	.178	0-.87	2:24	.113	.383	0-1.43	0:23	0	-	-
Dolomite	12:24	2.19	2.52	0-7.07	14:24	2.33	2.27	0-6.23	13:23	1.01	.731	0-2.09
Ca-dolomite	10:24	14.4	20.9	0-55.6	4:24	.214	.637	0-2.56	0:23	0	-	-
Siderite	9:24	.301	.531	0-2.07	14:24	.447	.476	0-1.46	4:23	.117	.286	0- 22
Ca-siderite	11:24	.887	1.80	0-8.18	8:24	.679	1.49	0-6.38	12:23	1.29	1.75	0-6.80
Pyrite	1:24	.145	.712	0-3.49	10:24	.878	1.13	0-3.33	19:23	2.63	1.85	0-6.79
Marcasite	1:24	.416	2.04	0-10.0	0:24	0	-	-	0:23	0	-	-
Gypsum	1:24	.245	1.20	0-5.87	0:24	0	-	-	1:23	.192	.941	0-4.61
Smectite	24:24	12.6	8.02	1.22-31.0	24:24	16.5	7.67	4.83-36.0	20:23	14.6	12.5	0-35.3
Illite	24:24	2.97	1.67	1.10-8.16	24:24	12.0	6.72	3.83-24.5	23:23	15.1	6.42	6.13-26.8
Chlorite	23:24	3.79	2.48	.74-10.2	24:24	11.4	6.94	2.73-24.5	22:23	13.5	9.50	0-26.8
Kaolinite	22:24	8.53	7.08	0-22.9	23:24	11.6	8.38	0-32.6	23:23	17.3	8.08	2.78-31.3

Northern Great Plains (next three columns). The values for these other Fort Union rocks are averages (geometric means) of 80 samples of the sandstone and shale from outcrop and 50 samples of the fine-grained rocks from cores. In all three studies taken as a whole, the rock samples were collected from many sites spread over an area hundreds of kilometers wide. Analytical and preparation procedures were identical in all three studies. Comparison of the data among the three studies shows clearly that the values of the sandstone and siltstone-plus-shale in this study are quite similar to corresponding rock types of the Fort Union Formation from other areas in the region. Possible exceptions are that sandstone from the Hanging Woman Creek site has noticeably lower boron and selenium concentrations and higher sodium concentration than the outcrop rocks of the Ebens and McNeal study (U.S.G.S., 1977, p. 185) with which comparison might be made; and selenium concentrations appear to be higher in fine-grained rocks from the Hanging Woman Creek site than in those of Hinkley and Ebens study (U.S.G.S., 1977, p. 169). It is clear that the average chemical values of rocks at the Hanging Woman Creek site are representative of the area in general.

In addition to having similar average values of elemental composition, the rocks at the Hanging Woman Creek site and the rocks of the broader region also have similar degrees of spread (total variance) about their average values and a similar pattern of chemical variation with respect to spatial location of the samples. This can be seen by comparing the values, between studies, of total variance and individual components of variance ("between holes" and "between samples within holes"; these values are not given here for the other studies listed in Table 58, so the reader must consult them directly). These similarities strongly indicate that, just as at the Hanging Woman Creek site, most of the chemical information about the rocks at other sites could have been obtained from a sampling and analysis program much less extensive than the one followed in this study.

Comparison of outcrop and drilled core samples.--In Table 58 the chemical values for sandstone and shale collected from outcrop (U.S.G.S., 1977, p. 185) are very close to the values for the corresponding rock types sampled from core in both the Hanging Woman Creek study and the 5-site study of Hinkley and Ebens (U.S.G.S., 1977, p. 169) (fifth column of the table).

Samples in both the Ebens and McNeal (U.S.G.S., 1977, p. 185) outcrop study and Hinkley and Ebens (U.S.G.S., 1977, p. 169) core study were taken over wide areas and represent large numbers of samples; moreover, the analytical methods used were identical to those used in this study. The similarity suggests strongly that in potential mining sites where the overburden material is exposed as outcrop within or near the area to be disturbed, at least some samples may be collected from the outcrop for lithologic classification and possible chemical analysis with confidence that the results will be similar to results from the more expensive core samples.

Table 58.--Selected elements from the Fort Union Formation, in three Hanging Woman Creek rock types compared to rocks and soils from other locations in and near the Fort Union coal region.

[Values are geometric means, or arithmetic averages of geometric means of subgroups. All data reported on dry weight basis. N.R., not reported]

	Hanging Woman Creek Rocks, This Study			Rocks from outcrop Ebens & McNeal, 1977 (80 samples each type)		Fine-grained rocks, from cores, Hinkley & Ebens, 1977 (50 samples)	C-horizon soils Hanging Woman Site, Tidball, 1978.	C-horizon soils, Powder River Basin, Tidball & Ebens, 1976	Subsoils of Powder River Basin, Connor, Keith & Anderso 1976
	Sandstone	Siltstone and shale	Dark shale	Sandstone	Shale				
As------	3.8	6.1	7.6	4.4	5.1	3.6	7.3	N.R.	N.R.
B-------	26	58	64	51	98	59	41	24—/	26
Co------	6.9	13	16	5.4	9.1	8.7	9.5—/	7.3	6.3
Cr------	59	96	109	45	84	72	59—/	46	49
Cu------	13	51	54	13	34	38	35—/	17	16
Hg------	.031	.063	.11	.032	.060	.10	.03	N.R.	.023
Mo------	5.0	8.7	8.5	5.0	8.1	6.1	N.R.	N.R.	<3
Na------	.84	.64	.54	.49	.42	.64	.72	.47	N.R.
Pb------	3.3	13.9	22	5.2	15	11	N.R.	N.R.	17
Se------	.042	.21	.30	.19	N.R.	.16	N.R.	N.R.	N.R.
V-------	59	131	148	46	97	86	N.R.	N.R.	87
Zn------	60	110	125	44	80	100	N.R.	N.R.	61

—/ Averaged from values for distinct soil types or regions.

RECLAMATION OF SPOIL AREAS

Suitability of Hanging Woman Creek overburden rocks for use as soil material.--Perhaps the single most important statement to be made about the lack of potential chemical harmfulness of a potential soil replacement material (overburden rock) is that it is chemically and mineralogically similar to soils of the region which successfully support desirable stands of the native vegetation. It is clear from the data of Table 58 that the sandstone of the Fort Union Formation at the Hanging Woman Creek site is chemically similar to a large number of subsoils from this site and from other parts of the Fort Union coal region (three right-hand columns of table; studies by Tidball, 1978; Tidball and Ebens, 1976; and Connor, Keith, and Anderson, 1976). Furthermore, the similarity of nearby subsoils is almost as great in the case of siltstone and shale from the Hanging Woman Creek site.

Judged from bulk chemistry based on analysis of total rock and soil samples, it appears that much of the overburden rock at the Hanging Woman Creek site could be used to replace the soils of the site or region. At the present limited stage of knowledge of reclamation chemistry and toxicity of elemental concentrations in soil, we feel that it is a very complex matter to set actual "red flag" or hazard level concentration limits in soils for particular elements. Some progress has been made in this matter for certain elements, most notably molybdenum and selenium, but for these and almost all other elements of interest, different soil conditions and even different points of view have the strongest influence on the assignment of maximum permissible levels. Varying soil pH, mineralogy, moisture regime and temperature, as well as the varying uptake abilities of different plant species and the hardiness and dietary preferences of various animal species, must be taken into account in determining acceptable ranges of whole-soil concentrations of chemical elements. The situation is only somewhat simpler for determining acceptable availability levels of the elements.

Relative volumes of the rock types and options for use in reclamation.--Table 59 shows the relative volume abundance of the lithologic constituents of the rock column at the Hanging Woman Creek site, both by individual hole cores and for all cores taken together. In general, sandstone is sufficiently abundant (about one-third of the overburden rock) and is present in sufficiently thick, continuous, and recognizable units to allow it to be used as needed for plant growth medium on top of the refill column, and for the material most likely to contact ground water at the bottom of the refill column. In much of the overburden rock column, strata of siltstone are sufficiently thick to be utilized in the same way, if desired. Units of dark shale and other shale are more commonly intermixed with each other and with sandstone and siltstone over short vertical distances, but the relative volumes of either pure or intermixed zones of shale are small enough that these rocks could practically be segregated into the middle part of the refill material and separated from both plant roots and the ground-water zone by a thickness of sandier rock at top and bottom.

