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MIB ADSORPTION IN DRINKING WATER TREATMENT

BY

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THESIS

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WE HEREBY RECOMMEND THAT THE THESIS BY

THOMAS EDWARD TOKUO GILLOGLY

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BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Snoeyink
Director of Thesis Research

Head of Department

Committee on Final Examination†

Snoeyink
Chairperson

Roger A. Minear

† Required for doctor's degree but not for master's.

O-517

"We are healed of a suffering only by experiencing it in full." (Marcel Proust)

Abstract

MIB ADSORPTION IN DRINKING WATER TREATMENT

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Department of Civil and Environmental Engineering
University of Illinois at Urbana-Champaign. 1998
Vernon L. Snoeyink, Advisor

The objective of this research was to provide the tools necessary to determine the effectiveness of activated carbon, in the presence or absence of free chlorine, for the removal of 2-methylisoborneol (MIB) in a drinking water treatment plant.

An alternative approach to analyzing concentrations of (MIB) was developed for use in laboratory-scale experiments. MIB synthesized with radiolabeled-^{14}C (^{14}C-MIB), could be analyzed by liquid scintillation counting, a technique suitable for the rapid collection and analysis of radiolabeled compounds. Using this technique, a 2.5 mL sample aliquot containing ^{14}C-MIB could be analyzed with a 3.0 ng/L limit of detection with greater than 89% confidence, without any sample concentration. This analysis could be used in the presence or absence of free chlorine.

The percent MIB removed by activated carbon, either powdered (PAC) or granular (GAC), was independent of the influent MIB concentration in natural water. It was determined that the adsorption of MIB was controlled by the quantity of natural organic matter adsorbed. Based on these experimental findings and supported by competitive adsorption theory, one protocol was developed to determine the minimum PAC dose required to reduce a known concentration of MIB to a desired level. A second protocol was also developed to determine the remaining GAC bed life for the mitigation of an MIB taste and odor episode. The results from these protocols indicated that adsorption

by activated carbon alone might not provide sufficient protection against taste and odor caused by MIB. It was suggested that an alternative or combination of technologies (ozone, advanced oxidation, biological reduction, adsorption) be investigated to determine which is the most effective.

It was observed that chlorine had a deleterious effect on the ability of both PAC and GAC to adsorb MIB. From this, it was encouraged to avoid contacting activated carbon with chlorine.

"It is better to deserve honors and not have them
than to have them and not deserve them." (Mark Twain)

Dedication

To my grandfather:

May I one day be half the man you saw in me.

"Be anything you want to be;
just be the best that you can be."
-Tokuo Yamamoto

"I am a part of all that I have met" *(Lord Alfred Tennyson)*

Acknowledgments

Looking back to see how I have gotten to where I am today, I am reminded of the countless people who have influenced my life. While it is impossible to address every one of them here, there are a select few who have played a pivotal role during the past few years. First and foremost is my advisor, Dr. Vernon L. Snoeyink. His sage insight and timeless patience has guided me through my development here at the University of Illinois. Without him, I might actually think that I understand something about adsorption.

My gratitude also goes out to the members of my committee, Dr. Richard Larson. Dr. Benito Mariñas and Dr. Roger Minear. Their endurance, support and insight have been most~~ly~~ appreciated.

The "Snoeyink Research Group", both past and present, has been a source of inspiration, insight, and insanity. I have been fortunate enough to be a part of this fine collection of minds...and people. Those who have shared my office, and thus my life, deserve an additional thank you, and more than likely a couple of apologies. In particular, Carlos "Maestro" Campos has been a true friend, helping me though both my personal and professional careers. A special thank you goes to Joseph Elarde, who worked with me countless days, and nights, on this project and constantly provided a unique perspective on research and life.

The City of Chicago, Department of Water, has been kind enough to serve as the primary funding source for this project, without which, this thesis would not have been possible.

Last, but not least, my wife, Mai, and my family has been there every step of the way. Their encouragement, consolation, and patience have been without bounds; their understanding and forbearance, infinite.

"A place for everything, everything in its place." (Benjamin Franklin)

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"Perplexity is the beginning of knowledge." (Kahlil Gibran)

Introduction

Most utilities considering employing an activated carbon system, as well as some utilities which have one installed, are perplexed. These utilities are not sure how effective their adsorptive systems will be. While many factors contribute to a particular systems effectiveness, answering two questions would go far to alleviate some of their confusion. These two questions are, "how much powdered activated carbon (PAC) will be necessary," and, "how long will granular activated carbon (GAC) adsorbers last?" For the treatment of organoleptic problems, determining how much PAC is necessary to mitigate predicted levels of earthy-musty contamination, generally indicates if powdered or granular activated carbon should be used. Should GAC be selected, due to large required doses of PAC, ascertaining how long a GAC adsorber would be effective typically indicates if the technology is economically feasible.

The occurrence of earthy-musty tastes and odors caused by compounds such as 2-methylisoborneol (MIB) and geosmin, commonly encountered in surface waters, is a problem water utilities around the world must face. Activated carbon, both powdered and granular, has been widely used for the mitigation of these unacceptable organoleptic occurrences, but this technology has yielded mixed results. The wide variability in the effectiveness of activated carbon appears related to the magnitude and periodic nature of the influent concentration, the concentration and characteristics of the natural organic matter, and the presence or absence of free chlorine.

It is the purpose of this study to obtain the fundamental data necessary to determine the key factors that influence activated carbon performance and dosage requirements for earthy-musty taste and odor control in a water treatment plant using free chlorine as a disinfectant. This will be accomplished by investigating the influences of the influent MIB concentration, natural organic matter, and free chlorine on PAC and GAC.

"If you steal from one author, it's plagiarism.
If you steal from two, it's research." (Wilson Mizner)

A Musty Review

Of the odors in water supplies, the earthy or musty descriptors are most frequently observed, though they are often masked by stronger odors (Mallevialle *et al.*, 1987; McGuire *et al.*, 1981). 2-Methylisoborneol (MIB) alias 1,2,7,7-tetramethhyl-*exo*-bicyclo(2.2.1.)heptan-2-ol alias 2-exo-hydroxy-2-methylbornane is frequently associated with the earthy-musty tastes and odors. While this compound is the focus of the paper, other causative agents of earthy-musty complaints exist.

The presence of MIB has been detected the world over. However, it has not been until relatively recently that this compound has been readily identifiable at the concentrations typically encountered in the environment. While the sensory analysis of water was initially more sensitive than chemical analysis, the variability inherent to sensory perception often cast doubts on the results.

People's perception of the odor in the water varies greatly between individuals. This range of sensitivities varies up to a factor of 10,000 or more (Cees *et al.*, 1974). With this wide range of perception, questions of degree of treatment arose. Should the water be treated so that some of the people are satisfied? Most of the people? All of the people?

In 1925 the US Public Health Service's drinking water standards stated that the taste of drinking water be "generally acceptable". This was amended in 1946 to state that drinking water should be "not objectionable", and again in 1962 to "not offensive". In the early 1970s, the World Health Organization (WHO) wrote that the "absence of color and of any disagreeable taste or smell are of the utmost importance in public supplies of water." 1984 brought the draft of the WHO guidelines for drinking water quality stated that the drinking water "not be offensive for most of the consumers served." (Bartels *et* *al.*, 1989; Sano, 1988; Mallevialle *et al.*, 1987). These descriptors, however publicly comforting, were still vague in determining to what absolute concentrations a water should be treated. Zoeteman *et al.* (1980) suggested that the water be treated to a level such that only five percent of the population could detect the compounds. The 1984 draft guidelines for drinking water by the WHO did suggest that the musty odor compounds be decreased to less than ten percent of the odor threshold concentration (OTC) (Sano, 1988). The OTC corresponds to a fifty percent detection by the population; ten percent of the OTC corresponds to approximately fifteen percent of the consumers still being able to detect the odor (Cees *et al.*, 1974). This was later generalized by the final guidelines, stipulating that only the most sensitive (five percent) of the population are permitted to detect an offensive taste. To attain these goals, an extensive amount of information must be collected.

2-METHYLISOBORNEOL

The mid-1960s brought great developments in the arena of chemical analysis of tastes and odors. It was not until this time that the specific compounds that were possibly causing the offensive organoleptic qualities were isolated and analyzed. Gerber and Lechevalier (1965) were the first to isolate a "new" compound, which they named geosmin; "ge" from Greek, meaning earth, and "osmin" meaning odor. Later, Gerber (1968) was able to publish the structure of geosmin, but there was a musty compound that was showing up in their research that had yet to be identified. In 1969, Medsker *et al.* (1969) isolated and identified this other compound produced by actinomycetes as MIB (Figure 1). MIB was not a new compound, as it had been earlier synthesized by Zelinsky (1901). Collins *et al.* (1970) confirmed that *Streptomyces odorifer*, an actinomycete, produced both geosmin and MIB. At the same time of these developments, acrid odors (Henley *et al.*, 1969; Gaines and Collins, 1963) and musty odors besides MIB were also being isolated and identified (Dougherty *et al.*, 1967; Dougherty *et al.*, 1966; Morris *et al.*, 1963).

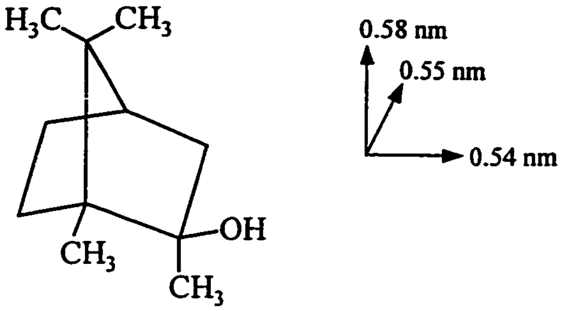

Figure 1 - 2-Methylisoborneol

Physical Properties

This research was important in identifying the problem. The structural properties of this compound and others account for their sensory activity (Veijanen, 1992; Mallevialle, 1987; Gerber, 1983; Gerber, 1968). While the structure is important, other physical and chemical properties are also critical to determine possible analytical and treatment methods, as well as understand how they persist in the environment.

Table 1 - Boiling Point of MIB

Boiling Point (°C)	Source
207	Wako (1994)
196.7	Pirbazari *et al.* (1992)
208-209	Zelinsky (1901)

Table 2 - MIB Melting Point

Melting Point (°C)	Source
162-163	Wako (1994)
162.1-163.3	Pribazari *et al.* (1992)
158-160	Medsker *et al.* (1969)

Table 3 - Physical Properties of MIB

Solubility (mg/L)	194.5
Vapor Pressure (atm)	6.68×10^{-5}
Henry's Law Constant (atm m^3/mol)	5.76×10^{-5}
Log K_{OW}	3.13
Density (g/cm^3)	0.929
Refractive Index	1.47

Odor Threshold

Table 4 shows some of the MIB OTCs reported in the literature. It should be noted that this concentration has systematically decreased over time. It is believed that this correlation is generally related to the analytical detection limits and not to population sensitization. While the results of sensory evaluation techniques typically vary from population to population, and between replicate analyses within a given population, an appropriate MIB OTC, based on the more recent studies would be 5 ng/L.

Table 4 - Odor Threshold Concentration of MIB

Odor Threshold Concentration (ng/L)	Source
6.3	Young *et al.*, 1996
5	Ito *et al.*, 1988
4 (trained), 12 (untrained)[1]	Sano, 1988
29	Amoore, 1986
20	Zoeteman *et al.*, 1980
30-40	Persson, 1980
100	Wood and Snoeyink, 1977
100	Rosen *et al.*, 1970
100	Medsker *et al.*, 1969

While several technologies have been applied to remove MIB from drinking water, activated carbon has been the treatment most frequently utilized. In comparison to granular activated carbon (GAC), powdered activated carbon (PAC) has been more frequently applied (Gillogly *et al.*, 1998; Huang *et al.*, 1996; Wittmeyer *et al.*, 1995; Simpson and MacLeod, 1991; Lalezary *et al.*, 1986). However, GAC has also been regularly employed (Pirbazari *et al.*, 1993; Lalezary *et al.*, 1986; Chudyk *et al.*, 1979; Herzing *et al.*, 1977).

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[1] Trained personnel consisted of 25 to 36 water examination laboratory staff members; 46 untrained panelists were randomly selected from the water treatment plant's distribution area (Sano, 1988). Trained personnel tend to be more aware of various attributes of the water, and as a result the perceived OTC of a trained panel is typically lower than an untrained panel (Meilgaard *et al.*, 1991).

Synthesis

Zelinski (1901) first reported the synthesis of 2-methylisoborneol. Since then, several researchers have performed similar syntheses by reacting methylmagnesium halides or methyllithium with camphor to produce MIB (Wood and Snoeyink, 1977).

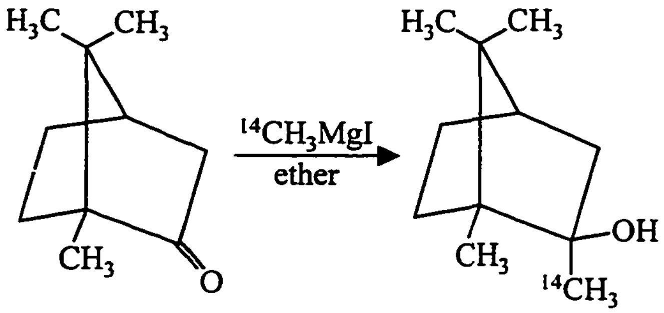

Figure 2 – Synthesis of ^{14}C-MIB from *d*-Camphor

Radiolabeled ^{14}C-MIB was used extensively through the research presented in this thesis. This particular material, prepared by American Radiolabeled Chemical, Inc. (St. Louis, MO), was formed by reacting ^{14}C-labeled methylmagnesium iodide with the *d*-camphor enantiomer. The *d*-camphor was selected after Wood and Snoeyink's (1977) determination that naturally occurring MIB exists in the R form. A radiochemical purity of 100 percent was determined by the manufacturer using high performance liquid chromatography (HPLC). The chemical purity was determined to be greater than 99% by gas chromatography at the University of Illinois. Gas chromatography-mass spectroscopy was used to verify that the compound received from American Radiolabeled Chemicals, Inc. was 2-^{14}methylisoborneol.

Adsorption by Activated Carbon

For a given water and target organic micropollutant, activated carbons have displayed a wide range of capacities for the target compound; MIB is no exception (Gillogly *et al.*, 1997; Newcombe and Drikas, 1995). Currently the adsorption mechanism controlling the uptake of MIB by activated carbons has not been verified. However, it is believed that in addition to the physical size and chemical nature of MIB, the pore size distribution and the surface chemistry of the activated carbon plays a critical role in determining how MIB adsorbs.

Several researchers (Newcombe and Drikas, 1995; Chudyk *et al.*, 1979; and Pendleton *et al.*, 1997) have been able to show a strong correlation between the surface area/micropore volume of PAC (coal-, coconut-, lignite-, and peat-based) and MIB adsorption capacity. While the data collected from wood-based PACs did not fit this same trend, an increase in the surface area/micropore volume of the wood-based PACs still yielded higher adsorption capacities. It was concluded from additional analyses that the porosity of the carbon could not account for the differences observed with the wood-based carbon, indicating the differences were probably due to surface chemistry (Pendleton *et al.*, 1997).

It has been proposed that surface oxides play a critical role in the adsorption of organic compounds by activated carbon. Boehm (Eley *et al.*, 1966) developed a set of titrations to categorize the surface oxides into four groups: strongly acidic carboxyl, weakly acidic carboxyl, phenolic and carbonyl. Based upon these titrations, Snoeyink *et al.* (1974) and McGuire and Suffet (1984, 1980) correlated increases in concentrations of these functional groups to increasing reaction between free chlorine and activated carbon. The increasingly oxidized carbons were then correlated to decreasing adsorption quantities of phenol, *para*-nitrophenol, *n*-butanol, 1,4-dioxane, nitromethane, and methyl ethyl ketone.

Lalezary *et al.* (1988), and Lalezary-Craig *et al.* (1986) showed that PAC was less effective for MIB if it was applied together with chlorine. Gillogly *et al.* (1998b, submitted 1998) reacted varying amounts of free chlorine with activated carbon and found decreasing removals of MIB for increased amounts of free chlorine reacted. These findings are consistent with a study that reported a decrease in MIB adsorption capacity with increasing hydrophilic sites, as determined by water adsorption isotherms (Pendleton *et al.* 1997).

Together these studies suggest that MIB adsorption by activated carbon probably occurs by hydrophobic interaction (sorption to non-polar hydrocarbon-like sites) with the carbon surface. As a result, free chlorine reacting with the surface of the carbon (forming >C=O, -OH and-COOH groups) increases the hydrophilicity of the carbon surface. For more hydrophilic surfaces, less MIB would be expected to adsorb, as it would be more difficult for the MIB to displace the adsorbed water molecules to reach the non-polar adsorption sites.

"The only limit to our realization of tomorrow will be our doubts of today. Let us move forward with strong and active faith."
(Franklin Delano Roosevelt)

Objectives

It was the hypothesis of the author that the methods currently used to determine how effective powdered and granular activated carbon are for the removal of naturally occurring episodes of MIB are too complex and often do not take into consideration how other treatment process affect the effectiveness of the carbon. Therefore, it was the objective of this research to develop simple tools to determine the effectiveness of activated carbon, in the presence or absence of free chlorine, for the removal of 2-methylisoborneol in a drinking water treatment plant. Discussed in the next five chapters, this objective was met by collecting the fundamental data to realize the following goals:

- Demonstrate liquid scintillation counting of ^{14}C-MIB is a technique suitable for rapid collection and analysis of low spiked concentrations of MIB in natural water environments that do not oxidize the MIB;
- Develop a method to determine the minimum powdered activated carbon dose required to reduce a given MIB concentration to a specific level in natural water;
- Confirm that the method to determine the minimum PAC dose required to mitigate an earthy-musty taste and odor episode is independent of the PAC's starting material, natural water source, or naturally occurring MIB concentration;
- Determine the effect of free chlorine on 2-methylisoborneol adsorption by powdered activated carbon;
- Verify that the removal efficiency of MIB by a GAC adsorber is unrelated to the concentration of MIB in natural water;

- Show that the GAC adsorber removal efficiency of MIB is dependent on the mass of chlorine reacted per mass of activated carbon and/or the amount of previously adsorbed background organic matter;
- Demonstrate that the immediate performance potential of GAC, as determined in laboratory scale columns, is independent of bed dimensions for a given EBCT.
- Postulate a protocol to assess the immediate performance potential of a GAC filter/adsorber based upon the elements of research that proved significant.

Submitted: *Water Science and Technology*, October 1997

"I look on that man as happy, who, when there is a question of success, looks into his work for a reply." (Ralph Waldo Emerson)

A Simplified Method to Determine the PAC Dose Required to Remove MIB

by

Thomas E.T. Gillogly[*], Vernon L. Snoeyink[*], Gayle Newcombe[**], Joseph R. Elarde[*]

ABSTRACT

Equilibrium data obtained from a natural water with several different initial concentrations of 2-methylisoborneol (MIB) plot as a single line on a percent remaining, C_e/C_0 x 100%, versus carbon dose, C_c, plot. This indicates that the percent removal of MIB is independent of its initial concentration in natural water for a given PAC dose. The relationship is specific for each type of PAC, and it is not valid at very high MIB concentrations, however. These data show that, predicting the minimum amount of carbon necessary to effectively mitigate any MIB episode, may be accomplished by analyzing a single bottle-point isotherm. The robustness of this approach was shown through the use of four water sources, fourteen different carbons, and MIB concentrations ranging from 45 ng/L to 178 μg/L.

KEYWORDS

^{14}C-MIB; 2-Methylisoborneol; Activated Carbon; Closed-Loop Stripping Analysis (CLSA); Scintillation Counting

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[*] University of Illinois, 205 N. Mathews Avenue, Urbana, Illinois 61801 (V.L. Snoeyink served as an advisor to the project; J.R. Elarde, a masters student, assisted in collecting data from the domestic waters)

[**] Australian Water Quality Centre, Private Mail Bag, Salisbury South Australia 5108, Australia (G. Newcombe collected the data obtained from the Australian waters)

INTRODUCTION

The effective application of activated carbon up to this point has required either complex predictive mathematical modeling with its corresponding calibration experimentation, or extensive trial-and-error testing. Researchers have long been developing and modifying these theories and models to predict adsorbent material capacities for a variety of contaminants. Earthy-musty tastes and odors produced by geosmin and 2-methylisoborneol (MIB) have recently gained considerable attention as two compounds responsible for consumer complaints the world over.

Accurately describing the competitive adsorption between the background organic matter and the compound of interest has made predictions difficult. One approach utilizes the Equivalent Background Compound (EBC) model, (Najm *et al.*, 1991a; Najm *et al.*, 1991b; Knappe *et al.*, 1993; Qi, 1994; Gillogly *et al.*, 1997) while another employs Fictive Components (FCs) (Frick and Sontheimer, 1983; Crittenden *et al.*, 1985; Smith and Weber, 1990). Both have been applied successfully; however, they require several experiments for calibration, and confirmation, as well as an understanding of how to manipulate the models. This requires specially trained personnel and time, when time may be a critical factor. Other researchers have attempted to determine if a physical characteristic of the carbon could determine *a priori*, how effectively MIB could be removed (Chudyk *et al.*, 1979). Unfortunately, it was determined that characteristics such as surface area and micropore volume could not be consistently used (Newcombe *et al.*, 1994).

The carbon dose required to mitigate a particular organic contamination problem in a water supply generally depends on the adsorptive capacity of the carbon. Unfortunately, the adsorptive capacity is dependent upon the initial contaminant concentration, which can vary widely. Large data sets are required to fully characterize such systems, and collection of these data for compounds that cause earthy-musty odor is complicated by an analysis procedure that is difficult and time consuming.

Fortunately, recent studies have shown that a single isotherm may be sufficient to yield the necessary information to determine a particular carbon's feasibility. The research contained herein follows a recent development of Knappe (1996). He showed that a unique relationship existed for adsorption of a trace compound such as atrazine in the presence of natural organic matter. If the initial concentration of the trace compound was less than a certain level, approximately 50 μg/L for atrazine, its percent removal at equilibrium for a given carbon dose in a particular natural water is independent of the compounds initial concentration. Thus, for a given carbon dose, the amount of trace compound adsorbed is directly proportional to its initial concentration. The following study has investigated how this trend may be applied to MIB adsorption for a variety of activated carbons and waters.

MATERIALS AND METHODS

2-Methylisoborneol

The concentration of 2-methylisoborneol (MIB) was determined by one of two methods. Those experiments using the Kankakee River or Lake Michigan as its water source relied upon ^{14}C labeled MIB (^{14}C-MIB). These tests were analyzed by mixing 2.5 mL filtered sample aliquots with 18 mL of scintillation cocktail (Ecoscint, National Diagnostics, Manville, NJ) in scintillation vials. The resulting fluorescence was then measured in a liquid scintillation counter (Tri-Carb Model 1600CA, Packard Instrument Co., Downers Grove, IL). This method is described in greater detail in "Kinetic and Equilibrium Studies of ^{14}C-MIB Adsorption on PAC in Natural Water" (Gillogly *et al.*, 1997).

Experiments utilizing Hope Valley Reservoir and Myponga Reservoir water analyzed MIB as per Method 6040B "Closed-Loop Stripping, Gas Chromatographic/Mass

Spectrometric Analysis" (Standard Methods, 1995), with an additional modification to incorporate deuterated standards.

Activated Carbons

The activated carbons employed in this study were Cecarbon (Elf Atochem North America, Philadelphia, PA), F-400 (Calgon Carbon Corp., Pittsburgh, PA), WPL (Calgon Carbon Corp., Pittsburgh, PA), WPH (Calgon Carbon Corp., Pittsburgh, PA), prototype carbon (not commercially available), ASTM M325 (Haycarb Holdings, Victoria, Australia), Picatif PCO (PICA, Levallois, France), Picazine (PICA, Levallois, France), P1100 (PICA, Levallois, France), P1300 (PICA, Levallois, France), W20 (Norit Americas Inc., Atlanta, GA), Hydrodarco-B (Norit Americas Inc., Atlanta, GA), Watercarb (Acticarb, Dunnellon, FL), and Nuchar SA-20 (Westvaco Chemicals, Covington, VA). Granular activated carbon samples were ground so that ≥95% passed a #325 U.S. Standard mesh (44 μm diameter).

Waters

Several natural water sources were drawn upon in this study, including: Hope Valley Reservoir (South Australia, Australia; 5.0 mg/L DOC), Kankakee River (Illinois, USA; 4.0 mg/L DOC), Lake Michigan (Illinois, USA; 1.8 mg/L DOC), Myponga Reservoir (South Australia, Australia; 5.8 mg/L DOC). Prior to use, these waters were passed through a 1 μm filter for particulate removal. Any water not immediately used was stored in the dark at 4°C to limit biological activity.

RESULTS AND DISCUSSION

The difficulty in predicting the amount of an organic contaminant that can be removed for a particular carbon dose has been in describing the reduction of adsorptive capacity due to competing background organics. The familiar equilibrium solid-phase concentration of MIB, q_e, versus the MIB equilibrium solution concentration, C_e, plot, shows how the amount of MIB adsorbed per unit mass of activated carbon changes with the initial concentration (see Figure 1). Typically several experiments are necessary to calibrate and verify a competitive adsorption model, so that the model can be used to predict the capacity of a particular carbon dose for an initial concentration of interest. This process can have many steps, take a considerable amount of time, and requires personnel knowledgeable of the model and its operation.

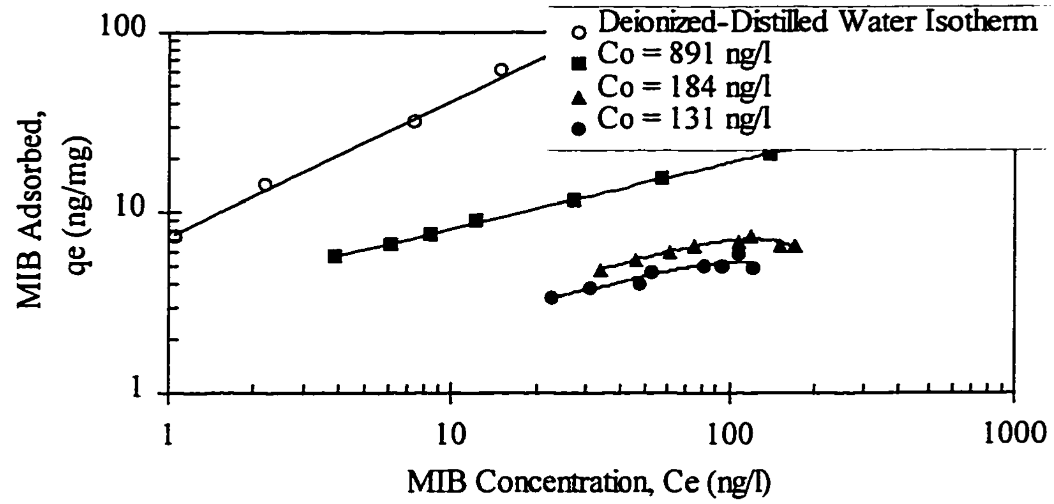

Figure 1 - Hydrodarco-B adsorption isotherms in Kankakee River water

Following a recent development of Knappe (1996), it has been shown that if the natural water equilibrium data are plotted as percent remaining, C_e/C_0 x 100%, versus carbon dose, C_c, instead of q_e versus C_e, the data plot as a single line if the initial concentrations of the trace compound are sufficiently low. This behavior of the data is predicted from the Ideal Adsorbed Solutions Theory if the solid phase concentration of the competing background organic matter at a given carbon dose is not affected by trace levels of the target compound (Knappe, 1996). This behavior of the data indicates that the percent removal of a trace organic is independent of its initial concentration in natural water for a given PAC dose. From this type of plot, the minimum carbon dose required to achieve a desired removal can be quickly obtained for any reasonable initial concentration without the need for mathematical models. As shown in Figure 2, the Hydrodarco-B MIB adsorption data in Kankakee River water for the initial concentrations of 131, 184 and 891 ng/L, now fall on the same line. A similar trend is also seen with WPH PAC.

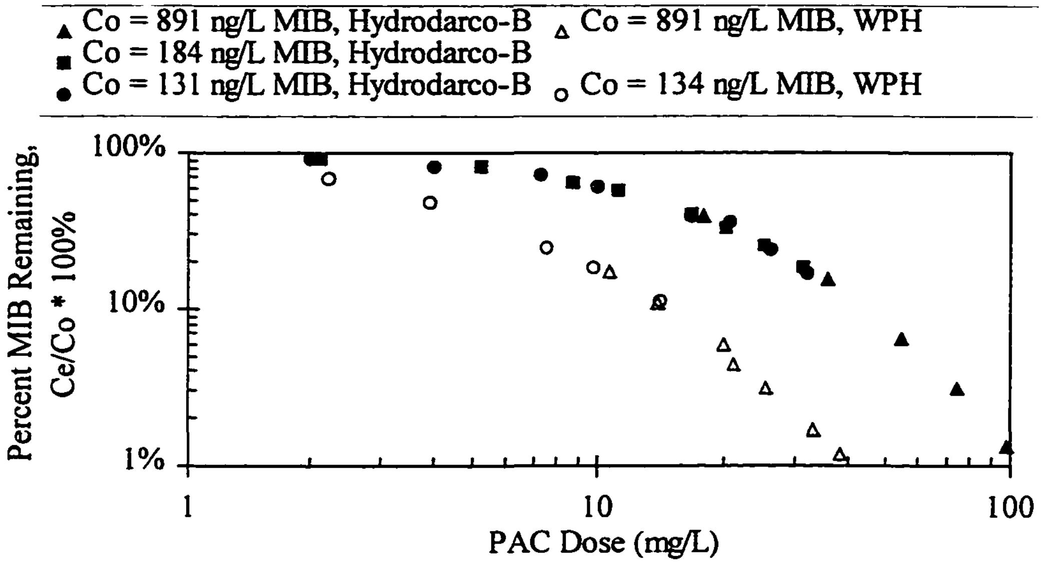

Figure 2 - PAC adsorption isotherms in Kankakee River water

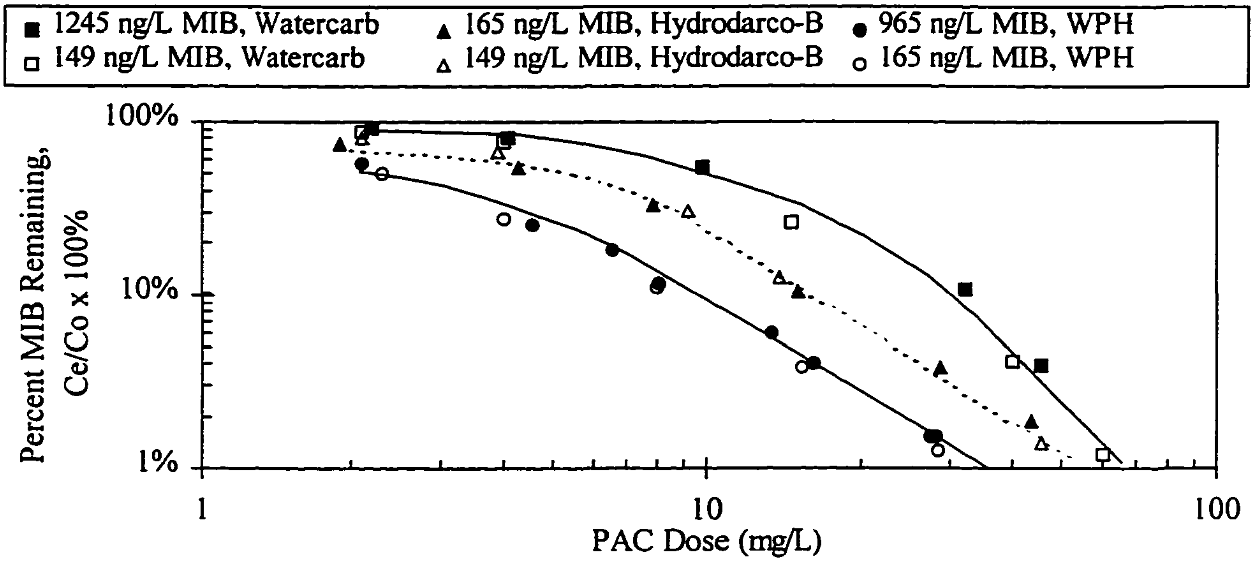

Figure 3 - PAC adsorption isotherms in Lake Michigan water

Additional isotherms run in Lake Michigan water using Watercarb, Hydrodarco-B and WPH PAC also show that the adsorption data for each carbon plot as a single line (refer to Figure 3). Critical information can be extracted from these plots quickly and easily. For example, if the MIB C_0 is 100 ng/L and it must be reduced to 5 ng/L, a removal of 95% is required (C_e/C_0 x 100% = 5%). Drawing upon the data in Figure 3, a carbon dose of 12.5 mg/L WPH would be required for a 95% removal. The data in Figure 2 and 3 can now be used to compare the minimum carbon doses required to remove 95% of the MIB from Kankakee River water and Lake Michigan water, as shown in Table 1. Substantially more competition between natural organic matter and MIB occurs in Kankakee River water than in Lake Michigan water.

Table 1 - PAC dose required to remove 95% of the MIB initially present

Water Source	WPH	Hydrodarco-B	Watercarb
Kankakee River	20.3	61	-
Lake Michigan	12.5	22	38

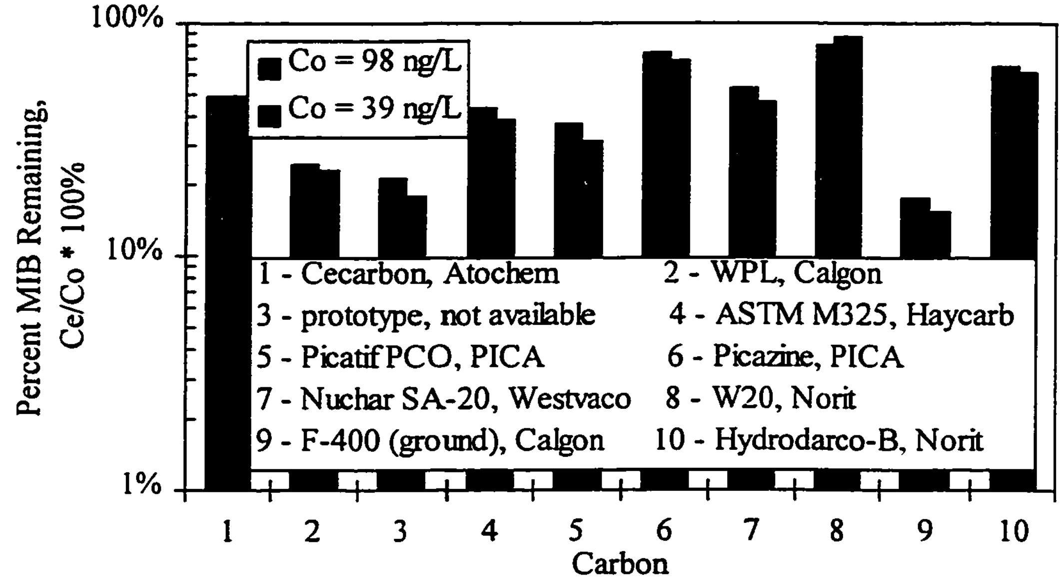

Figure 4 - Comparison of 10 carbons; 13.2 mg/L PAC in Hope Valley water

To show the differences which can exist between carbons, ten activated carbons made from a wide variety of starting materials (coal, coconut, wood, peat, lignite) were analyzed using two initial MIB concentrations and a PAC dose of 13.2 mg/L in water from the Hope Valley Reservoir. As seen in Figure 4, the difference in percent remaining for the two initial concentrations was less than 7% for all carbons, with an average difference of 4%. The carbons removed from 13 to 85% of the MIB, however, showing a great variability in adsorptive capacity. This difference emphasizes the importance of evaluating carbons on a cost per unit MIB removed basis rather than on a cost per unit weight basis.

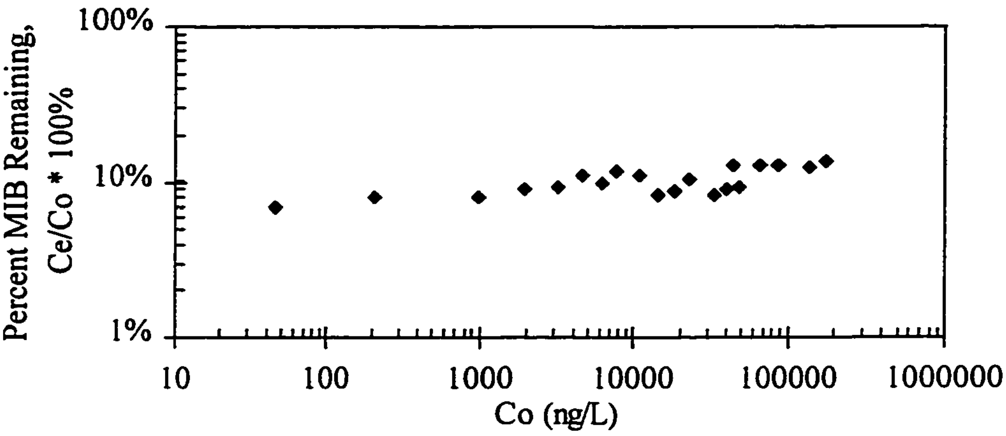

Figure 5 - MIB removed by 13.2 mg/L P1300 from Myponga Reservoir water

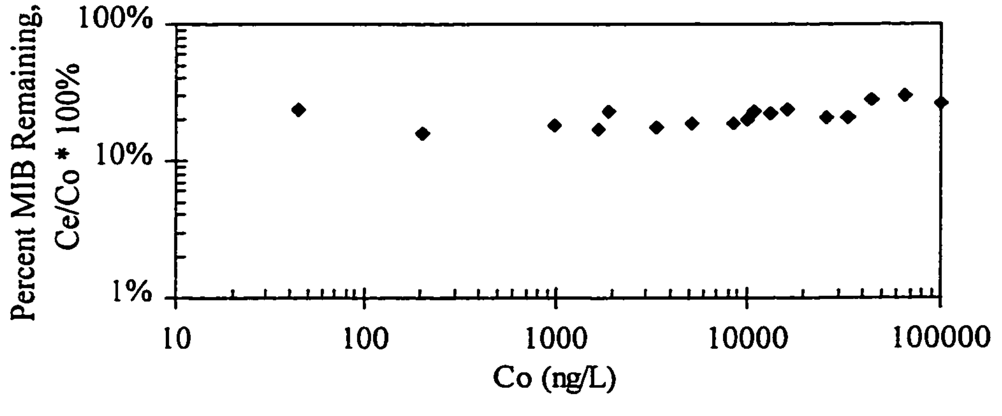

Figure 6 - MIB removed by 13.2 mg/L P1100 from Myponga Reservoir water

Two final series of experiments were performed to show that the percent MIB removed by one carbon dose was constant over a wide range of initial MIB concentrations.

Myponga Reservoir water was spiked with MIB between 45 ng/L and 178 μg/L. To the spiked water, 13.2 mg/L of P1300 or P1100 was added and allowed to come to equilibrium. While these MIB concentrations covered three to four orders of magnitude, the percent remaining showed an impressive consistency (see Figures 5 and 6). Over this wide range, the difference in the measured maximum and minimum percent remaining was less than 6.6% for P1300, with an average of 10.2% remaining. While a larger difference, 13.7%, was observed between the maximum and minimum percent remaining with P1100, average 21.6% remaining, the approach yields excellent reproducibility.

CONCLUSIONS

These data support a simplification in the procedure for determining the PAC dose required to remove a desired amount of MIB. It has been shown that for a given water/carbon system, a particular carbon dose a will remove a fixed percentage of the MIB initially present. This has been shown to hold true regardless of the activated carbon's starting material, brand of carbon, carbon dose, natural water source, or initial concentration of MIB. However, the relationship is specific for each natural water and type of PAC. The calculated dosage is a minimum dosage, and will be higher in a specific treatment plant if the method of PAC application does not result in the achievement of equilibrium.

This implies that predicting the minimum amount of carbon necessary to effectively mitigate any MIB episode may be accomplished by analyzing a single bottle-point isotherm. This test may also serve as a rapid method for comparing carbons, or for determining at what point another technology should be investigated for the control of earthy-musty taste and odor episodes.

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"Nothing can have value without being an object of utility" (Karl Marx)

Kinetic and Equilibrium Studies of ^{14}C-MIB Adsorption on PAC in Natural Water

by

Thomas E.T. Gillogly*, Vernon L. Snoeyink*, Joseph R. Elarde*,
Claude M. Wilson**, Earl P. Royal**

INTRODUCTION

Anthropogenic and biogenic taste and odor problems have plagued water sources over the ages. In prehistoric times, people relied upon their senses to warn them of dangerously contaminated water. Even today we are influenced by our senses to determine if a particular food or drink has spoiled or become contaminated. Additionally, the awareness of pollutants in our environment has brought us to a state of hypersensitivity to off-flavors and odors. These objectionable tastes and odors are often presumed to be due to toxic substances (Jensen *et al*, 1994). A study in The Netherlands showed a 45 percent decrease in water consumption due to people disliking the taste (Cees *et al.*, 1974). Another survey of US consumers, showed that greater than 15 percent of the respondents used either bottled water or a home-treatment device. The majority of these people indicated that their action was due to bad smelling or tasting tap water (Manwaring *et al.*, 1986). Earlier, the Gallup Poll showed the most common complaint with drinking water to be taste (Gallup, 1973).

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Of the odors in water supplies, the earthy or musty descriptors are most frequently observed, though they are often masked by stronger odors (Mallevialle and Suffet, 1987; McGuire *et al.*, 1981). The two compounds most frequently associated with earthy-musty odors are MIB and geosmin. These compounds are problematic due to their odor threshold concentrations in the low nanogram/L levels and resistance to chemical oxidation. Chlorine and potassium permanganate by themselves are generally considered ineffective. As a result, many utilities have used granular activated carbon (GAC) and powdered activated carbon (PAC). Recently, Suffet *et al.* (1996) reported that utilities responding to a survey considered activated carbon to be the most effective taste and odor control process. Of those utilities, PAC was used more than six times as often as GAC.

Because MIB is frequently present, and more weakly adsorbed than other common earthy or musty compounds, including geosmin, it is reasonable to use it as the target compound in laboratory studies (Lalezary *et al.*, 1986). The analysis of MIB has often handicapped the development of solutions to the taste and odor problem. Although it has been successfully used by many, the Closed Loop Stripping Analysis (CLSA) procedure is inefficient, laborious and time consuming due to requirements of large sample sizes, the need for prolonged stripping of the sample, and extended time for chromatographic analysis (Standard, 1992). This method often yields low reproducibility at low MIB concentrations, creating special problems in adsorption studies.

OBJECTIVES AND APPROACH

The objective of this study was to develop a method which could be easily employed to determine the necessary amount of PAC required to mitigate earthy-musty taste and odor episodes. This study shows that radiolabeled MIB can be used to circumvent most analytical problems discussed above. It has also been shown that both kinetics of MIB adsorption and capacity in the presence of natural organics are important factors in determining the performance of a PAC in a water treatment plant. In order to achieve the objective, five commercially available PACs were studied in Lake Michigan water. Laboratory kinetic data were analyzed using the pseudo single-solute homogeneous surface diffusion model (HSDM) (Traegner and Suidan, 1989; Qi *et al.*, 1994). The equilibrium results were analyzed using a new approach that involves a percent adsorbate remaining at equilibrium versus carbon dose plot. The results from this research were compared to those obtained by Huang *et al.* (1996) using the traditional CLSA analysis.

The HSDM model assumes instantaneous equilibrium between the adsorbent and adsorbate at the outer surface of the particle, and that the intraparticle migration of the adsorbate is controlled by surface diffusion. Determination of the kinetic parameters (liquid film mass transfer coefficient - k_f, surface diffusion coefficient - D_s) for the batch system is accomplished by minimizing the difference between the concentration versus time data collected in a batch test, and that predicted by the HSDM. This comparison between the model prediction and data requires inputs of parameters which can be determined directly (initial MIB concentration - C_o, carbon concentration - C_c, particle diameter - d_p, particle density - ρ_p) and experimentally (Freundlich coefficients - K, 1/n). Once the model is calibrated it can be used to predict adsorption as a function of time in different types of reactors, such as plug flow and continuous stirred tank reactors.

The experimentally determined parameters are calculated using the Freundlich isotherm equation (Freundlich, 1906):

$$q_e = KC_e^{1/n} \qquad [1]$$

where q_e = Solid phase concentration of MIB in equilibrium with C_e;
K = Freundlich isotherm constant;
C_e = Equilibrium liquid phase concentration of MIB;
$1/n$ = Freundlich isotherm constant.

A new method for interpreting both kinetic and equilibrium data for trace compounds in natural waters follows the recent development of Knappe (1996). He showed that a unique relationship existed for adsorption of a trace compound such as atrazine in the presence of natural organic matter. If the initial concentration of the trace compound was less than a certain level, approximately 50 µg/L in the case of atrazine, the trace compound percent removal at equilibrium for a given carbon dose in natural water is independent of its initial concentration (Knappe *et al.*, 1996). Thus, for a given carbon dose, the amount of trace compound adsorbed is directly proportional to its initial concentration. Additionally, the data in this study have demonstrated that the percent removal at any given time for a given carbon dose in natural water, is independent of the MIB initial concentration. Therefore, by plotting the percent of trace compound remaining versus carbon dose for a given contact time, the minimum amount of carbon required to reduce the trace compound to a desired concentration, may be quickly obtained without the need for mathematical models. In order to use this plot, it is important to establish that the range of initial concentrations of interest is less than the value above which this relationship is no longer valid.

MATERIALS AND METHODS

2-Methylisoborneol

The ^{14}C-labeled 2-methylisoborneol (^{14}C-MIB) (American Radiolabeled Chemicals, St. Louis, MO) was selected due to ease of analysis and small sample size requirements. Analysis of ^{14}C-MIB samples was accomplished by mixing 2.5 mL aliquots with 18 mL of scintillation cocktail (Ecoscint, National Diagnostics, Manville, NJ) in scintillation vials. The resulting fluorescence was then measured in a liquid scintillation counter (Tri-Carb Model 1600CA, Packard Instrument Co., Downers Grove, IL). The specific activity (55 mCi/mmol) of the ^{14}C-MIB yielded a detection limit, with a confidence level greater than or equal to 89%, of 4.5 ng/L without the use of a concentration step (Skoog and Leary, 1992).

The compound was received predissolved in purge and trap grade methanol at a concentration approximately 18.3 µg/µL (chemical purity ≥ 99% confirmed by GC-MS analysis, 100% radiochemical purity confirmed by HPLC). Stock solutions of 100 ng/µL were subsequently prepared by spiking 5.4 µL of the received solution into 1 mL of purge and trap grade methanol. The compound and all solutions were stored at 4°C.

Water

Natural Water. Lake Michigan water (see Table 1 for composition) was used as the natural water source to study competitive effects between background organic material and MIB. Water was collected from a line running from the South Water Production Plant (Chicago, IL) crib to the shore plant. The water was shipped to the University of Illinois in 208 L (55 gal) stainless steel drums, where it was stored at 4°C in the dark to limit biological activity. (The crib is located two miles off shore in water 32 to 35 feet deep; the water is drawn near the bottom.)