Table 59.--Abundance, in percent, of different rock types in the Fort Union Formation cores of drilled holes at Hanging Woman Creek site.

Hole number	Sand-stone	Silt-stone	Shale and mudstone	Dark shale	Coal
20	14	26	23	9	16
21	39	14	17	5	25
23	18	18	31	12	20
25	22	9	31	13	26
27	42	15	19	8	16
All core	28	16	24	10	22

Generally the dark shale contains the largest concentrations of trace elements and sandstone the smallest (Figures 41, 43). Sandstone generally has the widest spread in its chemical data because, despite the visible presence of the sand-size grains (both quartz and feldspar) in these rocks, the remainder of the material which they contain may be mineralogically varied and may include much or little clay. This fact emphasizes the need for using the greatest possible care in inspection before classifying a rock of the Fort Union Formation as a sandstone, to be sure that it is not simply an unstructured, slightly gritty rock of another class with a large fraction of layer silicate minerals and high concentrations of minor and trace elements.

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R-mode Factor Analysis of Extractable Elements in A- and C-horizon Soils from the Northern Great Plains

by

James M. McNeal, Ronald C. Severson, and Larry P. Gough

Introduction

The manner by which extractable elements occur in soils has received little attention. Attempts to relate total soil chemistry to plant chemistry have met with little success (Gough and Severson, 1976; Severson and Gough, 1978; Shacklette, Sauer, and Miesch, 1970). More success has been obtained in relating plant composition to the composition of soil extracts (Lindsay and Norvell, 1969; Randall, Schulte, and Corey, 1976; Rule and Graham, 1976; Shuman and Anderson, 1974). Results from most of these studies are difficult to apply to native vegetation or uncultivated soils because they are usually concerned with applications of fertilizer in either greenhouse experiments or controlled field plot experiments.

A better understanding of the occurrence of extractable elements in soil will provide information that may result in the formulation of an extract which provides for better relationships between plant chemistry and extractable element chemistry. In this study, the occurrence of elements in various extracts of both A- and C-horizon soils is examined using R-mode factor analysis.

Experimental Procedures

Samples of both A and C soil horizons were collected at 21 locations of diverse soil chemistry in the Northern Great Plains. Sample locations are shown on Figure 33. The less-than-2-mm fraction was used for analysis. Table 60 lists the variables determined on the whole soil. Details of the analytical procedures and choice of sample sites is given in Severson and others (1977).

Table 61 lists the extracts used and the elements determined in each extract. Overall, 90 variables were measured in the A-horizon soils and 79 were measured in the C-horizon soils. Note that the HCl extract was not used on the C-horizon soils. A substantial portion of the large amount of calcite in the C horizon would be dissolved by the HCl, and the elements in the calcite would mask the elements from other sources. There are two reasons for not being able to determine all 12 elements in the extracts. The first is that the element was part of the leaching solution (Ca in DTPA, Na in EDTA, and Mg in $MgNO_3$). The second reason is that some elements in some extracts had high interferences or were present in levels below the detection limit. This was the situation for Co, Cu, Fe, and Ni in the hydroquinone extract. Details

Table 60.--Variables determined on soils of the Northern Great Plains

[Abbreviations used in figures, tables, and text are given in parentheses]

Total Element Content	Mineralogy	Chemical and Physical Properties
Al (Al-t)	Quartz	Sand
C (C-t)	Plagioclase (Plag)	Silt
Ca (Ca-t)	Microcline (K-spar)	Clay (clay-s)
Cu (Cu-t)	Clay (clay-m)	Cation Exchange Capacity (CEC)
Fe (Fe-t)	Calcite	
K (K-t)	Dolomite	pH
Mg (Mg-t)		C-carbonate (C-CO_3)
Mn (Mn-t)		C-organic (C-org)
Na (Na-t)		C-heating to 550°C (C-550)
Zn (Zn-t)		C-walkley-black (C-wb)

Table 61.--Elements determined in soil extracts of the Northern Great Plains.

[Abbreviations for the extracts used in the text are given in parentheses]

Extractable Elements	DTPA (d)	EDTA (e)	HCl (h)*	Extract Hydroquinone (q)	$MgNO_3$ (m)	Oxalate (o)
Ca		x	x	x	x	x
Cd	x	x	x	x	x	x
Co	x	x	x		x	x
Fe	x	x	x		x	x
K	x	x	x	x	x	x
Mg	x	x	x	x	x	x
Mn	x	x	x	x	x	x
Na	x	x	x	x	x	x
Ni	x	x	x	x	x	x
Pb	x	x	x	x	x	x
Zn	x	x	x	x	x	x

*Extract was not used for C-horizon soil.

of the extraction procedure are given elsewhere (Gough and others, 1978; Severson and others, 1977). The chemical analysis of the extracts was performed by atomic absorption spectrophotometry. The standards were prepared by adding known amounts of the elements to solutions that had the same composition as the extracting solution.

A description of each extract is as follows:

DTPA: 0.005 M DTPA (diethylenetriaminepentaacetic acid) in 0.01 M calcium chloride and 0.1 M triethanolamine at pH 7.30 (Lindsay and Norvell, 1969).

EDTA: 0.01 M EDTA (ethylenediaminetetraacetic acid) in 0.1 M ammonium acetate at pH 7.0 (Randall and others, 1976).

HCl: 0.1 M HCl (Randall and others, 1976)

Hydroquinone: 0.2% hydroquinone ($C_6H_6O_2$) in 1 M ammonium acetate at pH 7.0 (Randall and others, 1976).

$MgNO_3$: 1.0 M magnesium nitrate (Randall and others, 1976)

Oxalate: 0.2 M ammonium oxalate at pH 3.0 (McKeague and Day, 1966).

These six extracts were chosen because they represent a wide range of modes of extraction. They range in approximate order of degree of extraction from weak to strong: $MgNO_3$, DTPA, EDTA, hydroquinone, oxalate, and HCl.

The $MgNO_3$ is a neutral salt that only dissolves readily soluble minerals, and has a weak ion exchange capability. The Mg^{2+} ion can replace readily exchangeable cations, but the solution has no complexing or chelating agents to aid in the ion exchange. The DTPA solution has an exchangable cation, Ca^{2+}, and also uses DTPA as a chelating agent. The chloride will also serve as a complexing agent. EDTA is very similar to DTPA as EDTA also serves as a chelating agent, while the ammonium, NH_4^+, cation exchanges with other cations, and the acetate, $C_2H_3O_2^-$, serves as a complexing agent. Due to the similarity of extraction methods, DTPA and EDTA would be expected to give similar results. Hydroquinone (HQ) is a weak reducing agent and will reduce Mn oxides, but not Fe oxides. Oxalate is a strong reducing agent capable of dissolving manganese as well as iron oxides. The ammonium ion can also serve to replace readily exchangeable elements. The oxalate treatment is light sensitive. In light it dissolves well crystallized Fe and Mn oxides, whereas in darkness it dissolves only the more amorphous Fe and Mn oxides. Because elements available to plants are more likely to be associated with the more amorphous Fe and Mn oxides, the experiment was performed in darkness. The HCl extract is capable of dissolving some of the more insoluble minerals by keeping the cations in solution by complexing them with chloride. HCl does not have a great ion-exchange capacity.

Factor Analysis

R-mode factor analysis attempts to express large numbers of variables in terms of fewer "master" variables or factors. These factors commonly describe physical or chemical processes which exert controlling influences on the variables. Three steps in a factor analysis are: (1) the calculation of a correlation matrix, (2) the extraction of the initial factors, called principal components, and (3) the rotation of the principal components to a "final" solution. These steps are considered in some detail by Harmon (1967) and Comrey (1973).

The final solution used here is based on the varimax criterion, which was used to rotate the principal components factor matrix. The varimax rotation is orthogonal--which means that the resulting factors are independent (uncorrelated) of each other. Generally, this rotation produces factors with either high or low factor loadings and minimizes intermediate factor loadings. A common problem with factor analysis is that there are no set rules to determine the number of factors to rotate. Both Comrey (1973) and Spencer (1967) rotate various numbers of factors until "simple structure" is obtained--that is, a situation where the factors are most easily described and understood. This practice was followed for this report with the result that about 75% of the total variation in the data was described.

A brief explanation of some of the terms used in factor analysis will be useful. The factor loading is a number between -1.00 and +1.00 and is the degree to which a variable "loads" (roughly analogous to correlation) on each of the rotated factors. The square of a factor loading is an estimate of the percentage of the total variance of a variable that is explained by the factor. Similarly, the factor loadings may be thought of as having values above which the loadings are significantly different than zero and values below which the loadings are not significant. Consequently, values above 0.50 may be considered significant and values above 0.70 may be considered highly significant.

A rotated communality is the sum of squares of loadings of a variable on all rotated factors. The square of a communality is the percentage of the total variance of a variable accounted for by the factors. Clearly, a communality increases as the number of factors that are rotated increases. The percentage of the total variance accounted for by each factor is the relative importance of that factor. If enough factors are rotated, 100 percent of the total variance of a variable will be accounted for and the communality will be 1.00.

Analytical error also plays a part in factor analysis. For example, if the analytical error of an element is 20 percent, then rotating increasing numbers of factors until more than 80 percent of the

Table 62.--Factor analysis loading and communalities for total and extractable element content for four varimax factors for A-horizon soils of the Northern Great Plains.

[Factor; see text for explanation of each factor. Extract abbreviations: m, $MgNO_3$; d, DTPA; e, EDTA; h, HCl; q, hydroquinone; o, oxalate; t, total]

Element	Extract	Factor 1	2	3	4	Communalities
Cd	d	.67	.11	.28	.11	.55
	e	.78	.35	.33	-.02	.84
	h	.31	-.47	.40	.25	.54
	q	.20	.15	-.19	-.31	.19
	m	.32	.38	.29	.02	.33
	o	-.03	.22	.79	-.06	.67
Ca	t	-.19	.61	-.16	-.16	.46
	e	.38	.72	.11	-.50	.92
	h	.31	.78	-.07	-.38	.86
	q	.26	.76	.06	-.52	.92
	m	.47	.72	.10	-.43	.93
	o	.52	.60	-.34	.08	.75
Co	d	.27	-.01	.80	-.06	.70
	e	.53	.22	.18	-.45	.56
	h	-.09	-.70	.34	.29	.69
	m	.38	.59	-.07	-.29	.58
	o	.10	-.14	.92	-.12	.89
Cu	t	.39	.61	.41	-.35	.81
	d	.40	.30	.65	-.42	.85
	e	.28	.30	.68	-.36	.76
	h	-.42	-.60	.45	.24	.80
	m	.43	.80	-.14	-.14	.86
	o	.24	.14	.84	-.24	.84
Fe	t	.28	.80	.30	-.29	.89
	d	.12	-.65	.70	.03	.93
	e	.16	-.74	.58	.17	.93
	h	-.18	-.75	.33	.42	.88
	m	.75	.21	-.07	.19	.66
	o	.25	.11	.80	-.15	.73

Table 62.--(Continued)

Element	Extract	Factor 1	Factor 2	Factor 3	Factor 4	Communalities
K	t	.01	.13	-.14	-.19	.07
	d	.86	.07	.25	-.20	.85
	e	.89	.12	.23	-.21	.90
	h	.85	-.15	.31	.12	.85
	q	.89	.16	.20	-.22	.90
	m	.86	.16	.19	-.27	.88
	o	.90	.09	.20	-.12	.87
Mg	t	.16	.90	-.31	-.18	.97
	d	.17	.04	.16	-.42	.23
	e	.45	.66	.17	-.46	.89
	h	.38	.76	-.39	-.04	.87
	q	.50	.67	.13	-.42	.88
	o	.28	.75	-.15	-.48	.90
Mn	t	.34	.63	.49	.07	.76
	d	.12	-.07	.59	.43	.56
	e	.72	-.30	.39	.30	.85
	h	.05	-.49	.51	.48	.73
	q	.24	.41	.56	.36	.67
	m	.20	-.62	.50	.29	.76
	o	.12	-.15	.85	.00	.77
Na	t	-.75	.02	.06	.43	.75
	d	-.20	.13	.22	-.83	.80
	h	-.19	.35	.10	-.76	.75
	q	-.31	.18	.21	-.58	.52
	m	.00	.21	.26	-.79	.74
	o	.01	.52	-.24	-.48	.57
Ni	d	.19	.11	.85	.03	.77
	e	.00	-.08	.85	-.06	.73
	h	-.23	-.16	.80	.19	.76
	m	.25	.02	.33	-.08	.18
	o	.05	.11	.94	-.11	.90
Pb	d	.75	.36	-.08	-.32	.81
	e	.82	.37	-.02	-.25	.87
	h	-.04	-.42	-.07	-.03	.18
	q	.34	.48	-.02	-.67	.79
	m	.21	.65	.00	-.04	.46
	o	.17	-.28	.53	-.15	.42

Table 62.--(Continued)

Element	Extract	Factor 1	Factor 2	Factor 3	Factor 4	Communalities
Zn	t	.40	.72	.34	-.24	.87
	d	.85	-.13	.18	.07	.78
	e	.88	-.17	.15	.04	.83
	h	.16	-.64	.49	.47	.91
	q	.36	.40	.17	-.03	.32
	m	.43	-.66	.44	+.05	.82
	o	.26	-.17	.80	-.18	.76

Table 63.--Factor analysis results showing relative loadings of variables on four factors derived by varimax rotation for A-horizon soils of the Northern Great Plains.

[Some variables are negative; abbreviations are listed in Table 61]

Factor Loading	Factor Number and Interpretation				Percent variance explained
	1--Organic	2--Clay	3--Iron, manganese oxides	4--Sodium clay	
1.0					100
	C-org		Ni-o		90
	C-t		Co-o		
.9	C-wb, C-550, K-o	Mg-t			80
	K-e, K-8, Zn-e				
	K-m, K-d				
	Zn-d, K-h		Mn-o, Ni-d, Ni-e, Cu-o		
	Pb-e			Na-d	70
.8		Clay-m, Fe-t, Cu-m	Ni-h, Co-d, Zn-o, Fe-o		
	Cd-e	Ca-h, pH	Cd-O	Na-m	
		Ca-q, Mg-h		Na-h	60
	Fe-m, Pb-d, -Na-t	Mg-o, -Fe-e, -K-spar -Fe-h, -Quartz			
	Mn-e	Zn-t, Ca-e, Ca-m			
		-Co-h	Fe-d		
.7					50
	C.E.C.		Cu-e		
	Cd-d	Mg-q, Mg-e, -Zn-m		-Pb-q	
		Pb-m, clay-s, -Zn-h, -Fe-d	Cu-d	-Plag	
		Mn-t, -Mn-m	-Dolomite		40
		Cu-t, Ca-t, Al-t, Ca-o, -Cu-h			
.6					
		Co-m	-C-CO_3, Mn-d	Na-q	
		Water, -Sand, C-CO_3	Mn-q	-Sand	
	Co-e, sil, Ca-O	Na-o, Dolomite	Pb-o	Ca-q	30
	Mg-q, -Sand		Mn-h	Ca-e	
.5					
	Water	-Mn-h, Pb-q	Mn-t	Silt, Mg-o, -Na-o, -Mn-h	
	-Al-t, Ca-m	-Cd-h	-pH	Water, -Zn-h	
	Mg-e	C.E.C.		Co-e, -Mg-e	
	Cu-m, -Cuph, -Zn-m	-Pb-h		-Na-t, Ca-m, -Fe-h, -Mn-d	20
	Zn-t, Clay-s, Cu-d	Zn-q, Silt, Mn-q	Cu-t, Cd-h	Mg-q, Cu-d, Mg-d	
.4					
	Ca-e, Cu-t, Co-m, -Plag	Cd-m	Mn-e, Mg-h	C.E.C., Clay-m, Ca-h	
	Zn-q	C-550, Pb-e, Pb-d		Cu-e, -Mn-q	
	Mn-t	Cd-e, Na-h	Ni-m, Zn-t, -Ca-o	Cu-t, Al-t	
	Clay-m, Cd-m, Pb-q		Cd-e	Pb-d	
	Ca-h, Cd-h, -Na-q	-Mn-e, Cu-e, Cu-d	K-h, -Mg-t, Fe-t, Water	-Mn-e, Cd-q	10
.3					
	Percent of total variance explained by each factor				Sum in percent
	22.3	23.2	17.6	11.1	74.2

variance is explained often results in a factor that is due largely to analytical error. Such a factor contributes little to the understanding of physical and chemical processes that affect the occurrence of an element.