Table 1. Characteristics of Lake Michigan Water

pH	8.2
Alkalinity	117 mg/L as $CaCO_3$
Conductivity	281 µmhos
Turbidity	1.88 N.T.U.
Nitrogen, Total Kjeldahl	0.37 mg/L
Phosphate, Total	0.021 mg/L
Dissolved Organic Carbon	1.8 mg/L

Organic-free Water. Organic-free water for the single-solute isotherms was obtained by passing deionized Urbana, IL, tap water through a Milli-Q water system (Millipore Corp., Bedford, MA) which has three cartridges (activated carbon, ion exchange, ion exchange) and a 0.45µm filter. The water had a resistivity ≥ 18 megohm-cm and a dissolved organic carbon (DOC) content of 0.1-0.3 mg/L.

Activated Carbons

The PACs evaluated in this study were Cecarbon (Elf Atochem North America, Philadelphia, PA), WPH (Calgon Carbon Corp., Pittsburgh, PA), Hydrodarco-B (Norit Americas Inc., Atlanta, GA), Watercarb (Acticarb, Dunnellon, FL), and Nuchar SA-20 (Westvaco Chemicals, Covington, VA). (See Table 2.) Samples of these carbons were obtained from the inventory of the City of Chicago Department of Water, but were not collected in a fashion to assure that they were fully representative of the inventory. The PAC samples were stored in polyethylene bottles until used.

Table 2. Powdered Activated Carbon Properties

PAC	Starting Material	Iodine No. (mg/g)
Cecarbon	Bituminous Coal	1020
WPH	Bituminous Coal	800
Hydrodarco-B	Lignite	550
Watercarb	Wood	550
Nuchar SA-20	Wood	1000

Prior to use, samples were dried overnight in a 110°C oven, to remove excess water, and subsequently were cooled in a desiccator. Once cooled, the desired amount of carbon, not less than 2 mg, was weighed out on a 4-point scale (LIBROR AEU-210, Shimazdu Corp., Kyoto, Japan).

For experiments which required carbon slurries, a slurry of 10 mg/mL was used. These slurries were prepared by mixing 10 g of the particular carbon, prepared as above, in 1 L of organic-free water. The slurry was mixed with a magnetic stirring bar only when an aliquot was to be drawn. For the remaining time the slurry bottle was quiescent. This was to prevent grinding of the carbon between the storage vessel bottom and magnetic stirring bar, as the kinetics of adsorption is sensitive to particle diameter.[17, 18]

Equilibrium Isotherm Tests

Adsorption isotherms of ^{14}C-MIB on PAC were obtained in the laboratory using the bottle-point technique (Randtke and Snoeyink, 1983). Into 1 L, 500 mL, 250 mL, or 120 mL acid washed/baked 300°C bottles, a known mass of the oven dried carbon was added, along with a known volume of glass beads. Three of the bottles had no carbon, and were used to determine the initial concentration of ^{14}C-MIB. These bottles were then filled headspace free with the sample water using a 100 mL dispensing pipette (Brinkmann, Westbury, NY). The 120 mL bottles were then covered with a teflon faced silicone septum (Wheaton, Millville, NJ) and an aluminum crimp cap while the 1L, 500 mL and 250 mL bottles were covered with teflon tape (Fisher, Pittsburgh, PA) and a screw cap. These bottles were then agitated on a shaker table in the dark for 4 days. After the four days, samples were collected using a stainless steel needle (Aldrich Chemical Co., Milwaukee, WI) connected to a gas-tight, luer lock syringe (Hamilton Co., Reno, NV). The aliquot was then passed though a 0.22 µm conditioned nylon membrane syringe (Magna, Westboro, MA) supported in a syringe filter holder (Swinney Holder, Gelman Sciences, Ann Arbor, MI). To condition the filter, 5 mL of the sample was filtered and wasted prior to the collection of 2.5 mL into the scintillation vial. The glass beads were used to ensure adequate mixing in the headspace free bottles.

Isotherm solutions were prepared in a floating head delivery vessel (custom manufacture, University of Illinois, IL). For isotherms in natural water, the floating head delivery vessel was filled with Lake Michigan water. The water was chlorinated to 2.5 mg/L as Cl_2 and stirred for 6 to 8 hours. This killed most of the microorganisms, and allowed the water to come to room temperature. After stirring, the free chlorine was measured and subsequently dechlorinated with a stoichiometric amount of sulfurous acid (Fisher Scientific Co., Pittsburgh, PA). The pH of the solution was adjusted as needed back to 8.2 ± 0.1, with 1 M HCl or NaOH. The dechlorinated water was then spiked with a predetermined amount of ^{14}C-MIB and allowed to mix for 1 hour prior to filling the isotherm bottles.

Batch Kinetic Tests

The device used for the batch kinetic experiments was a jar test apparatus (Six Paddle Stirrer Model 7790-400, Phipps & Bird, Richmond, VA) and modified square jars (B-

KER^2, Phipps & Bird, Richmond, VA). Clear acrylic lids were manufactured for each individual jar to prevent loss of MIB through volatilization. These lids allowed for the experiments to be visually monitored and run with only a small fraction of the solution surface exposed to the atmosphere. In the jars, 2.6 L of Lake Michigan water (pH = 8.2) was brought to room temperature and spiked with ^{14}C-MIB to the desired initial concentration. The solutions were then stirred at 125 rpm for 5 minutes before the addition of carbon. Carbon was either added by aliquots of a carbon slurry, or by a weighed mass of oven dried, prewetted carbon. (To properly wet the carbon prior to the test, weighed carbon was soaked overnight in a small aliquot of organic-free water.) Samples were then withdrawn at predetermined time intervals up to 240 minutes. The samples were collected in the same fashion as described above in the equilibrium tests. To maintain the jars headspace free, unspiked Lake Michigan water was added to make up volume used in sampling. The resulting measurements were then adjusted for the amount of water added to the system.

Full-scale Treatment

During 1995, the City of Chicago, Department of Water, proactively started the application of approximately 2.4 mg/L of PAC in May, prior to the expected beginning of the taste and odor season. It was not until mid-July that analyses of the influent showed MIB. With the initial detection of MIB, carbon doses were continually increased to a maximum of 11 mg/L at the height of the taste and odor season. The PAC doses decreased along with the MIB, until a residual level of 1.2 mg/L PAC had been applied for approximately one month beyond the last detection of MIB. The effluent concentrations of MIB corresponding to a known dosage of PAC were not collected, therefore, direct comparison between the field data and laboratory predictions was not possible.

RESULTS AND DISCUSSION

Adsorption Equilibria

Watercarb PAC. The results from the four day isotherms are shown in the familiar equilibrium solid-phase concentration of MIB, q_e, versus the MIB equilibrium solution concentration, C_e, plot in Figure 1. This figure shows the effect of the background organics competing with the MIB. The adsorption capacity is much less in natural water than organic-free water, and decreases as the initial concentration of MIB used in the isotherm test decreases. Note that the isotherms in organic-free water (C_0 149 ng/L and 0.374 mg/L) yielded the same Freundlich parameters, indicating that they are not a function of initial MIB concentration. The background organic matter reduces the amount of MIB that can be adsorbed by occupying adsorption sites on the PAC. The capacity of PAC for MIB can be predicted through the use of competitive adsorption models, one of which is the Equivalent Background Compound (EBC) model (Najm *et al.*, 1991; Knappe *et al.*, 1993; Qi, 1992).

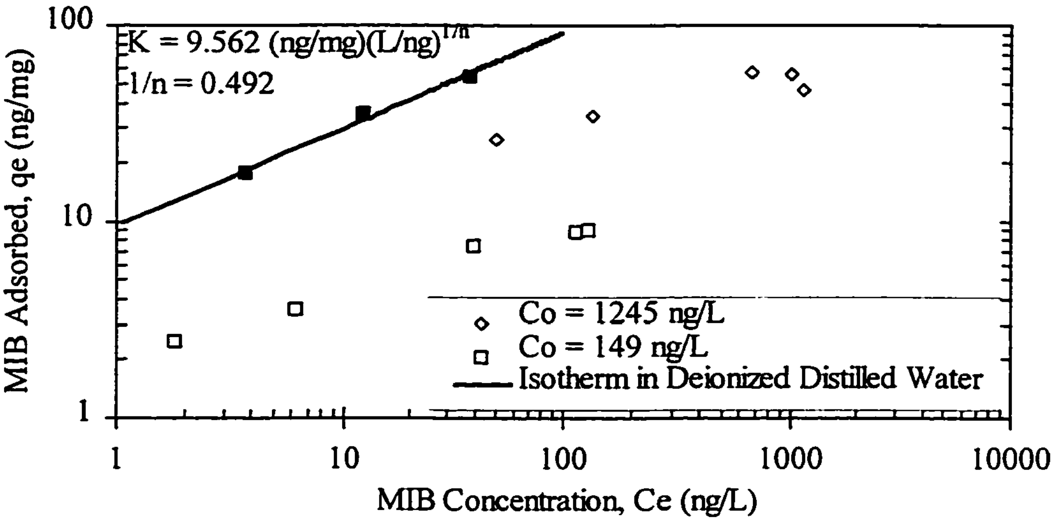

Figure 1. Effect of Initial MIB Concentration on the MIB Capacity of Watercarb PAC in Lake Michigan Water

Within the EBC model the complex mixture of the background organic matter is represented as a single "equivalent background compound". This allows the competition between the background organics and the target compound to be calculated by the ideal adsorbed solution theory (IAST). The parameters for the EBC (Freundlich - K_{EBC}, $1/n_{EBC}$, $C_{o,EBC}$) are determined by calculating the parameters for a single compound which would produce the same amount of competition observed between a single-solute and natural-water isotherms, for the target compound. The EBC model then uses these Freundlich EBC and the single-solute MIB Freundlich parameters, along with the IAST program to calculate isotherms for different initial concentrations of MIB in that particular natural water.

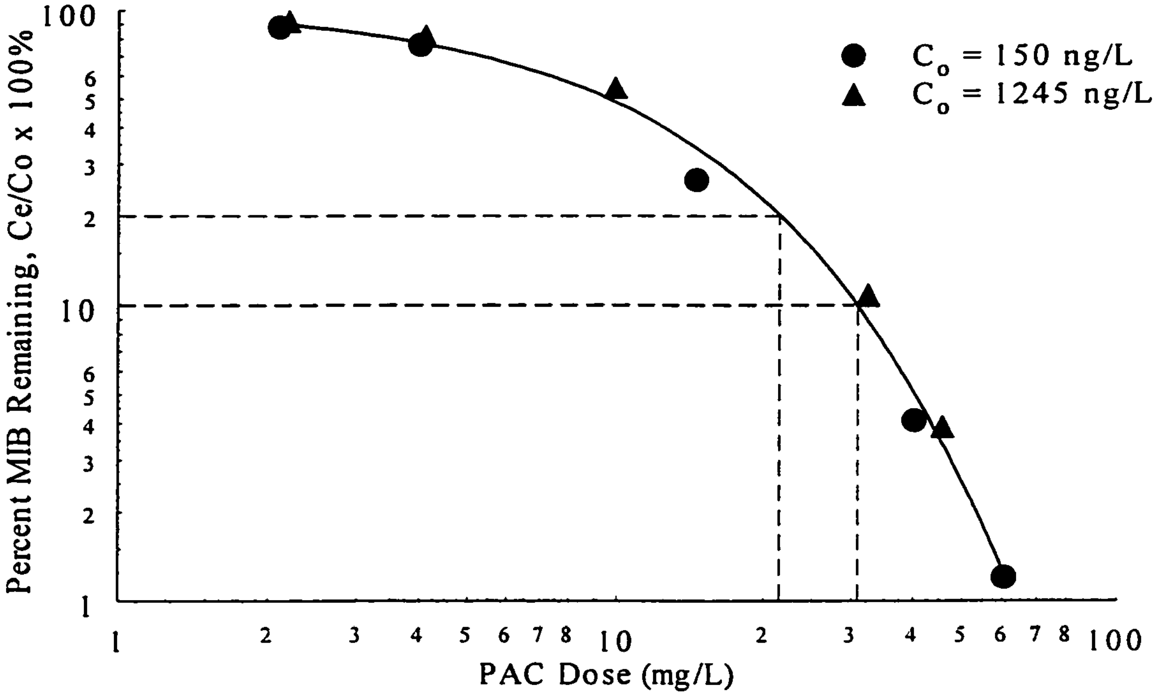

Figure 2. Percent MIB Remaining as a Function of Watercarb PAC Dose

It has been previously shown that if the natural water equilibrium data are plotted as percent remaining, C_e/C_0 x 100%, versus carbon dose, C_c, instead of q_e versus C_e, the data converge to a single line if the initial concentrations of the trace compound are sufficiently low (Knappe, 1996). This indicates that the percent removal of a trace organic is independent of its initial concentration in natural water for a given PAC dose. From this type of plot, the minimum carbon dose required to achieve a desired removal can be quickly obtained for any reasonable initial concentration without the need for mathematical models. As shown in Figure 2, the MIB data for initial concentrations of 150 and 1245 ng/L, almost an order of magnitude in difference, fall on the same line. A best fit line is also displayed on this figure. Calculations with the EBC model for this PAC-natural water system show that if MIB initial concentration, C_0, equals 4,000 ng/L, the PAC dose to remove 95% of the MIB is only 10% larger than the minimum dose calculated from the line of convergence, and it becomes progressively less as C_0 decreases. Based on these data, we have assumed that equilibrium data for initial concentrations less than 150 ng/L will similarly produce a single line on a C_e/C_0 x 100%versus C_e plot.

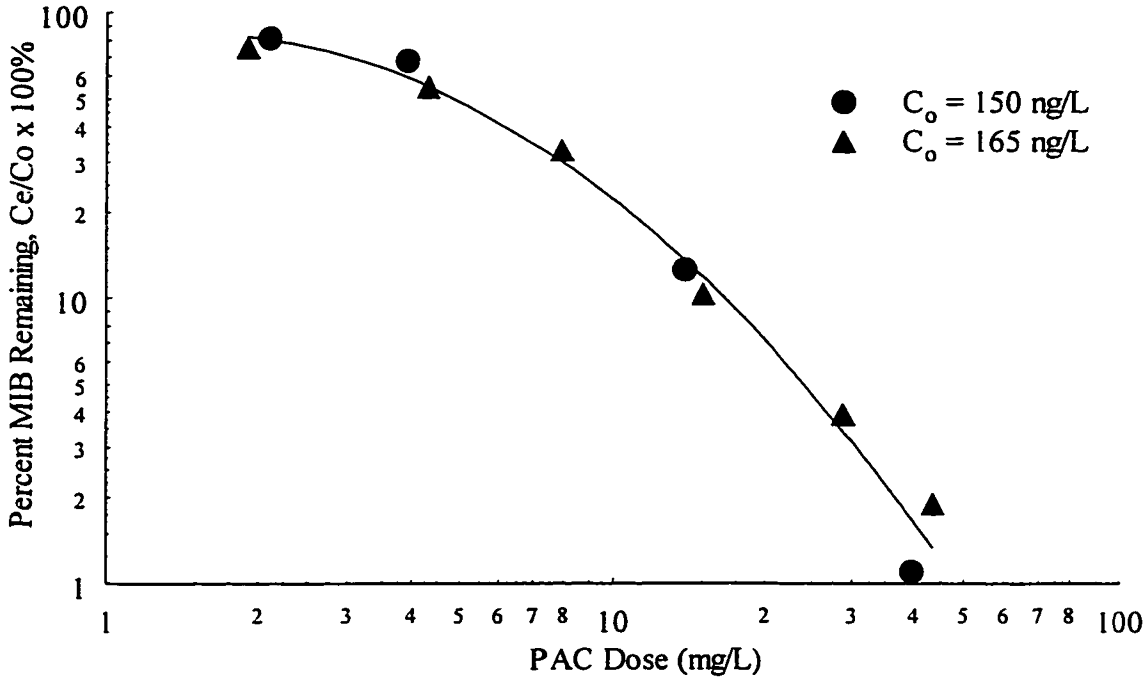

Figure 3. Percent MIB Remaining as a Function of Hydrodarco-B PAC Dose

Extracting critical information from these plots can be done quickly and easily. For example, if the MIB C_0 is 40 ng/L and it must be reduced to 4 ng/L, a removal of 90% is required (C_e/C_o x 100% = 10%). The figure shows that a carbon dose, of 31 mg/L of Watercarb PAC would be required. Similarly, 21.5 mg/L PAC would be required for 80% removal.

Hydrodarco-B PAC. The percent remaining versus carbon dose plot for Hydrodarco-B PAC is shown in Figure 3. The data in this plot show the minimum carbon dose for a given percent remaining, at equilibrium, of the initial MIB concentration. EBC model calculations for the PAC-natural water system show that if the MIB C_o = 200,000 ng/L, the PAC dose to remove 95% of the MIB is only 10% more than the minimum dose. Thus, the C_e/C_o x 100% versus C_c plots are independent of the initial MIB concentrations used in this study, as well as any concentration expected in natural water. These findings are consistent with the theoretical development of Knappe (1996) and his observation that the PAC dose required to remove a given percentage of atrazine converged to a minimum for $C_o < 50$ μg/L (Knappe *et al.*, 1996).

Adsorption Kinetics

Watercarb PAC. Headspace free batch kinetic tests at a pH of 8.2 were used to evaluate the MIB adsorption rate. Watercarb PAC was the first of the five PACs to be analyzed. Figure 4 shows the experimental data collected for a four hour batch kinetic test, with an MIB initial concentration of 175 ng/L and a 11.5 mg/L PAC dose. In order to analyze the data using the HSDM, the Freundlich parameters, K and 1/n, corresponding to the C_o and carbon dose of the kinetic test need to be known. A K value of 2.37 (ng/mg)(L/ng)$^{1/n}$ and a 1/n of 0.303 were calculated for this initial concentration from the C_e/C_o x 100% versus C_c plot. This was accomplished by generating a q_e versus C_e isotherm for this initial concentration by determining the C_e/C_o values corresponding to several carbon doses. The C_e/C_o value for each carbon dose was then used to calculate q_e, the surface concentration, as a function of C_e, using: $q_e = (C_o\text{-}C_e)/C_c$. The q_e versus C_e data were plotted on a log-log plot; the slope of the linear portion of the isotherm was used as the 1/n value. The q_e (mg/g) for the carbon dose of interest (11.5 mg/L) and the 1/n value were used in the Freundlich equation (see equation 1) to calculate K. The input of these

Freundlich values along with the batch kinetic data into the HSDM model yielded a surface diffusion coefficient, D_s, equal to $0.110\text{x}10^{-9}$ cm^2/min, as determined by the Levenberg-Marquardt algorithm, a nonlinear least squares optimization routine (International, 1991).

The HSDM fit to the data is also shown in Figure 4. Once the surface diffusion coefficient was determined, the HSDM was used to predict the percent removal of MIB as a function of time for a PAC dose of 34.6 mg/L. (See Figure 5.) The prediction is in acceptable agreement with the experimental data. Therefore, this approach to calibrating the HSDM can be used to give reasonable results.

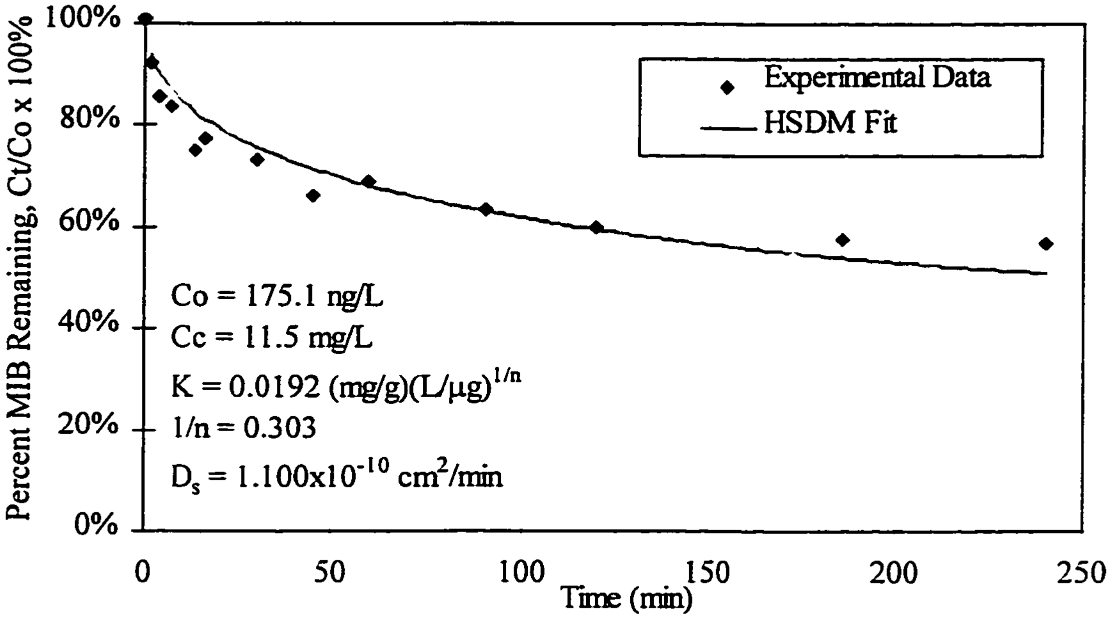

Figure 4. Batch Kinetic Test Data for MIB Adsorption with Watercarb PAC

The HSDM was able to give a better fit and prediction of the data in the Figures 4 and 5 if it was assumed that equilibrium was reached in 4 hours rather than 4 days. Using the 4-hour plateau values from the kinetic data for 3 to 4 different carbon doses, a $C_{4\text{-hour}}/C_o$ x 100% versus C_c plot was generated. (Refer to Figure 13.) From this plot and the procedure described above with the C_e/C_o x 100% versus C_c plot, K and 1/n values were generated. (See Table 3 for values.) By using these new values, a much better fit of the first 4 hours of data was obtained. (See Figure 6) A similar approach was employed by Huang *et al.* (1996). Its application was able to successfully simulate field data for the adsorption of MIB from Niagara River water.

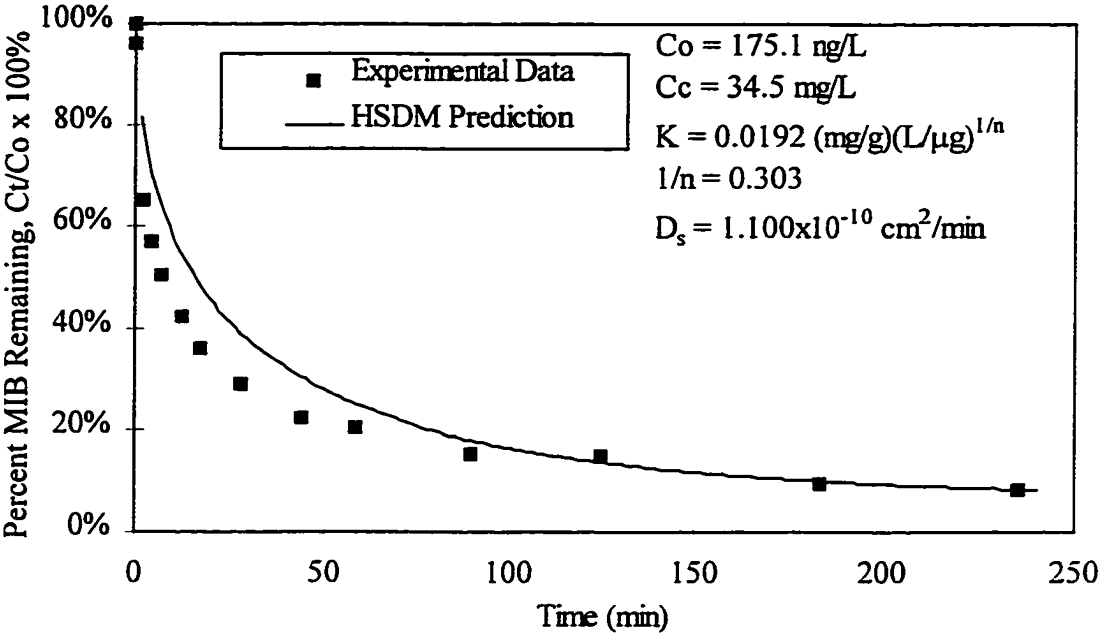

Figure 5. Comparison of the HSDM Prediction to Batch Kinetic Test Data for MIB Adsorption with Watercarb PAC

The difference in the agreement between measured and predicted values is a result of the difference between the pseudo-equilibrium reached within 4 hours and true equilibrium at 4 days. The slow increase in capacity after 4 hours is not consistent with a mechanism of uptake that can be characterized by a single surface diffusion coefficient for the entire kinetic curve. This "second step" may be another surface or pore diffusion controlled step in which MIB must pass through pores partially blocked by background organic matter. Using the approach that emphasizes the first 4 hours of data is most important if only short contact times are used for PAC in the full scale plant, but the true equilibrium data should be used i the PAC is to be used with very long contact times.

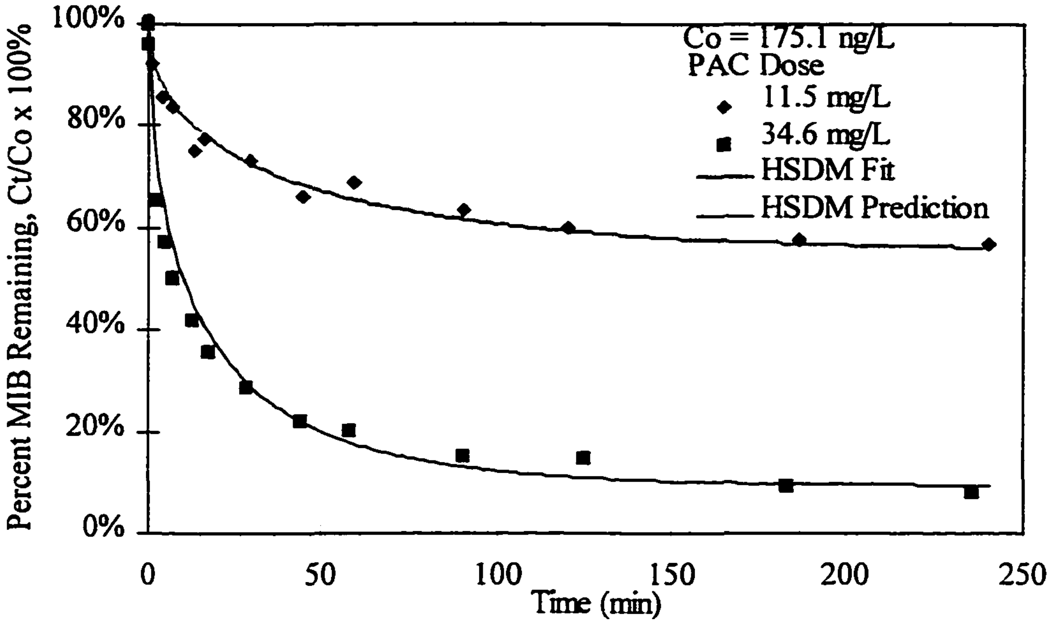

Figure 6. HSDM Fit and Prediction of Batch Kinetic Test Data for MIB Adsorption with Watercarb PAC, Based Upon 4-Hour Kinetic Test Plateau Values ($D_s = 3.69 \times 10^{-10}$ cm^2/min)

Table 3. 4 Hour Freundlich Isotherm Constants

PAC (mg/L)	K (ng/mg)(L/ng)$^{1/n}$	1/n
	(based upon kinetic test plateau values)	
Cecarbon	4.13	0.396
WPH	3.52	0.359
Nuchar SA-20	2.20	0.418
Hydrodarco-B	2.49	0.341
Watercarb	2.50	0.216

Hydrodarco-B PAC. The kinetic experiments were repeated using Hydrodarco-B. The fit and prediction of the first 4 hours of data, using true equilibrium data to calibrate the HSDM, was similar to that obtained with Watercarb PAC and are not shown here. However, a better fit and prediction of the first 4 hours of kinetic data was again obtained using 4-hour plateau values to obtain the Freundlich parameters for the HSDM. (See Figure 7.)

Additional batch kinetic tests were performed with 11.5 mg/L Hydrodarco-B to determine what effect changes in the initial concentration of MIB would have on the observed percent removal over time. Figure 8 shows the percent removal at any given time for a particular carbon dose, is not a function of the initial concentration of MIB. This is an important finding because it shows that the diffusion coefficient is not a function of initial concentration. Therefore, percent removal versus time predictions is valid for any MIB concentration typically encountered in natural water. Based upon this information, the percent remaining at equilibrium, C_e/C_0 x 100%, versus C_c plot described above may be expanded to a percent remaining at a fixed time, C_t/C_0 x 100%, versus C_c plot, which will not change as C_0 changes. (See Figure 9) This family of curves was developed using the HSDM that was calibrated with the data in Figure 7. From this new plot, the amount of Hydrodarco-B required to reduce various episodes to the threshold odor concentration, given different amounts of contact time in an ideal reactor, may be quickly determined. (See Table 4.)

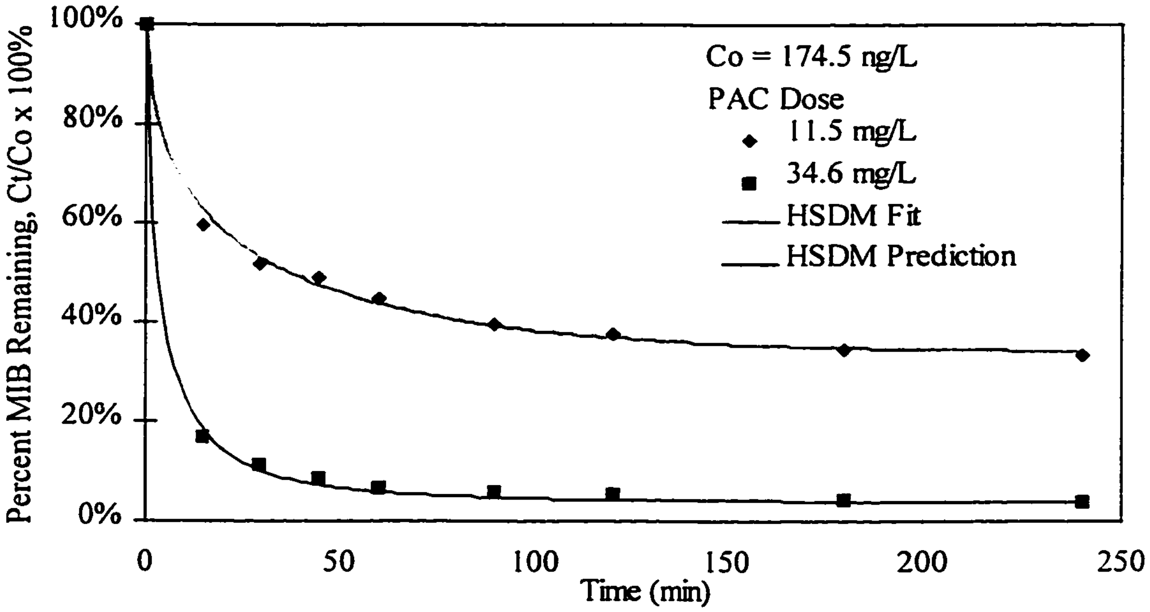

Figure 7. HSDM Fit and Prediction of Batch Kinetic Test Data for MIB Adsorption with Hydrodarco-B PAC, Based Upon Kinetic Test Plateau Values ($D_s = 3.80 \times 10^{-10}$ cm²/min)

Other Powdered Carbons. Kinetic tests were run with the remaining three carbons in order to observe trends between carbons, without doing the extensive equilibrium tests previously done with Watercarb and Hydrodarco-B. Initial MIB concentrations varied from 170 to 175 ng/L, and a pH of 8.2 ± 0.1 was used in these evaluations.

For each carbon, batch kinetic tests with two different carbon doses were performed. A 4-hour response to an additional two carbons doses was also obtained, though the full kinetic response for these doses was not developed. Figures 10 through 12 show the first 4 hours of kinetic data for Nuchar SA-20, WPH, and Cecarbon, respectively. These figures also show the HSDM fit and prediction of the kinetic data based upon the available 4-hour data shown in Figure 13. The Freundlich parameters that were obtained from the data in Figure 13 are given in Table 4.

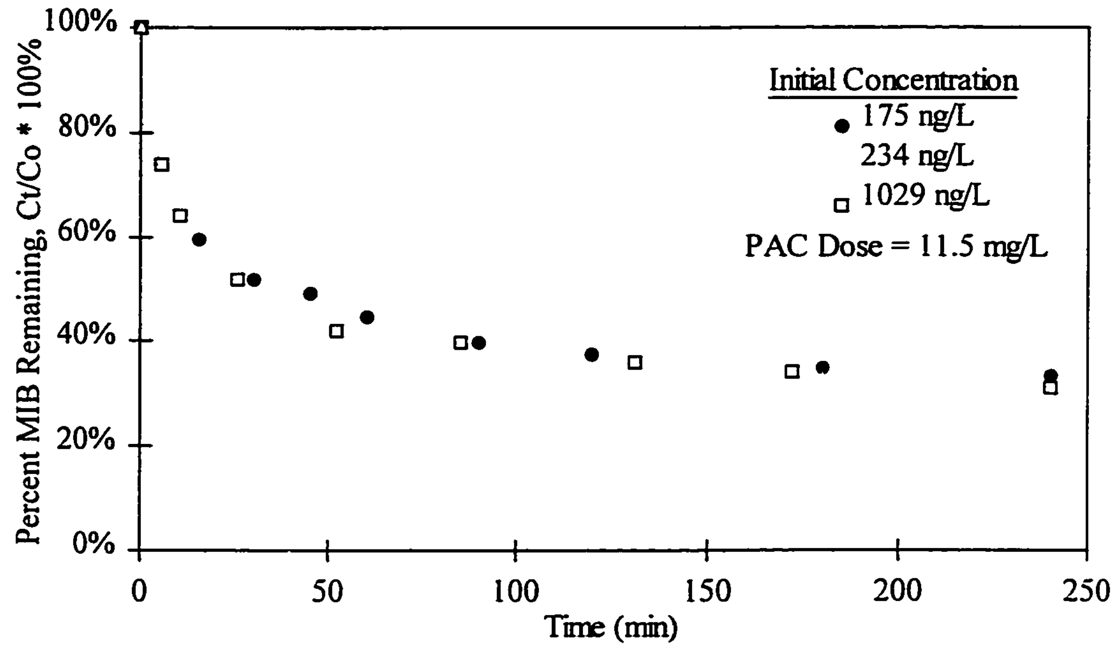

Figure 8 Effect of Initial MIB Concentration on Percent Removal versus Time for Hydrodarco-B PAC

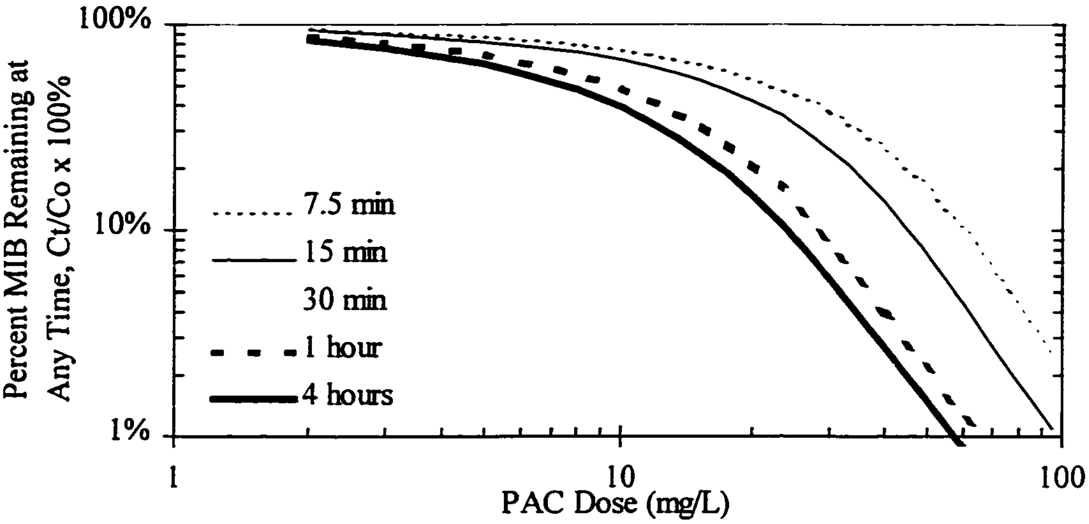

Figure 9 Percent MIB Remaining as a Function of Contact Time versus Hydrodarco-B Dose

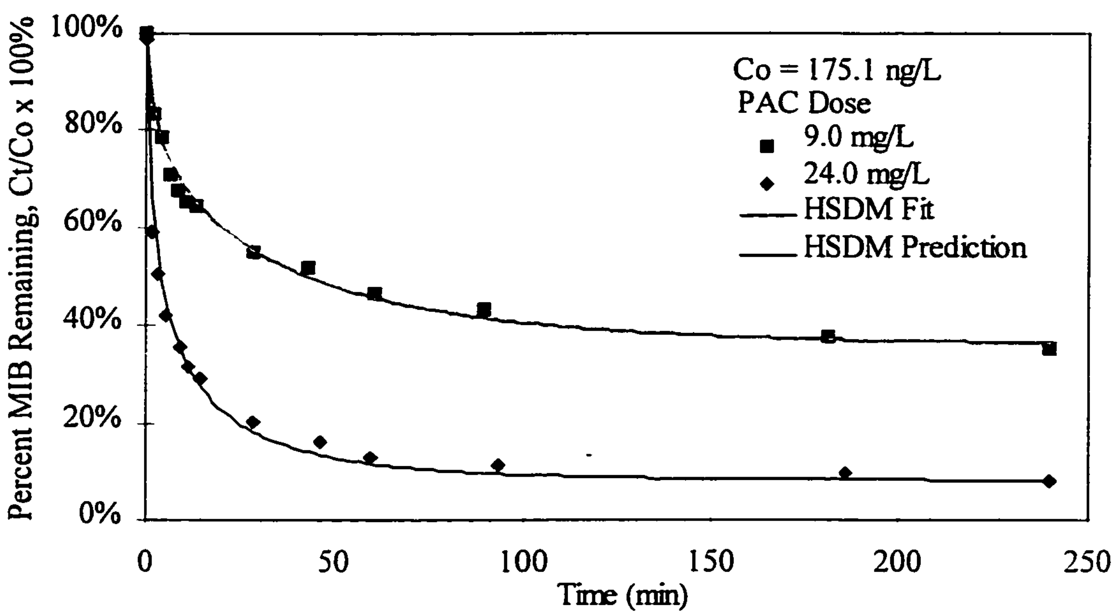

Figure 10. HSDM Fit and Prediction of Batch Kinetic Test Data for MIB Adsorption with Nuchar SA-20 PAC, Based Upon Kinetic Test Plateau Values ($D_s = 3.55 \times 10^{-10}$ cm^2/min)

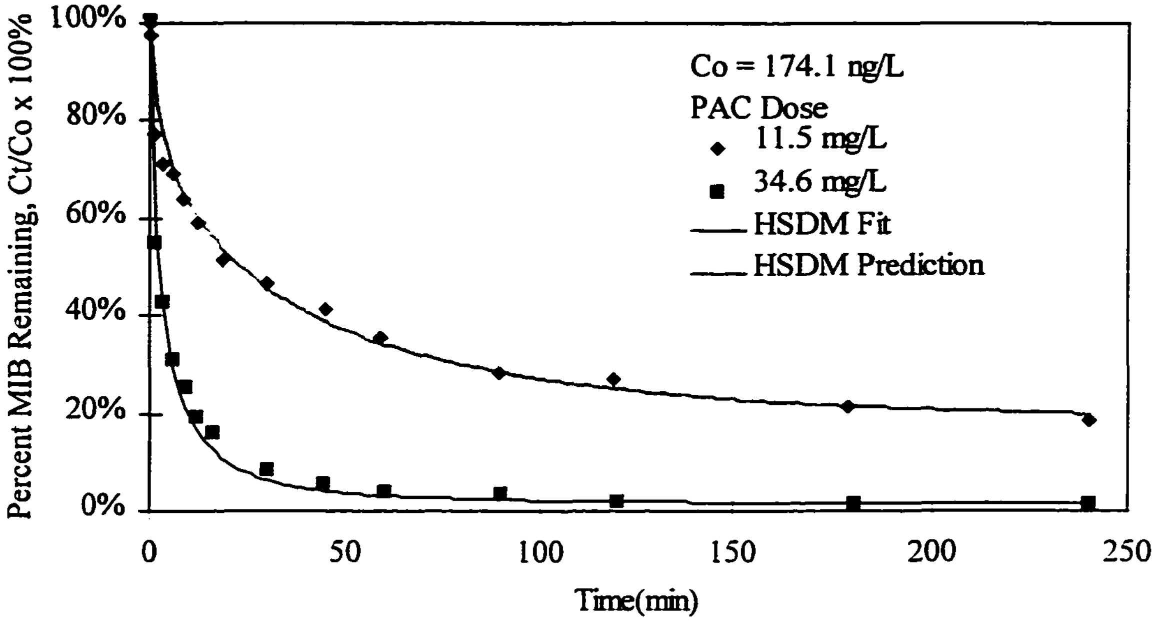

Figure 11. HSDM Fit and Prediction of Batch Kinetic Test Data for MIB Adsorption with WPH PAC, Based Upon Kinetic Test Plateau Values ($D_s = 2.08 \times 10^{-10}$ cm²/min)

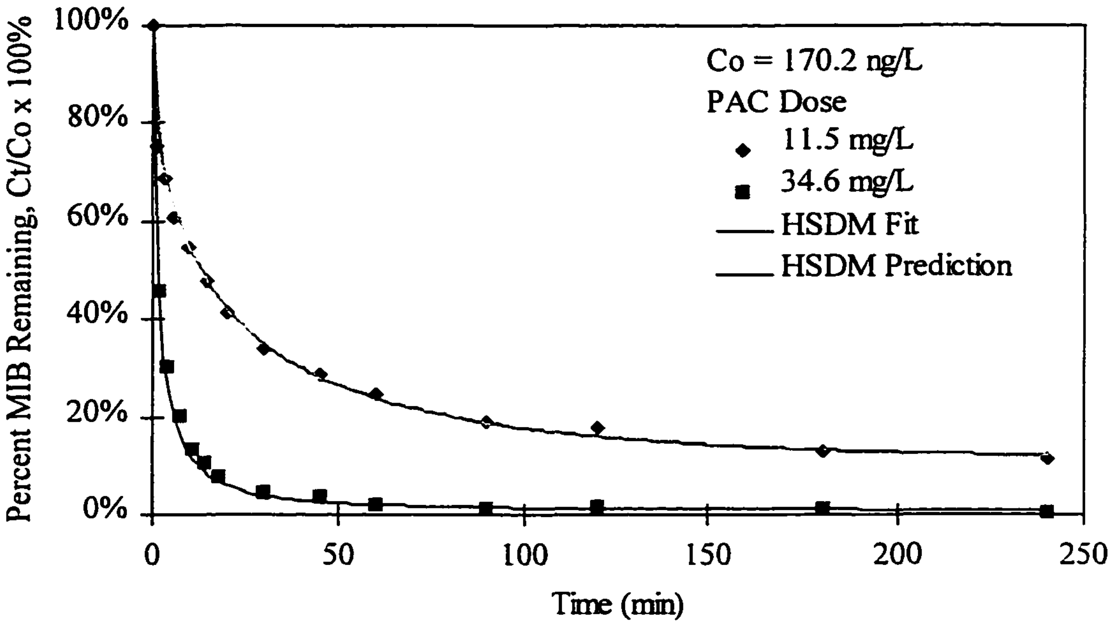

Figure 12. HSDM Fit and Prediction of Batch Kinetic Test Data for MIB Adsorption with Cecarbon PAC, Based Upon Kinetic Test Plateau Values ($D_s = 1.73 \times 10^{-10}$ cm²/min)

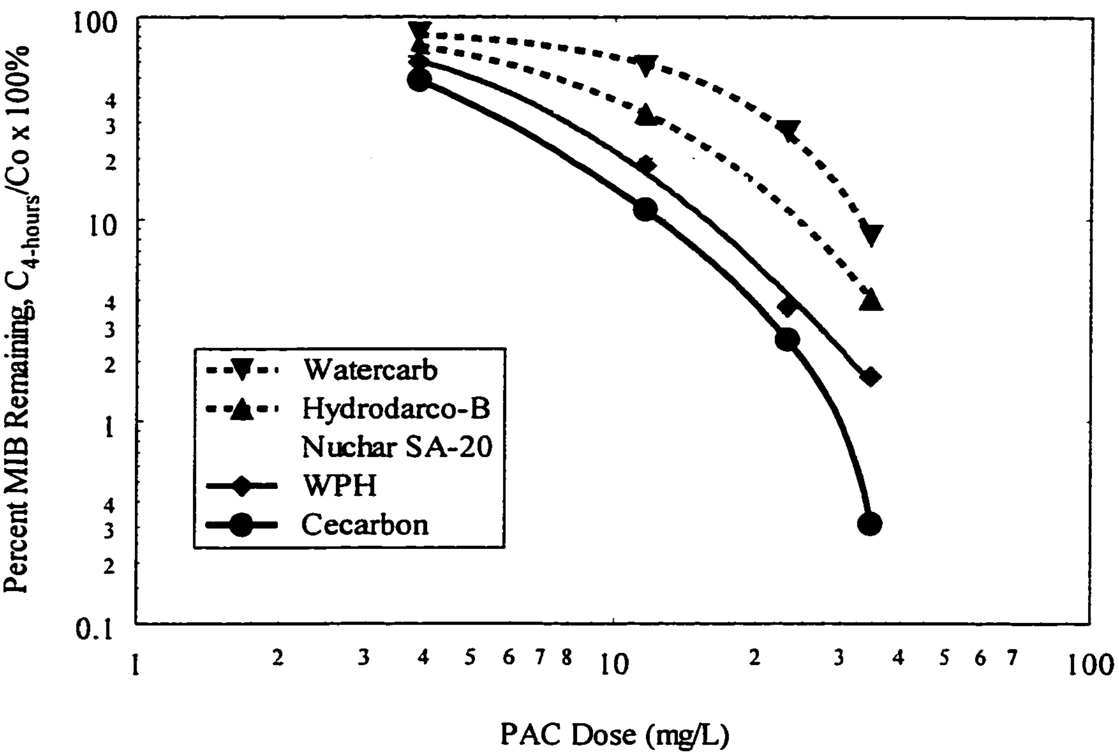

Figure 13. Percent MIB Remaining After 4 Hours of Contact for All Five PACs

Table 4. Required Hydrodarco-B Dose (mg/L) to Reduce the MIB Concentration to 5 ng/L for Different MIB Episodes and Contact Times*

Contact Time	Initial Concentration		
	100 ng/L	50 ng/L	25 ng/L
7.5 min	77	61	44
15 min	58	44	32
30 min	44	34	25
1 hour	36	28	21
4 hours	32	23	17

* These doses have been calculated assuming contact takes place in an ideal reactor.

From Figure 13, the minimum required dose for each PAC, with 4 hours of contact, can quickly be determined for any initial concentration. Table 5, gives an example of reducing initial concentrations of 100, 50 and 20 ng/L down to 5 ng/L (95%, 90%, 80% removal, respectively) in 4 hours.

Table 5. Required PAC Dose to Reduce the MIB Concentration to 5 ng/L for Different MIB Episodes and 4 Hours of Contact Time*

Carbon mg/L	Initial Concentration		
	100 ng/L	50 ng/L	25 ng/L
Cecarbon	18	13	8
WPH	24	18	12
Nuchar SA-20	30	22	15
Hydrodarco-B	32	23	17
Watercarb	38	33	27

* These doses have been calculated assuming contact takes place in an ideal reactor.