Results

A Horizon

Four factors were rotated for the study of the A horizon. These four factors explain a reasonably high amount of the variance (74.2%). Additional factors either appear to be due to noise or error in the data or add little additional information that is useful in interpreting the data. The results are summarized in Table 62 and 63. Table 62 lists the factor loadings for each variable on each of the four factors, and Table 63 gives the relative loadings for all of the variables on each of the four factors.

Factor 1 is strongly related to organic carbon based on the high loadings of C-org, C-t, C-wb, and C-550 (Table 63). The moderately high loadings of CEC indicates that extractable elements that load on factor 1 may occur largely in exchange sites in the organic material. The exchange sites of clay material are of less importance because of the low loading of clay on this factor. Extractable elements associated with exchange sites on organic materials include K with high loadings by all extracts, and both Pb and Zn from the DTPA and EDTA extracts.

Factor 2 is more difficult to interpret than factor 1. The highest loadings on this factor are for Mg-t, followed by clay-m, Fe-t, pH, microcline and negative quartz, and finally clay-s. It seems reasonable to relate this factor to clay minerals (perhaps Mg-rich montmorillonites) and, to a lesser extent, to carbonate materials. The high positive relationship of pH indicates that clay minerals and Fe and Mn minerals are more stable in basic than in acidic solutions. This suggests that the Fe and Mn minerals are carbonates. This seems reasonable because dolomite, Mg-t and Ca-t, and C-CO_3 are also moderately loaded on this factor. Microcline and quartz are negatively related to this factor and probably serve as dilutants to the amount of clay and carbonate present. This factor also has a moderately low loading with CEC, indicating that perhaps the extractable elements that load positively (Ca, Mg, Fe, Mn) may occur in exchange sites on clay minerals. It is not likely that the carbonate minerals have large amounts of exchangeable cations.

Factor 3 is related mainly to oxalate-extractable transition metal cations plus a few transition metals removed by other extracts. Oxalate dissolves Fe and Mn oxides, and the transition metals loading on this factor are probably associated with these oxides. The negative association with pH, dolomite, and C-CO_3 supports this interpretation because the transition metals would probably not occur as carbonates. If they did occur as carbonates, then they would exhibit a positive relationship with carbonates rather than the negative one that is indicated.

Factor 4 is clearly dominated by all extractable forms of Na; however, a few other loadings on physical and chemical properties are moderately high. The physical and chemical properties that are positively related to extractable Na are clay-s, silt, CEC, and clay-m. This indicates that some clay minerals with a moderate ion-exchange capacity probably have Na in readily exchangeable sites. As the clay mineralogy was not determined, the clay mineral associated with exchangeable Na cannot be identified. It is interesting to note the similarity between loadings of exchangeable Ca and, to a lesser extent, exchangeable Mg with exchangeable Na on this factor. Few of the exchangeable transition metals are related to this factor, and exchangeable Mn is negatively related to exchangeable Na.

Discussion for A-Horizon Soils

Factor 1 is related to organic carbon and will be referred to as the organic factor. Factor-2 is less clearly defined, but is apparently related to both clay minerals and Fe-t and Mn-t, with a smaller contribution from carbonate minerals. For brevity, this factor will be referred to as the clay factor. Factor 3 will be called the Fe and Mn oxide factor because it is related to the oxyhydroxides of both Fe and Mn. Factor 4, like factor 2 is a clay-minerals factor, but with a large contribution from extractable Na. In order to distinguish between the two factors, this fourth factor will be called the Na-clay factor.

To aid in the discussion of how each of the extractable elements relate to a factor, the factor loadings are presented by element for each extract, and the communalities are listed in Table 62. It is important to recall that the varimax method of rotating the principal components results in factors that are independent of each other. Consequently, the four factors as described are independent of each other.

Each major element has its own readily exchangeable mode of occurrence. Each of the major elements (Na, K, Ca, and Mg) load similarly on a given factor. The highest to lowest significant factors for each element are summarized in Table 64. For a given major element, it means that any extract will provide a similar amount of information on "availability." Multiple regression techniques may be used to find an equation relating the same element between each of the extracts.

The transition metals (Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn) removed by the oxalate extract have high loadings on the Fe and Mn oxide factor and, generally, have insignificant loadings on the other factors. This demonstrates that oxalate is very specific in dissolving elements held by the Fe and Mn oxides and that other extracts do not readily remove the elements from these oxides. All the transition metals generally have similar loadings on each of the factors for the DTPA and EDTA

Table 64.--The relative order of importance of factor loadings on elements for all extracts. Factors derived by R-mode factor analysis and varimax rotation in some A- and C-horizon soils of the Northern Great Plains.

Element	Soil Horizon	
	A	C
Ca	clay >> organic ≈ Na-clay	CEC
Cd	organic ≈ Fe-Mn oxide	carbonate (-) > Na-x
Co	Fe-Mn oxide > organic	carbonate (-) > CEC ≈ Fe-Mn
Cu	Fe-Mn oxide > clay ≈ organic	carbonate (-) ≈ clay ≈ CEC ≈ Fe-Mn
Fe	clay > Fe-Mn oxide	carbonate (-) > clay
K	organic	clay
Mg	clay > Na-clay ≈ organic	clay > carbonate
Mn	Fe-Mn oxide > Na-clay > clay	carbonate (-) >> CEC (-)
Na	Na-clay >> clay	Na-x
Ni	Fe-Mn oxide	carbonate (-)
Pb	organic > clay > Na-clay	CEC > Fe-Mn ≈ clay
Zn	organic > Fe-Mn oxide ≈ clay	Fe-Mn ≈ carbonate ≈ CEC

extracts, indicating that these two extracts give similar information for both the transition metals and major elements. Each element, however, has different loadings on the various factors, indicating that the occurrence of these metals is generally not related in the sites attached by DTPA and EDTA. With few exceptions, the relatively weak ion exchange extract ($MgNO_3$) had its highest loadings for the transition metal ions on the clay and organic factors. Presumably, therefore, transition metals absorbed by clays and organics are the most readily exchangeable. In general, the loadings of the transition metals of the HCl extract were not similar to the loadings of the metals for any other extract. The transition metals of the HCl extract were derived largely from clays, with smaller amounts being derived from the other three factors. The HCl extract is not specific for any of the factors. For the transition metals, hydroquinone was the poorest extract in terms of generally having the lowest communalities and having the lowest number of significant factor loadings. The loadings of elements measured in the hydroquinone extract are generally different from those of any other extract for the transition metals. It appears that hydroquinone is not a particularly good extract in terms of having strong relations either with a factor or with the various transition metals.

C Horizon

Seven factors are needed to explain both the occurrence of the extractable elements and a reasonable amount (77.2 percent) of the total variance. The additional factors required for the C horizon (as compared with the A horizon) may be due to the fact that C-horizon soils more closely represent the chemistry and mineralogy of several different types of bedrock. A-horizon soils tend to be more homogeneous because they are more completely weathered, may be mixed by transportation, and are dominated by biologic activity and accumulation of organic matter. In addition, the development of soil horizon features results in differences between the A and C soil horizons. For example, the organic carbon content of the well-developed A horizon is 1.9% (Severson and others, 1977, p. 56) and the organic factor (see Table 63) explains over 22% of the total variance of the data set, while in the C-horizon the organic carbon content is much lower at 0.65% (Severson and others, 1977, p. 56), with no organic-rich layer, and the organic factor explains only about 6% of the total variance. Also, the A and C horizons contain 0.035 and 0.45% carbonate carbon, respectively (Severson and others, 1977, p. 56), indicating that the C horizon has an accumulation of carbonates. There is no carbonate factor for the A horizon, but the carbonate factor for the C horizon explains nearly 22% of the total variance of the data set; nearly 50% more than the next most important factor.

Table 66 shows the relative loadings of the variables on the seven factors. Table 65 is a listing of the factor loadings by element on each extract for each of the seven factors. The communalities of the variables are also given in Table 65.

Table 65.--Factor analysis loadings and communalities for total and extractable element content for seven varimax factors. C-horizon soils of the Northern Great Plains.

[Factor; see text for explanation of each factor. Extract abbreviations: T, total; d, DTPA; e, ETDA; q, hydroquinone; m, $MgNO_3$; o, oxalate]

		Factor							
Element	Extract	1	2	3	4	5	6	7	Communality
Ca	T	.73	.41	.21	-.10	-.27	.00	.22	.88
	e	-.14	.06	-.88	-.16	-.03	-.10	-.19	.87
	q	.14	.01	-.91	-.18	-.01	-.14	-.18	.92
	m	-.27	+.04	-.88	-.07	-.17	-.12	-.09	.92
	o	-.08	-.20	-.23	.27	-.43	-.47	-.44	.78
Cd	d	-.65	.00	-.10	-.04	-.31	.28	-.13	.63
	e	-.67	-.16	-.32	-.04	-.20	.12	-.02	.63
	q	-.48	.30	.33	.24	-.07	-.12	.67	.53
	m	-.18	.11	-.42	.31	-.27	.21	-.09	.45
	o	-.13	-.36	-.18	.58	.02	-.33	-.08	.63
Co	d	-.41	.06	-.28	+.01	-.25	-.02	.50	.56
	e	.11	.50	-.18	-.37	.29	-.29	-.29	.68
	m	-.37	-.25	-.54	-.39	-.07	.05	.07	.66
	o	-.79	.13	-.07	-.09	.15	.22	.20	.76
Cm	T	.17	.47	-.05	.33	-.17	-.66	-.17	.85
	d	-.03	.71	.08	.23	-.09	-.46	-.08	.79
	e	-.08	.34	.19	.39	-.10	-.26	-.17	.42
	m	.28	.26	-.68	.07	.16	-.41	-.20	.85
	o	-.88	.11	-.19	.26	.07	-.03	.01	.90
Fe	T	.20	.00	-.26	.32	-.08	-.78	-.16	.85
	d	-.55	.37	.30	.25	-.20	-.40	.04	.80
	e	-.63	.34	.19	.39	-.10	-.26	-.18	.77
	m	.13	.44	-.29	.30	-.42	.26	-.08	.64
	o	-.91	-.05	-.25	.17	.07	-.06	-.01	.92
K	T	.07	-.11	-.36	.42	-.09	.11	-.42	.52
	d	-.29	.87	-.08	.16	-.01	.00	.05	.87
	e	-.23	.88	-.08	-.20	.13	.05	-.02	.90
	q	-.35	.88	-.20	.03	.04	.00	.04	.95
	m	-.11	.78	-.24	.04	.27	.13	.12	.78
	o	-.52	.71	-.05	.23	-.06	.19	.04	.87

Table 65.--Continued

Element	Extract	Factor 1	 2	 3	 4	 5	 6	 7	Communality
Mg	T	.77	.55	.20	-.04	-.09	-.02	-.07	.95
	d	.39	.53	.00	-.04	.06	-.26	.29	.59
	e	.44	.73	-.09	.18	.13	-.17	.07	.82
	q	.31	.49	-.09	.37	.11	.04	-.26	.55
	o	.34	.52	.11	.12	.46	-.20	-.09	.68
Mn	T	.05	-.31	.02	.22	-.31	-.64	.14	.68
	d	-.58	.18	.05	-.16	-.43	-.55	.10	.91
	e	-.68	.44	.42	-.15	-.27	-.11	.01	.94
	q	-.72	-.09	-.19	-.07	-.10	-.31	.23	.73
	m	-.67	.25	.48	-.12	-.23	-.07	.10	.83
	o	-.90	-.11	-.22	.07	.17	.15	.11	.94
Na	T	-.04	-.36	.03	.16	.08	-.01	.86	.90
	d	-.04	.24	.10	.91	-.05	-.12	.13	.92
	q	-.02	.18	.08	.91	-.05	-.10	.14	.89
	m	-.06	.24	.11	.88	-.06	-.17	.09	.89
	o	-.15	.15	.07	.92	-.06	-.13	-.05	.92
Ni	d	-.66	-.06	.18	.02	-.41	.06	.27	.72
	e	-.76	.03	.27	.02	-.13	.10	.07	.69
	m	-.23	-.26	-.33	.49	-.03	-.35	.30	.68
	o	-.92	-.04	-.18	.08	.13	.04	.16	.92
Pb	d	-.10	.33	-.18	-.04	.07	-.69	.03	.63
	e	-.13	.42	-.62	-.08	-.14	-.42	-.14	.80
	q	-.07	.16	-.73	.14	.16	-.08	.07	.62
	m	-.16	-.24	-.68	-.22	-.39	.08	.07	.76
	o	-.71	.21	.26	.04	.01	-.09	-.01	.62
Zn	T	.19	.14	-.07	.39	-.28	-.77	-.08	.89
	d	-.55	.20	.03	.45	-.09	-.37	.09	.70
	e	-.13	.42	-.62	-.08	-.14	-.42	-.11	.61
	q	-.12	-.16	-.14	-.19	.04	-.36	-.62	.61
	m	+.05	.11	-.37	.30	-.56	-.22	-.00	.60
	o	-.73	.09	.05	.17	.26	.14	-.18	.70

[Some variables are negative; abbreviations are listed in Table 62]

Factor Loading	1--Carbonate	2--Clay	3--Cation exchange capacity	4--Sodium	5--Organic	6--Total iron, manganese	7--Plagioclase	Percent variance explained
1.0								100
								90
	-Ni-o			Na-o, Na-q, Na-d				
.9			Ca-q					80
	-Mn-o, -Fe-o	K-q, K-e	Ca-e, Ca-m					
	-Cu-o	K-d					Na-t	
	Calcite							70
.8								
	pH	-Sand						
	-Co-o	Clay-s, K-m	-Water		C-wb	Fe-t		60
	Mg-t, -Ni-e					Zn-t		
							Plag	
	Ca-t, -Mn-q, -Zn-o	Clay-m, Mg-e	Pb-q					
.7	Dolomite, -Pb-o	Cu-d, K-o			C-org			50
	-Mn-e		Cu-m, Pb-m					
	C-t, C-CO$_3$, -Cd-d,		C.E.C.			Pb-t		
	-Cd-e, -Ni-d,	Silt				Cu-t		
	-Mn-m					Mn-t		40
	-Fe-e		Pb-e					
.6	-Quartz			Cd-o				
	-Mn-d, -Zn-e				Zn-m		Zn-q	
		-Quartz	-Fe-e			Mn-d		30
	C-550, -Zn-d, -Fe-d	Mg-t				Al-t		
	-K-o	C-550, Mg-d, Mg-o						
.5		Co-e						
	-Cd-q	C-CO$_3$, Mg-q	-Mn-m	Ni-m			Co-d	
		-Cu-t						
	Mg-e	Mn-e, Fe-m, C.E.C.		Zn-d	Tot-C, Silt, -Mg-O	Cu-d, K-spar, -Ca-o		20
		Pb-e, -K-spar	-Dolomite, -Mn-e, Cd-m	K-t	C-550	C-org		
	-Co-d	Ca-t			Mn-d, Fe-m, Ca-o	Pb-e	-Ca-o	
.4					Ni-d	Fe-d, Cu-m		
	Mg-d	C-t		-Co-m, Zn-t, Cu-e	Co-m, Pb-m			
	-Co-m, -C.E.C.	Dolomite, Fe-d, -Cd-o	K-t, Zn-m, Al-t	Zn-e, -Co-e, Mg-q		Zn-d, Zn-q		
		-Na-t		Al-t		Zn-d, Zn-q	-Al-t	
	-K-q, Mg-o	Cu-e				-Ni-m		
		Pb-d	-Cd-q, Cd-e, Ni-m	Cu-t, Fe-t	Clay-m	Cd-o	-C-550	
	Mg-q	Cd-q, -Mn-t	-C-t, -Fe-d, -Plag	Fe-m, Cd-m, Zn-m	Cd-d, Mn-t	Mn-q, C-wb		10
.3								
	Percent of total variance explained by each factor							Sum in Percent
	21.7	15.8	11.5	8.8	6.4	8.0	5.0	77.2