The data for the higher carbon doses of each PAC were compared to the results obtained in Niagara River water, another Great Lakes water, by Huang *et al.* (1996). For a PAC dose of 30 mg/L in Niagara River water (pH = 8.3; TOC ≈ 2.5 mg/L), the percent MIB remaining after 1.5 hours depended on the brand of carbon used. Watercarb and Nuchar SA-20 were found to remove 83 and 95% of the MIB, respectively. For the same dose and amount of time in Lake Michigan water (pH = 8.2; TOC ≈ 1.8 mg/L), Watercarb and Nuchar SA-20 were predicted to remove 81 and 94%, respectively.

Using the maximum possible PAC dosage for the Chicago water treatment plants (12 mg/L PAC), a comparison of all five powdered activated carbons is shown in Figure 14. Each curve represents the HSDM model prediction for that PAC under plug flow conditions. At 4 hours, the predicted percent MIB remaining for the carbons ranges from 10 to more than 40 percent. Modeling the system as a completely mixed reactor to account for an exponential residence time distribution of PAC, decreases the percent remaining to 6 to more than 35 percent. An actual water treatment plant would probably have conditions somewhere between plug flow and completely mixed. More importantly, these wide range of percent removals imply that the selection of a particular PAC should not be based solely upon cost per weight, but should instead be founded upon a cost per unit MIB removal.

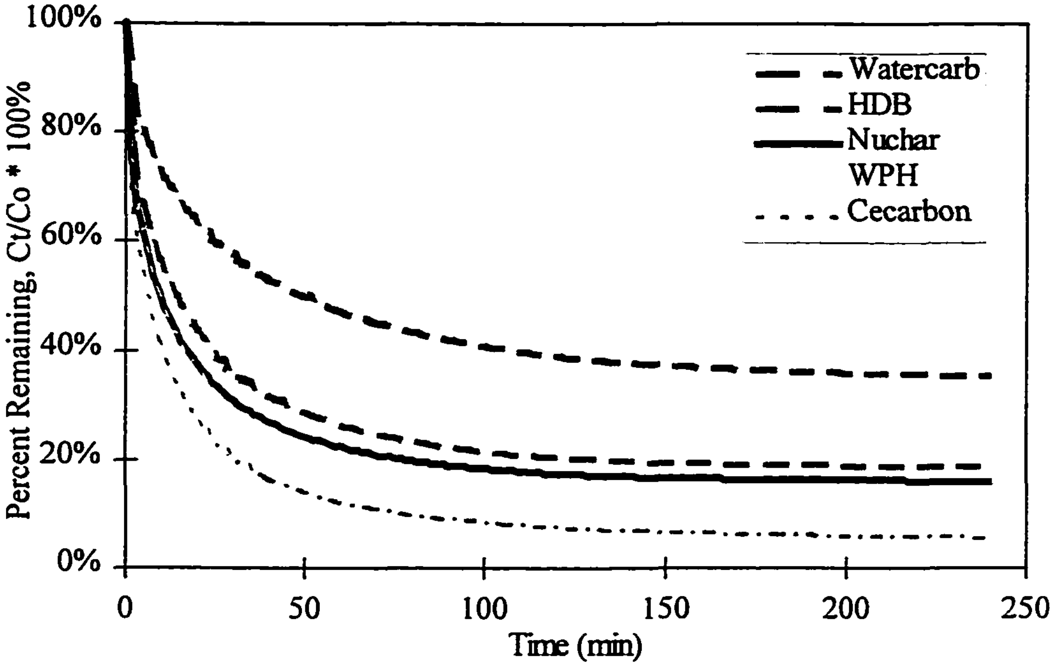

Figure 14. Comparison of HSDM Predictions for All Five PACs, Based Upon Kinetic Test Plateau Values of MIB Adsorption

A comparison of Figure 13 to Figures 2 and 3 shows, that there can be significant differences between the amount of PAC required for 4 hours versus 4 days of contact. For a 90% removal, increasing the dose of Watercarb PAC by 7%, or 2 mg/L, would be required if the contact time was decreased from 4 days to 4 hours. This difference is larger with Hydrodarco-B PAC, which would require increasing the dose 45%, or 7.5 mg/L, for this same decrease in contact time. This emphasizes the importance of having an extended contact time to minimize the carbon dose. Increased contact time may be available if PAC is applied directly to a filter, or in a solids contact clarifier.

The methodologies presented here can be utilized to choose the most cost effective PAC. It must be remembered that conditions in the full-scale plant may lead to results that vary somewhat from laboratory experiments. Specifically, if the PAC is very dense, more of it may settle out early in a sedimentation basin, thus shortening the effective contact time for that carbon and reducing the amount adsorbed. Further, a difference in the particle size distribution of the PAC relative to the sample of PAC used in the laboratory tests may affect kinetics. Some interaction with treatment chemicals used at the plant, although probably unavoidable, may also affect performance, as may hydraulic short circuiting. These issues make it necessary to obtain full-scale plant data on MIB removal to compare to the predicted performance in order to assess the importance of these factors. The data presented here are also specific to Lake Michigan water. Different results would be expected if another water source were to be used.

CONCLUSIONS

The use of ^{14}C-MIB allows for reproducible, accurate, and timely data collection. The protocol for data collection and analysis developed above is a viable tool to investigate the effects of alternative waters, carbons and types of natural organic matter, on the kinetics of MIB adsorption and the equilibrium capacity. Using this material, and a scintillation counter to determine concentration, it was found that:

- For a given PAC dose in natural water, the percent MIB adsorbed at equilibrium is independent of the initial MIB concentration. This is supported in theory by a competitive adsorption model (EBC) and confirmed by both kinetic and equilibrium batch experiments.
- For any given PAC dose in natural water, and any fixed time of contact, the percent MIB adsorbed in an ideal reactor is independent of the initial MIB concentration. Thus for any contact time of interest, the PAC dose required to mitigate any MIB episode for any contact time of interest, may be quickly determined from a C_t/C_0 x 100% versus C_c plot.

ACKNOWLEDGMENTS

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"Men love to wonder and that is the seed of our science." (Ralph Waldo Emerson)

Effect of Chlorine on 2-Methylisoborneol Adsorption by Activated Carbon

by

Thomas E.T. Gillogly*, Vernon L. Snoeyink*,
Andrea Holthouse*, Claude M. Wilson**, Earl P. Royal**

INTRODUCTION

Musty or earthy odors, generally attributed to 2-methylisoborneol (MIB) and geosmin, are the most frequently observed odors in water supplies (Mallevialle and Suffet, 1981). Surveys of utilities have found that the use of activated carbon seems to be one of the most effective methods for the control of tastes and odors (Suffet *et al.*, 1996; Sigworth, 1957). However, the activated carbon is often applied without a full understanding as to how other treatment chemicals may affect adsorption.

The application of chlorine as a part of the water treatment process is still a common practice for disinfection, taste and odor control and ammonia removal. As a result, chlorine is one of the chemicals that often comes into contact with activated carbon. When free chlorine, monochloramine and dichloramine contact activated carbon, they oxidize its surface and in the process are converted primarily to Cl^- and other products (Snoeyink and Suidan, 1975). Oxidation of the surface of activated carbon results in a

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* University of Illinois, 205 N. Mathews Avenue, Urbana, Illinois 61801 (V.L. Snoeyink served as an advisor to the project; A. Holthouse, an undergraduate student, assisted in collecting data)

** City of Chicago, Department of Water, 1000 East Ohio Street, Chicago, Illinois 60611 (C.M. Wilson and E.P. Royal provided information about the problem in Lake Michigan) decrease in adsorptive capacity for a variety of organic compounds (Snoeyink and Suidan, 1975; McGuire and Suffet, 1984; McGuire and Suffet, 1980; Snoeyink *et al.*, 1974; Coughlin, 1970; Coughlin and Ezra, 1968). Also, activated carbon catalyzes many types of reactions with aqueous chlorine (McGuire and Suffet, 1984; Hwang *et al.*, 1990, Jackson *et al.*, 1987; Voudrais *et al.*, 1985; McCreary *et al.*, 1982; Snoeyink *et al.*, 1981, McCreary and Snoeyink, 1981). MIB, however, is very difficult to oxidize and is not directly affected by chlorine (Glaze *et al.*, 1990;Lalezary *et al.*, 1986). The purpose of this article is to show the effect of reacting a range of amounts of free chlorine with a unit mass of PAC on the ability of the PAC to adsorb MIB. Previous research of Lalezary *et al.* (1988), and Lalezary-Craig *et al.* (1986), showed that PAC is less effective for MIB if it is applied together with chlorine, and the findings reported herein expand on this research to show the effect on kinetics and equilibria, and the impact of allowing a short time of PAC contact before chlorine is added.

MATERIALS AND METHODS

2-Methylisoborneol

Concentration Determination. The ^{14}C-labeled 2-methylisoborneol (^{14}C-MIB) (American Radiolabeled Chemicals, St. Louis, MO) was selected due to ease of analysis and small sample size requirements. Analysis of ^{14}C-MIB samples was accomplished by mixing 2.5 mL aliquots with 18 mL of scintillation cocktail (Ecoscint, National Diagnostics, Manville, NJ) in scintillation vials. The resulting fluorescence was then measured in a liquid scintillation counter (Tri-Carb Model 1600CA, Packard Instrument Co., Downers Grove, IL). The specific activity (55 mCi/mmol) of the ^{14}C-MIB yielded a detection limit of 4.5 ng/L, with a confidence level greater than or equal to 89%, without the use of a concentration step (Skoog and Leary, 1992).

Degradation Analysis. While the use of scintillation counting to determine the concentration of ^{14}C-MIB has been previously documented, its use is only valid if the

MIB is not oxidized to other compounds. To validate that MIB was not oxidized, selected samples were analyzed by gas chromatography-mass spectroscopy (5890 Series II Gas Chromatograph with a 5971 Series Mass Selective Detector, Hewlett-Packard Co., Palo Alto, CA) to determine if there were any breakdown products. Prior to GC-MS analysis, the organic compounds in the selected samples were concentrated using solid phase extraction (3M Empore C_{18} Extraction Disks for Environmental Analysis, St. Paul, MN) using the procedure recommended by the manufacturer.

Stock Solution. The compound was received predissolved in purge and trap grade methanol at a concentration of approximately 18.3 μg/μL (chemical purity ≥ 99% confirmed by GC-MS analysis, 100% radiochemical purity confirmed by high performance liquid chromatography (HPLC)). Stock solutions of 100 ng/μL were subsequently prepared by spiking 5.4 μL of the received solution into 1 mL of purge and trap grade methanol. The compound and all solutions were stored at 4°C.

Water

Natural Water. Lake Michigan water (see Table 1 for composition) was used as the natural water source to study competitive effects between background organic material and MIB. Water was collected from a line running from the South Water Production Plant (Chicago, IL) crib to the shore plant. The water was shipped to the University of Illinois in 208 L (55 gal) stainless steel drums, where it was stored at 4°C in the dark to limit biological activity. (The crib is located two miles off shore in water 32 to 35 feet deep; the water is drawn near the bottom.)

Table 1. Characteristics of Lake Michigan Water

pH	8.2
Alkalinity	117 mg/L as $CaCO_3$
Conductivity	281 μmhos
Turbidity	1.88 N.T.U.
Nitrogen, Total Kjeldahl	0.37 mg/L
Phosphate, Total	0.021 mg/L
Dissolved Organic Carbon	1.8 mg/L

Organic-free Water. Organic-free water for the single-solute isotherms was obtained by passing deionized Urbana, IL, tap water through a Milli-Q water system (Millipore Corp., Bedford, MA) which has three cartridges (activated carbon, ion exchange, ion exchange) and a 0.45μm filter. The water had a resistivity ≥ 18 megohm-cm and a dissolved organic carbon (DOC) content of 0.1-0.3 mg/L.

Activated Carbon

The PAC evaluated in this study was Hydrodarco-B (Norit Americas Inc., Atlanta, GA). A grab sample of this carbon was obtained from the inventory of the City of Chicago Department of Water. The PAC was stored in polyethylene bottles until used. Prior to use, samples were dried overnight in a 110°C oven to remove excess water, and subsequently were cooled in a desiccator. Once cooled, the desired amount of carbon, not less than 2 mg, was weighed out on a 4-point scale (LIBROR AEU-210, Shimazdu Corp., Kyoto, Japan).

For experiments that required carbon slurries, a slurry of 10 mg/mL was used. These slurries were prepared by mixing 10 g of the carbon, prepared as above, in 1 L of organic-free water. The slurry was mixed with a magnetic stirring bar only when an aliquot was to be drawn. For the remaining time the slurry bottle was quiescent. This was to prevent grinding of the carbon between the storage vessel bottom and magnetic stirring bar, as the kinetics of adsorption is sensitive to particle diameter (Najm *et al.* 1990; Mathews and Zayas, 1989).

The PAC was prepared in large batches for experiments that utilized carbon that had been oxidized prior to the experiment. $Ca(OCl)_2$ was added to 20 L of Milli-Q water to make up a 10 mg/L as Cl_2 solution. To the chlorine solution, dried PAC was added to give the desired mass ratio of chlorine to PAC. The mixture was allowed to mix for 2 days in the dark, or until all the chlorine had reacted, whichever was longer. The carbon was then filtered out of the mixture and dried overnight in a 110°C oven to remove excess water, and then cooled in a desiccator. For an experiment using the preoxidized carbon, a portion of the desired carbon was weighed out and wetted in 10 mL of Milli-Q water for 24 hours prior to its use.

Batch Kinetic Tests

The apparatus used for the batch kinetic experiments was a jar test apparatus with modified B-KER^2 square jars (Six Paddle Stirrer Model 7790-400, Phipps & Bird, Richmond, VA). Clear acrylic lids were manufactured for each individual jar to prevent loss of MIB through volatilization. These lids allowed for the experiments to be visually monitored and run headspace free. In the jars, 2.6 L of Lake Michigan water (pH = 8.2) was brought to room temperature and spiked with ^{14}C-MIB to the desired initial concentration. The solutions were then stirred at 125 rpm for 5 minutes before the addition of carbon. Carbon was either added as an aliquot of a carbon slurry, or as a weighed mass of oven dried, prewetted carbon. (To properly wet the carbon prior to the test, weighed carbon was soaked overnight in a small aliquot of organic-free water.) Samples were then withdrawn at predetermined time intervals up to 240 minutes. The samples were collected using a stainless steel needle (Aldrich Chemical Co., Milwaukee, WI) connected to a gas-tight, luer lock syringe (Hamilton Co., Reno, NV). The aliquot was then passed though a 0.22 μm conditioned nylon membrane syringe (Magna, Westboro, MA) supported in a syringe filter holder (Swinney Holder, Gelman Sciences, Ann Arbor, MI). To condition the filter, 5 mL of the sample was filtered and wasted prior to the collection of 2.5 mL into the scintillation vial. To maintain the jars headspace free, unspiked distilled deionized water was added to make up volume used in sampling. The resulting measurements were then adjusted for the amount of water added to the system.

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RESULTS AND DISCUSSION

Effect of Chlorine on MIB Adsorption and the Time of Addition of Chlorine Relative to PAC

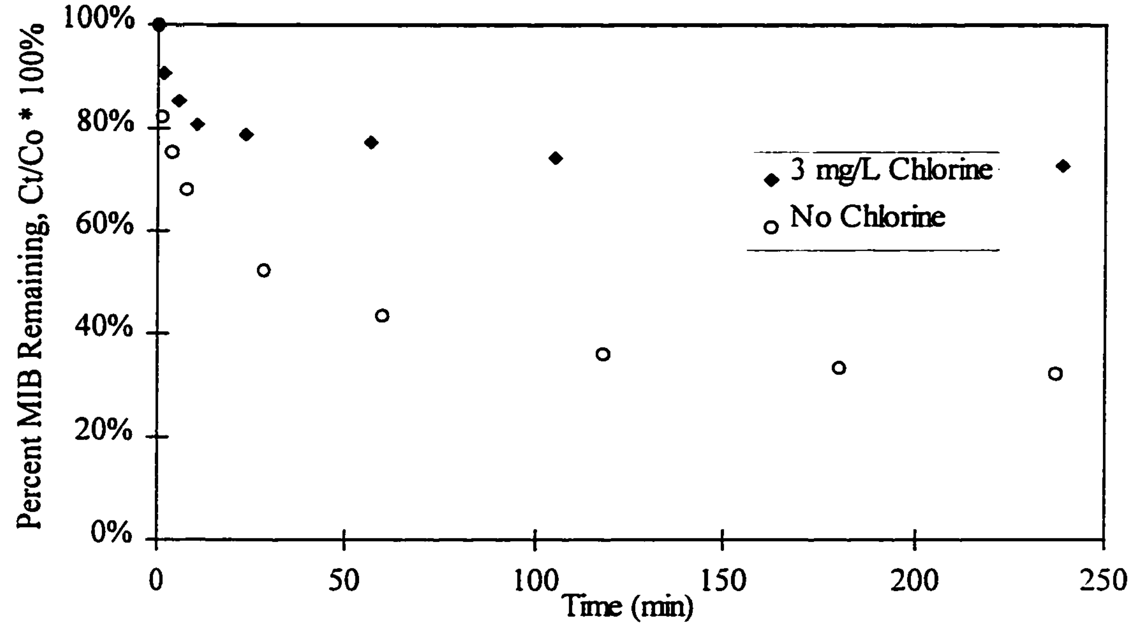

Figure 1 - Effect of Free Chlorine on MIB Adsorption

A series of experiments was carried out to show the effect of the presence of aqueous chlorine on the ability of PAC to adsorb MIB from Lake Michigan water, the effect of the initial chlorine concentration, and the effect of delaying the chlorine addition until after PAC had been added to simulate the effect of using an alternative point of chlorine addition. Application of chlorine at the same time that PAC was added dramatically reduced the amount of MIB adsorbed by activated carbon. The data shown in Figure 1 were obtained from two batch tests. The control, represented by the open circles, was performed by adding 11.5 mg/L Hydrodarco-B PAC to pH 7.4 Lake Michigan water spiked with ^{14}C-MIB. The other batch test was spiked with chlorine (3 mg/L as Cl_2) at the time of the addition of 11.5 mg/L Hydrodarco-B. The chlorine caused the percent MIB removed in 4 hours to be reduced from 68% to 26%, a 60% loss of capacity. A similar trend has been reported for Calgon WPH, by Lalezary-Craig *et al.* (1988). In

Weymouth plant influent water, 10 mg/L WPH PAC adsorbed 73% of the MIB in 4 hours. However, if 2 mg/L of chlorine was simultaneously dosed with the WPH, only 56% of the MIB was removed.

The simultaneous addition of 3 mg/L chlorine and 11.5 mg/L PAC to Lake Michigan water was repeated in another batch test. This time, however, the concentration of chlorine was monitored. Within 9 minutes more than 90% of the free chlorine had reacted, and by 90 minutes none was detectable. An additional 0.11 mg/L of combined chlorine as Cl_2 was measured at 9 minutes. This concentration slowly decreased to 0.03 mg/L as Cl_2, measured at 4 hours.

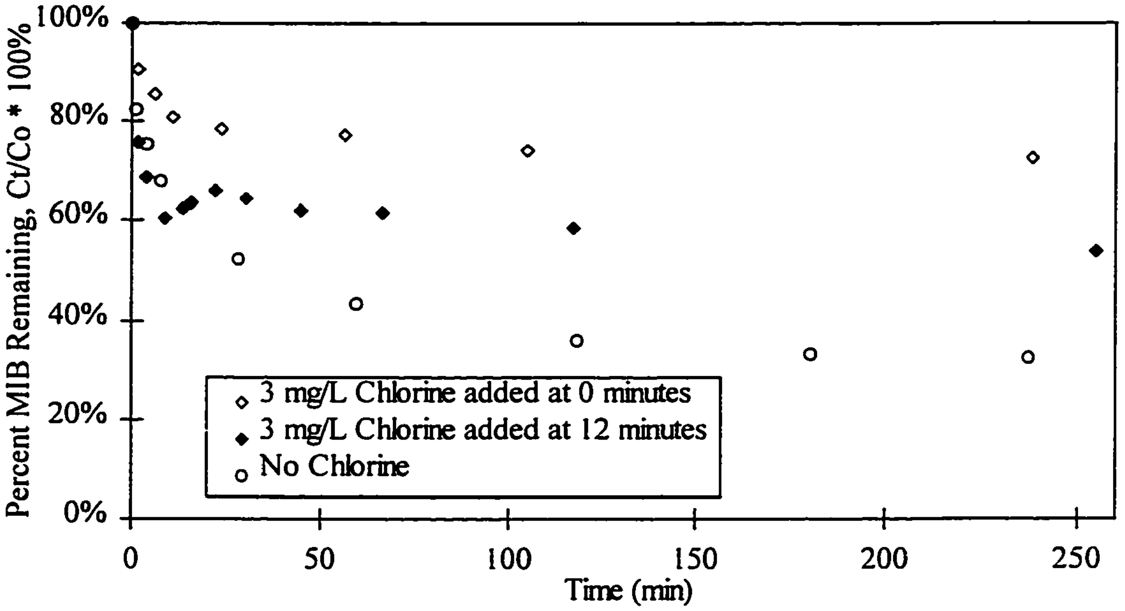

Figure 2 - Effect of Time of Chlorine Addition on MIB Adsorption

Experiments were then conducted to show the effect of adding chlorine a short time after the addition of PAC. Figure 2 compares the results obtained from adding 3 mg/L chlorine 12 minutes after the application of 11.5 mg/L PAC, to those collected from the first experiment with (3 mg/L of chlorine simultaneously with PAC) and without chlorine. From this figure it can be seen that delaying the time of addition of chlorine by 12 minutes was beneficial (46 percent removal versus 26 percent removal) even though there was a release of the previously adsorbed MIB as a result of the application of chlorine. While delaying the addition of chlorine improved MIB removal to 46 percent after 4 hours, removal was still far short of the 68 percent achieved when no chlorine was present. Two significant conclusions can be made from this experiment: 1) chlorine can oxidize adsorption sites containing MIB, thereby releasing the MIB back into the aqueous phase; 2) the later that chlorine is applied with respect to the addition of PAC, the greater the expected MIB removals

Several additional experiments were conducted to show the effect of chlorine doses of 0, 3 and 5 mg/L as Cl_2 on the MIB removal that could be achieved by several PAC doses. To this end, headspace free reactors containing pH 7.4 Lake Michigan water and MIB were dosed simultaneously with chlorine and PAC. The resulting MIB concentrations were monitored over time. The percent of MIB remaining at 4 hours as a function of PAC dose is shown in Figure 3. It has been previously shown that for a given PAC dose in natural water, and any fixed time of contact, the percent MIB adsorbed in an ideal reactor is independent of the initial MIB concentration (Mathews and Zayas, 1989). From this graph, the necessary amount of PAC necessary to remove any initial concentration of MIB down to threshold odor levels may be quickly determined when reasonable levels of chlorine and PAC are added simultaneously. Table 3 gives the amount of Hydrodarco-B required to reduce MIB to threshold odor levels (5 ng/L) for several different initial concentrations, given 4 hours of contact in an ideal reactor and initial chlorine concentrations of 0, 3 and 5 mg/L as Cl_2.

It can be observed that as the concentration of PAC increased, the lines in Figure 3 converged for the different initial concentrations of chlorine. This can be explained by looking at the mass of chlorine reacted per mass of PAC. (See Table 4) For a fixed initial concentration of chlorine, the amount of chlorine reacted per mass of PAC decreases as the carbon concentration increases. It would appear that below a given ratio of chlorine to carbon, the effect is negligible. Further research is necessary to determine if this ratio is specific to a given water or carbon.

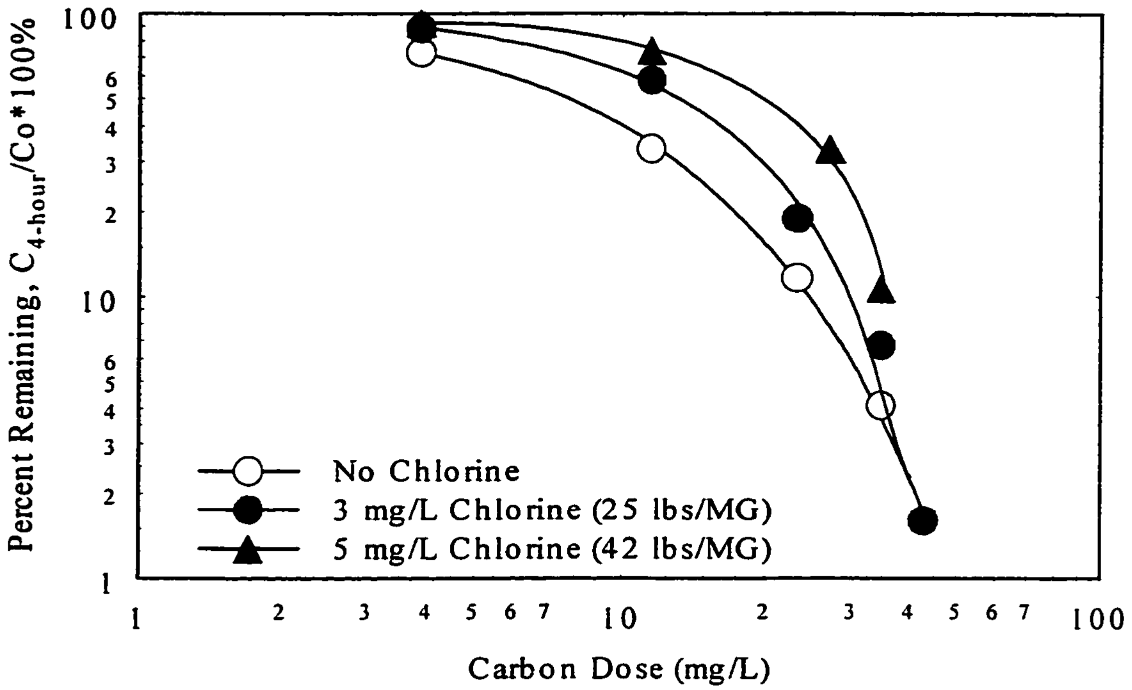

Figure 3 - Effect of a Fixed Initial Concentration of Chlorine on the 4-Hour MIB Adsorption Capacity: Percent Remaining Versus PAC Dose

Table 3 - Required PAC Dose (mg/L) to Reduce MIB Concentration To 5 ng/L with 4 Hours of Contact Time

Initial Chlorine Concentration	Initial MIB Concentration		
	20 ng/L	50 ng/L	100 ng/L
0 mg/L	15	24	32
3 mg/L	22	30	34
5 mg/L	29	36	38

Table 4 - Milligrams of Chlorine Reacted within 4 Hours per Milligram of PAC[2]

PAC (mg/L)	Initial Chlorine Concentration	
	3 mg/L	5 mg/L
3.85	0.73	1.18
11.5	0.26	0.43
23.1	0.13	0.22
34.6	0.09	0.14
46.2	0.06	0.11

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[2] For the lower PAC concentrations, not all of the chlorine initially present was reacted within 4 hours. These numbers indicate the actual amount reacted.

Cause of the Decrease in MIB Adsorption

There were several possible reasons for the observed decrease in MIB capacity caused by chlorine. Because it has been shown through many studies that activated carbon may catalyze many types of reactions with chlorine, it was important to establish that the radiolabeled MIB was not being catalytically degraded on the PAC (Hwang *et al.*, 1990, Jackson *et al.*, 1987; Voudrais *et al.*, 1985; McCreary *et al.*, 1982; Snoeyink *et al.*, 1981, McCreary and Snoeyink, 1981, Glaze *et al.* 1990). The experiment with addition of 3 mg/L of chlorine 12 minutes after the PAC was repeated and a solution sample was collected at 22 minutes, the time of maximum MIB release. Analysis of the sample by GC-MS showed no additional compounds that might have come from a chlorine-MIB reaction on the PAC surface indicating activated carbon does not catalyze a reaction between MIB and chlorine.

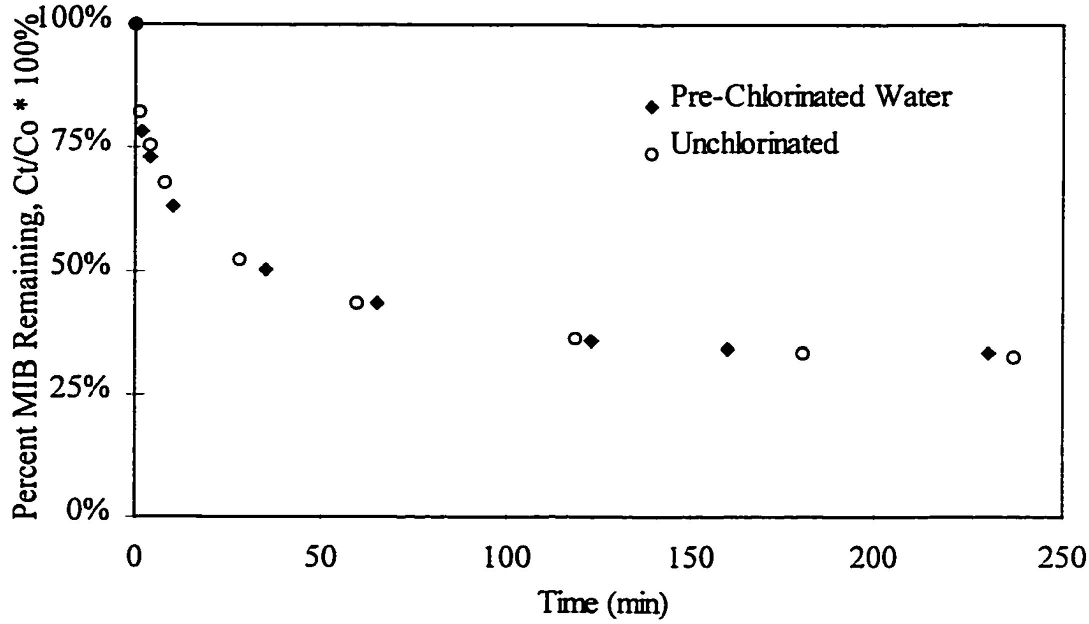

Figure 4 - Effect of Disinfection By Products on the Adsorption of MIB

An additional experiment was performed to verify that the observed chlorine effect was not attributable to increased competition for adsorption sites by disinfection-by-products (DBPs). Lake Michigan water was chlorinated with 5 mg/L as Cl_2 and allowed to react in the dark for 24 hours. The remaining free chlorine was dechlorinated by adding sulfite, after which the water was spiked with MIB and 11.5 mg/L PAC. The kinetic curves for MIB adsorption in the presence of DBPs (shown in Figure 4) indicated that they did not influence adsorption.

The most probable reason for the observed decrease in MIB capacity was the buildup of surface oxides. Previous studies have shown that increasing the amount of chlorine reacted per mass of activated carbon increased the concentration of surface oxides on the carbon, and correspondingly decreased the capacity of F-400 activated carbon to adsorb phenol and *p*-nitrophenol (PNP) (Snoeyink *et al.* 1974). However, the impact observed on the ability of Hydrodarco-B PAC to adsorb MIB was much greater than for phenol and *p*-nitrophenol, as shown in Table 5.

Table 5 - Single Solute Percent Capacity Reduction as a Function of Chlorine Reacted[3]

Compound / Carbon	Free Chlorine Reacted (mg Cl_2/mg carbon)	
	0.5	1
PNP / F-400[7]	29%	35%
Phenol / F-400[24]	54%	62%
MIB / Hydrodarco-B*	~75%	~92%

Factors Affecting the Decrease in MIB Adsorption

Experiments were conducted to determine the importance of the initial chlorine concentration versus the mass of chlorine reacted per gram of PAC for the decrease in MIB adsorption. (See Figure 5) In deionized-distilled water, chlorine was reacted with Hydrodarco-B in the absence of MIB. In one group of tests 5 mg of chlorine as Cl_2 was reacted with 11.5 mg PAC, with the chlorine applied in three different ways. First, 5 mg/L chlorine was reacted with 11.5 mg/L PAC; second, the chlorine was reacted with 11.5 mg/L PAC in two consecutive steps of 2.5 mg/L chlorine in each step; and third, the chlorine was applied to 11.5 mg/L PAC in 5 dosings of 1 mg/L chlorine each. For each test, subsequent additions of chlorine were not added until all of the previously dosed

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[3] This study, assuming plateau values in Figure 5 approximate equilibrium

chlorine had reacted. After all the chlorine had reacted, each of the three reactors were spiked with ^{14}C-MIB and monitored over time. Each means of application resulted in a 4-hour MIB removal about 23 percent, or a reduction in capacity of 75%, showing that initial chlorine concentration was not an important factor. Another group of tests looked at a total of 10 mg/L of chlorine reacted with 11.5 mg/L Hydrodarco-B. For this group 10 mg/L of chlorine added all at once, and 10 mg/L added in 5 additions of 2 mg/L was investigated. Both application methods resulted in an MIB removal of 8 percent, or a 92% reduction in MIB capacity, further substantiating that it is the amount of chlorine reacted, not its initial concentration, which determines the magnitude of the chlorine effect.

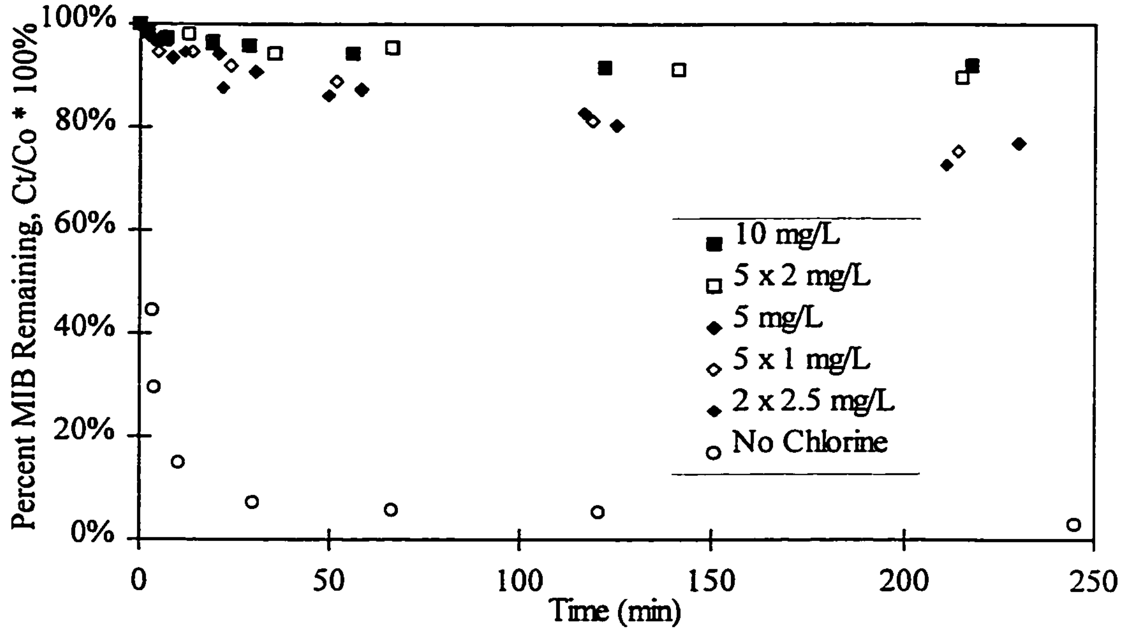

Figure 5 - Effect of Total Chlorine Dosed and Initial Concentration

Once it was determined that the mass of chlorine reacted per mass of activated carbon governed the decrease in capacity, additional experiments were run to determine how great of an effect could be expected for different ratios of chlorine reacted to PAC. Hydrodarco-B was preoxidized in DDI water with chlorine to PAC mass ratios of 0.5:1, 1:1 and 2:1, and subsequently dried. The adsorption of MIB in Lake Michigan water by these oxidized carbons was then monitored over time. With 11.5 mg/L Hydrodarco-B 68% of the MIB initially present was adsorbed in 4 hours. As the chlorine reacted to PAC ratio increased from 0.5, to 1.0 to 2.0, MIB removals of 49 percent, 31 percent, and 15 percent were observed, as shown in Figure 6. The trend observed in this figure further supports the hypothesis that the formation of surface oxides is reducing the capacity of the PAC for MIB.

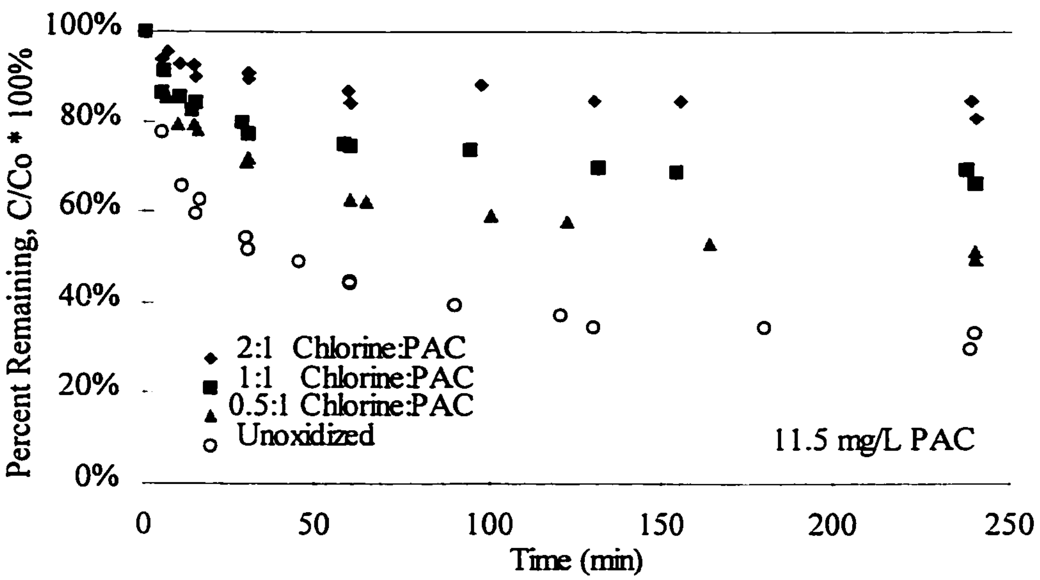

Figure 6 - Dependence of MIB Removal on Mass Chlorine Reacted Per Mass PAC

It was noticed that the percent removal for the PAC which had been preoxidized to a 1:1 chlorine to PAC mass ratio gave similar percent removals to the experiment with a simultaneous addition of 3 mg/L of chlorine with 11.5 mg/L of unoxidized PAC (0.26:1 chlorine to PAC mass ratio). It was determined that the drying step of the preoxidation process recovered some of the capacity that was lost during the oxidation process. Figure 7 shows the results from an experiment carried out in DDI water. In the first reactor, 5.8 mg/L PAC and 5.8 mg/L chlorine were allowed to react until all the chlorine had been reduced, prior to the addition of the MIB. This gave a 1:1 chlorine to PAC mass ratio carbon which had not been dried. The second reactor contained 5.8 mg/L of 1:1 chlorine to PAC mass ratio preoxidized carbon, which had been dried. The third reactor contained

5.8 mg/L of unoxidized PAC. The response of these three reactors to MIB was markedly different. The oxidized carbon which had not been dried removed only 11% of the MIB initially present, as compared to an 86% removal by the unoxidized PAC. This reduction in the 4-hour capacity due to oxidation, constitutes a 87% reduction in capacity. However, if the oxidized carbon is dried some of the capacity is recovered. In 4 hours the dried oxidized carbon is able to remove 38% of the MIB, a 56% loss of capacity.

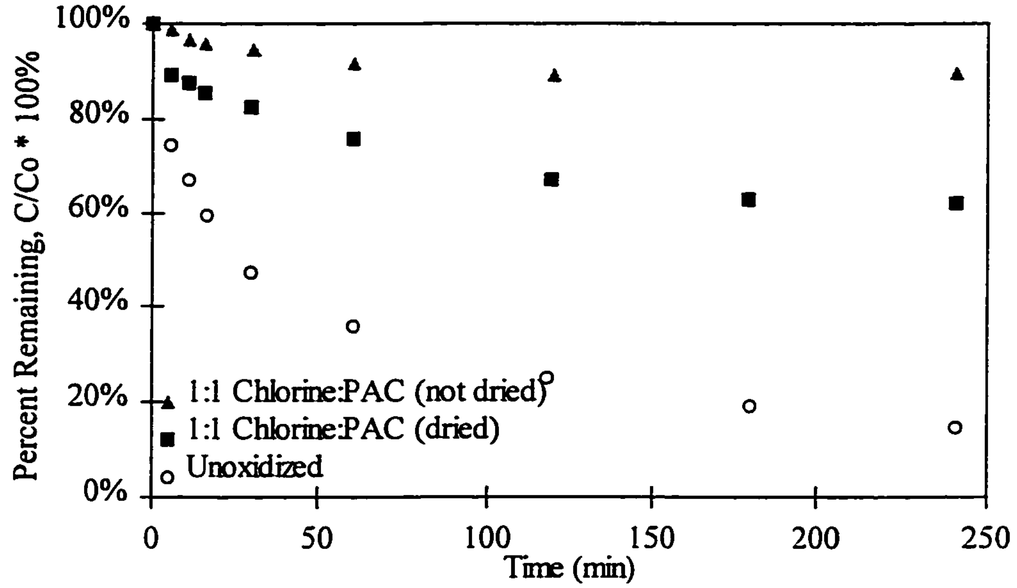

Figure 7 - Stability of Oxidized Adsorption Sites

It is believed that the drying process volatilized some of the weakly bound surface oxides. These easily volatilizable oxides may be surface carboxyl groups. It has been previously reported that the dechlorination capacity of activated carbon may be restored by heating to 500-700°C in an inert environment. During this heating primarily CO_2 was evolved, which can be derived from carboxyl groups.[7]

CONCLUSIONS

The conclusions are as follows:

- Activated carbon's adsorptive capacity for MIB is significantly reduced by free chlorine. While certain levels of chlorine must be added to satisfy federal disinfection regulations, the best efficiency will be achieved if contact between PAC and chlorine is minimized or eliminated. For reasonable concentrations of chlorine, the amount of chlorine reacted per unit mass of activated carbon determines the extent of reduction in MIB adsorption capacity.
- Chlorine can oxidize adsorption sites containing MIB. A release of MIB back into the aqueous phase was observed immediately after an addition of chlorine to a system in which activated carbon had previously adsorbed MIB.
- The later that chlorine is applied with respect to the addition of PAC, the greater the expected MIB removals. In Lake Michigan water, 11.5 mg/L of Hydrodarco-B was able to remove 68% of the MIB in 4 hours. If chlorine (3 mg/L as Cl_2) was simultaneously added with the PAC, only 26% of the MIB was removed in 4 hours. However, if the chlorine addition was delayed by 12 minutes 54% of the MIB was adsorbed in the same amount of time.
- Drying an oxidized carbon recovers a large portion of the lost MIB capacity. In deionized-distilled water 5.8 mg/L of unoxidized Hydrodarco-B removed 86% of the MIB initially present in 4 hours. If the carbon had been oxidized to a 1:1 chlorine to PAC mass ratio removed only 11% of the MIB in 4 hours. However, when this carbon had been reacted to the same chlorine to PAC mass ratio and was dried prior to MIB adsorption 38% of the MIB was adsorbed.

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"Few enterprises of great labor or hazard would be undertaken if we had not the power of magnifying the advantages we expect from them." (Samuel Johnson)

Determining the Remaining GAC Bed Life for Taste and Odor Control

by

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ABSTRACT

This study has developed an alternative approach to rapidly and effectively evaluate the remaining life of a GAC bed for the mitigation of taste and odor episodes. Using laboratory-scale columns packed with GAC taken from full-scale operating adsorbers, the approach was shown to simulate the performance of pilot-scale columns very well. It was concluded from this study that the maximum attenuation of a transient MIB load by GAC, reported as percent removal, was independent of the influent MIB concentration but dependent on the amount of natural organic matter adsorbed on its surface. It was also discovered that adsorption alone might be insufficient to provide full protection against typical MIB episodes.

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INTRODUCTION

One of the questions most frequently asked while using granular activated carbon (GAC) adsorbers is, "how much longer will it last?" Heilker (1979) indicated that taste and odor substances from algal blooms exhausted a biologically active bed after a four month run. Newcombe *et al.* (1994) concluded that even for a GAC filter exposed to periodic low nanogram per liter concentrations of 2-methylisoborneol (MIB) with an empty bed contact time (EBCT) of 20 minutes, 18 months was the longest that the filter could be expected to reduce MIB concentrations to below the odor threshold concentration. Additionally, GAC filter beds treating the same water with EBCTs of 6.5 and 13 minutes were expected to be exhausted within 10 months. After only seven weeks, geosmin, at periodic influent concentrations of hundreds of nanograms per liter, was observed in the effluent of a GAC system that had chlorine in the influent water (CH2M, 1987). In contrast, others have reported bed lives on the order of years for the removal of MIB and geosmin (Yagi *et al.* 1988; Suffet, 1980; Schulhof, 1979).

Predicting Bed Life

While not a simple task, many researchers have attempted the challenge of predicting the effective service life of GAC adsorbers. The most obvious first step was to determine the GAC capacity for the particular adsorbate of interest in batch systems. It was determined that GAC particle size had no noticeable effect on the equilibrium adsorption capacity (Najm *et al.* 1990; Weber and Wang, 1987; Thacker *et al.* 1983; Randtke and Snoeyink, 1983; Lee *et al.* 1981). While it was expected that carbons with higher adsorption capacities would have longer bed lives, it was found that adsorption kinetics had a dramatic impact on bed life and would often shift the expected order of breakthrough (Weber and Wang, 1987; Lee *et al.* 1981).

While equilibrium theory alone has been used to predict pilot- and full-scale column performance, the use of fixed bed mass transfer models that incorporate both kinetics and equilibrium is much more common. Mass transfer models have been used to develop equations that relate the operation of large-scale adsorbers and small-scale predictive columns (Crittenden *et al.* 1987; Crittenden *et al.* 1991). The test procedure, including the application of the scaling equations, is commonly referred to as the rapid small-scale column test (RSSCT). The RSSCT takes particle size, hydraulic loading, and empty bed contact time (EBCT) into account.

The hydraulic loading of the RSSCT is selected by assuming that intraparticle diffusion is either independent (constant diffusivity; CD-RSSCT) or proportional (proportional diffusivity; PD-RSSCT) to particle size. Unfortunately, it cannot be determined *a priori* whether proportional or constant diffusivity should be used. While both CD-RSSCT (Crittenden *et al.* 1987; Vidic *et al.* 1992; McGuire *et al.* 1991; Crittenden *et al.* 1986) and PD-RSSCT (Crittenden *et al.* 1991; Summers; *et al.* 1989) have been able to successfully predict breakthrough in known and unknown mixtures, there are many times when predictions have not been accurate (Crittenden *et al.* 1986; Summers *et al.* 1989; Speth and Miltner, 1981).

An alternative approach has recently been taken in applying the RSSCT. Using virgin GAC, Matsui *et al.* (1994) observed that the removal efficiency of intermittently applied pesticides (simazine, napropamid, bentazon, asulum, hymexazol) in natural water was not related to the concentration of the pesticide itself. Similarly, Namuduri and Summers (1991) found that the percent breakthrough of chloroform, 1,2-dichloroethene and 1,2-dichloropropane was generally insensitive to the input pulse concentration. These findings support and expand upon the results of other researchers who showed that the percent removal of a micropollutant from natural water by powdered activated carbon was independent of the micropollutant's initial concentration (Knappe *et al.* 1998, Gillogly *et al.* 1998, Gillogly *et al.* 1997; Graham *et al.* 1997).