The phases that dominate factor 1 are clearly the carbonate minerals, calcite, and dolomite (Table 66). This factor will be referred to as the carbonate factor. The variables with the highest positive loadings on this factor, in order of decreasing importance, are calcite, pH, Mg-t, Ca-t, dolomite, C-t, and C-CO_3. Less important loadings include silt, negative quartz (which probably occurs as a dilutant to the carbonates), and C-550. This factor explains nearly 22% of the total variance of the data set--a very large amount considering that there are 79 variables.

Factor 2 has its highest non-extract loading on sand (negative) with smaller loadings on both clay-s and clay-m (Table 66). Moderate loadings occur with silt, quartz (negative), Mg-t, C-550, C-CO_3, and CEC. This factor is primarily due to fine-grained material, including clay and silt, with sand (quartz) serving as a dilutant. This factor also has a minor contribution by carbonates. This is the second most important factor, and it accounts for nearly 16 percent of the total variance. Factor 2 is referred to as a clay factor.

Factor 3 has a high loading on water and a lesser, but important, loading on CEC. No other non-extract variables seem to have significant loadings on this factor. As the water variable represents the percentage weight loss on heating from air-dry to 105°C, it is not clear why water is not associated with other variables in addition to CEC. Perhaps both CEC and water are related to the surface area of the soil. This factor explains over 11% of total variance of the data set.

Factor 4 is dominated by very high loadings of extractable Na, and will be referred to as the extractable Na (Na-x) factor. This factor may be analogous to the Na-clay factor of the A horizon, although clay does not load on this factor. Soluble Na salts may also account for this factor, as these salts would be present in quantities too small to be detected by X-ray diffraction. It explains nearly 9% of the total variance.

Factor 5 is an organic factor with high loadings of C-wb and C-org, with small loadings on C-t, silt, and C-550. It explains about 6 percent of the variance in the data and will be referred to as the organic factor.

Factor 6 has moderately high loadings on Fe-t and Mn-t. This factor may represent Fe and Mn minerals from the underlying rocks, presumably largely unweathered. This factor explains about 8 percent of the total variance and will be called the Fe and Mn factor. It is dissimilar to the Fe and Mn oxide factor of the A horizon.

Factor 7 has high loadings of Na-t and plagioclase and is clearly related to that mineral. It explains only 5 percent of the total variance and will be referred to as the plagioclase factor.

Discussion for C-Horizon Soils

In general, all extracts for each of the major elements (Ca, K, Mg, Na) load on the same factors. A list of the major elements and the important factors in order of loading is given in Table 64. These factor loadings are analogous to the A horizon results for these same elements. The results suggest that the major elements are either readily exchangeable or highly soluble, or both. Any extract can be used to remove any of the four major elements from the soil, as these elements occur in the soil in a manner that is equally susceptible to attack by any of the extracts. For the transition metals (Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn), the DTPA and EDTA extracts generally all have similar loadings on the same factors (Table 65). This means that the same information on extractable elements can be obtained from either of these two extracts. This result is very similar to that obtained for DTPA and EDTA in A-horizon soils.

The oxalate extracts load almost exclusively on the carbonate factor for all of the transition metals except Cd. The large negative factor loadings suggest that when the oxalate extract is used it exclusively dissolves elements from the carbonate factor. The negative loadings of the oxalate extracts on the carbonate factor imply that, when the concentration of calcite and the pH are high, the concentration of oxalate-extractable elements is low. A possible explanation is that the higher the pH and carbonate content are in the soil, the greater the change in conditions of oxalate extract during the extraction process. If the acidic (pH 3) oxalate solution is made sufficiently more basic by dissolving carbonate, then either the Fe and Mn oxyhydroxides in the soil may not be dissolved or the released transition metals may be reprecipitated as carbonates or hydroxides. The result is that there will be negative relationships between the pH and carbonate content of the soil and between the concentrations of transition metals dissolved by the oxalate solution.

The $MgNO_3$ extract is the weakest of the extracts tested. In general, it has no high loadings on any of the factors for the transition metals. Rather, it has low to moderate loadings on several factors for each of the transition metals. These include, in order of decreasing importance, factors 3, 4, and 5. Presumably, the transition metals can be readily removed by ion exchange from these factors. Of lesser importance are the clay and organic factors, from which $MgNO_3$ generally removes very small amounts of the transition metals.

The removal of transition metal ions is similar for DTPA and EDTA, but not identical in terms of factor loadings. The loadings for these two extracts are not at all similar to the factor loadings of $MgNO_3$. Both DTPA and EDTA tend to be negatively loaded on the carbonate factors (similar to oxalate). Since the pH of both DTPA and EDTA is near neutral, the effect of a pH change would not be as strong as with oxalate. Consequently, it seems that the negative loadings for both DTPA and EDTA, as well as oxalate, must be due to the formation of insoluble transition metal carbonates or hydroxides. Both DTPA and EDTA also have several important, positive loadings on the clay factor.

These are on both the transition metals and the major elements. These loadings indicate that important amounts of some elements can be removed by ion exchange with complexing. There are only a few important loadings of either DTPA and EDTA on the transition metals for the remaining five factors. This means that DTPA and EDTA remove cations from clays and from soils low in both pH and carbonate by ion exchange. The other factors are generally not important.

Summary

Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn were extracted from samples of 21 A- and C-horizon uncultivated soils of the Northern Great Plains by DTPA, EDTA, hydroquinone, $MgNO_3$, and oxalate. In addition, HCl was used to extract these elements from the A-horizon soils. Other variables determined on each sample include a variety of soil chemical and physical properties, mineralogy, and total element content.

R-mode factor analysis demonstrates that nearly 75 percent of the total measured variation in A-horizon soils can be described in terms of four factors. The factors are: 1) organic content, 2) clay content, except Na-rich clay, 3) Fe and Mn oxides, and 4) Na-rich clay. Seven factors accounted for more than 75 percent of the total variance in C-horizon soils. The factors are: 1) carbonate content, 2) clay content, 3) cation exchange capacity, 4) extractable Na, 5) organic content, 6) Fe and Mn content, and 7) plagioclase. The four major elements--Ca, K, Mg, and Na--are each related to the same factor regardless of the extract, in both A- and C-horizon soils. The DTPA and EDTA extracts tend to give similar loadings on the same factors for the transition metals--Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn--in both A- and C-horizon soils. Transition metals in the oxalate extract tended to load positively on the Fe and Mn oxide factor for the A horizon, and negatively on the carbonate factor for the C horizon. Transition metals in the HCl, $MgNO_3$, and hydroquinone extracts loaded on various factors, depending on the soil horizon and the element.

References Cited

Anderson, B. M., and Keith, J. R., 1977, A new multi-traverse study of soil and sagebrush chemistry around the Dave Johnston Powerplant, Wyoming, p. 14-54, in U.S. Geol. Survey, Geochemical survey of the western energy regions, 4th annual progress report, July, 1977: U.S. Geol. Survey Open-file Rept. 77-872, 207 p.