Matsui *et al.* (1994) also found that the breakthrough curves for both intermittently and continuously applied pesticides were nearly identical. The effluent pesticide concentration was determined by the amount of background organic matter adsorbed on the GAC and not by the amount of pesticide adsorbed. Comparing columns exposed to intermittently and continuously applied pesticides, a difference in the percent pesticide removal was only found when the mass loading of pesticide was greater than about 50 percent of the loading at complete saturation of the GAC.

The RSSCT has proven useful for defining the behavior of fresh GAC but has not been used to determine the remaining life of an existing GAC adsorber due to particle size restrictions. RSSCTs typically use particles with geometric mean diameters less than 250 μm. While grinding fresh GAC to obtain the appropriate particle size does not alter its capacity, grinding partially saturated GAC will change its adsorptive properties because adsorption sites that were blocked by previously adsorbed compounds are now accessible.

Considering the inapplicability of the RSSCT, it was the objective of the authors to develop an alternative tool to rapidly and effectively evaluate the remaining life of GAC for mitigation of a taste and odor episode. The test should determine how effluent concentrations of taste and odor causing compounds change as influent concentrations change, without grinding the carbon. This test should also provide the information necessary to determine if the GAC is currently effective and if it will last through an impending taste and odor season, or if it is sufficiently spent to require regeneration or replacement.

MATERIALS AND METHODS

Pilot-Scale MIB Analysis. MIB and geosmin concentrations for the pilot-plant study were determined by Montgomery Watson Laboratories using Standard Method 6040B "Closed-Loop Stripping, Gas Chromatographic/Mass Spectrometric Analysis" (Standard, 1995). The detection limits were 3.0 and 5.0 ng/L for geosmin and MIB, respectively.

Laboratory-Scale MIB Analysis. Due to ease of analysis and small sample size requirements, ^{14}C-labeled 2-methylisoborneol (^{14}C-MIB) (American Radiolabeled Chemicals, St. Louis, MO) was utilized. Analysis of ^{14}C-MIB samples was accomplished by mixing sample aliquots with 18 mL of scintillation cocktail (Ecoscint, National Diagnostics, Manville, NJ) in scintillation vials. The resulting fluorescence was measured in a liquid scintillation counter (Tri-Carb Model 1600CA, Packard Instrument Co., Downers Grove, IL). It was not necessary to concentrate the sample for analysis. The compound was received predissolved in purge and trap grade methanol at an approximate concentration of 18.3 μg/μL (chemical purity ≥ 99% confirmed by GC-MS analysis, 100% radiochemical purity confirmed by high performance liquid chromatography - HPLC). Stock solutions of 100 ng/μL were subsequently prepared by spiking 5.4 μL of the received solution into 1 mL of purge and trap grade methanol. The compound and all solutions were stored at 4°C. The limit of detection for this analysis is 3.0 ng/L with greater than 89% confidence.

Virgin GAC. The virgin granular activated carbon used in this study was F-300 (Calgon Carbon Corp., Pittsburgh, PA).

Table 1 – Physical Characteristics of the Granular Activated Carbons

	Virgin	1 Years in Service	2 Years in Service
Effective size, mm	1.0	1.0	0.8
Uniformity coefficient	1.8	1.7	2.2

Preloaded GAC. When the pilot testing begun, the Hammond, Indiana and Michigan City, Indiana water treatment plants had been using F-300 GAC over sand in dual media filter-adsorbers for approximately 1 and 2 years, respectively. Both of these plants use Lake Michigan as their raw water source and are relatively near the Chicago, Illinois water treatment plants. Therefore, the concentration of the soluble organics in their raw waters should be similar (see Table 2). From each water treatment plant, representative samples of the entire GAC bed depth were collected for use in the studies. The samples were used immediately in the pilot study, and stored in 5 gallon sealed polyethylene containers until their use in the laboratory-scale experiments.

Additional preloaded GAC samples were collected from the Hammond, Indiana, Michigan City, Indiana, and Lake County, Illinois water treatment plants for laboratory experimentation. After collection, these samples were immediately used in the laboratory-scale experiments. GAC that had been in service for 0.2 and 3 years was collected from the Hammond, Indiana water treatment plant. Carbon from the Michigan City, Indiana water treatment plant was withdrawn after 4 years in service. The Lake County, Illinois water treatment plant also uses Lake Michigan water and was the source of GAC that had been in service for approximately 6 years.

Table 2 – Total Organic Carbon (TOC) in Water Treatment Plant Influent

Location	TOC
Chicago, Illinois	1.8-2.0
Hammond, Indiana	1.5-2.0
Michigan City, Indiana	1.5-2.5

Table 3 – Characteristics of Lake Michigan Water

pH	8.2
Alkalinity	117 mg/L as $CaCO_3$
Turbidity	2 NTU
Conductivity	281 µmhos

Water. The water used in both the pilot- and laboratory-scale experiments was drawn from a line running from the South Water Production Plant (Chicago, Illinois) crib to the shore plant. For the laboratory experiments, this untreated water was shipped to the University of Illinois in 208 L (55 gal) stainless steel drums, where it was stored at 4°C in the dark to limit biological activity. It was verified that the water collected for laboratory experiments did not contain a detectable concentration of MIB. (The crib is located 3.2

km [2 mi] offshore in water 9.6-10.5 m [32-35 ft] deep; the water is drawn near the bottom of the crib.)

Pilot-Scale GAC Columns. The pilot-scale columns consisted of 15.2 cm (6 inch) diameter columns, 53.3 cm (21 inches) of the selected GAC and 30.5 cm (12 inches) of sand (effective size - 0.5 mm; uniformity coefficient - 1.3). Each column was equipped with a slotted underdrain nozzle and a surface wash spray nozzle. The influent flow to the facility was equally distributed to the pilot filters through the use of a constant head box and flow splitting boxes.

A short distance downstream of the raw water pump, sodium hypochlorite was added to the raw water via a peristaltic pump. The chlorinated raw water then flowed through approximately 274 m of pipe to the test facility. A chlorine analyzer was used to monitor the chlorine residual of the raw water as it entered the test facility. The output of the peristaltic pump was adjusted to keep residuals in the desired range.

Laboratory-Scale GAC Columns. For the laboratory-scale experiments, GAC was packed into glass columns (Kontes, Vineland, New Jersey) with an inside diameter of 1.0 cm and a length of 30 cm. Each end was sealed with a threaded PTFE fitting equipped with 20 μm filters. The GAC was contained within a bed of glass beads by two 316 stainless steel, number 20 U.S. Standard mesh size (0.841 mm) screens. The glass beads were used to insure uniform flow through the GAC. The GAC beds were approximately 1 cm deep. A 12x14 U.S. Standard mesh (1.41 to 1.68 mm) size fraction of GAC particles was selected for use in the laboratory columns, because it was determined that these particles accounted for the largest fraction of the external surface area in the filters of the three water treatment plants. By using a representative size fraction rather than the same particle size distribution as the distribution in the full-scale plants, it was possible to more easily and rapidly obtain a laboratory column representative of the full-scale plant. The equivalency of performance was established using both approaches. Uniform packing of both glass beads and GAC particles was obtained through the use of a vibratory engraving tool (Vibro-Graver; Burgess, Chadwicks, New York) to vibrate the column as the column was being filled. A double plunger HPLC pump (Model 6000A; Waters Corporation, Milford, MA) was used to maintain constant low flow rates through the columns.

Feed solutions were prepared by filtering raw Lake Michigan water through a 0.45 μm membrane filter. Filtration of the water served to remove particulate and colloidal material that could otherwise plug or foul the laboratory columns. A taste and odor episode at the laboratory-scale was simulated by changing from this filtered Lake Michigan water to an influent solution of filtered Lake Michigan water spiked with ^{14}C-MIB to the desired influent MIB concentration. Feeding this spiked filtrate continued until the end of the episode, whereupon the influent was changed back to the unspiked filtrate.

Reaction of Chlorine with GAC. The reaction between chlorine and GAC was carried out prior to packing the carbon in the laboratory-scale columns. To react the chlorine with the GAC, a known mass of 12x14 U.S. Standard mesh size fraction GAC was placed in a steel mesh basket made from number 20 U.S. Standard mesh, 316 stainless steel (custom manufacture; University of Illinois, Urbana, Illinois). The basket, positioned towards the side of a 13-L glass carboy covered with aluminum foil, revolved at 20 rotations per minute. An overhead 3-blade teflon turbine rotating at 1550 rotations per minute ensured that a constant flow of the well mixed chlorine solution passed through the stainless steel basket. The rotation of the basket kept the GAC particles mixed, so that the reaction between the chlorine and the carbon particles was evenly distributed. A 13 L chlorine solution was prepared using calcium hypochlorite and 1.0 mM phosphate (buffered to pH 8.2). The pH was adjusted as needed with 0.5 N NaOH or HCl.

An initial concentration of approximately 10 mg/L free chlorine as Cl_2 was used to react with the carbon. Another setup identical to the first was operated in the absence of carbon to serve as a control. The chlorine residual of both vessels was monitored using Standard Method 4500-Cl F, "DPD Ferrous Titrimetric Method" (Standard, 1995). The amount of chlorine reacted with the carbon was adjusted according to the rate of chlorine decay in the control. If the residual reached 2 mg/L as Cl_2, and the desired chlorine reacted to carbon mass ratio had not yet been reached, the chlorine concentration was increased to approximately 7 mg/L as Cl_2. Once the desired amount of reaction had occurred, the basket was removed from the solution and rinsed with deionized-distilled water. The reacted GAC was then transferred to a column and packed as previously described.

RESULTS AND DISCUSSION

Pilot-scale MIB Removal

During the summer of 1996, Greeley and Hansen operated pilot-scale filters at the City of Chicago South Water Purification Plant to evaluate the effectiveness of GAC for the removal of MIB and geosmin. The naturally occurring MIB and geosmin concentrations in Lake Michigan were used to compare virgin and preloaded (1 year, 2 year) GAC. The one-year preloaded GAC was collected from Hammond, Indiana, and the two-year preloaded GAC was obtained from Michigan City, Indiana. Over the course of the three-month evaluation, influent geosmin concentrations were typically below the 3 ng/L detection limit. Thus, only MIB removal could be evaluated.

The influent MIB concentrations varied widely from day to day (see Figure 1). This natural variability increased the difficulty of using conventional predictive methods to determine the effectiveness of GAC. The data were analyzed by determining the percent MIB removed across each filter every time a sample was taken. These removals were then averaged for each filtration rate investigated. Filtration rates of 3, 4, and 5 gallons per square foot per minute (gfm) were used, corresponding to an EBCT (i.e. the volume of GAC bed/flow rate of applied water) of 4.4, 3.3 and 2.6 minutes, respectively. These rates were selected to span the projected range of filtration rates expected during the high water demand of the summer months.

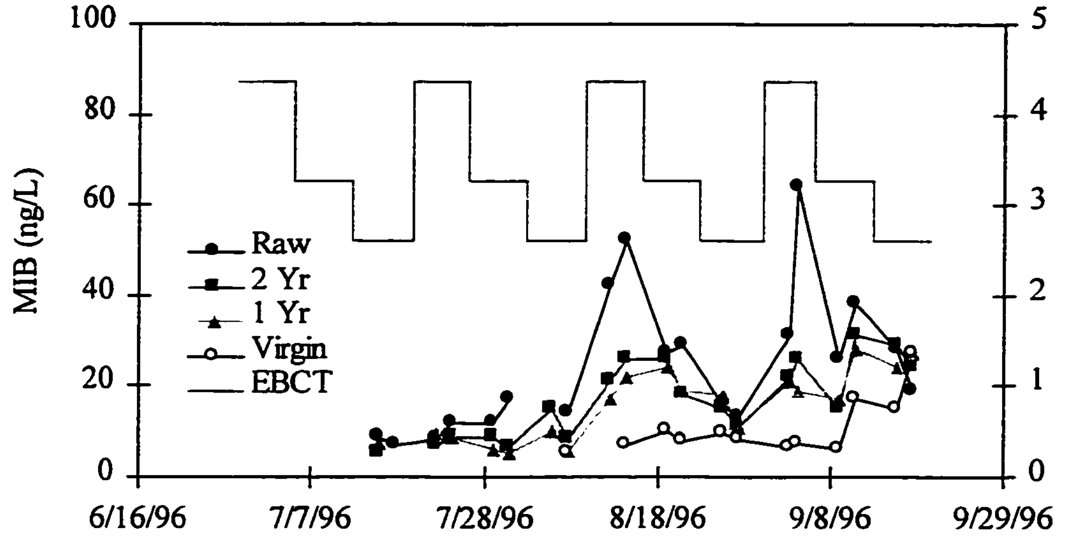

Figure 1 - MIB Removal by GAC: South Water Purification Plant Pilot Study

For the purpose of data analysis, the effluent samples in which MIB was not detected were assigned an MIB concentration of 2.5 ng/L (0.5 times the limit of detection). Table 4 shows the average percent removals obtained from the pilot study. The initial concentration range was 8 to 64 ng/L for the 4.4 minute EBCT, 12 to 38 ng/L for the 3.3 minute EBCT, and non-detectable to 28 ng/L for the 2.6 minute EBCT.

Table 4 - Summary of South Water Production Plant Pilot Study, Percent MIB Removal

Filtration Rate (gfm)	EBCT (min)	Average Percent Removals*		
		Virgin	1 yr preload	2 yr preload
3	4.4	83%	38%	39%
4	3.3	72%	37%	32%
5	2.6	34%	-24%	-45%

* Average of daily percent removals (less than detection limit effluents set to 0.5 times the limit of detection)

† EBCT: empty bed contact time (volume of GAC/flow rate)

‡ gfm: gallons per square foot per minute

It can be observed in Figure 1 that the changes in filtration rates seemed to coincidentally correspond to the natural fluctuation in the influent MIB concentration. As discussed later, it is believed that decreased removal efficiencies will be observed with decreasing influent concentrations. This is attributed to the desorption of a portion of the MIB adsorbed during periods of high influent concentration. For this reason, the dramatically reduced and negative removals observed with the 2.6 minute EBCT were not unexpected.

Laboratory-Scale Column MIB Removal

Pilot-plant studies give excellent data on GAC performance for a given history of MIB influent concentrations, but it is difficult to use these tests to accurately determine the effect of influent concentration because of it is highly variable in the influent water. Additionally, due to the cost and time for analysis of these earthy-musty compounds, samples were only collected twice per week. The goal of the laboratory-scale experiments was to develop a tool that would simulate the performance of the pilot-scale filters, yet not be encumbered by the difficulties often faced with larger scale experiments. The results discussed below indicate that pilot-scale performance may be reproduced using small-scale laboratory tests.

Effect of Service Time. The results of the pilot study were compared to the performance of the small-scale laboratory columns for a range of GAC preloading times. This was to determine if the laboratory columns could simulate the performance of the larger scale system, while simultaneously studying how the length of time that the GAC had been in use affects GAC performance. Each of these laboratory-scale (1.0 cm diameter) columns were prepared with a 12x14 US Standard mesh (1.41 to 1.68 mm) size fraction of GAC that had been in service from 0 to 6 years. A sieve analysis of the representative GAC samples from each of the three water treatment plants showed that the largest fraction of external surface area was in the 12x14 mesh size range; thus, the performance of this size range was likely to be the same as the full-scale adsorber. Each bed of GAC was approximately 1 cm deep.

Fresh GAC was first tested in these laboratory-scale columns at a 3.3 minute EBCT. Lake Michigan water spiked to 50 ng/L MIB was applied to the column for more than two days (> 873 bed volumes). After this period the influent was switched to unspiked Lake Michigan water. The effluent MIB concentration was monitored during the entire experiment. From these data (Figure 2) it can be seen that once the spiked influent was applied, the effluent concentration reached a pseudo-steady state within 6 hours (110 bed volumes). After this pseudo-steady state, or plateau, was reached, the effluent MIB concentration was essentially constant for the remainder of the two-day MIB application. While the effluent MIB concentration would be expected to slowly increase with a continued input of MIB and natural organic matter (NOM), it was felt that this initial plateau was representative of the ability of this GAC to remove the suddenly-appearing MIB during a taste and odor episode. After the influent was switched to Lake Michigan water without MIB, the effluent MIB concentration quickly dropped below the limit of detection. Less than three percent of the adsorbed MIB desorbed back into the aqueous phase, consistent with the fact that the surface coverage of the GAC with MIB was very low. Based upon these data, the remainder of the laboratory-scale GAC columns were evaluated at a two-day effluent plateau value.

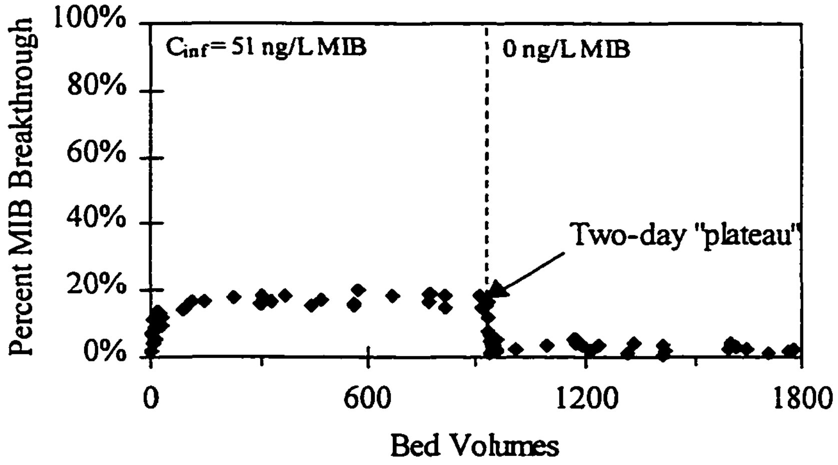

Figure 2 – Laboratory Column Two-Day Response to MIB (virgin GAC; 3.3 min EBCT)

Following this test with the virgin GAC, columns prepared with the carbons that had been collected from the different full-scale filters were evaluated at a 3.3 minute EBCT. The data show an increase in the percent MIB passing through the column with increasing service time (Figure 3). This figure also shows that the laboratory column data were in excellent agreement with the pilot study results.

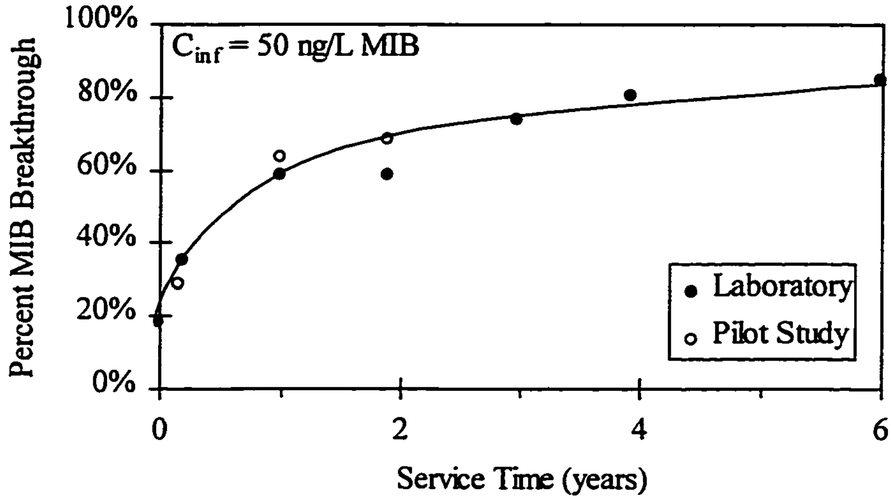

Figure 3 – Effect of Service Time on Percent MIB Breakthrough (3.3 Minute EBCT)

The observed increase in the effluent MIB concentration could have been attributed to several possible factors: 1) MIB adsorption, 2) NOM adsorption, 3) impact of treatment chemicals. The earthy-musty taste and odor problems in Lake Michigan are generally limited to the summer and early fall months. Even during this problematic time the MIB concentration rarely exceeds 50 ng/L. As a result, the amount of MIB adsorbed during the course of one year is a small fraction of the virgin capacity and is not expected to be the primary reason for the decreased effectiveness of the GAC. Based upon work presented later and the findings of other researchers, adsorption of NOM plays a major role in controlling the adsorption of MIB (Matsui *et al.* 1994; Knappe *et al.* 1998). In addition to NOM adsorption, the Hammond and Michigan City, Indiana water treatment plants allowed free chlorine onto their GAC beds. The deleterious effect of chlorine on the adsorptive capacity of activated carbon is well documented. Additional work specifically for MIB adsorption by GAC, presented later in this paper, confirms that the free chlorine should be considered a factor in the decrease of the GAC's effectiveness with increasing service time.

Using the same approach, the GAC was evaluated at a 4.4 minute EBCT. The two-day effluent concentration plateau values were used to calculate the percent MIB breakthrough for each of the carbons, and the results are shown in Figure 4. Comparing the data collected in the pilot study to the laboratory data, good agreement was again observed, except for the one-year service time. There is no apparent explanation for this difference.

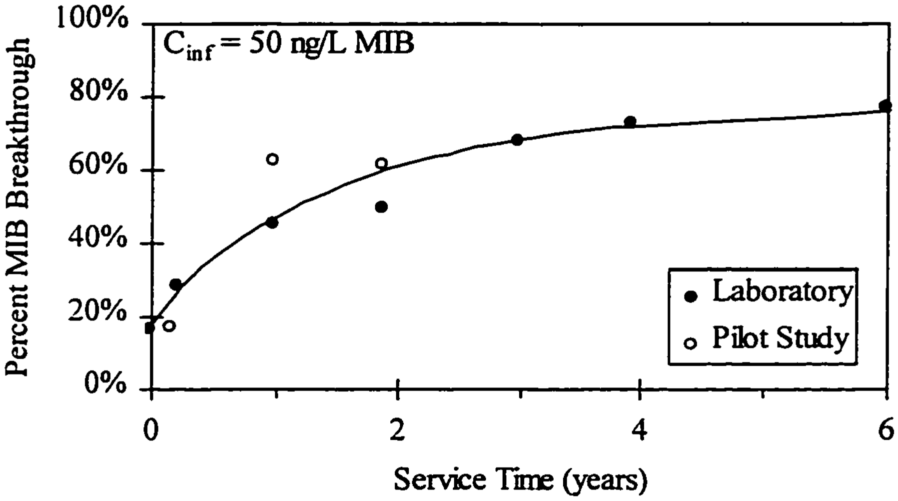

Figure 4 – Effect of Service Time on Percent MIB Breakthrough (4.4 Minute EBCT)

The 2.3 minute EBCT was the final contact time tested in this series of experiments, and the laboratory- and pilot-scale data are compared in Figure 5. There is poor agreement between the two sets of data. Evaluation of the pilot data shows that due to the natural fluctuations in the concentration of MIB in Lake Michigan, the majority of the data for this EBCT was obtained when the influent concentration was decreasing. As a result, it was very likely that desorption of previously adsorbed MIB was contributing to the MIB measured in the effluent. This effect should be considered when using these laboratory columns to evaluate the effectiveness of a given GAC. If a carbon sample is collected during or soon after the GAC is exposed to MIB the results could be biased by desorption, especially if the influent concentration is much lower than that of the previous exposure.

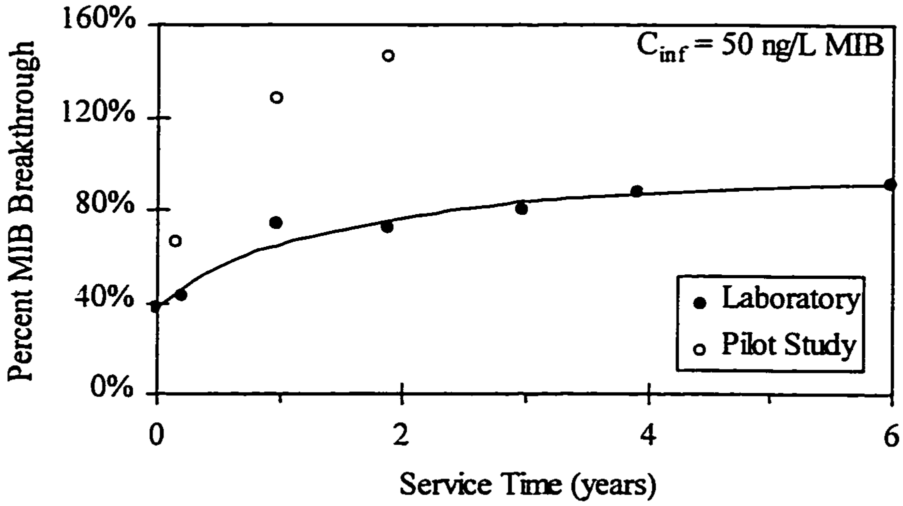

Figure 5 – Effect of Service Time on Percent MIB Breakthrough (2.3 Minute EBCT)

The EBCTs evaluated here (2.6, 3.3, 4.3) are typical of the contact times encountered with GAC filter caps in filter-adsorbers. These data suggest, however, that 28 ng/L was the maximum influent MIB concentration that fresh GAC with a 4.3 minute EBCT could reduce to threshold odor concentrations. This maximum concentration was lowered to less than 13 ng/L if a 2.6 minute EBCT was used. This indicates that adsorption alone may be insufficient to control MIB, and additional treatment technologies, such as ozone, advanced oxidation processes and biological oxidation, may be necessary to protect the consumer from unacceptable levels of tastes and odors. (Note: An additional laboratory-scale column, prepared with GAC that had been in service for 1 year, was operated at 4°C with a 3.3 minute EBCT. The percent MIB breakthrough was identical to the column operated at 25°C indicating biodegradation was not contributing to the observed removals.)

Laboratory Column Design

The excellent agreement between the pilot-plant results and the laboratory column data showed that short term lab tests can be used to effectively predict the results of large-scale systems. However, several questions about the design and methods of operation needed to be answered so that the laboratory column test could be used with confidence. Therefore, specific questions concerning the effect of the GAC column design (bed depth, column diameter and GAC particle size) on column performance were addressed. Also, the role of biological activity, influent MIB concentration and the concentration of chlorine were carefully examined.

Bed Depth. To determine if the bed depth affected GAC performance, four 1.0 cm diameter columns were packed with 12x14 GAC to depths between 0.8 and 3.3 cm. and each was operated with a different flow rate but the same EBCT. A solution containing approximately 50 ng/L MIB was applied to each column. The resulting MIB removal efficiency was calculated for each column using the two-day effluent concentration plateau. From the data presented in Figure 6, it can be seen that even the shortest GAC bed (0.8 cm) removed the same fraction of MIB as a bed approximately four times deeper (3.3 cm) when the columns were operated at the same EBCT. This means that this approach was not dependent on the bed depth or flow rate.

Column Diameter. The column diameter to particle diameter ratio can also affect column performance; short circuiting, and thus higher effluent concentrations, can result if this ratio is too small. In order to examine this effect, four 1.0 cm diameter columns and one 2.5 cm diameter column were packed with the same 12x14 GAC (1.41 to 1.68 mm particle diameter) that had been in service for one year. As seen in Figure 6, even though the 1.0 cm diameter columns had an average particle to column diameter ratio of only 6.5, they yielded the same removal as the larger column with a ratio of approximately 16.2. These data indicate that through proper packing of the GAC and the use of glass beads, low particle to column diameter ratios may be used.

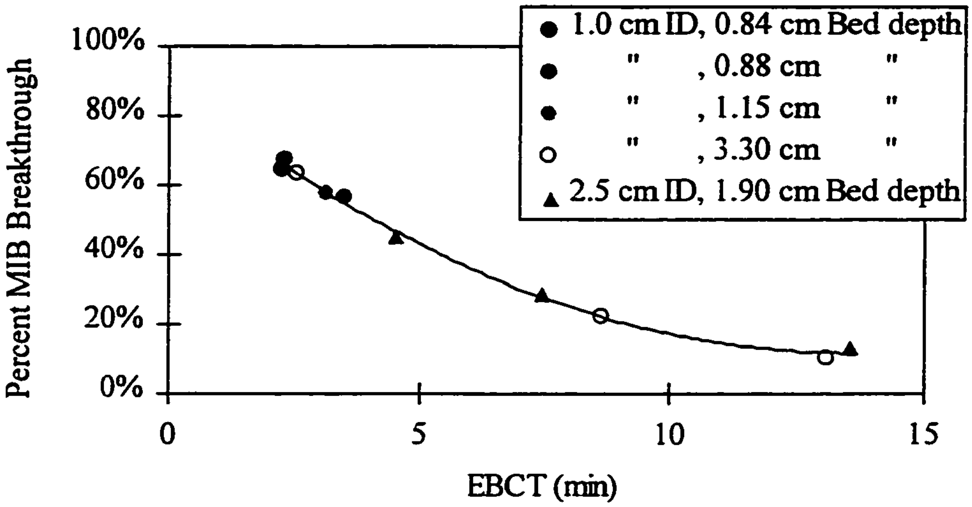

Figure 6 – Effect of GAC Bed Dimensions on Percent MIB Breakthrough (1 year service time)

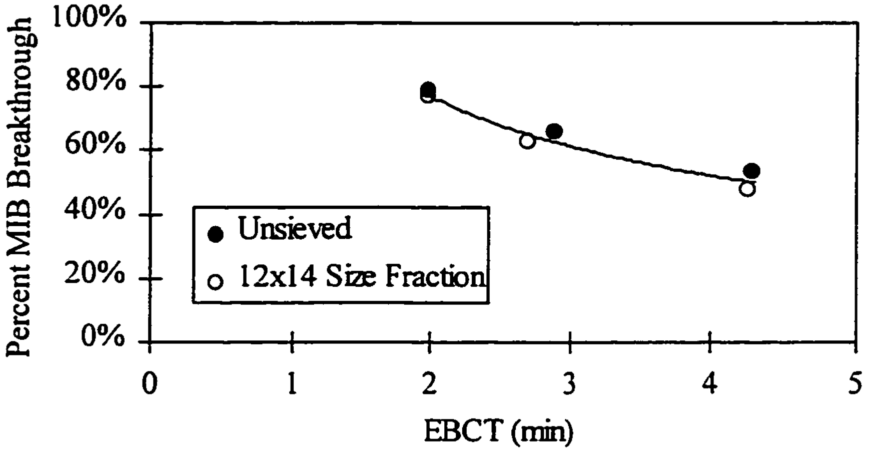

Figure 7 – Comparison of Sieved and Unsieved GAC (2 year service time)

It is interesting to note that even at contact times more typical of adsorbers, 10 to 15 minutes, approximately 85% of the MIB was removed for this carbon. This means that if threshold odor levels of approximately 5 ng/L MIB or less were desired, the GAC that had been in service for just one year could only be expected to control episodes less than approximately 30 ng/L MIB with ten minutes of contact.

GAC Particle Size. Ideally, a particle size distribution identical to the pilot- or full-scale adsorber would be used in these laboratory columns. However, by using a representative size fraction in the laboratory columns rather than the same particle size distribution as the full-scale plants, it was possible to more easily and rapidly obtain a laboratory column that could simulate a larger scale system. To test if the 12x14 mesh size fraction would yield results representative of the entire particle size distribution, two columns were prepared with GAC that had been in service for two years. The first column held an unsieved sample with the same particle size distribution as the full-scale filter. The second column was prepared with a 12x14 mesh size fraction of the same carbon. Both columns were fed an influent of Lake Michigan water spiked to approximately 50 ng/L MIB and monitored over time. The two-day effluent concentration plateau was used to calculate the percent MIB breakthrough at each EBCT evaluated. The close agreement between the results of the two columns indicated that the use of the 12x14 mesh size fraction was appropriate (see Figure 7).

Influent MIB Concentration

The issue of which influent MIB concentration to use is closely related to the question of the dependence of percent MIB breakthrough on influent concentration. If the percent breakthrough is independent of the concentration used, the influent concentration can be selected to provide easy-to-analyze sample concentrations. To test the dependence on influent concentration, the GAC that had been in service for one year was exposed to increasing influent concentrations of MIB. For approximately 2 days each, 25 ng/L, 51 ng/L and 100 ng/L MIB in Lake Michigan water were applied to the column with an EBCT of 3.1 minutes. The percent MIB passing through the GAC bed at each of the influent concentrations approached the same plateau value, approximately 55%.

The results of Figure 8 were encouraging because they demonstrated the independence of percent MIB breakthrough on the influent MIB concentration. However, the experiment only simulated step increases in taste and odor intensity. Figure 1 clearly shows through a taste and odor season, there may be several periods of alternating high and low concentrations of taste and odor causing compounds. As previously discussed, the data from the pilot study seemed to indicate that desorption might influence the effluent concentration.

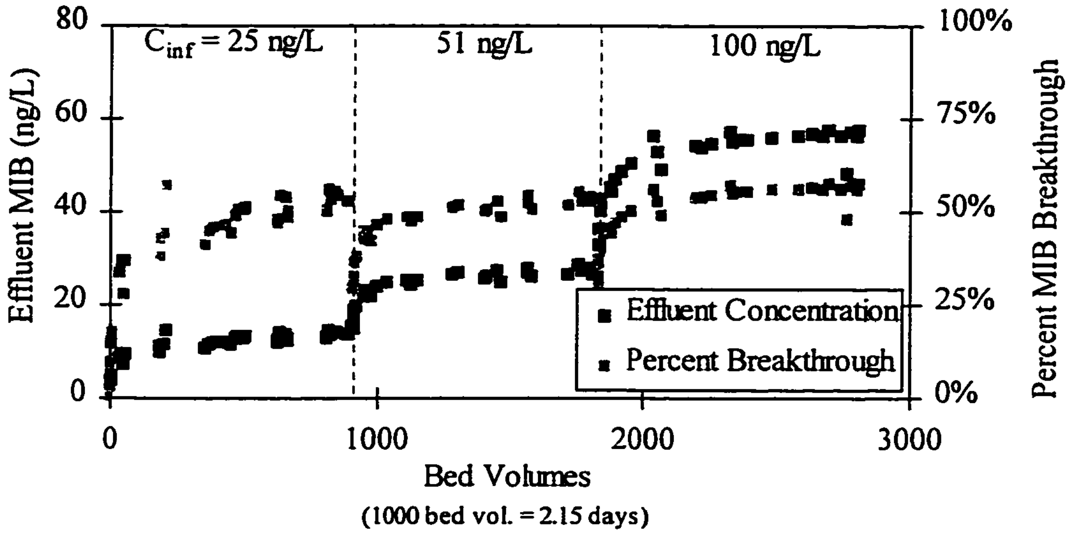

Figure 8 - Effect of Increasing Influent Concentration on Percent MIB Breakthrough (1 year service time; 3.1 min EBCT)

An additional experiment tested a variable influent MIB concentration on the GAC that had been in service for one year. The column was sequentially fed an influent of 52 ng/L, 25 ng/L and 100 ng/L MIB in Lake Michigan water, each for approximately two days. The resulting percent breakthroughs for the 2.3 minute EBCT were 66 percent, 77 percent and 68 percent, respectively (Figure 9). These data indicated that when the carbon experienced a decrease in the influent MIB concentration, desorbing MIB elevated the effluent concentration above that which would normally occur had the carbon not been pre-exposed to a higher influent concentration. This suggests that if a GAC sample is collected during or soon after it has been exposed to MIB, the minimum percent breakthrough could be biased by desorption if the laboratory column influent concentration is lower than that of the previous exposure.

Natural Organic Matter Loading

As previously stated, several researchers have reported that the loading of organic matter on activated carbon controls the adsorption of micropollutants. To support this hypothesis, specifically for the adsorption of MIB by GAC, an additional experiment was performed. A laboratory column was packed with 12x14 mesh virgin GAC. Deionized-distilled (DDI) water was continuously applied to the column with a 3.3 minute EBCT, periodically switching the influent to a batch of DDI water containing 50 ng/L MIB, for two days. The effluent MIB concentration was continuously monitored to determine what percentage of MIB in each simulated episode passed through the GAC. The percent MIB breakthrough for each application was approximately 9 percent

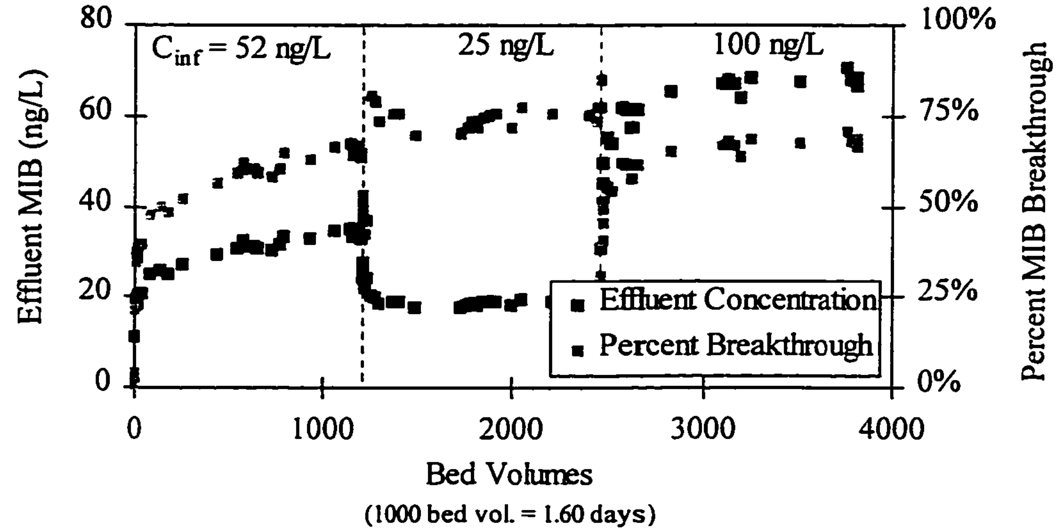

Figure 9 - Effect of Variable Influent MIB Concentrations on Percent MIB Breakthrough (1 year service time; 2.3 min EBCT)

Figure 10 compares the data collected during this experiment to the results previously obtained while evaluating the effect of service time on the percent MIB breakthrough. Starting with fresh carbon, twice as much MIB passed through the GAC in natural water than in DDI water. As the length of service time increased and additional NOM was adsorbed in the natural water system, the percent MIB passing through the column increased. No such increase was observed in the DDI system. The initial increase in the percent MIB breakthrough in the natural water system could not be attributed to the loading of MIB. Assuming the complete adsorption of a constant 50 ng/L MIB influent for 0.25 years with a 3.3 minute EBCT, a conservative estimate based on the data displayed in Figure 1, only 2.3 percent of the maximum MIB surface loading would have been utilized. As a result, a portion of the decrease in the MIB removal efficiency was attributed to the adsorption of NOM. It is likely that the reaction of chlorine with the GAC contributed to this decrease in MIB removal efficiency. The effect of chlorine on the ability of GAC to remove MIB is discussed below. [Note: The maximum MIB surface loading was determined from DDI water isotherms prepared with an unground 30x40 U.S. Standard mesh (0.420 to 0.595 mm diameter) size fraction of virgin GAC. The resulting Freundlich parameters for these single-solute isotherms were 8.738 (ng/mg)(ng/L)$^{-1/n}$ and 0.746 for K and 1/n, respectively.]

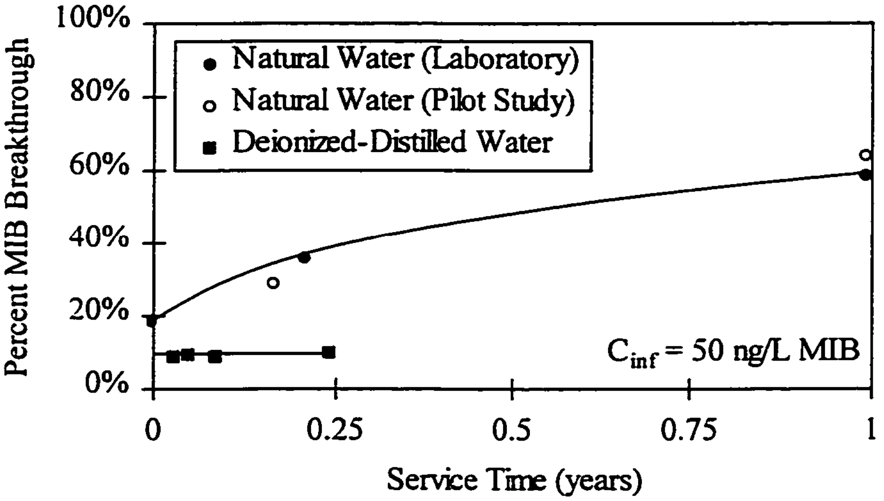

Figure 10 - Effect of Natural Organic Matter on MIB Breakthrough (3.3 min EBCT)

Effect of Chlorine

Many treatment plants with GAC beds that use free chlorine as a disinfectant have chlorine entering the activated carbon bed. When running the laboratory experiments, an important decision to be made is whether to include chlorine in the influent water to simulate field conditions. Several researchers have shown that chlorine reduces the adsorption capacity of activated carbon for numerous organic compounds (McGuire and Suffet, 1984; Snoeyink and Suidan, 1975; Snoeyink *et al.* 1974; Coughlin, 1970; Coughlin and Ezra, 1968). Lalezary *et al.* (1988) and Gillogly *et al.* (1998) have shown this specifically for powdered activated carbon and MIB. Based upon these results, a similar reduction in removal efficiency was expected between GAC and MIB once chlorine was allowed to react with the carbon.

To test this hypothesis, virgin GAC was reacted with chlorine [chlorine (as Cl_2) mass reacted to carbon mass ratio of 0.15 and 0.30] in a batch system before being transferred to a column. This allowed for uniform reaction of the chlorine with all carbon particles. As a result, these laboratory-scale columns are not representative of the entire depth of a GAC bed. However, these columns may simulate the performance of the top fraction of GAC in a full-scale system because most of the free chlorine entering such an adsorption system reacts with the GAC in the upper layer. Filtered Lake Michigan water was fed to these laboratory GAC beds, periodically switching to a 50 ng/L MIB Lake Michigan water solution for two-day intervals. The resulting breakthrough of each MIB episode is shown in Figure 11. [Note: A chlorine (as Cl_2) mass reacted to carbon mass ratio of 0.15 or 0.30 is equivalent to a water treatment plant with a 3.3 min GAC EBCT and 1.0 mg/L of chlorine as Cl_2 completely reacting with the carbon for 0.5 or 1.0 years, respectively.]

In a full-scale system, the chlorine would have reacted with aqueous and adsorbed NOM in addition to the GAC, so the approach used in this experiment does not exactly simulate a full-scale system reacting with chlorine. However, the laboratory results indicated the reaction of chlorine with GAC can significantly reduce the MIB adsorption efficiency, and thus the exposure of GAC to chlorine should be avoided if possible.

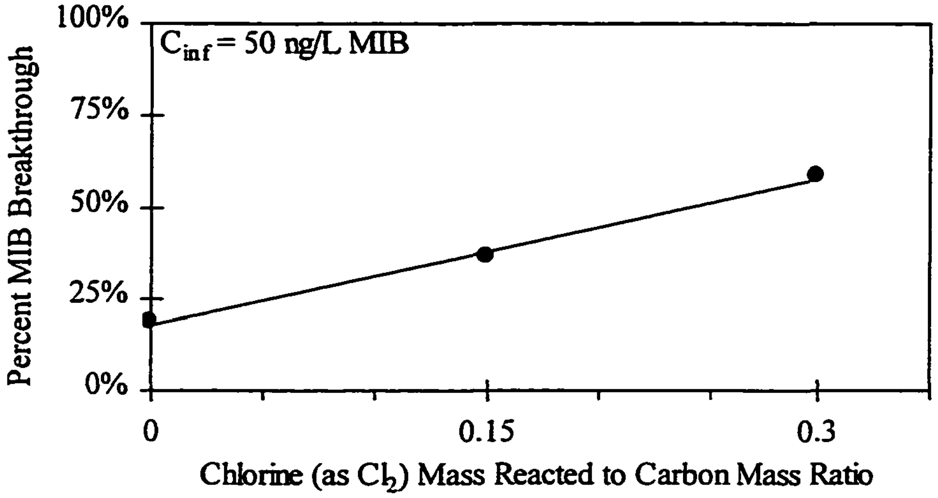

Figure 11 - Effect of Chlorine on MIB Removal Efficiency (3.3 min EBCT)

Biological Activity

It needed to be verified that the MIB removal observed in the laboratory-scale columns was not influenced by biological activity (i.e. no biodegradation of MIB). Several steps were taken to minimize the potential of a biological influence. All of the natural water used in the experiments was filtered through a 0.45 μm membrane filter. In addition to removing particulate and colloidal material that could otherwise plug or foul the laboratory columns, this filtration had the added benefit of removing potentially MIB degrading microorganisms present in the water. While this was probably sufficient for the limited time that the virgin GAC columns were operated, the preloaded GACs could themselves introduce attached microorganisms. However, the preloaded GAC samples were all collected before to the taste and odor season began. By collecting the samples at this time, the GAC and potentially attached microorganisms had not been exposed to MIB for 6 to 8 months. This meant that if an acclimation time were necessary for the MIB degrading microorganisms, the organisms would not already be acclimated when they were introduced into the experiment.

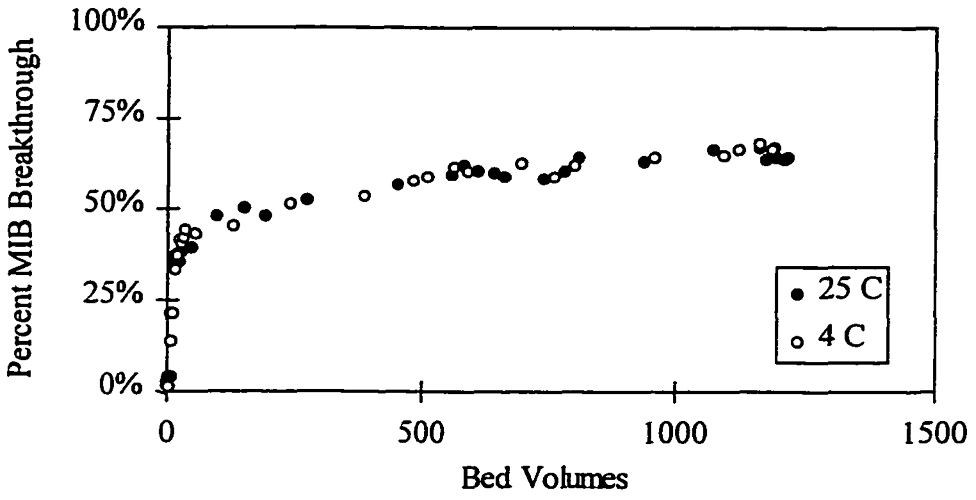

Figure 12 – Effect of Temperature on Percent MIB Breakthrough
(1 year service time; 2.3 min EBCT)

To verify that biological activity was not influencing the observed percent MIB breakthroughs, two columns were prepared with GAC that had been in service for 1 year. These laboratory-scale columns were operated at 4 and 25°C. If biological MIB degradation was present, it was expected that the column run in the 4°C temperature controlled cold room would have different results from the column operated at room temperature (25°C). Based on this assumption, Figure 12 indicates that biological activity was not influencing the observed percent MIB breakthroughs. Additional work, presented in the following chapter, shows that all of the trends observed in these laboratory-scale columns were predicted using competitive adsorption models, further indicating the percent MIB breakthroughs were not influenced by biological activity.