Bohn, H. L., and Aba-Husayn, M. N., 1971, Manganese, iron, copper, and zinc concentrations of Sporobolus wrightii in alkaline soils: Soil Sicence, v. 112, no. 5, p. 348-350.

Cashion, W. B., and Donnell, J. R., 1972, Chart showing correlation of selected key units in the organic-rich sequence of the Green River Formation, Piceance Basin, Colorado, and Uinta Basin, Utah: U.S. Geol. Survey Oil and Gas Inv. Chart OC-65.

Christianson, G. A., and Jacobson, G. A., 1971, Report on molybdenosis in farm animals and its relationship to a uraniferous lignite ashing plant, Division of Environmental Engineering, North Dakota State Dept. Health, Bismark 58505, 9 p. (unpublished manuscript).

Coffman, C. B., and Miller, J. R., 1973, Response of corn in the greenhouse to soil applied zinc and a comparison of three chemical extractions for determining available zinc: Soil Sci. Soc. Am. Proc., v. 37, p. 721-724.

Cohen, A. C., Jr., 1959, Simplified estimators for the normal distribution when samples are singly censored or truncated: Technometrics, v. 1, p. 217-237.

Comrey, A. L., 1973, A first course in factor analysis: Academic Press, New York, 316 pp.

Connor, J. J., Keith, J. R., and Anderson, B. M., 1976, Trace-metal variation in soils and sagebrush in the Powder River Basin, Wyoming and Montana: J. Research U.S. Geol. Survey, v. 4, no. 1, p. 49-59.

Culbertson, W. C., Hatch, J. R., and Affolter, R. H., 1978, Geology and coal resoures of the Hanging Woman Creek EMRIA site, Big Horn and Powder River Counties, Montana: U.S. Geol. Survey Open-file Rept. 78-506.

Dane, Carle, H. and Bachman, George O., 1965, Geologic map of New Mexico: U.S. Geol. Survey (2 sheets).

Dollahite, J. W. , Rowe, L. D., Cook, L. M., Hightower, Dan, Bailey, F. M., and Kyzar, J. R., 1972, Copper deficiency and molybdenosis intoxication associated with grazing near a uranium mine:

Southwestern Vet. 9:47-50.

Donnell, J. R., and Blair, R. W., Jr., 1970, Resource appraisal of three oil-shale zones in the Green River Formation, Piceance Creek Basin, Colorado: Colorado School of Mines Quart., v. 65, no. 4, p. 73-87.

Dye, W. B., and O'Harra, D. L., 1959, Molybdenosis, Nevada Agr. Exp. Sta. Bull. 207, 32 p.

Ebens, R. J., Erdman, J. A., Feder, E. L., Case, A. A., and Selby L. A., 1973, Geochemical anomalies of a claypit area, Callaway County, Missouri, and related metabolic imbalance in beef cattle: U.S. Geol. Survey Prof. Paper 807, 24 p.

Erdman, J. A., and Ebens, R. J., 1978, A comparison of the element content of crested wheatgrass grown on soils and on reclaimed spoils at the Dave Johnston Mine, Wyoming: J. Range Manage. (in press).

Erdman, J. A., Ebens, R. J., and Case, A. A., 1978, Molybdenosis: a potential problem in ruminants grazing on coal mine spoils: J. Range Manage. 31:34-36.

Erdman, J. A., and Gough, L. P., 1977, Variation in the element content of *Parmelia chlorochroa* from the Powder River Basin of Wyoming and Montana: The Bryologist, v. 80, no. 2, p. 292-303.

______1978, Mineral composition of wheat from coal-mine spoils and farms in the Northern Great Plains, USA: Proc., International Congress for Energy and the Ecosystem: Economics; Ecology and Planning of Coal Resource Development, June, 1978, Grand Forks, ND (in press).

Gatehouse, S., Russell, D. W., and Van Moort, J. C., 1977, Sequential soil analysis in exploration geochemistry: Jour. Geochem. Exploration, v. 8, p. 483-494.

Gough, L. P., and Erdman, J. A., 1977, Influence of a coal-fired powerplant on the element content of *Parmelia chlorochroa*: The Bryologist, v. 80, no. 3, p. 492-501.

Gough, L. P., McNeal, J. M., and Severson, R. C., 1977, Availability of DTPA-extracted elements to native plants in the Northern Great Plains: Agron. Abstracts, Amer. Soc. Agron., Madison, Wisc.

Gough, L. P., and Severson, R. C., 1976, Impact of point source emissions from phosphate processing on the element content of plants and soil, Soda Springs, Idaho, *in D. D. Hemphill, ed., Trace substances in environmental health-x:* Columbia, Mo., Univ. Missouri, p. 225-233.

Gough, L. P., Severson, R. C., and McNeal, J. M., 1978, Extractable and total-soil element concentrations favorable for native plant growth in the Northern Great Plains (Abs.): International Congress for Energy and the Ecosystem, June 12-16, Univ. of North Dakota, Grand Forks, N. D., p. 67.

Hale, M. E., 1974, *Bulbothrix*, *Parmelina*, *Relicina*, *Xanthoparmelia*, four new genera in the Parmelaceae (Lichenes): Phytologia, v. 28, no. 5, p. 479-490.

Halstead, R. L., Finn, B. J., and MacLean, A. J., 1969, Extractability of nickel added to soils and its concentration in plants: Can. Jour. Soil Sci., v. 49 p. 335-342.

Haq, A. U., and Miller, M. H., 1972, Prediction of available soil Zn, Cu, and Mn using chemical extractants: Agron. Jour., v. 64, p. 779-782.

Harmon, H. H., 1967, Modern factor analysis: 2nd ed., Univ. of Chicago Press, Chicago, 474 pp.

Harms, T. F., 1976, Analysis of plants and plant ashes by methods other than emission spectroscopy, *in* Miesch, A. T., Geochemical survey of Missouri--methods of sampling, laboratory analysis, and statistical reduction of data: U.S. Geol. Survey Prof. Paper 954-A, p. 17-18.

Hinkley, Todd K., Ebens, Richard J., and Boerngen, Josephine G., 1978, Overburden chemistry and mineralogy of Hanging Woman Creek, Big Horn Country, Montana and recommendations for sampling at similar sites: U.S. Geol. Survey Open-file Rept. 78-393.

Hite, R. J., and Dyni, J. R., 1967, Potential resources of dawsonite and nahcolite in the Piceance Creek Basin, northwest Colorado, *in* Symposium on oil shale, 4th: Colorado School of Mines Quart., v. 62, no. 3., p. 25-38.

Hodgson, J. F., 1963, Chemistry of the micronutrient elements in soils: Advances in Agronomy, v. 15, p. 119-159.

Huffman, Claude, Jr., and Dinnin, J. I., 1976, Analysis of rocks and soils by atomic absorption spectrometry and other methods, *in* Meisch, A. T., Geochemical survey of Missouri - methods of sampling, laboratory analysis and statistical reduction of data: U.S. Geol. Survey Prof. Paper 954A, p. A12-A14.

Jenne, Everett, A., and Luoma, Samuel N., 1977, Forms of trace elements in soils, sediments, and associated waters: an overview of their determination and biological availability, (in) Biological Implications of Metals in the Environment: CONF-750929, Tech. Info. Ctr., Energy Research and Development Administration, p.

110-143.

Klein, D. H., Andren, A. W., Carter, J. A., Emery, J. F., Feldman, C., Fulkerson, W., Lyon, W. S., Ogle, J. C., Talmi, Y., Van Hook, R. I., and Bolton, N., 1975, Pathways of thirty-seven trace elements through coal-fired power plant: Environ. Sci. and Technology, v. 9, p. 973-979.

Kubota, J., 1975, Areas of molybdenum toxicity to grazing in the western states: J. Range Manage. 28:252-256.

Leone, F. C., Nelson, L. S., Johnson, N. L., and Eisenstat, S., 1968, Sampling distributions of variance components 2, Empirical studies of unbalanced nested designs: Technometrics, v. 10, p. 719-737.