SUMMARY AND CONCLUSIONS

A test was developed to rapidly and effectively evaluate the remaining life of a GAC bed for the mitigation of a taste and odor episode. The results showed that adsorption alone may be insufficient to control MIB episodes. The need for additional treatments, such as ozone, advanced oxidation processes, or biological oxidation is evident, and additional research is necessary to determine which combination of these technologies can most effectively be used. Specific conclusions of this study are:

- Laboratory-scale columns simulated the performance of a pilot-plant very well. The test used a representative GAC size fraction (12x14 U.S. Standard mesh – 1.41 to 1.68 mm diameter) packed in a small laboratory column (1.0 cm diameter). The percent removal of MIB pulse-loadings was essentially the same in the laboratory columns as it was in the pilot-plant. These laboratory columns were also able to show the impact of variable influent MIB concentrations, the accumulation of natural organic matter and the reaction of GAC with free chlorine.

- Adsorption by GAC alone, will often provide insufficient protection against MIB taste and odor episodes. The laboratory- and pilot-scale experiments often showed that GAC would not reduce MIB to threshold odor concentrations. For short contact times (~ 4 minute EBCT), virgin GAC could only be expected to control episodes less than approximately 30 ng/L MIB. Even with longer contact times (~ 10 minute EBCT), a 30 ng/L MIB episode was the most MIB a GAC that had been in service for one year could reduce to acceptable levels.

- The maximum attenuation of a transient MIB load by granular activated carbon, reported as percent removal, was independent of the influent concentration but dependent on the surface loading of natural organic matter. The percent MIB removed by a bed of granular activated carbon was independent of the influent MIB concentration, for increasing influent concentrations. However, when the GAC had been exposed to higher influent concentrations, a subsequent and lower concentration episode was not removed at the same efficiency due to desorption and redistribution of MIB from the previous loading. Based upon these results, if a GAC sample was collected during or soon after it has been exposed to MIB, the minimum percent breakthrough observed in these laboratory-scale columns could be biased if the influent concentration selected for the test was too low.

- In natural water, MIB removal was controlled by the adsorption of the other adsorbable organic matter. In deionized-distilled water, a constant percent removal was observed for a series of simulated MIB episodes. However, for a natural water system, a significant decrease in MIB removal efficiency was observed and attributed to the adsorption of natural organic matter from Lake Michigan water. This indicated that for limited amounts of MIB accumulation, the breakthrough of continuous and intermittent MIB loadings would be similar, since the background organic matter was primarily controlling the removal efficiency.

- Chlorine has a deleterious effect on the ability of granular activated carbon to remove MIB. The greater the amount of chlorine allowed to react with the GAC, the lower the percent removals. Thus, the application of chlorine to GAC should be avoided if possible.

ACKNOWLEDGMENT

The authors would like to thank Gary Williams, Randy Russell and William Soucie for providing samples of GAC, and Kathryn Force for her assistance with the pilot-study.

*"Doing [research] without [publishing] is like winking at a girl in the dark.
You know what you are doing, but nobody else does." (Steuart H. Britt)*

Predicting GAC Performance

The water industry has long been attracted to predicting the performance of granular activated carbon. If the performance of GAC can be predicted, the technical and economic feasibility of activated carbon for a particular application can be decided. To obtain a prediction two general approaches have been utilized. The first approach uses laboratory-scale columns to simulate the performance of large-scale systems, as discussed in the previous chapter. The second approach utilizes the physical and adsorptive characteristics of an activated carbon, obtained from laboratory experiments, to initialize a predictive mathematical model. The use of one such model, "FS", will be discussed here.

PSEUDO SINGLE-SOLUTE HOMOGENEOUS SURFACE DIFFUSION MODEL

The program "FS", written by Yuasa (1982), has been used with some success (Knappe, 1996). By assuming axial dispersion through a GAC filter/adsorber was negligible (Weber and Liu, 1980), the program solves a system of equations for plug flow pseudo-single solute homogeneous surface diffusion (PFHSDM) through a fixed bed adsorber to model the adsorption rate of the target compound from natural water onto GAC. Pseudo single-solute homogeneous surface diffusion assumes that the rate at which the target compound is adsorbed from natural water by activated carbon can be modeled as if the target compound was the only compound present. To solve the PFHSDM, equilibrium [$K(C_{inf})$, $1/n$] and kinetic (D_s, k_f) parameters are needed. The pseudo single-solute $K(C_{inf})$ and $1/n$ can be determined using the equivalent background compound (EBC) method (Qi *et al.*, 1992). Once these parameters have been calculated the D_s and k_f can be determined from a short bed adsorber test.

PFHSDM Calibration and Use

Pseudo Single-Solute Capacity. The pseudo single-solute equilibrium capacity is determined by the EBC method. Initially it is assumed that a single hypothetical compound, the equivalent background compound, can represent the natural organic matter (NOM) in the water, besides the target compound. This allows competitive adsorption to be described by a bi-solute version of the ideal adsorbed solution theory (IAST). The bi-solute IAST may then be used to predict the equilibrium surface capacity of the target compound that a specific mass of activated carbon will adsorb for any given initial concentration of the target compound. This competitive capacity is equivalent to the pseudo single-solute equilibrium capacity for the particular system predicted. This approach is outlined in greater detail in the chapter discussing "Kinetic and Equilibrium Studies of ^{14}C-MIB Adsorption on PAC in Natural Water".

Critical to predicting a pseudo single-solute capacity, is precisely determining the single-solute and competitive adsorption equilibrium capacity of activated carbon for the target compound. Several researchers have reported that particle size had no noticeable affect on the equilibrium adsorption capacity of either ground or unground virgin GAC, for both single-solute and competitive systems (Najm *et al.*, 1990; Weber and Wang, 1987; Thacker *et al.*, 1983; Randtke and Snoeyink, 1983; Lee *et al.*, 1981). The time required to reach equilibrium, however, depends on particle size (Najm *et al.*, 1990). Therefore, the smallest attainable particle size should be used in the isotherms to minimize the time required for experimentation.

Other researchers studying atrazine (Knappe, 1996) and trichloroethene adsorption (Carter *et al.*, 1992) have found that grinding preloaded GAC can significantly alter its capacity. They agreed that this process increases the Freundlich K value by opening up adsorption sites previously blocked by preloaded natural organic matter. The researchers also observed a decrease in the slopes of the isotherms (1/n) with grinding, indicating an increase in site energy heterogeneity. For these reasons it was felt that grinding preloaded carbon would not yield adsorptive capacity parameters descriptive of the unground GAC.

Unfortunately, the role of particle size in preloading has not been completely characterized. Summers *et al.* (1990) determined that after 1 week of preloading, the capacity for *cis*-1,2-dichloroethene was independent of particle size. Carter *et al.* (1992) observed a convergence of trichloroethene capacity within 4 weeks of preloading for 30/40 and 80/100 size fractions of activated carbon. These studies seem to indicate that the influence of GAC particle size on the degree of preloading diminishes over time, but further study is needed.

Rate of Adsorption. Once the pseudo single-solute equilibrium capacity parameters had been calculated, the kinetic parameters could be determined from a short bed adsorber (SBA) test. The SBA test was designed such that immediate but not complete breakthrough was observed (i.e., the mass transfer zone of the target compound was longer than the depth of the GAC bed). Using the data collected from the SBA and the program "FS-SI", the D_s and k_f are calculated by performing a nonlinear least-squares optimization technique that minimizes the error between the experimental data and the model prediction from the pseudo single-solute PFHSDM (see Appendix D: FS-SI).

Model Prediction. Once the parameters describing the adsorption of the target compound by activated carbon have been determined, the program "FS" can then be used to predict the performance of a GAC bed. The model uses a moving-grid finite difference method to numerically solve the PFHSDM (see Appendix D: FS)

GAC Preparation. Prior to use, the virgin GAC was washed with deionized-distilled water to remove the fines. The carbon was then dried to remove the water and sieved to collect the desired size fractions (20x25 U.S. Standard mesh - 0.707 to 0.841 mm diameter, and 30x40 U.S. Standard mesh - 0.420 to 0.595 mm diameter). The sized virgin GAC was then rinsed again with deionized-distilled water to remove any fines generated during sieving, dried at 105 °C to remove the water, and stored in a desiccator until use.

The preloaded carbons collected from the water treatment plants were initially washed with deionized-distilled water to remove the fines. The washed carbon was then wet-sieved to obtain the size fractions of interest (12x14 U.S. Standard mesh – 1.14 to 1.68 mm diameter, 16x18 U.S. Standard mesh – 1.00 to 1.19 mm diameter, and 20x25 U.S. Standard mesh - 0.707 to 0.841 mm diameter). The 20x25 mesh fraction was the smallest size fraction of the preloaded GACs that could be collected that did not have a significant amount of sand. The wet-sieved GAC particles were then blotted to remove the excess water and immediately weighed out for use. Additional portions of the preloaded sized GAC were weighted out and dried to determine their moisture content. The weighed mass(es) of preloaded GAC were then adjusted by the corresponding moisture content to determine the dry mass of activated carbon used in the experiment.

ADSORPTION EQUILIBRIA RESULTS

Virgin GAC

The adsorption capacity of GAC for MIB was first evaluated for the virgin GAC. While these Freundlich K and 1/n were being determined using the bottle-point isotherm technique described in previous chapters, it was felt that the independence of capacity on GAC particle size should be verified for MIB. While additional information about the relationship between particle size and preloading was also necessary, this could only be evaluated with the preloaded GAC. Without considering the influence of these factors, there would be insufficient confidence in the results obtained.

Headspace-free deionized-distilled water bottle-point isotherms were prepared with 30x40 (0.420 to 0.595 mm diameter) and 20x25 (0.707 to 0.841 mm diameter) U.S.

Standard mesh GAC particles. After 25 days of agitation, a select number of the bottles were sampled and topped-off with deionized-distilled water. Once a total of 125 days had passed, the MIB concentration in all of the bottles was analyzed. The concentration of MIB from the bottles that had been previously sampled at 25 days was adjusted to account for the addition of the small volume of deionized-distilled water to keep the bottles headspace-free.

The data (Figure 1) show a difference in the MIB surface loading between the two GAC particle sizes after 25 days of agitation. An additional agitation of 100 days showed a significant increase in the MIB surface loading, indicating, 25 days was not long enough to reach equilibrium. The data after 125 days of agitation show the capacities of the two GAC size fractions converging. This convergence suggests that the virgin GAC's capacity for MIB was independent of particle size and the particles were in equilibrium with the aqueous MIB concentration. The corresponding Freundlich parameters for the virgin GAC single-solute isotherms at 125 days were 8.738 (ng/mg)(ng/L)$^{-1/n}$ and 0.746 for K and 1/n, respectively.

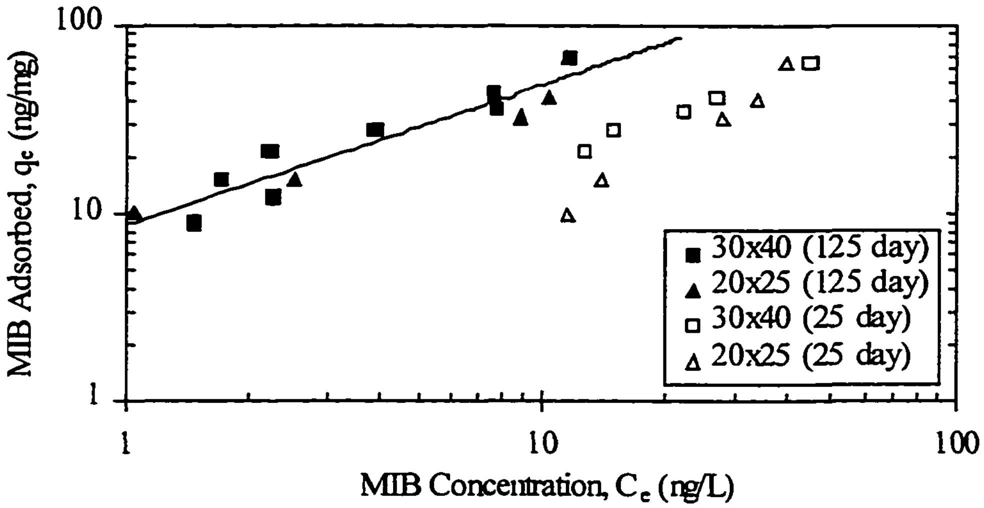

Figure 1 - Effect of Time and Particle Size on MIB Surface Loading (virgin GAC)

These isotherms draw attention to a potential problem with the use of mathematical models. Even when using a 30x40 mesh fraction of particles, 25 days was an insufficient amount of time to reach equilibrium. Should the Freundlich K and 1/n be determined prior to equilibrium, the parameters assumed for equilibrium could be significantly different than the true values. This low value would affect all subsequent parameter determinations, ultimately affecting the final GAC performance prediction.

Using the 20x25 mesh size fraction of virgin GAC an additional isotherm was prepared with Lake Michigan water. Again a difference was noted between the 25 and 125 day MIB surface loading (Figure 2). The data collected at 125 days were used for the EBC method.

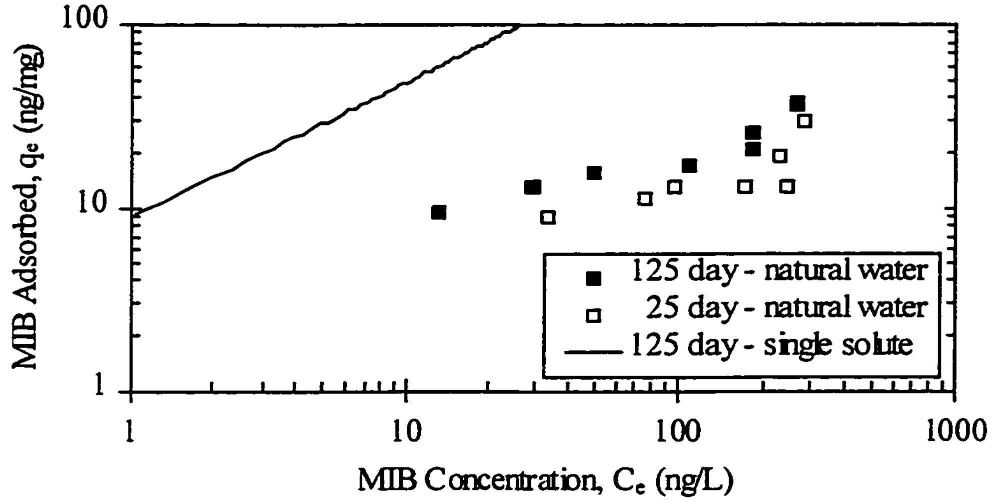

Figure 2 - Effect of Time on MIB Surface Loading (virgin 20x25 GAC; C_o = 341 ng/L)

Table 1 lists the Freundlich parameters and initial concentration of the EBC as determined by the EBC method. Applying these EBC and single-solute parameters to the bi-solute version of the IAST, an isotherm was predicted for an initial MIB concentration of 53.3 ng/L (Figure 3). At complete saturation, the carbon in a fixed bed of GAC should come to equilibrium with the influent MIB concentration. To determine the competitive adsorption parameters for this condition, the MIB surface loading (q_e) at the initial MIB concentration of the isotherm ($C_e \approx C_o$) predicted by the IAST was obtained by extrapolating from the MIB surface loadings corresponding to low carbon doses (100, 50 and 5 μg/L). Applying these values to the Freundlich equation, with 1/n equivalent to the slope of the single-solute isotherms, the competitive capacity Freundlich K was determined for this initial concentration. Table 2 lists these predicted competitive capacity Freundlich parameters.

Table 1 - Equivalent Background Compound Freundlich Parameters

GAC	Virgin	1 Year Preload	2 Year Preload
K, (mmol/g)(μmol/L)$^{-1/n}$	2.64×10^{-2}	2.74×10^{-2}	1.78×10^{-3}
1/n	0.0171	0.796	0.841
C_o, μmol/L	4.53×10^{-4}	6.90×10^{-3}	7.89×10^{-2}

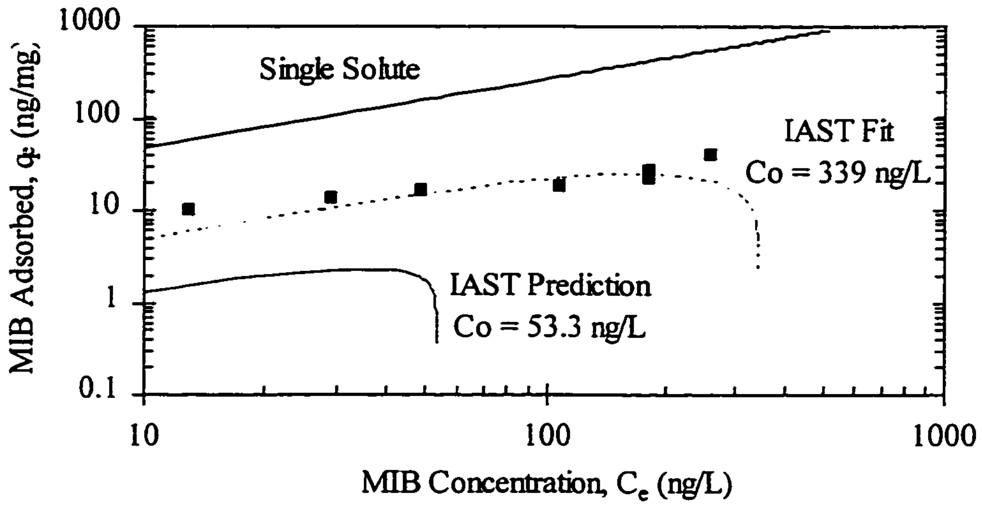

Figure 3 - IAST Fit and Prediction (virgin GAC)

Table 2 – Natural Water Freundlich Parameters

GAC	Virgin	1 Year Preload	2 Year Preload
C_e, ng/L ($\approx C_{inf}$)	53.3	51.7	51.7
K, (ng/mg)(ng/L)$^{-1/n}$	0.0191	0.1215	0.1945
1/n	0.7459	0.6471	0.5882

Preloaded GAC

While the same general approach was used to determine the competitive adsorption Freundlich parameters for the preloaded GACs, additional tests were necessary to obtain information about the relationship between particle size and degree of preloading. If the degree of preloading were dependent on size of the particles, the equilibrium MIB capacity would be dependent on particle size. Should a particle size/MIB capacity dependence exist, further experimentation would be necessary to determine which size fraction of particles would yield an MIB capacity representative of the entire distribution of particle sizes.

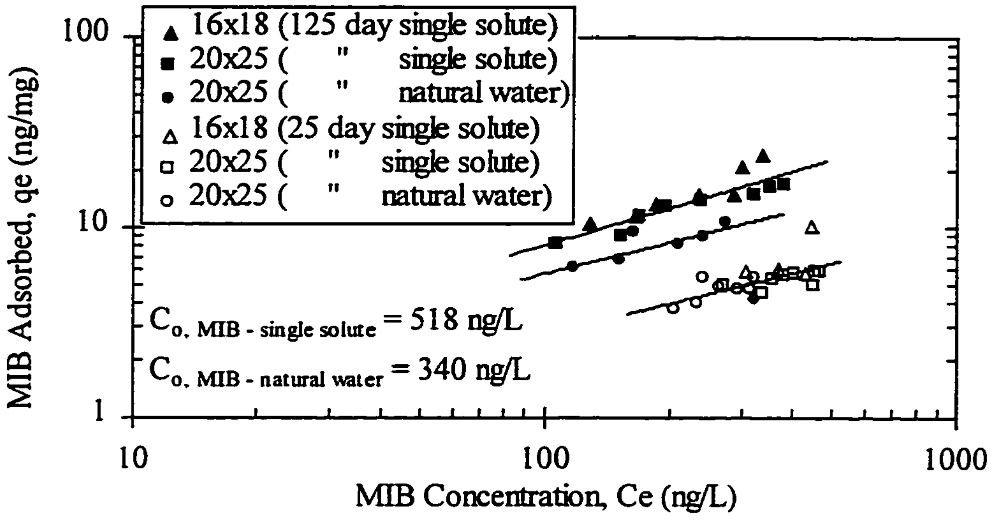

Figure 4 - Effect of Time and Particle Size on Surface MIB Loading (1 year service time)

For both the 1 and 2 year preloaded GACs, 25 and 125 day single-solute and natural water isotherms were analyzed (Figure 4 and 5, respectively). As expected for both activated carbons, the initial 25 days of agitation was insufficient to reach equilibrium. There was no significant difference between the MIB surface loadings of the 12x14, 16x18 or 20x25 mesh GAC size fractions after 125 days of agitation. This suggests that for these carbons the degree of preloading is independent of particle size. Based upon the available data, this conclusion cannot be substantiated for preloading times less than one year.

The single-solute Freundlich parameters were obtained from the 125-day isotherms. A K and 1/n of 0.4126 $(ng/mg)(ng/L)^{-1/n}$ and 0.6471, respectively, were recorded for the 1 year preloaded GAC. Slight differences were observed for the 2 year preloaded GAC (K = 0.4602 $(ng/mg)(ng/L)^{-1/n}$ and 1/n = 0.5882). The EBC method was then applied to the 125-day natural water isotherms. The resulting Freundlich EBC parameters and predicted competitive MIB equilibrium capacities are listed in Tables 1 and 2, respectively.

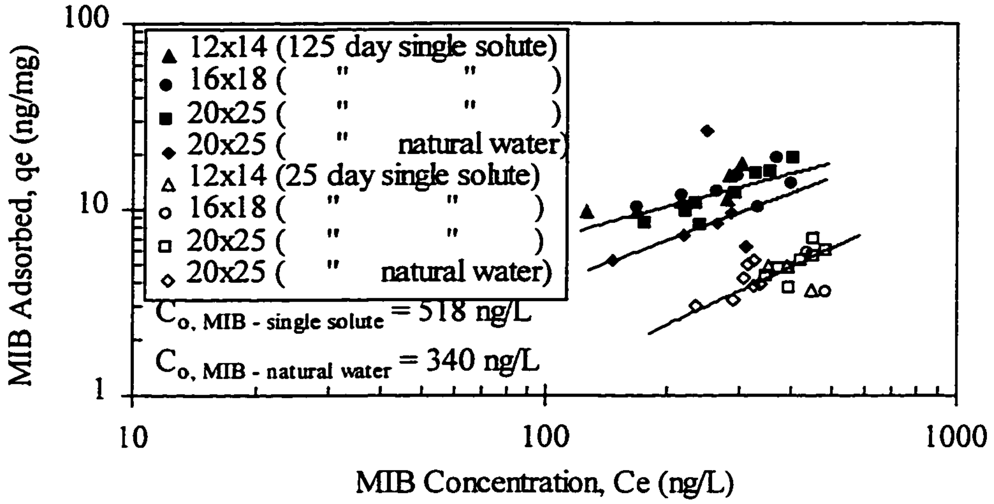

Figure 5 - Effect of Time and Particle Size on MIB Surface Loading (2 year service time)

It is interesting to note that after 25 days of agitation there was no observable competition. Focusing on the 1 year preload GAC (see Figure 6), the single-solute and natural water MIB isotherms could be characterized by a single set of Freundlich parameters. Knappe (1996) saw similar results with atrazine. The natural water and single-solute atrazine isotherms were compared after 28 days of agitation, from which it was concluded that there was no competition with the preloaded GACs tested. Isotherms of longer duration were not tested to verify that equilibrium had been reached.

It is understandable that for preloaded GAC isotherms of "short" contact times, competition might not be readily apparent. In both the single-solute and natural water isotherms the NOM already adsorbed, or preloaded, onto the GAC would be present. The additional adsorbable organic matter contributed by a short contact time in the natural water isotherm is likely to be small in comparison to the quantity of previously adsorbed NOM. Finally, based upon the results obtained in previous chapters, concluding that the quantity of NOM adsorbed controls the adsorption of MIB, the amount of MIB adsorbed and its corresponding competition would be characterized by comparing a small or undetectable difference in two large quantities of adsorbed NOM.

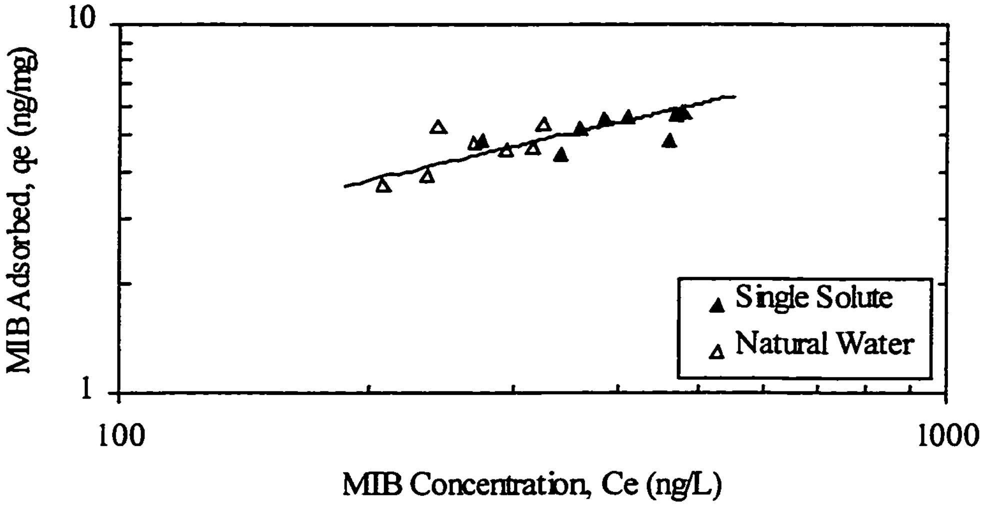

Figure 6 –Adsorptive Competition at 25 days (1 year preload, 20x25 mesh GAC)

GAC PHYSICAL CHARACTERISTICS

Some of the physical properties of the GAC and GAC beds needed to be determined before the adsorption kinetics could be characterized. The skeletal density and particle porosity of the carbons were determined through mercury intrusion porosimitry (Autopore #9220; Micrometrics, Norcross, Georgia). A comparative skeletal density was determined by helium pycnometry (Accupyc 1330; Micrometrics, Norcross, Georgia). The skeletal density and particle porosity were used to calculate the GAC particle density used in the FS model. Table 3 lists the values obtained for the characterization of the GAC particles.

Some researchers have combined helium pycnometry with mercury intrusion porosimitry to determine the particle density. Table 3 indicates that this may lead to results different than if mercury intrusion porosimitry was used alone. It is expected that helium would be able to access pores smaller than mercury, leading to larger skeletal densities and particle porosities. While the "functional" porosity and skeletal density should be based only on the pores accessible to NOM and MIB would produce kinetic parameters most descriptive of the system, a technique to determine this was not readily available. For the work presented here only the data obtained by mercury intrusion porosimitry was considered.

Table 3 – GAC Particle Characteristics

GAC	Hg Intrusion Porosimitry			He Pycnometry
	Skeletal Density (g/mL)	Particle Porosity	Particle Density (g/mL)	Skeletal Density (g/mL)
Virgin	1.30	0.392	0.791	2.01
1 Year Preload	1.59	0.381	0.983	1.67
2 Year Preload	1.55	0.395	0.938	1.73

Additional information (GAC bed depth, bulk density) was required about the GAC beds used to determine the kinetic parameters, as well as the GAC beds to be predicted. The GAC bed depth was measured directly through the glass column; if variations in the depth were noted, an average was used. The bulk density of the GAC was calculated by the dividing the mass of GAC used to prepare the bed, by the volume of the bed.

ADSORPTION KINETICS RESULTS

To obtain the kinetic parameters D_s and k_f, a short bed adsorber was prepared for the virgin GAC. The preparation of the SBA was identical to the laboratory test columns discussed at length in the previous chapter. Since the PFHSDM assumes that the rate at which MIB was adsorbed from natural water by the GAC could be modeled as if the MIB was the only compound present, the competitive adsorptive capacity predicted for the influent MIB concentrations of the laboratory-scale columns was used as a pseudo single-solute adsorption capacity. Figure 7 shows the breakthrough curve obtained from this SBA test. While the film mass transfer coefficient ($k_f = 2.40\text{x}10^{-3}$ cm/s) calculated from this SBA was in the general range expected, the surface diffusion coefficient ($D_s = 1.63\text{x}10^{-6}$ cm²/s) was several orders of magnitude larger than expected, based on the kinetics for MIB adsorption onto PAC (see the chapter discussing "Kinetic and Equilibrium Studies of ^{14}C-MIB Adsorption on PAC in Natural Water"). The reason for this higher than expected surface diffusion coefficient was explored and is discussed later. These kinetic parameters were subsequently used to predict the performance of the laboratory scale results obtained in the previous chapter.

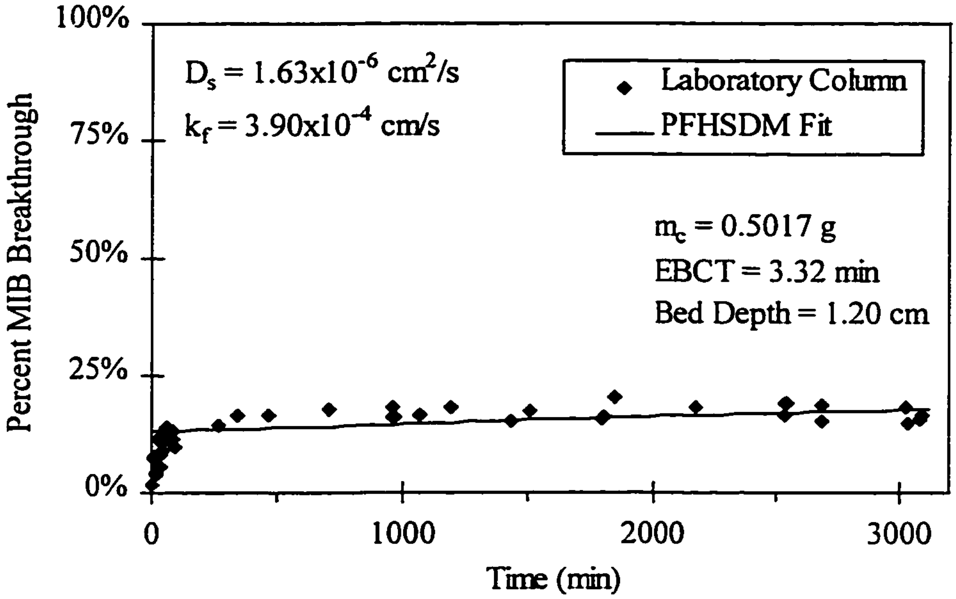

Figure 7 – Kinetic Parameters Determined with Laboratory Column (virgin GAC)

Similar fits were obtained for the preloaded GACs. The film mass transfer and surface diffusion coefficients obtained for the virgin and preloaded GAC are listed in Table 4.

(Note: the "SBA test" is actually one of the two-day spikes applied to the laboratory-scale columns. It was felt that the kinetic parameters obtained directly from these systems would be the most appropriate.)

Table 4 – MIB Adsorption Kinetic Coefficients

GAC	Virgin	1 Year Preload	2 Year Preload
D_s, cm^2/s	$1.63\text{x}10^{-6}$	$9.21\text{x}10^{-12}$	$7.86\text{x}10^{-12}$
k_f, cm/s	$3.90\text{x}10^{-4}$	$3.44\text{x}10^{-4}$	$2.23\text{x}10^{-4}$

It can be seen from this table that the film mass transfer coefficient is generally independent of the preloading time. This is consistent with k_f being dependent only on the flow rate of the system and the diameter of the GAC particles. The surface diffusion coefficient, however, dramatically changed after preloading. These data may indicate that the previously adsorbed NOM hinders the transport of MIB into the GAC particle. However, this will be discussed further later in the chapter.

GAC PERFORMANCE PREDICTIONS

Using the equilibrium and kinetic MIB adsorption parameters along with the GAC bed characteristics and experimental flow conditions, the performance of the laboratory-scale columns described in the previous chapter were predicted. Figure 8 shows the predicted percent MIB breakthrough for a virgin GAC bed exposed to a 2.6 or 4.5 min EBCT. The PFHSDM closely simulated the percent MIB breakthrough at two days (2880 minutes). The two-day percent MIB breakthrough value was used to characterize the GAC performance in the laboratory-scale columns used in the previous chapter, "Determining the Remaining GAC Bed Life for Taste and Odor Control".

Similar PFHSDM predictions were performed for the preloaded GAC. Figure 9 shows the PFHSDM fit and prediction of the GAC preloaded for 2 years. Similar fit and predictions of the 1 year preloaded GAC were also obtained. Additional predictions of the performance of the 1 year preloaded carbon were made for a range of EBCTs, between 2.3 and 13.5 minutes, and for two different column diameters (1.0 and 2.5 cm). Figure 10 shows that the PFHSDM was able to predict well the two-day percent MIB breakthrough of a wide variety of EBCTs and two different column diameters. Even at EBCTs over four times longer than what the model was calibrated at, there was only a 10 percent difference between the percent MIB breakthrough of the laboratory-scale column and the PFHSDM prediction.

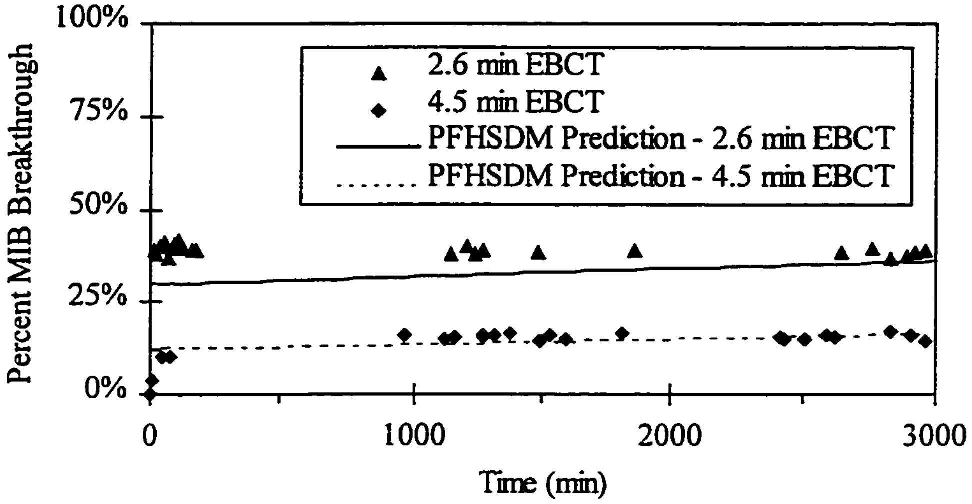

Figure 8 – PFHSDM Predictions of Virgin GAC Performance

A final set of predictions were made for the 1 year preloaded carbon to determine if the PFHSDM would predict that the percent MIB breakthrough was independent of the influent MIB concentration. Figure 11 clearly shows that the PFHSDM predicted the same percent MIB breakthrough for MIB influent concentrations of 25, 52 and 100 ng/L. It should be noted that this was based upon the 125-day isotherms. When the 25-day isotherm data were used, and no competition was evident, the PFHSDM did not predict the same percent MIB breakthrough, as expected.

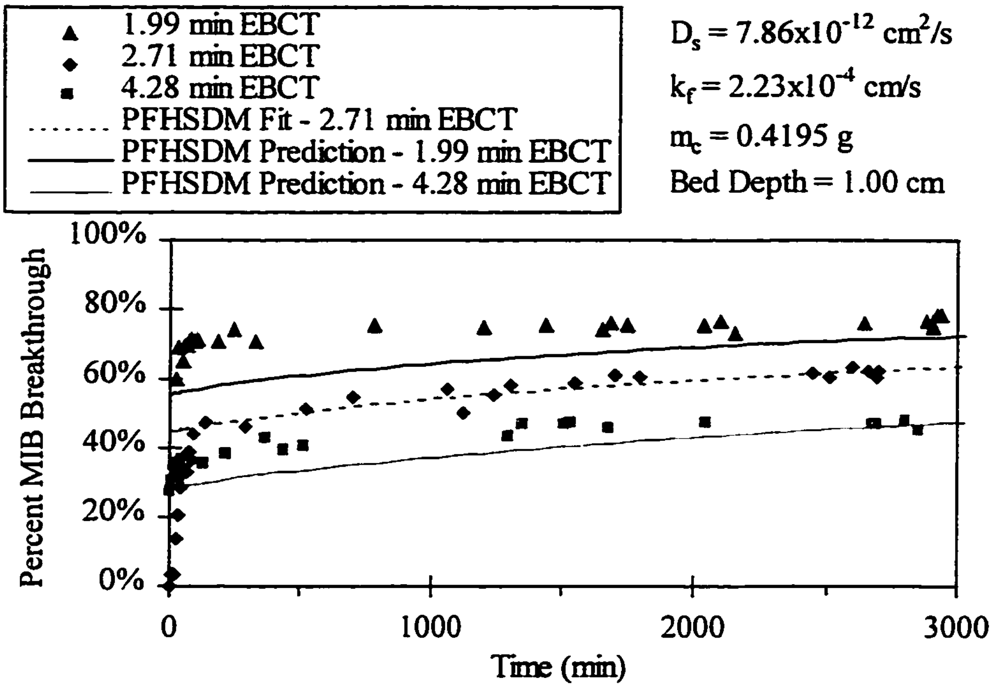

Figure 9 – PFHSDM Prediction of Preloaded GAC (2 year preload)

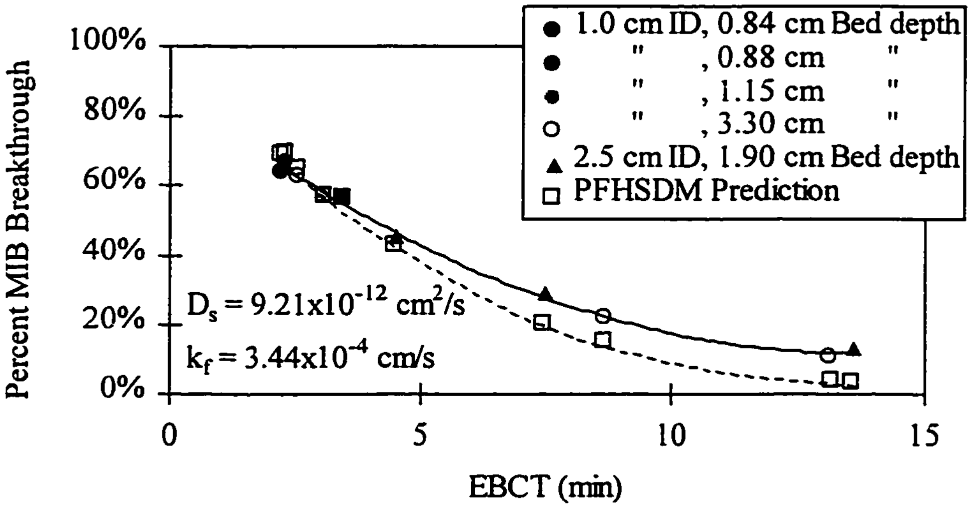

Figure 10 – The Influence of Bed Dimensions and EBCT on PFHSDM Predictions

(1 year service time)

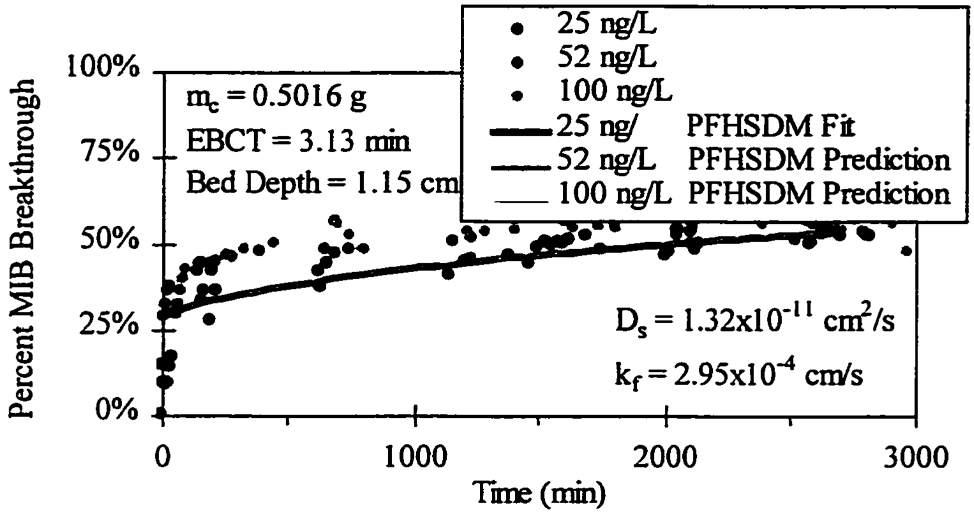

Figure 11 – Effect of the MIB Influent Concentration on PFHSDM Predictions

(1 year service time)

DIFFUSION LIMITATIONS

While the model was able to closely fit and predict the laboratory-scale column conditions presented in the preceding chapter, the modeling approach yielded some coefficients that did not seem to be physically realistic. The first question arose with the surface diffusion coefficient ($D_s = 1.63\times10^{-6}$ cm^2/s) obtained for the virgin GAC. As this value was considerably higher than expected, a sensitivity analysis was performed. Figure 12 indicated that if all of the other parameters were held constant, the fit obtained was generally insensitive to the surface diffusion coefficient. It was not until D_s had been decreased several orders of magnitude did the shape of the breakthrough curve change significantly. This implied that the model presented the film diffusion coefficient (k_f = 3.90×10^{-4} cm/s) as the rate limiting step of adsorption. This was verified by increasing k_f to 1×10^{-1} cm/s and varying the surface diffusion coefficient (Figure 13).

Figure 13 shows that the breakthrough of MIB for a virgin GAC system with less film resistance ($k_f = 1\times10^{-1}$ cm/s) than originally proposed by the model ($k_f = 3.90\times10^{-4}$ cm/s) was sensitive to surface diffusion when $D_s \geq 1\times10^{-12}$ cm^2/s. This was supported by using a D_s of $1x10^{-12}$ cm^2/s and varying the film diffusion coefficient (Figure 14). For this D_s, $1x10^{-12}$ cm^2/s, the convergence of the MIB breakthroughs indicated that at these film diffusion coefficients, $k_f \geq 1x10^{-3}$ cm/s, the surface diffusion was the rate limiting step. Based upon the range of surface diffusions tested and assuming the mass transfer zone is longer than the bed depth a film resistance coefficient between 10^{-4} and 10^{-3} cm/s would be required to match the laboratory-scale columns. This correlates well with the $3.9x10^{-4}$ cm/s determined by the optimization routine for this model.

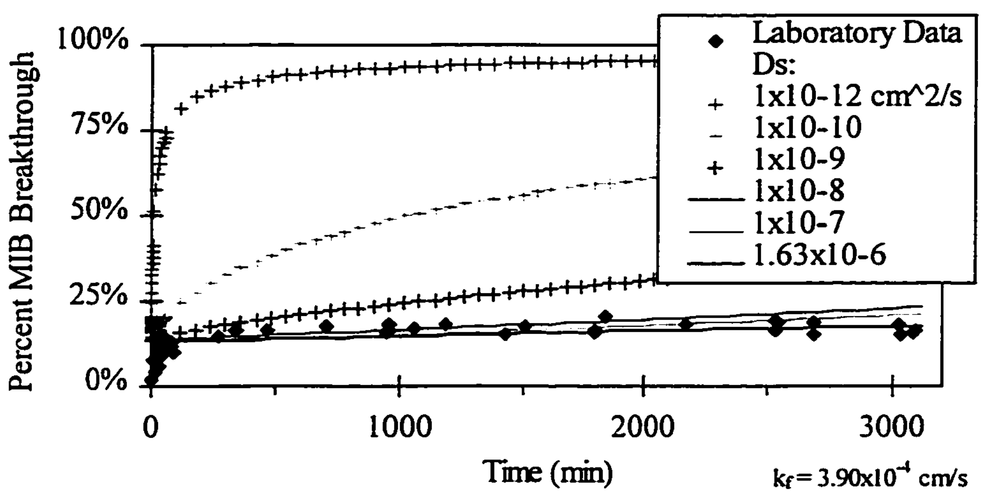

Figure 12 – Sensitivity of Percent MIB Breakthrough to the Surface Diffusion Coefficient

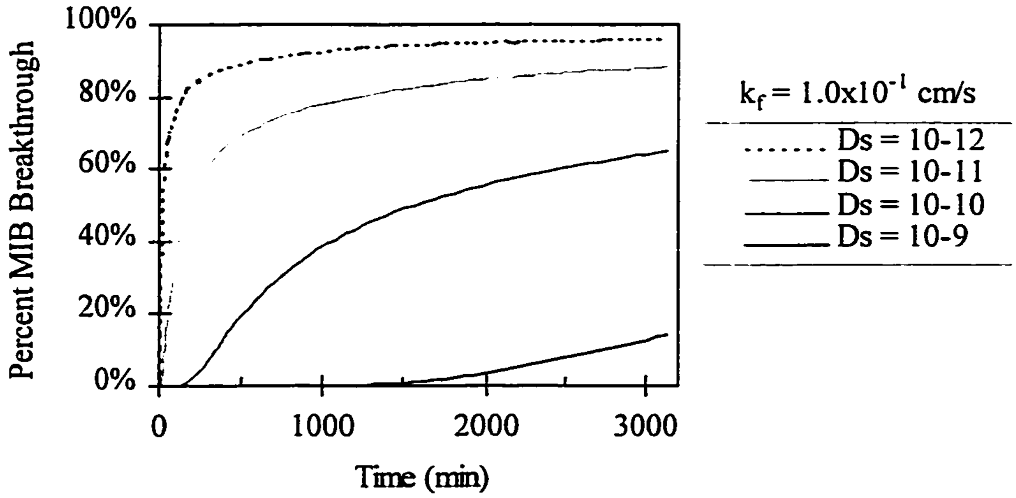

Figure 13 – MIB Breakthrough Sensitivity to Internal Diffusion with Less External Resistance

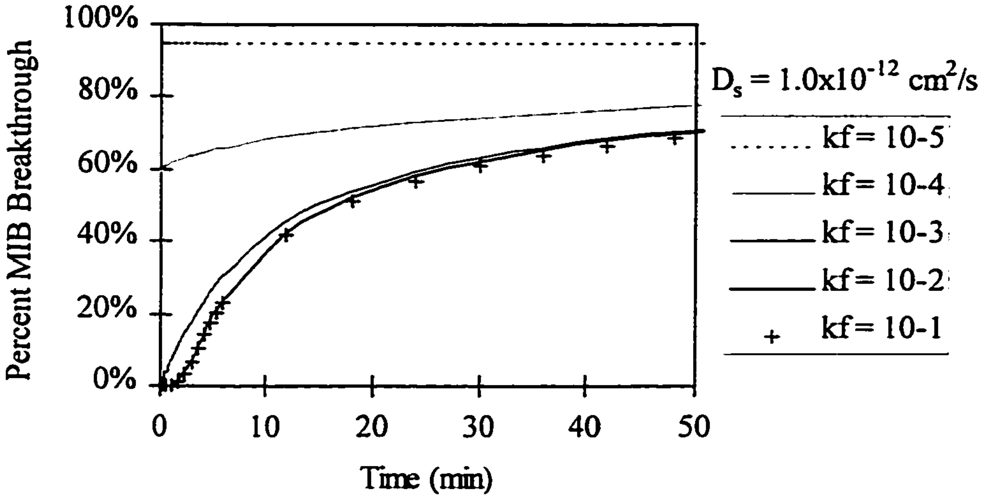

Figure 14 – Determining the Role of Film Resistance With Low Internal Diffusion

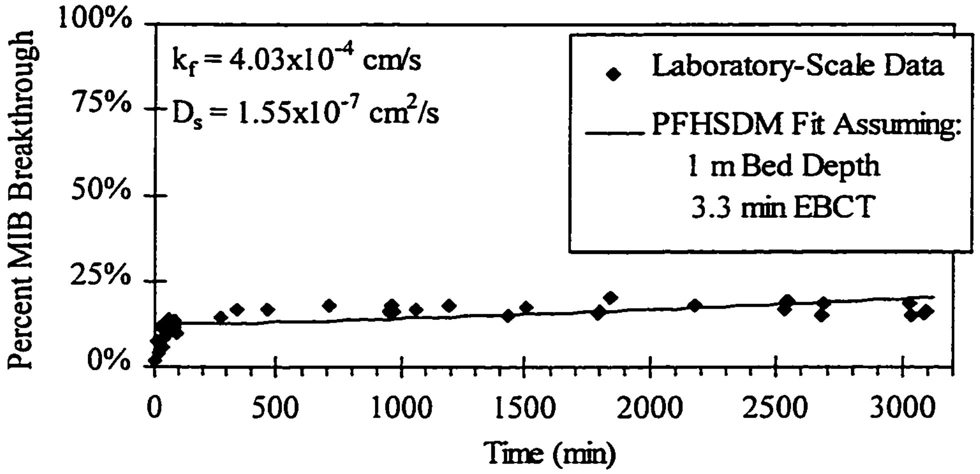

Figure 15 – Large Approach Velocity PFHSDM Fit

At such low approach velocities (0.361 cm/min) it is not unreasonable to expect film diffusion to have a significant effect on the breakthrough of MIB. The larger systems, however, operate at much higher velocities. This significant difference in flows was concerning. Assuming that the laboratory-scale columns do simulate the performance of larger-scale systems the model was initialized so that the model was trying to characterize a 1m deep bed with the same contact time (approach velocity = 301 cm/min). With k_f

and D_s equal to 4.03×10^{-4} cm/s and 1.55×10^{-7} cm^2/s, respectively, the model again assumes that film resistance is a limiting factor (Figure 15). All of these modeling results consistently indicate that MIB adsorption in GAC is a film diffusion controlled process.

CAPACITY LIMITATION

The data in Figures 3-5 indicate that the GAC capacity decreases with preloading time. The laboratory-scale column capacities predicted by the IAST, however, did not show the same trend (Table 5). The reason for this is due to the predicted effects of competition at equilibrium capacities close to the initial or influent MIB concentration. Assuming reversible adsorption, it is shown in Figure 3 that the MIB capacity dramatically decreases as the influent concentration is approached.

Table 5 – GAC Pseudo Single-Solute MIB Capacity

	Co = Ce (ng/L)	K (mg/g)(L/ug)^(1/n)
Virgin	53.29	0.003
1 yr preload	51.67	0.011
2 yr preload	51.67	0.011

It is believed that this dramatic decrease of capacity is due to the presence of a strongly adsorbing competing fraction of NOM that could displace previously adsorbed MIB. Figure 16 shows that the IAST prediction for the 1 year preloaded GAC did not show the same decrease of capacity at equilibrium concentrations close to the initial concentration. A similar IAST fit and prediction were obtained for the 2 year preloaded carbon. The IAST results of the preloaded carbons indicated that adsorbing an incremental amount of additional NOM to the preloaded carbons did not affect MIB adsorption as dramatically as with the virgin GAC. This resulted in the unexpected trend in the IAST predictions shown in Table 5. For the purpose of consistency, the IAST predictions presented in Table 5 were the capacity values used in the PFHSDM.

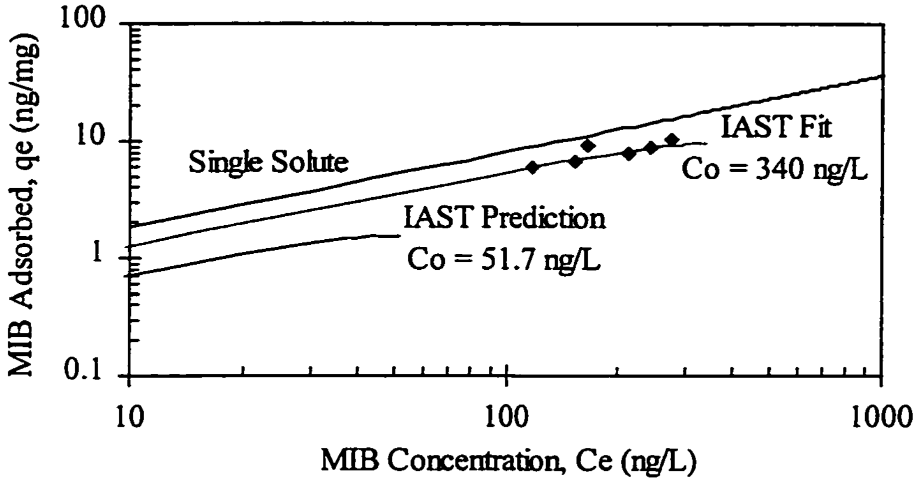

Figure 16 - IAST Fit and Prediction (1 year preload GAC)

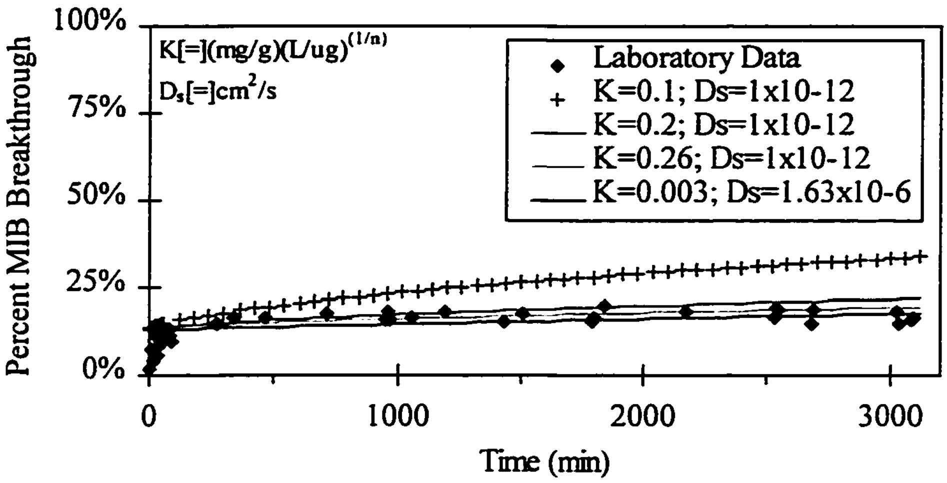

Figure 17 - Sensitivity of Percent MIB Breakthrough to the GAC Capacity

Instead of using the IAST predicted capacity determined at the influent concentration, and a capacity was determined from the portion of the isotherm parallel to the single solute for the virgin GAC a Freundlich K of 0.26 (mg/g)(L/µg)$^{1/n}$ could be obtained. If the film diffusion remained at 3.90x10^{-4} cm/s, a lower surface diffusion coefficient was selected (D$_s$ = 1x10^{-12} cm^2/s), and the Freundlich K was increased to 0.26, it can be seen that a reasonable fit can be obtained (Figure 17). It can be proposed that while the system is still primarily controlled by film diffusion, a more realistic surface diffusion can be obtained with a Freundlich K that is more physically reasonable.

SUMMARY AND CONCLUSIONS

Based on carefully collected equilibrium and kinetic MIB adsorption data, the plug flow pseudo single-solute homogeneous surface diffusion model was used to predict the two-day percent MIB breakthrough of laboratory-scale fixed bed GAC adsorbers. The model used the isotherm parameters from a batch test and determined the mass transfer parameters D_s and k_f by fitting the data from a laboratory-scale column test. Performance predictions were then made of the effect of changing EBCT and initial concentration. These model predictions closely matched the performance of the laboratory-scale columns at EBCTs close to the EBCT at which the model was calibrated. Even at EBCTs more than four times longer than the calibration EBCT, only a 10 percent difference was observed between the predicted and actual percent MIB breakthrough values. Additionally, the model was able to predict the performance of a larger diameter (2.5 cm) laboratory-scale column.

During the evaluation of the PFHSDM it was determined that poor predictions may be reached if sufficient time is not given for determining the equilibrium MIB adsorption parameters. It was also discovered that while satisfactory predictions were obtained the adsorptive parameters describing the system were not necessarily physically realistic. The model did indicate, however, that the adsorption of MIB in a fixed bed of GAC is controlled by film diffusion. Finally, the PFHSDM supported the findings reported in the previous chapter, which concluded, the percent MIB breakthrough was independent of the influent MIB concentration.

"I like work; it fascinates me. I can sit and look at it for hours." (Jerome K. Jerome)

Activated Carbon Testing Protocols

Developed from the work discussed in the previous chapters, protocols evaluating the use of powdered and granular activated carbon for MIB removal are described below.

POWDERED ACTIVATED CARBON

The protocol outlined here should provide the user with a method to assist in the selection of different PACs. The approach should also indicate the minimum PAC dose required to remove a desired fraction of MIB.

1. Obtain a representative sample of the natural water and powdered activated carbon(s) of interest;
2. Based upon the user's limit of MIB detection, select an initial concentration of MIB so that two to three logs of removal may be observed (the lower the concentration the better, however, make sure that at least 2 logs of removal can be analyzed);
3. Prepare a natural water isotherm with a range of carbon doses wide enough to remove the MIB to the analytical detection limit (PAC doses between 2.0 and 150 mg/L are often used; isotherms should be prepared headspace free to minimize losses due to volatilization; glass beads should be used in headspace free isotherms to insure proper mixing;);
4. Analyze the isotherm at a time representative of the PAC contact time expected in the water treatment facility;
5. Plot the results of the isotherm as percent MIB remaining ($C_t/C_o*100\%$) versus PAC dose on a log-log scale, and draw a line of best fit through the data;
6. Determine the influent and desired effluent MIB concentration to calculate the corresponding percent MIB remaining;

7. On the plot of the isotherm data, read horizontally across at the calculated percent MIB remaining until the line of best fit is intersected. At this point move vertically down to determine which PAC dose this corresponds.
8. The corresponding PAC dose read from the plot should indicate the minimum PAC dose required to reduce the concentration of MIB to the level selected in step #6.

(Note: the PAC dose determined from the graph is a minimum. Higher doses may be required due to interactions with other treatment chemicals, poor mixing conditions or shorter than expected contact times.)

GRANULAR ACTIVATED CARBON

This procedure can assist in determining the minimum amount of MIB expected to pass through a GAC filter/adsorber. This should indicate to the operator whether or not the activated carbon needs to be regenerated/replaced to serve as an effective barrier against tastes and odors.

1. Dewater the filter/adsorber of interest;
2. Collect a representative core sample;
3. Perform a sieve analysis to determine the GAC fraction which accounts for the largest fraction of the filter's external surface area (the carbon should be rinsed free of particulates if the filter was not backwashed prior to sampling);
4. Calculate the empty bed contact time (EBCT = bed volume/flow rate) of the large scale filter;
5. Select the flow rate to be used in the laboratory scale column (selection is often based on the pump used or the analytical sample volume requirements);
6. Using the information in #4 & 5, calculate the bed volume of the laboratory scale column to have the same EBCT as the large scale system;

7. Assuming an apparent bed density, and moisture content of the wet GAC, calculate the mass of wet GAC that should be weighed for the laboratory scale column (apparent bed density ~ 0.5 to 0.6; wet GAC moisture content ~ 30%);
8. Weigh the appropriate amount of the size fraction determined in step #3;
9. Prepare the laboratory column with the GAC centered in a bed of glass beads (make sure that the beads and GAC are well packed and do not have any air bubbles trapped between particles) and measure the actual bed dimensions;
10. Spike the influent natural water to the desired MIB concentration (note: the carbon's history may influence MIB removals; the influent concentration should be high enough so that desorption from previous exposure does not occur, however, it should not be so high that it significantly increases the carbons surface MIB concentration);
11. Set the flow rate for the actual bed dimensions determined in step #9 to obtain the EBCT determined for the larger scale system, and pass the spiked influent through the column at this flow rate for approximately two days to determine the effluent plateau concentration;
12. Normalizing this plateau value to the influent concentration will yield the minimum percent of MIB expected to pass through the larger scale column for any influent concentration (note: higher percentages of MIB may appear to pass through the larger scale column due to short circuiting, other treatment chemicals or previous loadings of MIB).

"In everything we ought to look to the end." (Jean de La Fontaine)

Summary and Conclusions

The work presented here has addressed the goals outlined for this study. To determine the effectiveness of activated carbon, in the presence or absence of free chlorine, for the removal of MIB in a drinking water treatment plant, two protocols were developed. One protocol was developed to determine the minimum PAC dose required to reduce a given MIB influent concentration to a specific level in natural water. The second protocol was used to determine the remaining life of an existing GAC bed for taste and odor control.

Through the development of these protocols it was found that:

- Liquid scintillation counting of ^{14}C-MIB was a technique suitable for the rapid collection and analysis of low concentrations of MIB in the presence and absence of free chlorine;
- The percent MIB removed by activated carbon, either powdered or granular, is independent of the influent MIB concentration, but dependent on the natural organic matter adsorbed;
- Chlorine has a deleterious effect on the ability of activated carbon, both powdered and granular, to adsorb MIB, and thus the contact of chlorine with activated carbon should be avoided;
- Adsorption by activated carbon alone does not appear to provide sufficient protection against taste and odor caused by MIB.

"My interest is in the future because I am going to spend the rest of my life there."
(Charles F. Kettering)

Future Research Needs

The results presented in this study have shown that adsorption by activated carbon alone does not appear to provide a sufficient barrier against taste and odor problems caused by MIB. Additional work is necessary to determine the best, or combination of, technologies that will mitigate the earthy-musty organoleptic problems caused by this compound. Circumstantial evidence from water treatment plants, such as the Lake County, Illinois WTP, indicates that MIB is "controlled" in advanced water treatment processes such as ozone followed by biologically active GAC filtration. In this particular case the GAC has been in place for over six years. Through this example, and others, it appears that determining where is the "removal" actually occurring, and what are the respective roles of, 1) adsorption, 2) biodegradation, 3) oxidation/advanced oxidation, is very important.

Assuming biodegradation is important, the following questions arise:

- While many organisms have been shown to degrade MIB, which organisms are responsible for its degradation to the low concentrations necessary to produce palatable water?
- What conditions are necessary to stimulate the growth of these desirable organisms? (e.g. water quality parameters, post ox/AOP DOC characteristics)
- Do these organisms require time to acclimate before they start degrading the seasonal occurrences of MIB? If so, how long do these organisms require to acclimate, and can this amount of time be reduced or eliminated so that the organisms have been "triggered" to degrade MIB as soon as it appears in the influent?

- Is the adsorbent capacity of the GAC required, beneficial or even necessary? (i.e. can an alternative/cheaper support media be used with an equal or superior effectiveness?)

Providing answers to these questions would help to determine the most effective approach to controlling MIB related taste and odor problems. Since the consumers' confidence in the quality and safety of their drinking water is directly connected to its aesthetics, these answers would also give the water treatment plants information critical to the production of water acceptable to the population they service.

"Only those things are beautiful which are inspired by madness and written by reason"

(André Gide)

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"It is surprising what a man can do when he has to,
and how little most men will do when he don't have to." (Walter Linn)

Appendix A (Mathematical Modeling)

A number of theories and formulations have been applied to the mathematical modeling of adsorption processes. This research has only relied upon the use of the Freundlich and Ideal Adsorbed Solution Theory (IAST) equilibrium models and two-resistance, homogeneous surface diffusion kinetic models. As a result, only these will be focused upon here.

ADSORPTION EQUILIBRIA MODELING

The use of the Langmuir (1918) isotherm has been used extensively in the representation of single-solute adsorption equilibria. The expression was later extended to a multi-component system by Butler and Ockrent (1930). Jain and Snoeyink (1973) also modified the Langmuir isotherm for a bi-solute system. However, an underlying assumption of the Langmuir expression is a constant adsorption site energy, which does not typically correlate well with adsorption into activated carbon. For highly heterogeneous surfaces, the Freundlich (1906) expression is generally more applicable, though the equation does not reduce to Henry's Law as the concentration approach zero.

$$q = KC^{1/n} \qquad \text{(A.1)}$$

where q = equilibrium solid phase concentration, ng adsorbate/mg adsorbent;
C = equilibrium liquid phase concentration, ng/L;
K = Freundlich constant, $(\text{ng/mg})(\text{L/ng})^{1/n}$;
$1/n$ = Freundlich constant, dimensionless.

While the Freundlich equation (see equation A.1) was originally empirically obtained, theory was later developed to explain it based on a heterogeneous adsorbent (Halsey and

Taylor, 1947). This equation has been typically used to describe single-solute systems and has been used in this fashion for all single-solute systems in this research. However, Crittenden *et al.* (1985) has incorporated the Freundlich equation into the ideal adsorbed solution theory (IAST) to model multisolute systems. The application of the IAST to a system with N components could then characterize that multisolute system by:

$$C_i = \frac{q_i}{\sum_{k=1}^{N} q_k} \left[\frac{\sum_{k=1}^{N} n_k q_k}{n_i K_i} \right]^{n_i} \qquad \text{(A.2)}$$

where C_i = equilibrium liquid phase concentration of component i;

q_i = equilibrium solid phase concentration of component i;

n_i and K_i = single solute Freundlich isotherm constants of component i.

The IAST was originally developed for the adsorption of gaseous mixtures (Myers and Prausnitz, 1965). Radke and Prausnitz (1972) later adapted it to dilute aqueous systems. Since the application of the Freundlich expression to the IAST, it has been extensively and successfully employed (Knappe, 1996; Crittenden *et al.*, 1985; Najm *et al.*, 1991; Schmidt, 1994; Qi *et al.*, 1994).

The application of the IAST to natural water systems has been limited by the unknown composition of the background organic matter. Two main approaches have been employed to deal with this problem. One approach as been to describe the background organics as a mixture of fictive components

Another approach has been to characterize the background organic matter as a single compound - the equivalent background compound (EBC). Using this method, natural water isotherms are performed for the target compound of interest. These are compared to the single-solute isotherm for that compound. The characteristics of the EBC are then assigned such that they yield the same amount of competition

Reduction of equation A.2 into a bi-solute system yields:

$$C_1 = \frac{q_1}{q_1 + q_2}\left[\frac{n_1 q_1 + n_2 q_2}{n_1 K_1}\right]^{n_1} \tag{A.3}$$

$$C_2 = \frac{q_2}{q_1 + q_2}\left[\frac{n_1 q_1 + n_2 q_2}{n_2 K_2}\right]^{n_2} \tag{A.4}$$

An isotherm bottle, a batch adsorption system, can be described by a mass balance equation:

$$q_i = \frac{C_{i,0} - C_i}{C_c} \tag{A.5}$$

solving for C_i:

$$C_i = C_{i,0} - q_i C_c \tag{A.6}$$

where $C_{i,0}$ = initial concentration of compound i;

C_c = carbon concentration in the isotherm bottle.

Using equation A.6 equations A.3 and A.4 can be rewritten for a bi-solute batch adsorption system as:

$$C_{1,0} - q_1 C_c - \frac{q_1}{q_1 + q_2}\left[\frac{n_1 q_1 + n_2 q_2}{n_1 K_1}\right]^{n_1} = 0 \tag{A.7}$$

$$C_{2,0} - q_2 C_c - \frac{q_2}{q_1 + q_2}\left[\frac{n_1 q_1 + n_2 q_2}{n_2 K_2}\right]^{n_2} = 0 \tag{A.8}$$

A method by Najam *et al.* (1991) groups all of the background organic matter (BOM) into a hypothetical compound called the equivalent background compound (EBC) so that a complex organic system can now be modeled as the bi-solute system described above. While the initial concentration and Freundlich parameters for the EBC are unknown they may be determined by the following procedure:

1. Determine Freundlich parameters, K_1 and $1/n_1$, for the target compound. by performing a single-solute isotherm (i.e., a MIB isotherm in organic-free water);
2. Collect isotherm data, q_1 versus C_e, for the target compound in natural water at two different initial concentrations that are low enough to observe competition;
3. Utilize the EBC program (Knappe *et al.*, 1993; Matsui, 1994) to solve for the EBC Freundlich parameters (K_2, $1/n_2$, $C_{2,0}$) (see Appendix D).

With the EBC Freundlich parameters determined, adsorbent capacity predictions for the target compound with any given initial concentration is possible. For these predictions we used a computer program of the IAST equations written by Qi (1992) and modified by Matsui (1994) (see Appendix D).

HOMOGENEOUS SURFACE DIFFUSION FOR A BATCH SYSTEM

The batch reactor adsorption of a target compound from natural water onto PAC may be described by a pseudo single-solute homogeneous surface diffusion model (HSDM). The basic assumptions made when applying the pseudo single-solute HSDM to this system are:

1. Intraparticle surface diffusion is the only rate limiting mechanism;
2. The surface diffusion coefficient is not a function of C_c or $C_{1,0}$ (i.e., BOM's effect on the adsorption rate of the target compound is constant).
3. Competitive effects are assumed to be fully accounted for by multi-solute equilibrium expressions (i.e., there are no multi-component diffusion interactions).

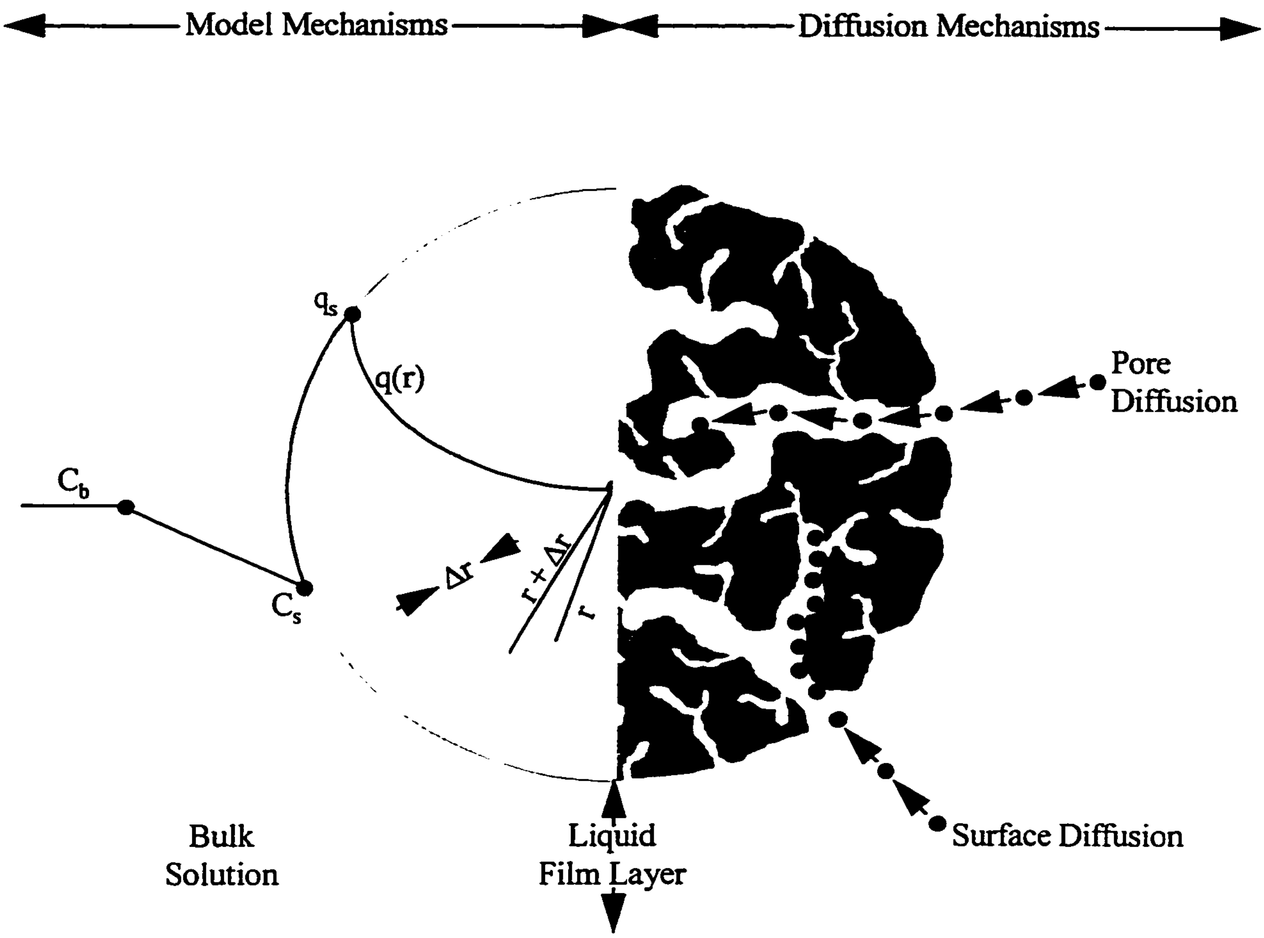

Figure 15. Adsorbate Transport Mechanisms Through an Activated Carbon Particle

This system of equations may be summarized as below:

$$\frac{\partial q}{\partial t} = D_s\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \qquad \text{(A.9)}$$

$$\text{at } t = 0,\ 0 \le r \le R:\ q = 0 \qquad \text{(A.10)}$$

$$\text{at } r = 0,\ t \ge 0:\ \frac{\partial q}{\partial r} = 0 \qquad \text{(A.11)}$$

$$\text{at } t \ge 0:\ \frac{dC_l}{dt} = -\frac{3C_c}{R^3}\frac{\partial}{\partial t}\int_0^R qr^2 dr \qquad \text{(A.12)}$$

$$\text{at } t \ge 0,\ r = R:\ C_s = C_l \qquad \text{(A.13)}$$

$$\text{at } t = 0:\ C_l = C_{l,0} \qquad \text{(A.14)}$$

where, D_s = surface diffusion coefficient;
r = radial distance;
t = time;
R = particle radius;
C_l = bulk liquid phase concentration of the target compound;
Cs = liquid phase concentration at the external surface of the particle.

D_s was determined by a fit to the batch kinetic data, by a computer search program, "SEARCH" (see Appendix D). The search program consisted of the Levenberg-Marquardt unconstrained optimization algorithm and the numerical solution of the HSDM (International, 1991; Matsui, 1994).

In order to solve this system of equations, a relationship between the liquid phase concentration, C_s, and the solid phase concentration at the external surface, q_s, was needed. Equation A.15 was used for this purpose:

$$q_s = K(C_{l,0},C_c)C_s^{1/n} \tag{A.15}$$

where, $K(C_{l,0},C_c)$ = the capacity parameter which is a function of initial concentration, $C_{l,0}$, and carbon dose, C_c;
$1/n$ = assumed to be the single-solute Freundlich constant.

$K(C_{l,0},C_c)$ was determined by:

1. Determining the Freundlich parameters for the EBC with respect to the target compound, as outlined in the previous section;
2. Finding the solid and liquid phase concentrations of the target compound at equilibrium by the IAST. This is dependent on the carbon dose, initial concentration, and Freundlich parameters of both the target compound and EBC;
3. Calculating $K(C_{l,0},C_c)$ using equation A.15 and the solid and liquid phase concentrations determined in Step 2.

Once $K(C_{1,0},C_c)$, $1/n$, D_s and k_f have been determined, the "HSDM" program can be used to solve for the liquid phase concentration for plug flow systems (Traegner and Suidan, 1988) (see Appendix D).

For applications where it is desired to model the system as a CSTR (e.g., rapid mix, flocculation basin), the single-solute HSDM assumptions previously used, can be incorporated into the mass balance of a CSTR. Additional assumptions including a non-rate limiting film mass transfer and an exponential age distribution of PAC in the reactor allow for the resulting equation:

$$C_{in} - C_{eff} - C_c K(C_{in}, C_c) C_{eff}^{1/n} \left[1 - \frac{6}{\pi^2} \sum_{i=1}^{\infty} \frac{1}{i^2} \frac{1}{1 + i^2 \pi^2 \frac{D_s}{R^2} \tau} \right] = 0 \qquad \text{(A.16)}$$

where, C_{in} = influent concentration;

C_{eff} = effluent concentration;

$K(C_{in}, C_c)$ = capacity parameter as a function of the influent concentration, C_{in}, and the carbon concentration, C_c. This is equivalent to $K(C_{1,0},C_c)$ as previously described;

t = average PAC residence time.

τ = hydraulic retention time of CSTR

This non-linear equation is solved in the computer program "CSTR" written by Traegner and Suidan (1991) (see Appendix D).

ADSORPTION THROUGH A GRANULAR ACTIVATED CARBON BED

Adsorption through a bed of GAC has also been modeled using the pseudo single-solute HSDM. The fundamental nondimensional equations for a fixed bed, assuming negligible longitudinal dispersion, are (Knappe, 1996; Smith 1991; Crittenden *et al.*, 1986):

Liquid-Phase (Smith 1991)

$$\frac{\partial \bar{c}(\bar{z},\bar{t})}{\partial \bar{t}} = -\frac{D_g}{\varepsilon}\frac{\partial \bar{c}(\bar{z},\bar{t})}{\partial \bar{z}} - D_g \frac{\partial \bar{q}_{avg}(\bar{z},\bar{t})}{\partial \bar{t}} \tag{A.17}$$

$$\text{at } \bar{z} = 0,\ \bar{c}(\bar{z},\bar{t}) = c_o(t) \tag{A.18}$$

$$\text{at } \bar{t} = 0,\ \bar{c}(\bar{z},\bar{t}) = 0 \tag{A.19}$$

where, $\bar{c}(\bar{z},\bar{t})$ = nondimensional liquid-phase MIB concentration: c(z,t)/$c_{0;}$

$\bar{z}$ = dimensionless axial distance;

$\bar{t}$ = dimensionless time: t/(τD_g);

$c_0(t)$ = influent concentration;

D_g = MIB distribution parameter: $Mq_e/V\varepsilon C_O$; $[M = (1-\varepsilon)V\rho]$

$\bar{q}_{avg}(\bar{z},\bar{t})$ = average MIB concentration within the GAC particles evaluated at the bed step:

$$\bar{q}_{avg}(\bar{z},\bar{t}) = 3\int \bar{q}(\bar{r},\bar{z},\bar{t})\bar{r}^2 d\bar{r} \tag{A.20}$$

where, $\bar{q}(\bar{r},\bar{z},\bar{t})$ = solid-phase concentration of solute as a function of dimensionless radial distance from the center of GAC particle, $\bar{r}$, length and time.

Solid-Phase (Smith 1991)

$$\frac{\partial \bar{q}(\bar{r},\bar{z},\bar{t})}{\partial \bar{t}} = \frac{2E_d}{\bar{r}}\frac{\partial \bar{q}(\bar{r},\bar{z},\bar{t})}{\partial \bar{r}} + E_d \frac{\partial^2 \bar{q}(\bar{r},\bar{z},\bar{t})}{\partial \bar{r}^2} \tag{A.21}$$

$$\text{at } \bar{r} = 0,\ \frac{\partial \bar{q}(\bar{r},\bar{z},\bar{t})}{\partial \bar{r}} = 0 \tag{A.22}$$

$$\text{at } \bar{r} = 1,\ \frac{\partial \bar{q}(\bar{r},\bar{z},\bar{t})}{\partial \bar{r}} = \mathrm{Sh}\left[\bar{c}(\bar{z},\bar{t}) - \bar{c}_s(\bar{z},\bar{t})\right] \tag{A.23}$$

or

$$\mathrm{St}\left[\bar{c}(\bar{z},\bar{t}) - \bar{c}_s(\bar{z},\bar{t})\right] = \frac{\partial}{\partial t}\int_0^1 \bar{q}(\bar{r},\bar{z},\bar{t})\bar{r}^2 d\bar{r} \tag{A.24}$$

$$\text{at } \bar{t} = 0, \ \bar{q}(\bar{r}, \bar{z}, \bar{t}) = 0 \tag{A.25}$$

where, E_d = surface diffusion modulus: $\frac{D_s D_g \tau}{R^2}$;

Sh = Sherwood number (ratio of film to surface diffusion): $\frac{k_f R}{D_s}$;

St = modified Stanton number (ratio of mass transport through the film to advection): $\frac{k_f}{\alpha R}\left(\frac{1-\varepsilon}{\varepsilon}\right)$;

τ = hydraulic retention time;

$\bar{c}(\bar{z}, \bar{t})$ = bulk liquid-phase MIB concentration for a given bed step;

$\bar{c}_s(\bar{z}, \bar{t})$ = liquid-phase MIB concentration at the surface of the GAC particle for a given bed step;

α = mole fraction ratio of solid- to liquid-phase MIB

A similar system of equations are solved in the computer program "FS" written by Yuasa (1982) (see Appendix D).

Appendix B (Raw Data)

SINGLE-SOLUTE PAC ISOTHERM DATA IN MILLI-Q WATER

Watercarb (mg/L)	MIB (ng/L)
8.3	3.7
3.9	12.2
2.0	37.4
0	149.11
0	149.29

HDB (mg/L)	MIB (ng/L)
43.8	2.3
20.1	1.1
10.2	2.2
4.4	7.3
2.2	14.8
0	149.11
0	149.29

HDB (mg/L)	MIB (ng/L)
495.8	609.1
464.2	641.7
417.5	718.8
387.5	743.1
343.3	877.7
304.2	914.4
268.3	1093.6
210.8	1159.3
152.5	1492.3
98.3	3213.7
55.8	8846.0
22.5	65698.0
0.0	365854.7
0.0	384502.9
0.0	373115.8

SINGLE-SOLUTE GAC ISOTHERM DATA IN MILLI-Q WATER

Virgin	GAC (mg/L)	MIB (ng/L)	
30x40		25-day	125-day
	57.9		1.5
	42.2		2.3
	33.5		1.7
	23.6	12.7	2.2
	18.1	15.0	3.9
	14.2	22.2	7.7
	11.8	26.7	7.5
	7.5	44.7	11.7
	0.0	522.8	517.7

Hammond	GAC (mg/L)	MIB (ng/L)	
20x25		25-day	125-day
	51.0	273.6	108.0
	40.9	340.7	154.7
	31.0	358.9	169.8
	25.0	384.7	197.9
	20.3	408.4	241.1
	13.3	458.0	324.3
	10.1	464.7	354.3
	7.9	476.6	387.6
	0.0	522.8	517.7

Virgin	GAC (mg/L)	MIB (ng/L)	
20x25		25-day	125-day
	51.5	11.6	1.1
	33.4	14.1	2.5
	15.7	27.7	8.9
	12.2	33.6	10.4
	7.5	39.4	11.6
	0.0	522.8	517.7

Hammond	GAC (mg/L)	MIB (ng/L)	
16x18		25-day	125-day
	36.8	307.0	127.8
	25.1	369.3	184.9
	15.4	434.2	284.4
	7.4	447.5	336.6
	30.8		164.5
	18.8		234.3
	10.3		300.3
	0.0	522.8	517.7

Michigan City	GAC (mg/L)	MIB (ng/L)	
		25-day	125-day
20x25	40.8	350.1	178.8
	34.4	396.5	243.2
	31.3	377.3	223.2
	26.4	397.9	237.3
	18.7	425.4	294.5
	12.3	455.9	332.6
	10.1	455.1	360.1
	5.8	489.0	409.7
	0.0	522.8	517.7

Michigan City	GAC (mg/L)	MIB (ng/L)	
		25-day	125-day
12x14	40.1		126.1
	35.4	350.1	167.9
	27.7	387.4	215.6
	21.1	445.1	278.5
	15.5		280.7
	12.4		300.3
	0.0	522.8	517.7

Michigan City	GAC (mg/L)	MIB (ng/L)	
		25-day	125-day
16x18	34.8		170.1
	25.8		219.7
	20.8		264.8
	18.3		333.4
	14.6	439.7	300.2
	8.7	492.5	400.6
	7.8		373.7
	0.0	522.8	517.7

COMPETATIVE GAC ISOTHERM DATA IN CHICAGO CRIB WATER

Virgin	GAC (mg/L)	MIB (ng/L)	
20x25		25-day	125-day
	0.0	343.9	339.7
	2.1	282.0	262.4
	6.0	231.0	185.2
	7.5	247.4	185.6
	13.4	171.3	109.0
	18.9	96.6	49.5
	24.0	75.7	29.3
	34.6	33.9	13.1

Hammond	GAC (mg/L)	MIB (ng/L)	
20x25		25-day	125-day
	0.0	343.9	339.7
	3.6	324.57	325.1
	6.0	315.78	276.7
	10.8	294.40	244.4
	15.8	268.41	212.6
	19.0	242.37	164.9
	27.9	235.14	152.5
	37.1	207.14	117.5

Michigan City	GAC (mg/L)	MIB (ng/L) 25-day	MIB (ng/L) 125-day
20x25	0.0	343.9	339.7
	2.3	334.7	
	3.5	325.4	247.0
	4.8	325.4	309.5
	5.8	314.4	284.5
	9.2	305.0	261.6
	16.9	289.3	218.4
	36.2	234.5	146.7

COMPETATIVE PAC ISOTHERM DATA IN CHICAGO CRIB WATER

Watercarb (mg/L)	MIB (ng/L)
60.3	1.8
40.2	6.2
14.6	39.3
4.0	113.8
2.1	130.3
0	145.8
0	149.8
0	151.8

HDB (mg/L)	MIB (ng/L)
39.4	1.6
13.8	18.7
3.9	100.6
2.1	121.3
0	145.8
0	149.8
0	151.8

Watercarb (mg/L)	MIB (ng/L)
30.7	14.2
4.6	123.6
2.2	141.0
0.0	165.0

HDB (mg/L)	MIB (ng/L)
43.4	3.1
28.8	6.4
15.0	17.0
7.9	54.3
4.3	90.3
1.9	124.2
0.0	165.0

Watercarb (mg/L)	MIB (ng/L)
45.7	49.1
32.4	134.0
9.9	677.3
4.1	1017.9
2.2	1143.1
0.0	1245.2

WPH (mg/L)	MIB (ng/L)
43.3	0.9
28.5	2.1
15.3	6.3
8.0	18.3
4.0	45.2
2.3	82.8
0.0	165.0

WPH (mg/L)	MIB (ng/L)
88.8	1.8
72.5	2.9
62.3	3.8
54.6	5.1
43.5	5.0
27.3	14.8
28.2	14.7
16.2	38.8
8.1	110.1
13.3	58.3
6.5	175.8
4.5	247.2
2.1	548.5
0.0	965.0

COMPETATIVE PAC ISOTHERM DATA IN KANKAKEE RIVER WATER

Hydrodarco-B (mg/L)	MIB (ng/L)
0.0	184.0
2.1	170.3
5.2	149.7
8.8	118.8
11.2	107.0
16.7	74.6
20.3	60.5
25.1	46.1
31.1	33.8

Hydrodarco-B (mg/L)	MIB (ng/L)
0.0	891.0
17.9	354.5
35.8	137.5
54.6	57.1
74.2	27.4
98.1	12.1
116.1	8.4
132.3	6.1
154.5	3.9

Hydrodarco-B (mg/L)	MIB (ng/L)
0.0	131.0
2.0	121.1
4.0	107.5
7.3	94.1
10.0	80.2
16.7	51.9
20.7	47.3
25.9	31.3
31.9	22.5

WPH (mg/L)	MIB (ng/L)
0.0	134.4
2.2	90.8
3.9	65.6
7.6	33.1
9.8	24.9
14.1	14.9

WPH (mg/L)	MIB (ng/L)
0.0	891.3
10.8	155.8
14.0	96.6
19.9	53.0
21.3	38.9
25.6	27.9
33.3	14.9
38.4	10.7
45.2	6.4
64.9	3.1

BATCH KINETIC PAC DATA IN CHICAGO CRIB WATER

HDB (mg/L)	Time (min)	MIB (ng/L)
0.00	0	174.5
11.54	15	103.7
11.54	30	90.5
11.54	45	85.7
11.54	60	77.7
11.54	90	69.1
11.54	120	65.4
11.54	180	60.5
11.54	240	57.9
23.08	240	0.0
3.85	240	125.3
34.62	0	
34.62	15	29.1
34.62	30	19.6
34.62	45	15.1
34.62	60	11.9
34.62	90	10.3
34.62	120	9.5
34.62	180	7.7
34.62	240	7.1

Watercarb (mg/L)	Time (min)	MIB (ng/L)
11.54	0.00	175.1
11.54	0.00	174.2
11.54	1.42	159.9
11.54	4.08	148.2
11.54	7.08	144.6
11.54	13.52	130.3
11.54	16.37	133.9
11.54	30.00	126.3
11.54	45.00	114.6
11.54	59.50	119.5
11.54	90.00	109.8
11.54	120.00	103.9
11.54	186.12	99.6
11.54	240.00	98.4
0.00	240.00	173.0
3.85	240.00	143.1
23.08	240.00	46.7
34.62	0.00	166.4
34.62	0.00	172.9
34.62	2.05	113.2
34.62	4.47	98.8
34.62	7.18	86.9
34.62	12.60	72.9
34.62	17.47	62.0
34.62	28.33	49.9
34.62	44.38	38.3
34.62	58.20	35.3
34.62	89.72	26.5
34.62	124.50	25.4
34.62	183.00	16.4
34.62	235.53	14.3

Nuchar (mg/L)	Time (min)	MIB (ng/L)
9.0	0.00	175.09
9.0	2.00	145.95
9.0	4.25	137.58
9.0	6.53	124.06
9.0	8.77	118.41
9.0	10.90	114.44
9.0	13.62	112.42
9.0	28.67	96.72
9.0	43.17	91.00
9.0	61.02	81.33
9.0	89.92	75.71
9.0	120.10	75.97
9.0	180.90	65.79
9.0	240.00	61.62
24.0	0.00	172.70
24.0	0.00	174.59
24.0	1.50	103.47
24.0	3.50	88.49
24.0	5.30	73.61
24.0	9.37	62.65
24.0	11.40	55.22
24.0	14.48	50.96
24.0	28.48	35.76
24.0	46.55	28.09
24.0	60.00	22.71
24.0	93.70	19.91
24.0	118.97	26.87
24.0	186.00	16.68
24.0	240.00	14.27
0.0	240.00	177.60
0.0	240.00	175.46
3.0	240.00	125.96
18.0	240.00	25.14

WPH (mg/L)	Time (min)	MIB (ng/L)
11.54	0.00	169.8
11.54	1.08	134.9
11.54	3.25	123.9
11.54	5.58	120.4
11.54	8.55	111.5
11.54	11.88	103.0
11.54	18.07	89.7
11.54	30.00	80.8
11.54	45.00	72.2
11.54	59.00	62.0
11.54	89.00	49.4
11.54	119.00	47.1
11.54	178.50	37.1
11.54	240.00	32.2
34.62	0.00	177.8
34.62	1.12	95.6
34.62	3.22	74.7
34.62	5.95	54.3
34.62	8.92	44.7
34.62	11.37	33.9
34.62	15.42	27.9
34.62	29.50	14.7
34.62	44.50	9.8
34.62	59.83	6.8
34.62	89.75	6.1
34.62	120.00	3.5
34.62	180.00	2.9
34.62	240.00	2.9
0.00	240.00	174.8
0.00	240.00	169.1
3.85	240.00	103.5
23.08	240.00	6.5

Cecarbon (mg/L)	Time (min)	MIB (ng/L)
11.54	0.00	170.2
11.54	1.00	128.5
11.54	3.12	116.9
11.54	5.57	103.1
11.54	9.22	92.7
11.54	14.07	81.1
11.54	19.97	70.4
11.54	30.00	57.8
11.54	45.00	49.0
11.54	60.00	41.7
11.54	90.00	32.7
11.54	120.00	30.2
11.54	180.00	22.2
11.54	240.00	19.0
34.62	0.00	177.6
34.62	1.70	81.2
34.62	3.75	53.8
34.62	6.95	36.1
34.62	10.37	23.6
34.62	13.85	18.4
34.62	17.83	13.7
34.62	29.55	7.7
34.62	45.00	6.2
34.62	60.00	3.9
34.62	90.00	2.4
34.62	120.00	2.7
34.62	180.00	2.5
34.62	240.00	0.6
0.00	240.00	164.5
3.85	240.00	84.9
23.08	240.00	4.4

BATCH KINETIC PAC DATA WITH CHLORINE IN CHICAGO CRIB WATER

Hydrodarco-B (11.5 mg/L)
No Cl_2 added

Time (min)	MIB (ng/L)
0.0	247.8
1.2	203.9
3.7	186.9
7.7	168.6
28.0	129.8
59.5	107.9
118.0	89.3
180.0	82.6
237.0	80.3

Hydrodarco-B (11.5 mg/L)
Cl_2 (3 mg/L) added at t = 0

Time (min)	MIB (ng/L)
0.0	250.5
1.5	227.5
5.6	213.9
10.4	202.7
23.4	197.1
56.3	193.4
105.0	186.1
238.5	182.1
470.0	152.5

Hydrodarco-B (11.5 mg/L)
Cl_2 (3 mg/L) added at t = 12

Time (min)	MIB (ng/L)
0.0	255.4
1.6	193.6
4.0	175.5
8.4	154.8
13.4	159.2
15.6	162.5
21.7	168.5
30.3	164.2
44.5	159.0
66.3	157.6
117.2	149.9
254.5	138.1
483.0	120.6

Hydrodarco-B (11.5 mg/L)
pre-Cl_2 (5 mg/L) added
dechlor after 24 hours
then added PAC ad MIB

Time (min)	MIB (ng/L)
0.0	246.3
1.5	192.9
4.1	180.2
10.0	155.2
35.0	123.6
65.0	107.3
122.5	87.8
160.0	84.0
230.0	82.3

4-hour MIB concentration (ng/L) with
varied initial Cl_2 concentrations

Hydrodarco-B (mg/L)	No Cl_2	Cl_2 (3 mg/L)	Cl_2 (5 mg/L)
0	252.1	252.1	252.1
3.8	183.5	223.0	232.6
11.5	83.7	146.1	185.7
23.1	29.4	47.6	
26.9			83.4
34.6	10.3	16.9	27.0
42.6	4.0	4.0	

BATCH KINETIC PAC DATA WITH CHLORINE IN DEIONIZED-DISTILLED WATER

Hydrodarco-B (11.5 mg/L)
No Cl_2 pre-reacted

Time (min)	MIB (ng/L)
0.0	244.5
3.0	109.0
3.6	72.1
10.0	36.4
30.0	17.8
66.0	14.3
120.2	13.2
244.5	7.5

Hydrodarco-B (11.5 mg/L)
Cl_2 (1 x 10 mg/L) pre-reacted

Time (min)	MIB (ng/L)
0.0	255.4
1.7	251.8
6.8	248.9
19.3	245.9
28.9	244.6
55.9	241.0
122.0	233.8
218.0	234.6

Hydrodarco-B (11.5 mg/L)
Cl_2 (5 x 2 mg/L) pre-reacted

Time (min)	MIB (ng/L)
0.0	255.4
2.3	251.0
6.6	247.7
13.1	250.5
19.5	246.5
35.3	240.2
66.0	243.6
141.3	232.5
215.0	229.3

Hydrodarco-B (11.5 mg/L)
Cl_2 (1 x 5 mg/L) pre-reacted

Time (min)	MIB (ng/L)
0.0	255.4
3.8	247.4
8.7	239.1
21.1	240.6
30.8	232.2
58.2	223.1
125.0	205.0
230.0	196.2

Hydrodarco-B (11.5 mg/L)
l_2 (2 x 2.5 mg/L) pre-reacted

Time (min)	MIB (ng/L)
0.0	255.4
2.7	248.1
12.0	241.7
21.9	223.8
49.5	220.1
116.5	211.2
211.0	185.7