LeRiche, H. H., and Weir, A. H., 1963, A method of studying trace elements in soil fractions: Jour. Soil Sci., v. 14, no. 2, p. 225-235.

Lindsay, W. L., and Norvell, W. A., 1969, Development of a DTPA micronutrient soil test: Madison, Wisconsin, Agronomy Ass., Am. Soc. Agronomy, p. 84.

Maker, H. J., Keetch, C. W., and Anderson, J. U., 1973, Soil associations and land classification for irrigation, San Juan County: New Mex. State Univ. Ag. Exp. Sta. Rept. no. 257, 44 p.

McKeague, J. A., and Day, J. H., 1966, Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils: Canadian Jour. Soil Sci., v. 46, no. 1, p. 13-22.

McNeal, J. M., Gough, L. P., and Severson, R. C., 1977, The mode of occurrence of DTPA- and EDTA-extractable elements in soils of the Northern Great Plains: Agron. Absracts, Amer. Soc. Argron., Madison, Wisc., 128 p.

Miesch, A. T., 1976, Geochemical survey of Missouri--methods of sampling, laboratory analysis, and statistical reduction of data in a geochemical survey of Missouri, with sections on laboratory methods: U.S. Geol. Survey Prof. Paper 954-A, 39 p.

Mitchell, R. L., 1972, Trace Elements in soils and factors that affect their availability: Geol. Soc. Am. Bull., v. 83, p. 1069-1076.

Myers, A. T., Havens, R. G., and Dunton, P. J., 1961, A spectrochemical method for the semiquantitative analysis of rocks, minerals, and ores: U.S. Geol. Survey Bull. 1084-I, p. 207-229.

Natrella, M. G., 1961, Experimental Statistics: U.S. Natl. Bur. Stds. Hdbk., no. 91, Wash., D. C.

Neiman, H. G., 1976, Analysis of rocks, soils, and plant ashes by emission spectroscopy, in Meisch, A. T., Geochemical survey of Missouri - methods of sampling, laboratory analysis, and statistical reduction of data: U.S. Geol. Survey Prof. Paper 954-A, p. A14-A15.

Randall, G. W., Schulte, E. E., and Corey, R. B., 1976, Correlation of plant manganese with extractable soil manganese and soil factors: Soil Sci. Soc. America Jour., v. 40, no. 2, p. 282-287.

Rickmers, A. D., and Todd, H. N., 1967, Statistics--an introduction: New York, McGraw-Hill Book Co., 585 p.

Robb, W. A., and Smith, J. W., 1974, Mineral profile of oil shales in Colorado core hole no. 1, Piceance Creek Basin, Colorado, in Murray, D. K., ed., Guidebook to the energy resources of the Piceance Creek Basin, Colorado: Rocky Mountain Assoc. of Geologists twenty-fifth field conference, p. 91-100.

Roehler, H. W., 1974, Depositional environments of Eocene rocks in the Piceance Creek Basin, Colorado, in Murray, D. K., ed., Guidebook to the energy resources of the Piceance Creek Basin, Colorado: Rocky Mountain Assoc. of Geologists twenty-fifth field conference, p. 57-64.

Rule, J. H., and Graham, F. R., 1976, Labile soil pools of manganese, iron, and zinc as measured by plant uptake and DTPA equilibrium: Soil Sci. Soc. Amer. Jour., v. 40, pp. 853-857.

Safaya, N. M., 1978 Delineation of mine-spoils for specific nutrient stresses and screening plants for adaptability (Abs.): International Congress for Energy and the Ecosystem, June 12-16, Univ. of North Dakota, Grand Forks, N. D., p. 66.

Schafer, W. M., Nielsen, G. A., Dollhopf, D. J., and Hodder, R. L., 1976, Soil genesis, hydrological properties, and root characteristics of 2 to 52 year old stripmine spoils: Montana Agr. Res. Sta. Research Rept. 108 (progress rept. 1), 90 p.

Severson, R. C., and Gough, L. P., 1978, Environmental implications of element emissions from phosphate processing operations in southeastern Idaho: U.S. Geol. Survey Prof. Paper 1083, in press.

Severson, R. C., Gough, L. P., and McNeal, J. M., 1977, Availability of elements in soils to native plants, Northern Great Plains: U.S. Geol. Survey Open-file Rept. 77-847, 90 p.

Shacklette, H. T., Sauer, H. I., and Miesch, A. T., 1970, Geochemical environments and cardiovascular mortality rates in Georgia: U.S. Geol. Survey Prof. Paper, 574-C, 39 p.

Shuman, L. M., and Anderson, O. E., 1974, Evaluation of six extractants for their ability to predict manganese concentrations in wheat and soybeans: Soil Sci. Soc. America Proc., v. 38, no. 5, p.788-790.

Soil Survey Staff, 1975, Experimental Statistics: U.S. Natl. Bur. Stds. Hdbk., no. 91, Wash., D. C.

Sorenson, R. C., Oelsligle, D. D., and Knudsen, Delno, 1971, Extraction of Zn, Fe, and Mn from soils with 0.1 N hydrochloric acid as affected by soil properties, solution, soil ratio, and length of extraction period: Soil Sci., v. 111, no. 6, p. 352-359.

Spencer, D. W., 1967, Factor analysis II: A description of the application of oblique solutions: unpublished manuscript, Woods Hole Oceanographic Institute, Reference No. 67-59.

Tidball, R. R., 1978, Chemical and mineralogical evaluation of soils, Hanging Woman Creek EMRIA site, Big Horn County, Montana: U.S. Geol. Survey Open-file Rept. 78-346, 84 p.

Tidball, R. R., and Ebens, R. J., 1976, Regional geochemical baselines in soils of the Powder River Basin, Montana-Wyoming, in Laudon, R. B., ed., Geology and energy resources of the Powder River: Wyo. Geol. Assoc. Guidebook, Twenty-eighth Ann. Field Conf., Casper, Wyo., Sept., 1976, p. 299-310.

Thorton, I., 1974, Applied geochemistry in relation to mining and the environment. Preprint submitted at the Minerals and the Environment Symposium, London (June, 1974), 16 p.

Trudell, L. G., Beard, T. N., and Smith, J. W., 1970, Green River Formation lithology and oil shale correlations in the Piceance Creek Basin, Colorado: U.S. Bur. Mines Rept. Inv. 7357, 11 p.

U.S. Geological Survey, 1973, Draft environmental statement--proposed plan of mining and reclamation, Big Sky Mine, Peabody Coal Company, coal lease M-15965, Colstrip, Montana: U.S. Geol. Survey, Draft Environmental Statement DES 73-64, 214 p.

______1975, Geochemical survey of the western coal regions, 2nd Annual Progress Report: U.S. Geol. Survey Open-file Rept. 75-436, 132 p.

______1976, Geochemical survey of western energy regions (formerly Geochemical survey of western coal regions), 3rd Annual Progress Report, July, 1976: U.S. Geol. Survey Open-file Rept. 76-729, 138 p.

______1977, Geochemical survey of the western energy regions, 4th Annual Progress Report: U.S. Geol. Survey Open-file Rept. 77-872, 207 p.

VanTrump, George, Jr., and Miesch, A. T., 1977, The U.S. Geological

Survey Rass-Statpac system for management and statistical reduction of geochemical data: Computers and Geosciences, v. 3, p. 475-488.

Viets, Frank G., Jr., 1962, Chemistry and availability of micronutrients in soils: Ag. and Food Chem., v. 10, no. 3, p. 174-178.

Wahlberg, J. S., 1976, Analysis of rocks and soils by X-ray fluoresence, in Meisch, A. T., Geochemical survey of Missouri - methods of sampling, laboratory analysis, and statistical reduction of data: U.S. Geol. Survey Prof. Paper 954-A, p. A11-A12.

Waldrop, M., 1977, Strict law challenges strip mine operators: Chem. and Engineering News 55:18-19.

Whitaker, S. H., and Pearson, D. E., 1972, Geological map of Saskatchewan: Saskatchewan Dept. Mineral Resources and Saskatchewan research council, 1 sheet.