Hydrodarco-B (11.5 mg/L)
Cl_2 (5 x 1 mg/L) pre-reacted

Time (min)	MIB (ng/L)
0.0	255.4
4.6	241.3
13.7	241.7
24.3	235.1
51.7	226.8
119.0	207.3
214.0	192.6

2-DAY PERCENT MIB BREAKTHROUGH IN CHICAGO CRIB WATER FOR LABORATORY- AND PILOT-SCALE GAC COLUMNS

2.26 min EBCT

	Years in Service	Ceff/Cinf
Lab-scale	6	0.905
Columns	3.93	0.87
C_{inf}=50 ng/L	2.99	0.79
	1.8904	0.71
	0.9945	0.73
	0.2110	0.42
	0	0.37
G&H	0.1667	0.656
Pilot study	0.9945	1.27
	1.8904	1.45

4.36 min EBCT

	Years in Service	Ceff/Cinf
Lab-scale	6	0.77
Columns	3.93	0.722
C_{inf}=50 ng/L	2.99	0.675
	1.8904	0.49
	0.9945	0.45
	0.2110	0.28
	0	0.16
G&H	0.1667	0.17
Pilot study	0.9945	0.62
	1.8904	0.61

3.27 min EBCT

	Years in Service	Ceff/Cinf
Lab-scale	6	0.84
Columns	3.93	0.8
C_{inf}=50 ng/L	2.99	0.735
	1.8904	0.58
	0.9945	0.58
	0.2110	0.35
	0	0.18
G&H	0.1667	0.28
Pilot study	0.9945	0.63
	1.8904	0.68

2-DAY PERCENT MIB BREAKTHROUGH FOR A CONTINUOUSLY OPERATED DEIONIZED-DISTILLED WATER LABORATORY-SCALE GAC COLUMN (50 NG/L 2-DAY PULSES; 3.3 MIN EBCT)

Bed Vol	Ceff/Cinf
4962	0.080
8174	0.088
13876	0.082
18079	0.090

2-DAY PERCENT MIB BREAKTHROUGH IN CHICAGO CRIB WATER FOR DIFFERENT GAC BED DIMENSIONS (1 YEAR PRELOAD)

Col Dia (cm)	Bed Depth (cm)	EBCT (min)	Ceff/Cinf
1	0.88	2.35	0.67
	0.88	3.50	0.56
	0.84	2.29	0.64
	1.15	3.13	0.57
	3.3	8.69	0.22
	3.3	13.15	0.10
	3.3	2.59	0.63
2.5	1.9	13.56	0.13
	1.9	7.49	0.29
	1.9	4.51	0.45

2-DAY PERCENT MIB BREAKTHROUGH IN CHICAGO CRIB WATER FOR DIFFERENT GAC PARTICLE SIZE FRACTIONS (2 YEAR PRELOAD)

GAC size	EBCT	Ceff/Cinf
12x14	4.3	0.47
	2.7	0.62
	2.0	0.77
Unsieved	4.3	0.53
	2.9	0.65
	2.0	0.78

2-DAY PERCENT MIB BREAKTHROUGH IN CHICAGO CRIB WATER FOR GAC PREREACTED WITH FREE CHLORINE

Cl2:GAC	Ceff/Cinf
0:1	0.19
0.15:1	0.36
0.3:1	0.59

EFFLUENT MIB CONCENTRATION FROM A GAC COLUMN WITH A VARIABLE INFLUENT MIB CONCENTRATION IN CHICAGO CRIB WATER (1 YEAR PRELOAD; 2.3 MIN EBCT)

Cinf (ng/L)	Time	Bed Vol	MIB (ng/L)
51.2	5/4/98 10:40	0.0	0.0
	5/4/98 10:48	3.5	0.7
	5/4/98 10:56	7.0	1.7
	5/4/98 11:04	10.6	1.6
	5/4/98 11:12	14.1	10.7
	5/4/98 11:20	17.6	17.4
	5/4/98 11:28	21.1	18.8
	5/4/98 11:36	24.6	19.0
	5/4/98 11:44	28.1	18.0
	5/4/98 11:52	31.7	19.5
	5/4/98 12:37	51.4	20.0
	5/4/98 14:30	101.1	24.3
	5/4/98 16:30	153.9	25.5
	5/4/98 18:00	193.5	24.5
	5/4/98 21:00	272.6	26.6
	5/5/98 4:00	457.3	28.8
	5/5/98 8:00	562.7	30.2
	5/5/98 9:00	589.1	31.7
	5/5/98 10:00	615.4	30.8
	5/5/98 11:20	650.5	30.7
	5/5/98 12:00	668.1	30.1
	5/5/98 15:00	747.2	29.7
	5/5/98 16:30	786.7	30.9
	5/5/98 17:30	813.1	33.0
	5/5/98 22:30	944.8	32.2
	5/6/98 3:30	1076.6	34.0
	5/6/98 7:00	1164.5	34.3
	5/6/98 7:05	1166.6	34.4
	5/6/98 7:30	1177.1	32.6
	5/6/98 8:10	1193.8	34.2
	5/6/98 8:20	1198.0	32.8
	5/6/98 9:00	1214.8	32.5
	5/6/98 9:16	1221.8	33.0
24.7	5/6/98 9:24	1225.3	27.1
	5/6/98 9:32	1228.8	26.6
	5/6/98 9:40	1232.4	23.5
	5/6/98 9:44	1234.1	25.2
	5/6/98 9:56	1239.4	23.5
	5/6/98 10:04	1242.9	21.4
	5/6/98 10:12	1246.4	23.5
	5/6/98 11:11	1272.4	19.8
	5/6/98 12:00	1294.0	19.2
	5/6/98 13:00	1320.4	17.9
	5/6/98 15:30	1386.4	18.5
	5/6/98 16:45	1419.4	18.5
	5/6/98 20:20	1514.0	17.0
	5/7/98 5:00	1742.8	17.2
	5/7/98 6:20	1778.0	17.5
	5/7/98 7:00	1795.6	18.0
	5/7/98 8:30	1835.3	17.6
	5/7/98 9:30	1861.7	18.2
	5/7/98 11:00	1901.3	18.3
	5/7/98 12:15	1934.4	18.5
	5/7/98 15:30	2020.3	17.6
	5/7/98 17:30	2073.1	18.9
	5/7/98 23:30	2231.7	18.5
	5/8/98 7:00	2429.9	18.4
	5/8/98 8:20	2464.9	18.9
	5/8/98 8:30	2469.2	17.9
	5/8/98 9:13	2488.0	18.9

100.3	5/8/98 9:21	2491.5	20.8
	5/8/98 9:29	2495.1	30.0
	5/8/98 9:37	2498.6	40.2
	5/8/98 9:45	2502.1	44.7
	5/8/98 9:53	2505.6	48.9
	5/8/98 10:37	2524.9	54.8
	5/8/98 11:30	2548.2	53.5
	5/8/98 13:30	2601.0	61.4
	5/8/98 14:20	2622.9	60.9
	5/8/98 15:00	2640.5	56.8
	5/8/98 16:00	2666.9	60.7
	5/8/98 22:30	2838.2	64.5
	5/9/98 8:30	3101.9	66.3
	5/9/98 9:40	3132.6	67.5
	5/9/98 11:00	3167.8	66.4
	5/9/98 12:10	3198.6	63.2
	5/9/98 14:30	3260.1	67.8
	5/10/98 0:00	3510.8	67.1
	5/10/98 10:00	3774.3	70.1
	5/10/98 10:45	3794.1	67.2
	5/10/98 11:00	3800.7	67.7
	5/10/98 12:00	3827.0	67.8
	5/10/98 12:08	3830.5	66.0

EFFLUENT MIB CONCENTRATION FROM A GAC COLUMN WITH A VARIABLE INFLUENT MIB CONCENTRATION IN CHICAGO CRIB WATER (1 YEAR PRELOAD; 3.1 MIN EBCT)

inf (ng/L)	Time	Bed Vol	MIB (ng/L)
25.1	6/1/98 13:26	0.0	0.0
	6/1/98 13:30	1.3	3.6
	6/1/98 13:38	3.8	2.3
	6/1/98 13:46	6.4	2.2
	6/1/98 13:54	8.9	2.3
	6/1/98 14:02	11.5	3.5
	6/1/98 14:10	14.0	4.3
	6/1/98 16:00	49.1	8.3
	6/1/98 16:08	51.7	9.1
	6/1/98 16:30	58.7	6.8
	6/1/98 17:00	68.3	9.0
	6/1/98 23:52	199.7	10.5
	6/2/98 0:00	202.2	9.3
	6/2/98 0:30	211.8	11.0
	6/2/98 1:00	221.4	14.1
	6/2/98 8:30	364.9	10.2
	6/2/98 9:30	384.0	11.1
	6/2/98 10:00	393.6	11.3
	6/2/98 12:30	441.5	11.5
	6/2/98 13:50	467.0	11.0
	6/2/98 14:30	479.7	12.1
	6/2/98 15:00	489.3	12.6
	6/2/98 16:00	508.4	12.5
	6/2/98 16:30	518.0	12.7
	6/2/98 22:45	637.6	11.6
	6/2/98 23:00	642.4	11.8
	6/2/98 23:30	652.0	13.5
	6/3/98 0:30	671.1	13.4
	6/3/98 0:45	675.9	12.0
	6/3/98 1:00	680.7	12.5
	6/3/98 8:30	824.2	12.4
	6/3/98 8:38	826.8	12.6
	6/3/98 8:50	830.6	13.9
	6/3/98 9:20	840.2	13.2
	6/3/98 10:00	852.9	13.7
	6/3/98 10:30	862.5	13.4
	6/3/98 12:30	900.8	13.0
	6/3/98 13:26	918.6	14.7
	6/3/98 13:34	921.2	14.6
51.2	6/3/98 13:42	923.7	16.2
	6/3/98 13:50	926.3	18.4
	6/3/98 13:58	928.9	19.1
	6/3/98 15:45	963.0	21.4
	6/3/98 15:53	965.5	22.5
	6/3/98 16:01	968.1	22.6
	6/3/98 16:45	982.1	21.4
	6/3/98 18:00	1006.0	23.4
	6/3/98 20:00	1044.3	24.3
	6/4/98 0:15	1125.7	24.5
	6/4/98 1:00	1140.0	23.9
	6/4/98 2:00	1159.2	24.5
	6/4/98 8:45	1288.4	25.8
	6/4/98 10:00	1312.3	26.3
	6/4/98 15:20	1414.4	25.2
	6/4/98 15:45	1422.4	25.7
	6/4/98 17:30	1455.9	26.6
	6/4/98 18:30	1475.0	24.4
	6/4/98 23:30	1570.8	26.6
	6/4/98 23:38	1573.3	27.4
	6/5/98 0:30	1589.9	25.5
	6/5/98 7:30	1723.9	26.0
	6/5/98 9:30	1762.2	28.1
	6/5/98 10:30	1781.4	26.6
	6/5/98 12:00	1810.2	27.2
	6/5/98 12:15	1815.0	26.7
	6/5/98 12:30	1819.8	26.1
	6/5/98 13:26	1837.7	28.9

100.5	6/5/98 13:34	1840.2	32.2
	6/5/98 13:42	1842.8	35.9
	6/5/98 13:50	1845.4	39.7
	6/5/98 13:58	1847.9	42.3
	6/5/98 15:45	1882.0	44.0
	6/5/98 15:53	1884.6	44.4
	6/5/98 16:01	1887.1	44.6
	6/5/98 16:45	1901.2	46.3
	6/5/98 18:00	1925.1	48.0
	6/5/98 20:00	1963.4	49.7
	6/6/98 0:15	2044.7	55.7
	6/6/98 1:00	2059.1	52.5
	6/6/98 2:00	2078.2	48.5
	6/6/98 8:45	2207.4	53.6
	6/6/98 10:00	2231.3	53.3
	6/6/98 12:00	2269.6	53.9
	6/6/98 15:20	2333.4	56.4
	6/6/98 15:45	2341.4	54.4
	6/6/98 17:30	2374.8	55.1
	6/6/98 18:30	2394.0	54.9
	6/6/98 23:30	2489.7	55.5
	6/6/98 23:38	2492.2	55.4
	6/7/98 4:30	2585.4	55.8
	6/7/98 7:30	2642.8	56.3
	6/7/98 9:30	2681.1	55.7
	6/7/98 10:30	2700.2	57.0
	6/7/98 13:00	2748.0	55.6
	6/7/98 14:00	2767.2	47.7
	6/7/98 15:00	2786.3	56.5
	6/7/98 16:00	2805.5	55.8
	6/7/98 16:40	2818.2	57.2

KINETIC GAC DATA IN CHICAGO CRIB WATER

SBA	ime (min)	IB (ng/L)
	0.2	2.0
Virgin	0.5	2.8
30x40	0.8	2.2
(596.8 mg)	1.2	2.8
	1.5	5.3
Flow rate	1.8	7.6
7.76 mL/min	2.2	9.9
	2.5	13.2
Cinf	2.8	10.6
110.2 ng/L	3.2	12.0
	3.5	13.3
	3.8	12.9
	4.2	11.5
	4.5	11.8
	4.8	15.1
	10.0	15.8
	20.0	16.5
	30.0	21.9
	40.0	21.9
	50.0	24.5
	60.0	25.4
	75.0	27.1
	75.3	28.5
	90.0	31.3
	90.3	30.2
	105.0	32.1
	105.3	33.1
	120.0	32.9
	120.3	33.8
	145.0	37.0
	145.3	38.0
	210.0	42.4
	210.3	43.7
	240.0	45.3
	240.3	44.8
	270.0	45.3
	270.3	46.0
	285.0	45.1
	285.3	45.4
	315.0	51.1
	315.3	47.8
	345.0	53.8
	345.3	49.5
	375.0	53.4
	375.3	52.9
	405.0	55.4
	405.3	52.5
	435.0	52.2
	435.3	54.6
	465.0	55.9
	465.3	52.5
	495.0	55.0
	495.3	54.2
	525.0	55.5
	525.3	58.6
	555.0	59.2
	555.3	55.2
	585.0	59.6
	585.3	57.6
	595.0	61.6
	595.3	60.3

Batch	ime (min)	IB (ng/L)
	0.0	219.8
Virgin	5.0	214.8
20x25	15.0	203.6
(268.5 mg)	29.9	198.0
	44.8	188.5
Co	63.7	181.6
219.8 ng/L	123.5	164.5
	178.0	152.5
	235.0	140.7
	295.0	131.5
	360.0	121.8
	441.0	117.2
	515.0	106.5

SBA	ime (min)	IB (ng/L)
	0.0	0.9
Virgin	5.0	3.9
20x25	10.0	4.0
(501.7 mg)	15.0	2.1
	20.0	2.2
Flow rate	25.0	6.0
.28 mL/min	30.0	3.0
	35.0	4.3
Cinf	40.0	5.6
53.3 ng/L	45.0	4.7
	50.0	7.0
	55.0	6.2
	60.0	7.4
	65.0	6.6
	73.0	6.0
	80.0	6.9
	85.0	6.2
	90.0	5.2
	270.0	7.7
	342.0	8.8
	462.0	8.8
	707.0	9.4
	952.0	8.5
	959.0	9.7
	964.0	8.6
	1062.0	8.9
	1187.0	9.7
	1427.0	8.1
	1507.0	9.3
	1795.0	8.2
	1800.0	8.6
	1842.0	10.7
	2174.0	9.6
	2534.0	8.8
	2539.0	10.2
	2546.0	10.1
	2683.0	8.0
	2688.0	9.9
	3027.0	9.7
	3032.0	8.0
	3086.0	8.4
	3091.0	8.7

MIB SINGLE-SOLUTE FREUNDLICH PARAMETERS FROM GAC ISOTHERMS

25 day

GAC	K (ng/mg)(L/ng)^(1/n)	1/n
Virgin	2.8072	0.8228
Hammond - 1 yr	0.23118	0.5365
Michigan City - 2 yr	0.0099	1.0352

125 day

GAC	K (ng/mg)(L/ng)^(1/n)	1/n
Virgin	8.7383	0.7459
Hammond - 1 yr	0.4126	0.6471
Michigan City - 2 yr	0.4602	0.5882

EBC SINGLE-SOLUTE FREUNDLICH PARAMETERS FROM GAC ISOTHERMS

Based on 125 day

EBC	Virgin	1 yr	2 yr
K (mg/g)(L/ug)^(1/n)	23.48857	0.11181225	0.005322366
1/n	0.01710	0.7963007	0.84143995
Co (ug/L)	0.45270	6.9036	78.920173
K (mmol/g)(L/umol)^(1/n	0.026433217	0.027377355	0.001780019
1/n	0.01710	0.79630	0.84144
Co (umol/L)	0.000452697	0.0069036	0.078920173

Based on 25 day

EBC	Virgin
K (mg/g)(L/ug)^(1/n)	0.01495
1/n	0.00664
Co (ug/L)	0.10589
K (mmol/g)(L/umol)^(1/n	1.56544E-05
1/n	0.00664
Co (umol/L)	0.000105886

MIB PSEUDO SINGLE-SOLUTE FREUNDLICH PARAMETERS FOR GAC LABORATORY-SCALE COLUMNS

IAST	Cc (mg)	Ce (ng/L)	qe (ng/mg)	(ng/mg)(L/ng)^(1/n	(mg/g)(L/ug)^(1/n)
Virgin - 125	0	53.29	0.37	0.0191	0.00330
	501.7	0.29	0.11	0.2769	0.04787
Virgin - 25	0	53.29	0.53	0.0201	0.00592
	501.7	1.32	0.1	0.0796	0.02340
1 yr - 125	0	51.67	1.56	0.1215	0.01061
	356.3	0.80	0.14	0.1617	0.01413
1 yr - 125	0	25.09	0.76	0.0944	0.00825
	356.3	0.38	0.07	0.1309	0.01144
1 yr - 125	0	100.47	3.01	0.1524	0.01332
	356.3	1.61	0.28	0.2057	0.01797
2 yr -125	0	51.67	1.98	0.1945	0.01131
	419.5	1.82	0.12	0.0844	0.00491

PHYSICAL CHARACTERISTICS OF GACs USED

Hg Porisimitry	keletal Density (g/mL	article Porosity	Particle Density
Virgin	1.3004	0.3916	0.79116336
1 yr	1.5886	0.3814	0.98270796
2 yr	1.5492	0.3947	0.93773076

He Pycnometry	keletal Density (g/mL)
Virgin	2.012
1 yr	1.66516
2 yr	1.7271

COMPARISON OF CARBON BRANDS IN HOPE VALLEY RESERVOIR WATER (DATA PROVIDED BY GAYLE NEWCOMBE)

Activated Carbon Brand (13.3 mg/L)	Ce (ng/L) [Co = 98 ng/L]	Ce (ng/L) [Co = 39 ng/L]
Cecarbon	50	19
Calgon WPL	25	9
Australian Prototype	22	7
ASTM M325 from Haycarb	44	15
Picatif PCO	38	12
picazine	76	27
Nuchar SA, Westvaco	54	18
Norit W20	83	34
Calgon F400	18	6
Hydrodarco	67	24

EFFECT OF INITIAL CONCENTRATION IN MYPONGA RESEVOIR WATER (DATA PROVIDED BY GAYLE NEWCOMBE)

P1100	MIB	
(13.3 mg/L)	Co (ng/L)	Ce (ng/L)
	45.0	10.8
	205.0	32.8
	971.0	174.8
	1925.0	442.8
	1679.0	284
	3366.8	590
	5196.4	972
	8406.0	1576
	10021.3	2020
	10780.3	2450
	13370.1	3000
	16299.4	3850
	25763.8	5300
	33120.0	6800
	43997.2	12400
	65999.5	19650
	99013.0	25818

P1300	MIB	
(13.3 mg/L)	Co (ng/L)	Ce (ng/L)
	45.0	3.2
	206.0	16.5
	970.0	77.6
	1917.0	172.5
	3163.9	295
	4572.4	506
	6330.3	632
	7743.2	900
	10908.9	1210
	14333.7	1200
	18586.9	1650
	22824.3	2400
	33125.9	2700
	40482.2	3700
	47841.2	4400
	44008.8	5700
	66006.6	8550
	88009.6	11300
	139722.2	17400
	177829.8	24200

GREELEY AND HANSEN PILOT STUDY MIB DATA

	MIB Concentration (ng/L)				
Started 6/20/96	Raw	Virgin	1 yr old	2 yr old	EBCT (min)
7/1/96					4.36
7/3/96					4.36
7/8/96					3.27
7/10/96					3.27
7/15/96	8.6		7.5	5.1	2.62
7/17/96	7.0				2.62
7/22/96	8.3		9.7	6.8	4.36
7/24/96	12.0		8.7	8.8	4.36
7/29/96	12.0		6.1	8.8	3.27
7/31/96	17.0		5.3	6.6	3.27
8/5/96			10.0	15.0	2.62
8/7/96	14.0	5.3	5.8	8.3	2.62
8/12/96	42.0		17.0	21.0	4.36
8/14/96	52.0	7.1	22.0	26.0	4.36
8/19/96	27.0	10.0	24.0	26.0	3.27
8/21/96	29.0	7.9	19.0	18.0	3.27
8/26/96	16.0	9.8	18.0	15.0	2.62
8/28/96	13.0	8.5	11.0	11.0	2.62
9/3/96	31.0	6.5	21.0	22.0	4.36
9/4/96	64.0	7.4	19.0	26.0	4.36
9/9/96	26.0	6.1	17.0	15.0	3.27
9/11/96	38.0	17.0	28.0	31.0	3.27
9/16/96	28.0	15.0	24.0	29.0	2.62
9/18/96	19.0	27.0	27.0	24.0	2.62

Appendix C (Input/Output Files)

EBC OUTPUT FILES

```
                          Watercarb PAC

 PARAMETER #      1 == K  ; IG:    100.000000000000000
 PARAMETER #      2 == 1/n ; IG:     1.000000000000000
 PARAMETER #      3 == Co  ; IG:  10000.000000000000000
      3      10
EBC
 K  =   .33178046E+04 (mg/g)(ug/L)^-1/n
 1/n =   .49304968E+00
 C0  =   .34048691E+02 ug/L
 MW  =    .10000000E+04 g/mol
TARGET COMPOUND
 K  =   .28652000E+00 (mg/g)(ug/L)^-1/n
 1/n =   .49220000E+00
 C0  =   .15000000E+00 ug/L
 C0  =   .12452000E+01 ug/L
 MW  =    .16800000E+03 g/mol
   h2o-lo.dat  Co =  149.1 ng/L
   h2o-hi.dat  Co = 1245.2 ng/L
no,      Q-obs    Q-cal        C-obs    C-cal        AC-dose
Q( 1) = .2458E-02 .2441E-02 mg/g .1800E-02 .2787E-02 ug/l .6030E+02 mg/l
Q( 2) = .3577E-02 .3577E-02 mg/g .6200E-02 .6200E-02 ug/l .4020E+02 mg/l
Q( 3) = .7582E-02 .7692E-02 mg/g .3930E-01 .3770E-01 ug/l .1460E+02 mg/l
Q( 4) = .9050E-02 .6710E-02 mg/g .1138E+00 .1232E+00 ug/l .4000E+01 mg/l
Q( 5) = .9381E-02 .3983E-02 mg/g .1303E+00 .1416E+00 ug/l .2100E+01 mg/l
Q( 1) = .2617E-01 .2621E-01 mg/g .4910E-01 .4723E-01 ug/l .4570E+02 mg/l
Q( 2) = .3430E-01 .3563E-01 mg/g .1340E+00 .9094E-01 ug/l .3240E+02 mg/l
Q( 3) = .5736E-01 .6932E-01 mg/g .6773E+00 .5589E+00 ug/l .9900E+01 mg/l
Q( 4) = .5544E-01 .5501E-01 mg/g .1018E+01 .1020E+01 ug/l .4100E+01 mg/l
Q( 5) = .4641E-01 .3411E-01 mg/g .1143E+01 .1170E+01 ug/l .2200E+01 mg/l
F( 1) =   .74240E+00
F( 2) =   .16470E-03
F( 3) =   .21359E+00
F( 4) =   .33242E+00
F( 5) =   .34817E+00
F( 6) =   .20891E+00
F( 7) =   .67183E+00
F( 8) =   .72938E+00
```

```
F( 9) =    .83444E-01
F(10) =    .32458E+00
Error sum of squares =    .19678E+00
```

Hydrodarco-B PAC

```
PARAMETER #        1 == K  ; IG:     100.000000000000000
 PARAMETER #        2 == 1/n ; IG:      1.000000000000000
 PARAMETER #        3 == Co  ; IG:   10000.000000000000000
       3       10
EBC
K  =   .14737048E+04 (mg/g)(ug/L)^-1/n
1/n =   .61053013E+00
C0  =   .41283323E+03 ug/L
MW  =    .10000000E+04 g/mol
TARGET COMPOUND
K  =   .12231800E+01 (mg/g)(ug/L)^-1/n
1/n =   .72110000E+00
C0  =   .14920000E+00 ug/L
C0  =   .16500000E+00 ug/L
MW  =    .16800000E+03 g/mol
   149.2
   165.0
no,       Q-obs    Q-cal        C-obs    C-cal        AC-dose
Q( 1) = .3746E-02 .3676E-02 mg/g .1600E-02 .4360E-02 ug/l .3940E+02 mg/l
Q( 2) = .9457E-02 .9577E-02 mg/g .1870E-01 .1704E-01 ug/l .1380E+02 mg/l
Q( 3) = .1246E-01 .2194E-01 mg/g .1006E+00 .6364E-01 ug/l .3900E+01 mg/l
Q( 4) = .1329E-01 .2579E-01 mg/g .1213E+00 .9504E-01 ug/l .2100E+01 mg/l
Q( 1) = .3730E-02 .3704E-02 mg/g .3100E-02 .4232E-02 ug/l .4340E+02 mg/l
Q( 2) = .5507E-02 .5475E-02 mg/g .6400E-02 .7330E-02 ug/l .2880E+02 mg/l
Q( 3) = .9867E-02 .9867E-02 mg/g .1700E-01 .1700E-01 ug/l .1500E+02 mg/l
Q( 4) = .1401E-01 .1632E-01 mg/g .5430E-01 .3604E-01 ug/l .7900E+01 mg/l
Q( 5) = .1737E-01 .2326E-01 mg/g .9030E-01 .6497E-01 ug/l .4300E+01 mg/l
Q( 6) = .2147E-01 .2879E-01 mg/g .1242E+00 .1103E+00 ug/l .1900E+01 mg/l
F( 1) =    .13327E+01
F( 2) =    .34584E+00
F( 3) =    .10272E+01
F( 4) =    .83971E+00
F( 5) =    .62147E+00
F( 6) =    .40315E+00
F( 7) =    .11427E-03
F( 8) =    .82219E+00
F( 9) =    .86698E+00
F(10) =    .60892E+00
Error sum of squares =    .60032E+00
```

Calgon F-300 (virgin)

```
PARAMETER #       1 == K  ; IG: 1.000000000000000E-001
 PARAMETER #      2 == 1/n ; IG: 3.000000000000000E-001
 PARAMETER #      3 == Co  ; IG:    100.000000000000000
      3      14
EBC
 K  =   .23488573E+02 (mg/g)(ug/L)^-1/n
 1/n =  .17097794E-01
 C0  =  .45269657E+00 ug/L
 MW  =   .10000000E+04 g/mol
TARGET COMPOUND
 K  =   .15105000E+01 (mg/g)(ug/L)^-1/n
 1/n =  .74590000E+00
 C0  =  .33974000E+00 ug/L
 C0  =  .33974000E+00 ug/L
 MW  =   .16800000E+03 g/mol
   virg125.dat
   virg125.dak
 no,    Q-obs   Q-cal       C-obs   C-cal       AC-dose
 Q( 1) = .3683E-01 .1461E-01 mg/g .2624E+00 .3091E+00 ug/l .2100E+01 mg/l
 Q( 2) = .2576E-01 .2576E-01 mg/g .1852E+00 .1852E+00 ug/l .6000E+01 mg/l
 Q( 3) = .2055E-01 .2548E-01 mg/g .1856E+00 .1486E+00 ug/l .7500E+01 mg/l
 Q( 4) = .1722E-01 .1967E-01 mg/g .1090E+00 .7612E-01 ug/l .1340E+02 mg/l
 Q( 5) = .1536E-01 .1536E-01 mg/g .4950E-01 .4950E-01 ug/l .1890E+02 mg/l
 Q( 6) = .1294E-01 .1264E-01 mg/g .2930E-01 .3644E-01 ug/l .2400E+02 mg/l
 Q( 7) = .9441E-02 .9165E-02 mg/g .1307E-01 .2262E-01 ug/l .3460E+02 mg/l
 Q( 1) = .3683E-01 .1461E-01 mg/g .2624E+00 .3091E+00 ug/l .2100E+01 mg/l
 Q( 2) = .2576E-01 .2576E-01 mg/g .1852E+00 .1852E+00 ug/l .6000E+01 mg/l
 Q( 3) = .2055E-01 .2548E-01 mg/g .1856E+00 .1486E+00 ug/l .7500E+01 mg/l
 Q( 4) = .1722E-01 .1967E-01 mg/g .1090E+00 .7612E-01 ug/l .1340E+02 mg/l
 Q( 5) = .1536E-01 .1536E-01 mg/g .4950E-01 .4950E-01 ug/l .1890E+02 mg/l
 Q( 6) = .1294E-01 .1264E-01 mg/g .2930E-01 .3644E-01 ug/l .2400E+02 mg/l
 Q( 7) = .9441E-02 .9165E-02 mg/g .1307E-01 .2262E-01 ug/l .3460E+02 mg/l
 F( 1) =   .75471E+00
 F( 2) =   .48823E-05
 F( 3) =   .71363E+00
 F( 4) =   .75974E+00
 F( 5) =   .18172E-03
 F( 6) =   .55089E+00
 F( 7) =   .90071E+00
 F( 8) =   .75471E+00
 F( 9) =   .48823E-05
 F(10) =   .71363E+00
 F(11) =   .75974E+00
 F(12) =   .18172E-03
```

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F(13) =    .55089E+00
F(14) =    .90071E+00
Error sum of squares =    .39583E+00
```

Calgon F-300 (1 year preload)

```
PARAMETER #        1 == K  ; IG:      1.000000000000000

PARAMETER #        2 == 1/n ; IG:  3.000000000000000E-001

PARAMETER #        3 == Co  ; IG:     100.000000000000000

      3        14
EBC
 K  =    .11181225E+00 (mg/g)(ug/L)^-1/n
 1/n =   .79630070E+00
 C0  =   .69036052E+01 ug/L
 MW  =    .10000000E+04 g/mol
TARGET COMPOUND
 K  =    .36040000E-01 (mg/g)(ug/L)^-1/n
 1/n =   .64710000E+00
 C0  =   .33974000E+00 ug/L
 C0  =   .33974000E+00 ug/L
 MW  =    .16800000E+03 g/mol
   ham125.dat
   ham125.dak
 no,     Q-obs    Q-cal        C-obs    C-cal        AC-dose
 Q( 1) = .4061E-02 .9535E-02 mg/g .3251E+00 .3054E+00 ug/l .3600E+01 mg/l
 Q( 2) = .1050E-01 .9340E-02 mg/g .2767E+00 .2837E+00 ug/l .6000E+01 mg/l
 Q( 3) = .8830E-02 .8830E-02 mg/g .2444E+00 .2444E+00 ug/l .1080E+02 mg/l
 Q( 4) = .8046E-02 .8231E-02 mg/g .2126E+00 .2097E+00 ug/l .1580E+02 mg/l
 Q( 5) = .9204E-02 .7847E-02 mg/g .1649E+00 .1906E+00 ug/l .1900E+02 mg/l
 Q( 6) = .6711E-02 .6855E-02 mg/g .1525E+00 .1485E+00 ug/l .2790E+02 mg/l
 Q( 7) = .5991E-02 .5991E-02 mg/g .1175E+00 .1175E+00 ug/l .3710E+02 mg/l
 Q( 1) = .4061E-02 .9535E-02 mg/g .3251E+00 .3054E+00 ug/l .3600E+01 mg/l
 Q( 2) = .1050E-01 .9340E-02 mg/g .2767E+00 .2837E+00 ug/l .6000E+01 mg/l
 Q( 3) = .8830E-02 .8830E-02 mg/g .2444E+00 .2444E+00 ug/l .1080E+02 mg/l
 Q( 4) = .8046E-02 .8231E-02 mg/g .2126E+00 .2097E+00 ug/l .1580E+02 mg/l
 Q( 5) = .9204E-02 .7847E-02 mg/g .1649E+00 .1906E+00 ug/l .1900E+02 mg/l
 Q( 6) = .6711E-02 .6855E-02 mg/g .1525E+00 .1485E+00 ug/l .2790E+02 mg/l
 Q( 7) = .5991E-02 .5991E-02 mg/g .1175E+00 .1175E+00 ug/l .3710E+02 mg/l
 F( 1) =    .39109E+00
 F( 2) =    .24055E+00
 F( 3) =    .15030E-04
 F( 4) =    .16605E+00
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F( 5) =    .52636E+00
F( 6) =    .21254E+00
F( 7) =    .82628E-04
F( 8) =    .39109E+00
F( 9) =    .24055E+00
F(10) =     .15030E-04
F(11) =     .16605E+00
F(12) =     .52636E+00
F(13) =     .21254E+00
F(14) =     .82628E-04
Error sum of squares =    .80087E-01
```

Calgon F-300 (2 year preload)

```
PARAMETER #          1 == K  ; IG:       1.000000000000000

PARAMETER #          2 == 1/n ; IG:  3.000000000000000E-001
PARAMETER #          3 == Co  ; IG:     100.000000000000000
        3          12
EBC
K  =    .53223659E-02 (mg/g)(ug/L)^-1/n
1/n =   .84143995E+00
C0  =    .78920173E+02 ug/L
MW  =     .10000000E+04 g/mol
TARGET COMPOUND
K  =    .26760000E-01 (mg/g)(ug/L)^-1/n
1/n =   .58820000E+00
C0  =    .33974000E+00 ug/L
C0  =    .33974000E+00 ug/L
MW  =     .16800000E+03 g/mol
   mich125.dat
   mich125.dak
no,       Q-obs    Q-cal         C-obs    C-cal          AC-dose
Q( 1) = .2650E-01 .9608E-02 mg/g .2470E+00 .3061E+00 ug/l .3500E+01 mg/l
Q( 2) = .6304E-02 .9333E-02 mg/g .3095E+00 .2949E+00 ug/l .4800E+01 mg/l
Q( 3) = .2676E-01 .9129E-02 mg/g .1845E+00 .2868E+00 ug/l .5800E+01 mg/l
Q( 4) = .8491E-02 .8491E-02 mg/g .2616E+00 .2616E+00 ug/l .9200E+01 mg/l
Q( 5) = .7178E-02 .7300E-02 mg/g .2184E+00 .2164E+00 ug/l .1690E+02 mg/l
Q( 6) = .5332E-02 .5332E-02 mg/g .1467E+00 .1467E+00 ug/l .3620E+02 mg/l
Q( 1) = .2650E-01 .9608E-02 mg/g .2470E+00 .3061E+00 ug/l .3500E+01 mg/l
Q( 2) = .6304E-02 .9333E-02 mg/g .3095E+00 .2949E+00 ug/l .4800E+01 mg/l
Q( 3) = .2676E-01 .9129E-02 mg/g .1845E+00 .2868E+00 ug/l .5800E+01 mg/l
Q( 4) = .8491E-02 .8491E-02 mg/g .2616E+00 .2616E+00 ug/l .9200E+01 mg/l
Q( 5) = .7178E-02 .7300E-02 mg/g .2184E+00 .2164E+00 ug/l .1690E+02 mg/l
Q( 6) = .5332E-02 .5332E-02 mg/g .1467E+00 .1467E+00 ug/l .3620E+02 mg/l
```

```
F( 1) =   .70626E+00
F( 2) =   .33278E+00
F( 3) =   .10014E+01
F( 4) =   .70650E-04
F( 5) =   .13602E+00
F( 6) =   .30580E-04
F( 7) =   .70626E+00
F( 8) =   .33278E+00
F( 9) =   .10014E+01
F(10) =   .70650E-04
F(11) =   .13602E+00
F(12) =   .30580E-04
Error sum of squares =    .27180E+00
```

IAST OUTPUT FILES

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                              Watercarb PAC

   PROPERTIES of COMPONENTS

COMPONENT    K (mg/g)(ug/L)**-1/n   1/n    CO (ug/l)  MW(dalton)

EBC           3.1985   .37386    21.004     1000.000

MIB           .28652   .49220    1.2452      168.000

    IAST PREDICTION

DOSAGE          EBC                MIB

(mg/l)    C ug/l   q mg/g    C ug/l   q mg/g

 .00    21.0     9.91      1.24520    .03286
 .05    20.5     9.82      1.24354    .03312
 .10    20.0     9.73      1.24186    .03338
 .15    19.6     9.64      1.24015    .03364
 .20    19.1     9.56      1.23842    .03390
 .25    18.6     9.47      1.23666    .03417
 .30    18.2     9.38      1.23487    .03444
 .40    17.3     9.21      1.23120    .03499
 .50    16.5     9.04      1.22743    .03555
 .60    15.7     8.87      1.22353    .03612
 .80    14.2     8.53      1.21537    .03729
1.00     12.8     8.21      1.20669    .03851
1.20     11.5     7.89      1.19749    .03976
1.50     9.86     7.43      1.18265    .04170
1.70     8.87     7.14      1.17205    .04303
2.00     7.57     6.72      1.15510    .04505
2.20     6.82     6.45      1.14310    .04641
2.40     6.14     6.19      1.13055    .04777
2.70     5.25     5.83      1.11074    .04980
3.00     4.51     5.50      1.08983    .05179
3.50     3.52     5.00      1.05283    .05496
4.00     2.78     4.56      1.01368    .05788
5.00     1.80     3.84       .93160    .06272
6.00     1.22     3.30       .84857    .06611
8.00     .637     2.55       .69322    .06900
10.00     .375     2.06       .56236    .06828
12.50     .218     1.66       .43498    .06482
15.00     .138     1.39       .34090    .06029
```

```
 20.00   .667E-01  1.05       .21982     .05127
 30.00   .233E-01  .699       .10875     .03788
 50.00   .605E-02  .420       .04122     .02408
 70.00   .247E-02  .300       .02121     .01749
100.00    .955E-03  .210       .01038     .01235
200.00    .150E-03  .105       .00256     .00621


                         Hydrodarco-B PAC

      PROPERTIES of COMPONENTS

COMPONENT    K (mg/g)(ug/L)**-1/n  1/n    CO (ug/l)  MW(dalton)

 EBC             1473.7    .61053    412.83     1000.000

 MIB             1.2232    .72110    1.0000      168.000

       IAST PREDICTION

DOSAGE          EBC               MIB

  (mg/l)    C ug/l    q mg/g    C ug/l    q mg/g

   .00    413.       .583E+05  1.00000     .03003
   .05    15.8       .794E+04   .99677     .06471
   .10    5.29       .408E+04   .99167     .08332
   .15    2.75       .273E+04   .98551     .09663
   .20    1.72       .206E+04   .97857     .10714
   .25    1.20       .165E+04   .97104     .11584
   .30    .891       .137E+04   .96303     .12324
   .40    .557       .103E+04   .94590     .13524
   .50    .387       825.      .92772     .14457
   .60    .287       688.      .90883     .15195
   .80    .179       516.      .86997     .16254
  1.00     .124      413.       .83081     .16919
  1.20     .924E-01  344.        .79227     .17311
  1.50     .641E-01  275.        .73680     .17547
  1.70     .522E-01  243.        .70181     .17541
  2.00     .400E-01  206.        .65264     .17368
  2.20     .343E-01  188.        .62213     .17176
  2.40     .297E-01  172.        .59339     .16942
  2.70     .245E-01  153.        .55348     .16538
  3.00     .206E-01  138.        .51718     .16094
  3.50     .160E-01  118.        .46384     .15319
  4.00     .129E-01  103.        .41825     .14544
```

5.00	.894E-02	82.6	.34542	.13092
6.00	.664E-02	68.8	.29072	.11821
8.00	.414E-02	51.6	.21574	.09803
10.00	.288E-02	41.3	.16798	.08320
12.50	.200E-02	33.0	.12905	.06968
15.00	.148E-02	27.5	.10320	.05979
20.00	.925E-03	20.6	.07169	.04642
30.00	.476E-03	13.8	.04216	.03193
50.00	.206E-03	8.26	.02122	.01958
70.00	.119E-03	5.90	.01341	.01409
100.00	.663E-04	4.13	.00822	.00992
200.00	.213E-04	2.06	.00316	.00498

Calgon F-300 (virgin)

PROPERTIES of COMPONENTS

COMPONENT	K (mg/g)(ug/L)**-1/n	1/n	CO (ug/l)	MW(dalton)
EBC	23.489	.17098E-01	.45270	1000.000
MIB	1.5105	.74590	.53290E-01	168.000

IAST PREDICTION

DOSAGE	EBC		MIB	
(mg/l)	C ug/l	q mg/g	C ug/l	q mg/g
.00	.453	23.2	.05329	.00037
.05	.610E-24	9.05	.05326	.00051
.10	.151E-41	4.53	.05323	.00064
.15	.759E-52	3.02	.05318	.00074
.20	.374E-59	2.26	.05313	.00081
.25	.803E-65	1.81	.05307	.00088
.30	.188E-69	1.51	.05301	.00093
.40	.927E-77	1.13	.05288	.00103
.50	.199E-82	.905	.05273	.00111
.60	.466E-87	.754	.05258	.00118
.80	.230E-94	.566	.05225	.00130
1.00	.495-100	.453	.05189	.00140

1.20	.116-104	.377	.05151	.00148
1.50	.250-110	.302	.05090	.00159
1.70	.166-113	.266	.05047	.00166
2.00	.124-117	.226	.04980	.00174
2.20	.471-120	.206	.04934	.00180
2.40	.291-122	.189	.04887	.00184
2.70	.298-125	.168	.04815	.00191
3.00	.629-128	.151	.04740	.00196
3.50	.770-132	.129	.04614	.00204
4.00	.315-135	.113	.04485	.00211
5.00	.686-141	.905E-01	.04225	.00221
6.00	.163-145	.754E-01	.03968	.00227
8.00	.830-153	.566E-01	.03481	.00231
10.00	.184-158	.453E-01	.03050	.00228
12.50	.409-164	.362E-01	.02597	.00219
15.00	.985-169	.302E-01	.02231	.00207
20.00	.507-176	.226E-01	.01697	.00182
30.00	.269-186	.151E-01	.01093	.00141
50.00	.298-199	.905E-02	.00593	.00095
70.00	.862-208	.647E-02	.00388	.00071
100.00	.761-217	.453E-02	.00245	.00051
200.00	.191-234	.226E-02	.00098	.00026
268.50	.633-242	.169E-02	.00066	.00020
500.10	.101-257	.905E-03	.00029	.00011
500.40	.976-258	.905E-03	.00029	.00011
501.00	.910-258	.904E-03	.00029	.00011
501.70	.839-258	.902E-03	.00029	.00011
593.90	.435-262	.762E-03	.00023	.00009
596.80	.327-262	.759E-03	.00023	.00009
786.40	.322-269	.576E-03	.00016	.00007

Calgon F-300 (1 year preload)

PROPERTIES of COMPONENTS

COMPONENT	K (mg/g)(ug/L)**-1/n	1/n	CO (ug/l)	MW(dalton)
EBC	.11181	.79630	6.9036	1000.000

```
MIB          .36040E-01 .64710    .51670E-01   168.000

IAST PREDICTION

DOSAGE        EBC            MIB

 (mg/l)   C ug/l   q mg/g   C ug/l   q mg/g

  .00    6.90     .517      .05167    .00156
  .05    6.88     .515      .05159    .00156
  .10    6.85     .514      .05151    .00156
  .15    6.83     .512      .05144    .00156
  .20    6.80     .511      .05136    .00156
  .25    6.78     .509      .05128    .00156
  .30    6.75     .508      .05120    .00156
  .40    6.70     .505      .05104    .00156
  .50    6.65     .502      .05089    .00156
  .60    6.60     .499      .05073    .00156
  .80    6.51     .493      .05042    .00156
 1.00    6.42     .487      .05011    .00156
 1.20    6.33     .482      .04979    .00156
 1.50    6.19     .474      .04933    .00156
 1.70    6.11     .468      .04901    .00156
 2.00    5.98     .461      .04855    .00156
 2.20    5.90     .456      .04824    .00156
 2.40    5.82     .451      .04793    .00156
 2.70    5.71     .443      .04747    .00156
 3.00    5.59     .436      .04700    .00156
 3.50    5.42     .425      .04624    .00155
 4.00    5.25     .415      .04548    .00155
 5.00    4.93     .394      .04399    .00154
 6.00    4.65     .376      .04254    .00152
 8.00    4.15     .344      .03974    .00149
10.00     3.74     .316      .03711    .00146
12.50     3.32     .287      .03408    .00141
15.00     2.97     .262      .03132    .00136
20.00     2.43     .224      .02659    .00125
30.00     1.75     .172      .01966    .00107
50.00     1.08     .117      .01190    .00080
70.00     .755     .878E-01   .00801    .00062
100.00     .507     .640E-01   .00504    .00047
200.00     .224     .334E-01   .00189    .00025
268.50     .157     .251E-01   .00122    .00019
356.30     .111     .191E-01   .00080    .00014
500.10     .730E-01  .137E-01   .00048    .00010
500.40     .730E-01  .137E-01   .00048    .00010
501.00     .729E-01  .136E-01   .00048    .00010
```

```
501.70   .727E-01  .136E-01   .00047    .00010
593.90   .590E-01  .115E-01   .00037    .00009
596.80   .586E-01  .115E-01   .00036    .00009
786.40   .416E-01  .873E-02   .00024    .00007
```

Calgon F-300 (2 year preload)

```
     PROPERTIES of COMPONENTS


COMPONENT    K (mg/g)(ug/L)**-1/n  1/n    CO (ug/l)  MW(dalton)


 EBC           .53224E-02 .84144     78.920      1000.000


 MIB           .26760E-01 .58820     .51670E-01    168.000
      IAST PREDICTION

 DOSAGE         EBC              MIB

 (mg/l)    C ug/l   q mg/g    C ug/l   q mg/g    C ug/l   q mg/g

  .00    78.9     .203      .05167    .00198
  .05    78.9     .203      .05157    .00198
  .10    78.9     .203      .05147    .00197
  .15    78.9     .203      .05137    .00197
  .20    78.9     .203      .05128    .00196
  .25    78.9     .203      .05118    .00196
  .30    78.9     .203      .05108    .00196
  .40    78.8     .203      .05089    .00195
  .50    78.8     .203      .05070    .00194
  .60    78.8     .203      .05051    .00194
  .80    78.8     .203      .05013    .00192
 1.00     78.7     .203      .04976    .00191
 1.20     78.7     .203      .04939    .00190
 1.50     78.6     .203      .04885    .00188
 1.70     78.6     .203      .04850    .00187
 2.00     78.5     .203      .04797    .00185
 2.20     78.5     .203      .04763    .00184
```

2.40	78.4	.203	.04729	.00182
2.70	78.4	.203	.04679	.00181
3.00	78.3	.203	.04630	.00179
3.50	78.2	.203	.04550	.00176
4.00	78.1	.202	.04473	.00173
5.00	77.9	.202	.04326	.00168
6.00	77.7	.202	.04187	.00163
8.00	77.3	.201	.03933	.00154
10.00	76.9	.201	.03706	.00146
12.50	76.4	.200	.03454	.00137
15.00	75.9	.199	.03233	.00129
20.00	75.0	.197	.02860	.00115
30.00	73.1	.194	.02312	.00095
50.00	69.6	.187	.01649	.00070
70.00	66.3	.180	.01265	.00056
100.00	61.9	.170	.00922	.00042
200.00	50.3	.143	.00451	.00024
268.50	44.4	.129	.00320	.00018
356.30	38.3	.114	.00225	.00014
419.50	34.8	.105	.00182	.00012
500.10	31.1	.956E-01	.00144	.00010
500.40	31.1	.956E-01	.00144	.00010
501.00	31.1	.955E-01	.00144	.00010
501.70	31.0	.955E-01	.00144	.00010
593.90	27.6	.864E-01	.00114	.00009
596.80	27.5	.862E-01	.00113	.00008
786.40	22.2	.721E-01	.00076	.00006

HSDM INPUT/OUTPUT FILES

Watercarb PAC

IN:

```
0  1   1        /IPRC,IPRI,IPRO    (do not change)
1.7512D-04     /C0   (initial concentration in mg/L)
11.5385D-03    /CCONC (carbon concentration in g/l)
0.369030D-09   /DS    (surface diffusion coefficient in cm2/min)
1.000000D+13   /XKF   (film mass transfer coefficient in cm/min)
1.1146733D-2   /XK    (Freundlich K value in (mg/g)(ug/l)^-1/n)
0.2162         /XN    (Freundlich 1/n)
5.0D-04        /RADP  (particle radius in cm)
0.74D0         /RHOP  (particle density in g/cm3) (do not change for PAC)
10             /NCP              (do not change)
0.1D-04  2  2  /TOL,METH,MITER    (do not change)
1.0D-50        /DTINIT           (do not change)
1.5D0          /DTOUT  (time increment in min)
240.000D0      /TFINAL (final time in min)
10000          /ITMAX            (do not change)
```

Out:

```
C0   = .175120E-03        TFINAL           =       27.00  .734666
 CCONC =  .115385E-      .240000E+03               28.50  .729375
01                        NULL                      30.00  .724317
 CD   = .503930E+00         .00 1.000000            31.50  .719472
                           1.50  .924126            33.00  .714826
 DS   =  .36903E-09        3.00  .895187            34.50  .710364
 XKF  =  .10000E+14        4.50  .873973            36.00  .706075
 BIOT =  .41923E+15        6.00  .856734            37.50  .701947
 RADP =  .50000E-03        7.50  .842029            39.00  .697970
 RHOP =  .74000E+00        9.00  .829123            40.50  .694136
 XK   =  .49630E-01       10.50  .817574            42.00  .690437
 XN   =  .21620E+00       12.00  .807098            43.50  .686864
 TFAC =  .14761E-02       13.50  .797498            45.00  .683411
 NTOT =  11               15.00  .788627            46.50  .680071
 TOL  =   .100000E-04     16.50  .780378            48.00  .676840
 METH =  2                18.00  .772667            49.50  .673711
 MITER =  2               19.50  .765426            51.00  .670680
 DTINIT =    .100000E-    21.00  .758600            52.50  .667743
49                        22.50  .752146            54.00  .664895
 DTOUT              =     24.00  .746026            55.50  .662132
.150000E+01               25.50  .740208            57.00  .659451
```

58.50	.656848
60.00	.654320
61.50	.651865
63.00	.649479
64.50	.647159
66.00	.644904
67.50	.642711
69.00	.640577
70.50	.638501
72.00	.636480
73.50	.634513
75.00	.632598
76.50	.630734
78.00	.628918
79.50	.627149
81.00	.625426
82.50	.623747
84.00	.622111
85.50	.620517
87.00	.618963
88.50	.617448
90.00	.615971
91.50	.614532
93.00	.613128
94.50	.611759
96.00	.610424
97.50	.609122
99.00	.607853
100.50	.606614
102.00	.605406
103.50	.604228
105.00	.603078
106.50	.601956
108.00	.600862
109.50	.599794
111.00	.598752
112.50	.597736
114.00	.596744
115.50	.595776
117.00	.594831
118.50	.593910
120.00	.593010
121.50	.592132
123.00	.591275
124.50	.590439
126.00	.589623
127.50	.588826
129.00	.588049
130.50	.587290
132.00	.586549
133.50	.585826
135.00	.585121
136.50	.584432
138.00	.583759
139.50	.583103
141.00	.582462
142.50	.581837
144.00	.581226
145.50	.580630
147.00	.580048
148.50	.579480
150.00	.578926
151.50	.578384
153.00	.577856
154.50	.577340
156.00	.576837
157.50	.576345
159.00	.575865
160.50	.575397
162.00	.574939
163.50	.574493
165.00	.574057
166.50	.573631
168.00	.573216
169.50	.572810
171.00	.572414
172.50	.572028
174.00	.571651
175.50	.571282
177.00	.570923
178.50	.570571
180.00	.570229
181.50	.569894
183.00	.569567
184.50	.569248
186.00	.568937
187.50	.568633
189.00	.568336
190.50	.568046
192.00	.567764
193.50	.567487
195.00	.567218
196.50	.566955
198.00	.566698
199.50	.566447
201.00	.566202
202.50	.565962
204.00	.565729
205.50	.565501
207.00	.565278
208.50	.565061
210.00	.564849
211.50	.564641
213.00	.564439
214.50	.564242
216.00	.564049
217.50	.563861
219.00	.563677
220.50	.563497
222.00	.563322
223.50	.563151
225.00	.562984
226.50	.562821
228.00	.562662
229.50	.562507
231.00	.562355
232.50	.562207
234.00	.562062
235.50	.561921
237.00	.561783
238.50	.561649
240.00	.561517

Hydrodarco-B PAC

In:

```
0 1 1      /IPRC,IPRI,IPRO    (do not change)
1.7445D-04    /C0   (initial concentration in mg/L)
11.5385D-03   /CCONC (carbon concentration in g/l)
0.380000D-09  /DS   (surface diffusion coefficient in cm2/min)
1.000000D+13  /XKF  (film mass transfer coefficient in cm/min)
2.62498017D-2 /XK   (Freundlich K value in (mg/g)(ug/l)^-1/n)
0.3409        /XN   (Freundlich 1/n)
5.0D-04       /RADP  (particle radius in cm)
0.74D0        /RHOP  (particle density in g/cm3) (do not change for PAC)
10         /NCP           (do not change)
0.1D-04 2 2 /TOL,METH,MITER   (do not change)
1.0D-50       /DTINIT          (do not change)
1.5D0         /DTOUT  (time increment in min)
240.000D0     /TFINAL (final time in min)
10000         /ITMAX           (do not change)
```

Out:

```
C0   = .174450E-03            NULL                          33.00  .516881
 CCONC =  .115385E-              .00 1.000000               34.50  .510619
01                              1.50  .857824               36.00  .504647
 CD   = .957393E+00             3.00  .805903               37.50  .498944
                                4.50  .768709               39.00  .493491
 DS   =  .38000E-09             6.00  .739048               40.50  .488274
 XKF  =  .10000E+14             7.50  .714167               42.00  .483275
 BIOT =  .21430E+15             9.00  .692651               43.50  .478484
 RADP =  .50000E-03            10.50  .673665               45.00  .473887
 RHOP =  .74000E+00            12.00  .656664               46.50  .469473
 XK   =  .27658E+00            13.50  .641272               48.00  .465231
 XN   =  .34090E+00            15.00  .627216               49.50  .461154
 TFAC =  .15200E-02            16.50  .614291               51.00  .457231
 NTOT = 11                     18.00  .602335               52.50  .453455
 TOL  =    .100000E-04         19.50  .591224               54.00  .449818
 METH =  2                     21.00  .580855               55.50  .446313
 MITER =  2                    22.50  .571146               57.00  .442934
 DTINIT =    .100000E-         24.00  .562025               58.50  .439676
49                             25.50  .553433               60.00  .436532
 DTOUT              =          27.00  .545320               61.50  .433496
.150000E+01                    28.50  .537643               63.00  .430566
 TFINAL             =          30.00  .530365               64.50  .427736
.240000E+03                    31.50  .523454               66.00  .425001
```

67.50	.422358
69.00	.419803
70.50	.417333
72.00	.414943
73.50	.412632
75.00	.410395
76.50	.408230
78.00	.406134
79.50	.404105
81.00	.402140
82.50	.400237
84.00	.398393
85.50	.396607
87.00	.394877
88.50	.393200
90.00	.391575
91.50	.390000
93.00	.388473
94.50	.386993
96.00	.385558
97.50	.384166
99.00	.382817
100.50	.381509
102.00	.380239
103.50	.379008
105.00	.377814
106.50	.376656
108.00	.375532
109.50	.374442
111.00	.373384
112.50	.372358
114.00	.371362
115.50	.370396
117.00	.369459
118.50	.368549
120.00	.367666
121.50	.366810
123.00	.365978
124.50	.365172
126.00	.364389
127.50	.363629
129.00	.362891
130.50	.362176
132.00	.361481
133.50	.360807
135.00	.360152
136.50	.359517
138.00	.358900
139.50	.358301
141.00	.357720
142.50	.357156
144.00	.356608
145.50	.356077
147.00	.355560
148.50	.355059
150.00	.354573
151.50	.354101
153.00	.353642
154.50	.353197
156.00	.352765
157.50	.352345
159.00	.351938
160.50	.351543
162.00	.351159
163.50	.350786
165.00	.350424
166.50	.350073
168.00	.349732
169.50	.349401
171.00	.349079
172.50	.348767
174.00	.348464
175.50	.348170
177.00	.347885
178.50	.347607
180.00	.347338
181.50	.347077
183.00	.346823
184.50	.346576
186.00	.346337
187.50	.346105
189.00	.345879
190.50	.345660
192.00	.345448
193.50	.345241
195.00	.345041
196.50	.344846
198.00	.344657
199.50	.344473
201.00	.344295
202.50	.344122
204.00	.343954
205.50	.343791
207.00	.343632
208.50	.343479
210.00	.343329
211.50	.343184
213.00	.343043
214.50	.342906
216.00	.342774
217.50	.342645
219.00	.342519
220.50	.342398
222.00	.342280
223.50	.342165
225.00	.342054
226.50	.341946
228.00	.341841
229.50	.341739
231.00	.341640
232.50	.341544
234.00	.341450
235.50	.341360
237.00	.341272
238.50	.341186
240.00	.341103

Nuchar SA-20 PAC

In:

```
0 1 1       /IPRC,IPRI,IPRO    (do not change)
1.7509D-04    /C0   (initial concentration in mg/L)
9.00000D-03   /CCONC (carbon concentration in g/l)
0.355130D-09  /DS   (surface diffusion coefficient in cm2/min)
1.000000D+13  /XKF  (film mass transfer coefficient in cm/min)
3.9332237D-2  /XK   (Freundlich K value in (mg/g)(ug/l)^-1/n)
0.4176        /XN   (Freundlich 1/n)
5.0D-04       /RADP (particle radius in cm)
0.74D0        /RHOP (particle density in g/cm3) (do not change for PAC)
10            /NCP           (do not change)
0.1D-04 2 2 /TOL,METH,MITER   (do not change)
1.0D-50       /DTINIT          (do not change)
1.5D0         /DTOUT (time increment in min)
240.000D0     /TFINAL (final time in min)
10000         /ITMAX           (do not change)
```

Out:

```
C0   = .175090E-03          NULL                        33.00  .534285
 CCONC =  .900000E-           .00 1.000000              34.50  .528364
02                           1.50  .860750              36.00  .522718
 CD  = .976598E+00           3.00  .810360              37.50  .517326
                             4.50  .774429              39.00  .512170
 DS   = .35513E-09           6.00  .745869              40.50  .507237
 XKF  = .10000E+14           7.50  .721974              42.00  .502511
 BIOT = .17534E+15           9.00  .701356              43.50  .497979
 RADP = .50000E-03          10.50  .683197              45.00  .493630
 RHOP = .74000E+00          12.00  .666963              46.50  .489454
 XK   = .70396E+00          13.50  .652286              48.00  .485440
 XN   = .41760E+00          15.00  .638901              49.50  .481580
 TFAC = .14205E-02          16.50  .626605              51.00  .477865
 NTOT= 11                   18.00  .615244              52.50  .474288
 TOL  =   .100000E-04       19.50  .604693              54.00  .470841
 METH = 2                   21.00  .594856              55.50  .467518
 MITER= 2                   22.50  .585650              57.00  .464313
 DTINIT =    .100000E-      24.00  .577007              58.50  .461220
49                          25.50  .568869              60.00  .458235
 DTOUT              =       27.00  .561189              61.50  .455352
.150000E+01                 28.50  .553924              63.00  .452565
 TFINAL             =       30.00  .547038              64.50  .449873
.240000E+03                 31.50  .540501              66.00  .447270
```

67.50	.444752
69.00	.442317
70.50	.439960
72.00	.437679
73.50	.435470
75.00	.433331
76.50	.431259
78.00	.429252
79.50	.427307
81.00	.425421
82.50	.423593
84.00	.421821
85.50	.420102
87.00	.418435
88.50	.416818
90.00	.415250
91.50	.413728
93.00	.412251
94.50	.410817
96.00	.409426
97.50	.408076
99.00	.406765
100.50	.405492
102.00	.404256
103.50	.403056
105.00	.401890
106.50	.400758
108.00	.399659
109.50	.398591
111.00	.397554
112.50	.396546
114.00	.395567
115.50	.394615
117.00	.393691
118.50	.392793
120.00	.391920
121.50	.391073
123.00	.390249
124.50	.389448
126.00	.388671
127.50	.387915
129.00	.387180
130.50	.386466
132.00	.385772
133.50	.385097
135.00	.384442
136.50	.383805
138.00	.383185
139.50	.382583
141.00	.381998
142.50	.381429
144.00	.380876
145.50	.380339
147.00	.379816
148.50	.379308
150.00	.378815
151.50	.378334
153.00	.377868
154.50	.377414
156.00	.376973
157.50	.376544
159.00	.376127
160.50	.375722
162.00	.375328
163.50	.374945
165.00	.374572
166.50	.374210
168.00	.373858
169.50	.373516
171.00	.373183
172.50	.372860
174.00	.372545
175.50	.372239
177.00	.371942
178.50	.371653
180.00	.371372
181.50	.371098
183.00	.370833
184.50	.370574
186.00	.370323
187.50	.370079
189.00	.369841
190.50	.369610
192.00	.369386
193.50	.369167
195.00	.368955
196.50	.368749
198.00	.368548
199.50	.368353
201.00	.368163
202.50	.367978
204.00	.367799
205.50	.367624
207.00	.367455
208.50	.367290
210.00	.367129
211.50	.366973
213.00	.366821
214.50	.366674
216.00	.366530
217.50	.366391
219.00	.366255
220.50	.366123
222.00	.365995
223.50	.365870
225.00	.365749
226.50	.365631
228.00	.365516
229.50	.365405
231.00	.365297
232.50	.365191
234.00	.365089
235.50	.364989
237.00	.364892
238.50	.364798
240.00	.364706
241.50	.364617

WPH PAC

In:

```
0  1   1      /IPRC,IPRI,IPRO    (do not change)
1.7411D-04    /C0   (initial concentration in mg/L)
11.5385D-03   /CCONC (carbon concentration in g/l)
0.20778D-09   /DS   (surface diffusion coefficient in cm2/min)
1.000000D+13  /XKF   (film mass transfer coefficient in cm/min)
4.2080508D-2  /XK    (Freundlich K value in (mg/g)(ug/l)^-1/n)
0.3592        /XN    (Freundlich 1/n)
5.0D-04       /RADP  (particle radius in cm)
0.74D0        /RHOP  (particle density in g/cm3) (do not change for PAC)
10        /NCP              (do not change)
0.1D-04  2  2 /TOL,METH,MITER    (do not change)
1.0D-50       /DTINIT           (do not change)
1.5D0         /DTOUT  (time increment in min)
240.000D0     /TFINAL (final time in min)
10000         /ITMAX            (do not change)
```

Out:

```
CO    = .174110E-03          NULL                      33.00  .438869
 CCONC =  .115385E-           .00  1.000000             34.50  .431434
01                           1.50  .836167              36.00  .424331
 CD   = .148837E+01          3.00  .776214              37.50  .417538
                             4.50  .733108              39.00  .411032
 DS    =  .20778E-09         6.00  .698727              40.50  .404795
 XKF  =  .10000E+14          7.50  .669845              42.00  .398809
 BIOT  =  .25210E+15         9.00  .644837              43.50  .393060
 RADP  =  .50000E-03        10.50  .622742              45.00  .387531
 RHOP  =  .74000E+00        12.00  .602937              46.50  .382212
 XK    =  .50313E+00        13.50  .584986              48.00  .377089
 XN    =  .35920E+00        15.00  .568575              49.50  .372152
 TFAC  =  .83112E-03        16.50  .553467              51.00  .367392
 NTOT =  11                 18.00  .539479              52.50  .362798
 TOL   =    .100000E-04     19.50  .526464              54.00  .358362
 METH  =  2                 21.00  .514303              55.50  .354078
 MITER =  2                 22.50  .502901              57.00  .349935
 DTINIT =    .100000E-      24.00  .492178              58.50  .345929
49                          25.50  .482064              60.00  .342052
 DTOUT              =       27.00  .472503              61.50  .338299
.150000E+01                 28.50  .463444              63.00  .334664
 TFINAL             =       30.00  .454843              64.50  .331141
.240000E+03                 31.50  .446662              66.00  .327726
```

67.50	.324414
69.00	.321200
70.50	.318081
72.00	.315053
73.50	.312111
75.00	.309253
76.50	.306476
78.00	.303776
79.50	.301151
81.00	.298597
82.50	.296112
84.00	.293694
85.50	.291340
87.00	.289048
88.50	.286815
90.00	.284641
91.50	.282521
93.00	.280456
94.50	.278443
96.00	.276480
97.50	.274566
99.00	.272699
100.50	.270877
102.00	.269100
103.50	.267365
105.00	.265672
106.50	.264020
108.00	.262406
109.50	.260830
111.00	.259291
112.50	.257788
114.00	.256320
115.50	.254886
117.00	.253484
118.50	.252114
120.00	.250775
121.50	.249466
123.00	.248187
124.50	.246937
126.00	.245713
127.50	.244517
129.00	.243348
130.50	.242204
132.00	.241085
133.50	.239990
135.00	.238919
136.50	.237872
138.00	.236846
139.50	.235843
141.00	.234861
142.50	.233900
144.00	.232959
145.50	.232038
147.00	.231137
148.50	.230254
150.00	.229390
151.50	.228544
153.00	.227715
154.50	.226904
156.00	.226109
157.50	.225331
159.00	.224569
160.50	.223822
162.00	.223091
163.50	.222375
165.00	.221673
166.50	.220986
168.00	.220313
169.50	.219653
171.00	.219007
172.50	.218374
174.00	.217753
175.50	.217145
177.00	.216549
178.50	.215965
180.00	.215393
181.50	.214832
183.00	.214283
184.50	.213744
186.00	.213216
187.50	.212698
189.00	.212190
190.50	.211693
192.00	.211205
193.50	.210727
195.00	.210259
196.50	.209799
198.00	.209349
199.50	.208907
201.00	.208474
202.50	.208050
204.00	.207633
205.50	.207225
207.00	.206825
208.50	.206433
210.00	.206048
211.50	.205671
213.00	.205301
214.50	.204938
216.00	.204583
217.50	.204234
219.00	.203892
220.50	.203557
222.00	.203228
223.50	.202906
225.00	.202589
226.50	.202279
228.00	.201975
229.50	.201677
231.00	.201384
232.50	.201097
234.00	.200816
235.50	.200540
237.00	.200269
238.50	.200004
240.00	.199744

Cecarbon PAC

In:

```
0  1  1      /IPRC,IPRI,IPRO    (do not change)
1.7024D-04    /C0   (initial concentration in mg/L)
11.5385D-03   /CCONC (carbon concentration in g/l)
0.172720D-09  /DS   (surface diffusion coefficient in cm2/min)
1.000000D+13  /XKF  (film mass transfer coefficient in cm/min)
6.3553424D-2  /XK   (Freundlich K value in (mg/g)(ug/l)^-1/n)
0.3956        /XN   (Freundlich 1/n)
5.0D-04       /RADP (particle radius in cm)
0.74D0        /RHOP (particle density in g/cm3) (do not change for PAC)
10            /NCP            (do not change)
0.1D-04  2  2 /TOL,METH,MITER   (do not change)
1.0D-50       /DTINIT           (do not change)
1.5D0         /DTOUT  (time increment in min)
240.000D0     /TFINAL (final time in min)
10000         /ITMAX            (do not change)
```

Out:

```
C0   = .170240E-03          NULL                   33.00  .331793
 CCONC =  .115385E-           .00 1.000000         34.50  .324288
01                           1.50  .789472         36.00  .317168
 CD  = .213813E+01           3.00  .715149         37.50  .310402
                             4.50  .662451         39.00  .303966
 DS   = .17272E-09           6.00  .621069         40.50  .297836
 XKF  = .10000E+14           7.50  .586787         42.00  .291990
 BIOT = .21111E+15           9.00  .557465         43.50  .286410
 RADP =  .50000E-03         10.50  .531856         45.00  .281078
 RHOP =  .74000E+00         12.00  .509146         46.50  .275979
 XK   = .97710E+00          13.50  .488779         48.00  .271097
 XN   = .39560E+00          15.00  .470345         49.50  .266420
 TFAC =  .69088E-03         16.50  .453537         51.00  .261936
 NTOT = 11                  18.00  .438118         52.50  .257632
 TOL  =    .100000E-04      19.50  .423902         54.00  .253499
 METH =  2                  21.00  .410737         55.50  .249527
 MITER =  2                 22.50  .398499         57.00  .245706
 DTINIT =    .100000E-      24.00  .387083         58.50  .242030
49                          25.50  .376403         60.00  .238491
 DTOUT              =       27.00  .366385         61.50  .235080
.150000E+01                 28.50  .356966         63.00  .231792
 TFINAL             =       30.00  .348093         64.50  .228622
.240000E+03                 31.50  .339715         66.00  .225563
```

67.50	.222609
69.00	.219756
70.50	.216999
72.00	.214334
73.50	.211756
75.00	.209262
76.50	.206847
78.00	.204509
79.50	.202244
81.00	.200048
82.50	.197920
84.00	.195856
85.50	.193853
87.00	.191909
88.50	.190022
90.00	.188191
91.50	.186411
93.00	.184681
94.50	.183001
96.00	.181367
97.50	.179779
99.00	.178233
100.50	.176730
102.00	.175267
103.50	.173843
105.00	.172457
106.50	.171106
108.00	.169791
109.50	.168510
111.00	.167262
112.50	.166046
114.00	.164860
115.50	.163703
117.00	.162576
118.50	.161476
120.00	.160402
121.50	.159355
123.00	.158333
124.50	.157336
126.00	.156362
127.50	.155411
129.00	.154482
130.50	.153575
132.00	.152689
133.50	.151824
135.00	.150979
136.50	.150152
138.00	.149344
139.50	.148555
141.00	.147783
142.50	.147028
144.00	.146291
145.50	.145569
147.00	.144863
148.50	.144173
150.00	.143498
151.50	.142837
153.00	.142191
154.50	.141559
156.00	.140940
157.50	.140334
159.00	.139741
160.50	.139161
162.00	.138593
163.50	.138037
165.00	.137492
166.50	.136959
168.00	.136436
169.50	.135925
171.00	.135424
172.50	.134933
174.00	.134452
175.50	.133981
177.00	.133520
178.50	.133067
180.00	.132624
181.50	.132190
183.00	.131765
184.50	.131348
186.00	.130939
187.50	.130538
189.00	.130145
190.50	.129760
192.00	.129382
193.50	.129012
195.00	.128649
196.50	.128294
198.00	.127945
199.50	.127603
201.00	.127267
202.50	.126938
204.00	.126615
205.50	.126299
207.00	.125989
208.50	.125684
210.00	.125386
211.50	.125093
213.00	.124806
214.50	.124524
216.00	.124248
217.50	.123976
219.00	.123710
220.50	.123449
222.00	.123193
223.50	.122942
225.00	.122696
226.50	.122454
228.00	.122217
229.50	.121984
231.00	.121755
232.50	.121531
234.00	.121311
235.50	.121095
237.00	.120883
238.50	.120675
240.00	.120471
241.50	.120271

FS MODEL INPUT

Calgon F-300 (virgin)

```
(F-S)MODEL MIB Virgin 125 day isotherm pseudo single solute data and Ce = to Cinf
Hg skeletal density
 0.0033       / A  K  ((mg/g)(L/ug)**(1/n))
 0.7459       / B  1/n
 0.05329      / C0  Co  influent concentration (ug/L)
     12       / IR0 Initial division parameter, more than 10 recommended
 0.3614       / U   Approach velocity (cm/min)
 0.1545       / DIA Diameter of adsorbent (cm)- Ave for 12x14 size fraction is 0.1545
cm
 0.7912       / RS  Apparent particle density of adsorbent (g/cm**3)
 0.5323       / RB  Bulk density of bed (g/cm**3)
 3.9013400E-04  / AKF Kf  film transfer coefficient (cm/sec)
 1.6257934E-06  / DS  Surface diffusion coefficient (cm**2/sec)
    0.00      / DB  Dispersion coeffisient of flow through bed (cm**2/sec)
  1.00E-05    / DELT initial time step (hr)  DTMIN
   0.101      / DELTMX Maximum time step (hr)
DTMAX=MIN(DTMAX,DTMIN*10*N)
 51.6000      / TEND Total run time (hr)
     0.1      / DELZ Initial difference of bed depth (cm)
 1.20         / ZEND Total bed depth (cm)
 1.0          / DTUBE Diameter of column (cm)
     10       / IITM Frequency of output eg. 10 means 1 out of 10 time-steps
32            / NDATA Number of experimental data  //   less than 10 ignored
50.00  0.00699742    / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
55.00  0.006179173    / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
60.00  0.00738303    / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
65.00  0.006574189    / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
73.00  0.00597226    / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
80.00  0.006931584    / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
85.00  0.006160363
90.00  0.005191634
270.00 0.007721615
342.00 0.008784395
462.00 0.008784395
707.00 0.009442754
952.00 0.008483431
959.00 0.00965437
964.00 0.008596292
1062.00         0.008869041
```

1187.00	0.009668478
1427.00	0.0080602
1507.00	0.009282867
1795.00	0.008244493
1800.00	0.008640473
1842.00	0.010721902
2174.00	0.009645651
2534.00	0.008802926
2539.00	0.010204083
2546.00	0.010061937
2683.00	0.00799066
2688.00	0.009879177
3027.00	0.009706571
3032.00	0.007980507
3086.00	0.008354069
3091.00	0.008714404

Calgon F-300 (1 year preload)

(F-S)MODEL MIB Hammond 125 day isotherm pseudo single solute data and Ce = to Cinf Hg skeletal density

0.00825 / A K ((mg/g)(L/ug)**(1/n))
0.6471 / B 1/n
0.02509 / C0 Co influent concentration (ug/L)
12 / IR0 Initial division parameter, more than 10 recommended
0.3671 / U Approach velocity (cm/min)
0.1545 / DIA Diameter of adsorbent (cm)- Ave for 12x14 size fraction is 0.1545 cm
0.9827 / RS Apparent particle density of adsorbent (g/cm**3)
0.5653 / RB Bulk density of bed (g/cm**3)
2.9514371E-04 / AKF Kf film transfer coefficient (cm/sec)
1.3153105E-011 / DS Surface diffusion coefficient (cm**2/sec)
0.00 / DB Dispersion coeffisient of flow through bed (cm**2/sec)
1.00E-05 / DELT initial time step (hr) DTMIN
0.101 / DELTMX Maximum time step (hr) DTMAX=MIN(DTMAX,DTMIN*10*N)
45.000 / TEND Total run time (hr)
0.1 / DELZ Initial difference of bed depth (cm)
1.15 / ZEND Total bed depth (cm)
1.0 / DTUBE Diameter of column (cm)

```
    10      / IITM Frequency of output eg. 10 means 1 out of 10 time-steps
30          / NDATA Number of experimental data //   less than 10 ignored
154   0.008255592   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
162   0.009050663   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
184   0.006832832   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
214   0.009020773   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
626   0.010509291   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
634   0.009349562   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
664   0.011011441   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
694   0.014096079   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
1144  0.010180502   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
1204  0.011131001   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
1234  0.011346208   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
1384  0.011537503   / TDATAI(I) CDI(I)  Time(min)   Conc.(ug/L)
1464  0.011011441
1504  0.012135302
1534  0.012565716
1594  0.012535826
1624  0.012697232
1999  0.011612756
2014  0.011836403
2044  0.013462413
2104  0.013396656
2119  0.012039654
2134  0.012470069
2584  0.012434201
2592  0.012571694
2604  0.013862938
2634  0.013229272
2674  0.013731423
2704  0.013426545
2824  0.013031999
```

Calgon F-300 (2 year preload)

```
(F-S)MODEL MIB michigan city 125 day isotherm pseudo single solute data and Ce = to
Cinf Hg skeletal density
 0.01131       / A   K  ((mg/g)(L/ug)**(1/n))
 0.5882        / B   1/n
 0.05167       / C0  Co  influent concentration (ug/L)
     12      / IR0 Initial division parameter, more than 10 recommended
 0.3686        / U   Approach velocity (cm/min)
```

```
 0.1545        / DIA Diameter of adsorbent (cm)- Ave for 12x14 size fraction is 0.1545
cm
 0.9377        / RS  Apparent particle density of adsorbent (g/cm**3)
 0.5341        / RB  Bulk density of bed (g/cm**3)
 2.2296223E-04  / AKF Kf  film transfer coefficient (cm/sec)
 7.8588405E-012 / DS  Surface diffusion coefficient (cm**2/sec)
    0.00      / DB  Dispersion coeffisient of flow through bed (cm**2/sec)
  1.00E-05     / DELT initial time step (hr)  DTMIN
    0.101      / DELTMX Maximum time step (hr)
DTMAX=MIN(DTMAX,DTMIN*10*N)
 52            / TEND Total run time (hr)
     0.1       / DELZ Initial difference of bed depth (cm)
 1.00           / ZEND Total bed depth (cm)
 1.0           / DTUBE Diameter of column (cm)
      10       / IITM Frequency of output eg. 10 means 1 out of 10 time-steps
17             / NDATA Number of experimental data  //   less than 10 ignored
136     0.02449206    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
286     0.024050761    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
526     0.026674698    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
706     0.028463745    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
1066    0.029656443    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
1126    0.025893274    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
1246    0.028525985    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
1306    0.030100857    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
1546    0.030398003    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
1696    0.031729215    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
1786    0.031348869    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
2446    0.031741101    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
2506    0.031169743    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
2596    0.032694285    / TDATAI(I) CDI(I)  Time(min)    Conc.(ug/L)
2656    0.032051119
2688    0.03142346
2696    0.032199926
```

Appendix D (Computer Models)

EBC: EQUILIBRIUM PARAMETER SEARCH COMPUTER PROGRAM

```
C   PROGRAM EBCM
C
C  This program incorporates data from several isotherms to determine the
C  Freundlich parameters for the EBC.
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      REAL*8 MWS(10),MCS(10,50)
      CHARACTER*16 INPUT(10),OUTPUT
C
      COMMON PARS(50),QS(10,3,50),CES(10,3,50),
     &      XKS(10),XNS(10),C0(10,10),
     &      MCS,VS(10,50),NDS(10),NCS(10),SSQ,IPS(4),MWS,NDSETS
C
      COMMON /BLOCK2/QD(10,3,50),CD(10,3,50),CMEAN,ERRREL,ITMAX
C
      DIMENSION X(30),XGUESS(30),XSCALE(30),FSCALE(500),
     &        IPARAM(6),RPARAM(7),FVEC(500),FJAC(500,30),FDD(500)
C
      EXTERNAL FCN,LSJAC,DNEQBJ,DU4LSF
      EXTERNAL FS
C
      ERRREL=0.001
      ITMAX=100
C
      OPEN(UNIT=1,FILE='EBC.IN',STATUS='OLD')
C
      K=0
    5 CONTINUE
      K=K+1
C ****************************************************************
C  Read in the name of the data file
C ****************************************************************
      READ(1,1000) INPUT(K)
      IF (INPUT(K).NE.'NULL') THEN
       NDSETS=K
       GOTO 5
      ELSE
C ****************************************************************
C  Name of output file
C ****************************************************************
       READ(1,1000) OUTPUT
C        READ(1,*) (IPS(I),I=1,4)
      ENDIF
C
      DO 101 I=1,4
      IPS(I)=1
```

```
  101 CONTINUE
C
      WRITE(*,*) ' YOUR INPUT DATA FILES ARE:'
      WRITE(*,*) (INPUT(JJ),JJ=1,NDSETS)
      WRITE(*,*) ' YOUR OUTPUT DATA FILE IS:'
      WRITE(*,*) OUTPUT
C
      DO 45 JJ=1,NDSETS
C
       OPEN(JJ,FILE=INPUT(JJ),STATUS='OLD')
C
       READ (JJ,*) NDS(JJ),NCS(JJ)
       DO 20 I=1,NDS(JJ)
         READ (JJ,*) MCS(JJ,I),VS(JJ,I),(CES(JJ,J,I),J=1,NCS(JJ))
         MCS(JJ,I)=MCS(JJ,I)/1000.0D0
         VS(JJ,I)=VS(JJ,I)/1000.0D0
   20  CONTINUE
C
       DO 40 I=1,NCS(JJ)
         IF(JJ.EQ.1) THEN
          READ (JJ,*) XKS(I),XNS(I),C0(JJ,I),MWS(I)
          XKS(I)=XKS(I)*(1000.0D0/MWS(I))*
     &             MWS(I)**XNS(I)
          XNS(I)=1.0D0/XNS(I)
          ELSE
          READ (JJ,*) DUMXKS,DUMXNS,C0(JJ,I),DUMMWS
         ENDIF
         C0(JJ,I)=C0(JJ,I)/MWS(I)
         DO 30 J=1,NDS(JJ)
           CES(JJ,I,J)=CES(JJ,I,J)/MWS(I)
           QS(JJ,I,J)=(C0(JJ,I)-CES(JJ,I,J))*VS(JJ,J)/MCS(JJ,J)
           CEQ=CES(JJ,I,J)*MWS(I)
           QEQ=QS(JJ,I,J)*MWS(I)/1000
           WRITE(*,*) CEQ,QEQ
   30    CONTINUE
   40  CONTINUE
C
   45 CONTINUE
C
      I=2
      NDAT=0
      CMEAN=0
      DO 46 JJ=1,NDSETS
         NDAT=NDAT+NDS(JJ)
         DO 31 J=1,NDS(JJ)
         CMEAN=CMEAN+CES(JJ,I,J)
   31 CONTINUE
   46 CONTINUE
      CMEAN=CMEAN/NDAT
C
      OPEN (NDSETS+1,FILE=OUTPUT,STATUS='OLD')
C     WRITE (NDSETS+1,*) (XKS(I),I=1,NCS(1))
C     WRITE (NDSETS+1,*) (XKS(I),I=1,NCS(2))
C     WRITE (NDSETS+1,*) (QS(1,2,I),I=1,NDS(1))
```

```
C     WRITE (NDSETS+1,*) (QS(2,2,I),I=1,NDS(2))
C
      K=0
      PARS(1)=XKS(1)
      IF(IPS(1) .EQ. 1) THEN
        K=K+1
        XGUESS(K)=PARS(1)
        XGUESS1=XGUESS(K)/
     &  ((1000.0/MWS(1))*MWS(1)**(1.0/XNS(1)))
        WRITE(*,*) ' PARAMETER # ',K,' = K ','; IG: ',XGUESS1
      WRITE(NDSETS+1,*) 'PARAMETER # ',K,' = K ','; IG: ',XGUESS1
      END IF
C
      PARS(2)=XNS(1)
      IF(IPS(2) .EQ. 1) THEN
        K=K+1
        XGUESS(K)=PARS(2)
        XGUESS2=1.0/XGUESS(K)
        WRITE(*,*) ' PARAMETER # ',K,' = 1/n','; IG: ',XGUESS2
      WRITE(NDSETS+1,*) 'PARAMETER # ',K,' = 1/n','; IG: ',XGUESS2
      END IF
C
      PARS(3)=C0(1,1)
      IF(IPS(3) .EQ. 1) THEN
        K=K+1
        XGUESS(K)=PARS(3)
        XGUESS3=XGUESS(K)*MWS(1)
        WRITE(*,*) ' PARAMETER # ',K,' = Co',' ; IG: ',XGUESS3
      WRITE(NDSETS+1,*) 'PARAMETER # ',K,' = Co',' ; IG: ',XGUESS3
      END IF
C
      N=K
      M=0
      DO 70 JJ=1,NDSETS
        M=M+NDS(JJ)
   70 CONTINUE
C     WRITE (NDSETS+1,*) (XGUESS(I),I=1,N)
      WRITE (NDSETS+1,*) N,M
      WRITE (*,*) N,M
C   ****************************************************************
C   Call to the search routine
C   ****************************************************************
      DO 150 I=1,N
        XSCALE(I)=1.0D0
  150 CONTINUE
      DO 160 J=1,M
        FSCALE(J)=1.0D0
  160 CONTINUE
      LDFJAC=M
C
      XGUESS(1)=XGUESS(1)
      XGUESS(2)=XGUESS(2)**2
      XGUESS(3)=XGUESS(3)
C
```

```
      CALL DU4LSF(IPARAM,RPARAM)
      IPARAM(3)=400
      IPARAM(4)=2500
C
      CALL DUNLSF(FCN,M,N,XGUESS,XSCALE,FSCALE,
     &           IPARAM,RPARAM,X,FVEC,FJAC,LDFJAC)
C
      CALL FCN(M,N,X,FDD)
C
C ***************************************************************
C Send results to output file
C ***************************************************************
      X(1)=(ABS(X(1)))
      X(2)=(ABS(X(2)))**0.5
      X(3)=(ABS(X(3)))
C
      WRITE(NDSETS+1,1000) 'EBC'
      K=0
      IF (IPS(1).EQ.1) THEN
       K=K+1
       XKOUT=X(K)/
     &  ((1000.0/MWS(1))*MWS(1)**(1.0/XNS(1)))
       ELSE
       XKOUT=PARS(1)/
     &  ((1000.0/MWS(1))*MWS(1)**(1.0/XNS(1)))
      ENDIF
       WRITE (NDSETS+1,1003) XKOUT
C
      IF (IPS(2).EQ.1) THEN
       K=K+1
       XNOUT=1.0D0/X(K)
      ELSE
       XNOUT=1.0D0/PARS(2)
      ENDIF
      WRITE (NDSETS+1,1004) XNOUT
C
      IF (IPS(3).EQ.1) THEN
       K=K+1
       C0OUT=X(K)*MWS(1)
      ELSE
       C0OUT=PARS(3)*MWS(1)
      ENDIF
      WRITE (NDSETS+1,1005) C0OUT
      WRITE (NDSETS+1,1001) MWS(1)
C
      WRITE(NDSETS+1,1000) 'TARGET COMPOUND'
      XKOUT2=XKS(2)/
     &     ((1000.0/MWS(2))*MWS(2)**(1.0/XNS(2)))
      XNOUT2=1.0/XNS(2)
      WRITE (NDSETS+1,1003) XKOUT2
      WRITE (NDSETS+1,1004) XNOUT2
      DO 249 JJ=1,NDSETS
      C0OUT2=C0(JJ,2)*MWS(2)
      WRITE (NDSETS+1,1005) C0OUT2
```

```
 249 CONTINUE
   WRITE (NDSETS+1,1001) MWS(2)
C
   DO 248 JJ=1,NDSETS
   WRITE (NDSETS+1,1002) INPUT(JJ)
 248 CONTINUE
C
   WRITE(NDSETS+1,*) 'no,      Q-obs    Q-cal          '
  & ,'C-obs    C-cal        AC-dose'
   DO 250 JJ=1,NDSETS
    DO 200 J=1,NDS(JJ)
      Q   =QS(JJ,2,J)*MWS(2)/1000.0
      QOUT=QD(JJ,2,J)*MWS(2)/1000.0
      CEQ=CES(JJ,2,J)*MWS(2)
      XMCSJ=MCS(JJ,J)*1000.0
      CEQOUT=CD(JJ,2,J)*MWS(2)
      WRITE (NDSETS+1,1006) J,Q,QOUT,CEQ,CEQOUT,XMCSJ
 200  CONTINUE
 250 CONTINUE
C
   DO 210 I=1,M
    WRITE (NDSETS+1,1007) I,FVEC(I)
 210 CONTINUE
C
   WRITE (NDSETS+1,1008) SSQ
C
 1000 FORMAT(A)
 1001 FORMAT(1X,'MW  = ',E17.8,' g/mol')
 1002 FORMAT(1X,A20)
 1003 FORMAT(1X,'K   = ',E17.8,' (mg/g)(ug/L)^-1/n')
 1004 FORMAT(1X,'1/n = ',E17.8)
 1005 FORMAT(1X,'C0  = ',E17.8,' ug/L')
 1006 FORMAT(1X,'Q(',I2,') = ',E10.4,E10.4,' mg/g'
  &             ,E10.4,E10.4,' ug/l',E10.4,' mg/l')
 1007 FORMAT(1X,'F(',I2,') = ',E14.5)
 1008 FORMAT(1X,'Error sum of squares = ',E14.5)
C
   STOP '  all done'
   END
C-----------------------------------------------------------------
C  ******************************************************************
C  This subroutine evaluates the function that defines the least
C  squares problem
C  ******************************************************************
   SUBROUTINE FCN(M,N,X,F)
C
   IMPLICIT DOUBLE PRECISION (A-H,O-Z)
   REAL*8 MW(10),XMC(10,50)
C
   COMMON PAR(50),Q(10,3,50),CES(10,3,50),
  &     XK(10),XN(10),C0(10,10),
  &     XMC,V(10,50),ND(10),NC(10),SSQ,IPS(4),MW,NDSETS
C
   COMMON /BLOCK1/JJ,J,K
```

```
      COMMON /BLOCK2/QD(10,3,50),CD(10,3,50),CMEAN,ERRREL,ITMAX
C
      DIMENSION F(M),X(N)
     &        ,XI(10),XIGUESS(10),XIG1(10),XIG2(10)
      DIMENSION QQ(10),QQD(2),FF(2)
C
      DIMENSION XSCALE(2),FSCALE(2)
     &  ,IPARAM(6),RPARAM(5),FVEC(2)
      EXTERNAL FCNIAS,LSJAC,DNEQBJ,DZBREN
      EXTERNAL FS
C
      DATA ICALL/0/
C
C       WRITE(*,*) 'FCN IN DUNLSF'
      ICALL=ICALL+1
C ****************************************************************
C If trouble, limit the parameters to the smallest value of 10D-30
C ****************************************************************
C
      X1=(ABS(X(1)))
      X2=(ABS(X(2)))**0.5
      X3=(ABS(X(3)))
C
      IF (X1.LT.0.000001) X1=0.000001
      IF (X2.LT.0.01) X2=0.01
      IF (X3.LT.0.000001) X3=0.000001
C
      IF (IPS(1).EQ.1) XK(1)=X1
      IF (IPS(2).EQ.1) XN(1)=X2
      IF (IPS(3).EQ.1) THEN
      DO 117 JJ=1,NDSETS
      C0(JJ,1) =X3
  117 CONTINUE
      ENDIF
      X11=X1/
     &  ((1000.0/MW(1))*MW(1)**(1.0/X2))
      X22=1.0/X2
      X33=X3*MW(1)
      WRITE(*,*) X11,X22,X33
C
      I=0
      DO 115 JJ=1,NDSETS
       NN=NC(JJ)
       DO 110 J=1,ND(JJ)
       I=I+1
C
        DO 100 K=1,NN
        QMAX1 = C0(JJ,K)*V(JJ,J)/XMC(JJ,J)
        QMAX2 = XK(K)*C0(JJ,K)**(1.0/XN(K))
          IF(QMAX1.LE.QMAX2) THEN
          QMAX=QMAX1
          ELSE
          QMAX=QMAX2
          ENDIF
```

```
      QEST=QMAX*1.00001
      QMIN=0
      EABS=0
      EREL=0.002
      MAXFN=100
C       F1=FS(QMIN)
C       F2=FS(QEST)
C       WRITE(*,*) JJ,J,K,QEST
C       WRITE(*,*) F1,F2
C       WRITE(*,*) C0(JJ,K),V(JJ,J),XMC(JJ,J)
C       WRITE(*,*) XK(K),XN(K)
       CALL DZBREN(FS,EABS,EREL,QMIN,QEST,MAXFN)
C       WRITE(*,*) JJ,J,K,QEST
       QQ(K)=QEST
 100   CONTINUE
C
C       WRITE(*,*) JJ,J,(QQ(K),K=1,NN),' QQ'
C
      KMAX=1000
      PD=1.1
      MR=1
      FMAX=1.0D99
C
      FMIN1=FMAX
      NFLG=0
      DO 202 K2=1,KMAX
       QQD(2)=QQ(2)/PD**(K2-1)
       FABS=FMAX
       DO 203 K1=1,KMAX
        QQD(1)=QQ(1)/PD**(K1-1)
        CALL FCNIAS(NN,QQD,FF)
         FABSB=FABS
         FABS=(FF(1)/C0(JJ,1))**2
   &        +(FF(2)/C0(JJ,2))**2
C          FABS=DABS(FF(1))+DABS(FF(2))
         IF(FABS.LT.FMIN1) THEN
          FMIN1=FABS
          XIG1(1)=QQD(1)
          XIG1(2)=QQD(2)
          K11=K1
          K22=K2
          NFLG=1
         ELSE
          IF(FABS.GT.FABSB) GO TO 205
         ENDIF
203     CONTINUE
205     IF(K2-K22.GE.MR.AND.NFLG.EQ.1) GO TO 204
202    CONTINUE
204    CONTINUE
C
      FMIN2=FMAX
C       GO TO 304
      NFLG=0
      DO 302 K1=1,KMAX
```

```
          QQD(1)=QQ(1)/PD**(K1-1)
          FABS=FMAX
          DO 303 K2=1,KMAX
            QQD(2)=QQ(2)/PD**(K2-1)
            CALL FCNIAS(NN,QQD,FF)
             FABSB=FABS
             FABS=(FF(1)/C0(JJ,1))**2
    &           +(FF(2)/C0(JJ,2))**2
C              FABS=DABS(FF(1))+DABS(FF(2))
             IF(FABS.LT.FMIN2) THEN
               FMIN2=FABS
               XIG2(1)=QQD(1)
               XIG2(2)=QQD(2)
               K11=K1
               K22=K2
               NFLG=1
             ELSE
               IF(FABS.GT.FABSB) GO TO 305
             ENDIF
303         CONTINUE
305         IF(K1-K11.GE.MR.AND.NFLG.EQ.1) GO TO 304
302       CONTINUE
304       CONTINUE
C
        IF(FMIN1.LT.FMIN2) THEN
         XIGUESS(1)=XIG1(1)
         XIGUESS(2)=XIG1(2)
         ELSE
         XIGUESS(1)=XIG2(1)
         XIGUESS(2)=XIG2(2)
        ENDIF
C
C           WRITE(*,*) JJ,J,(QQ(K),K=1,NN),' QQ'
C           WRITE(*,*) K11,K22,'  k1, k2'
C           WRITE(*,*) JJ,J,(XIGUESS(K),K=1,NN),' XIG'
C
C       CALL DNEQNJ(FCNIAS,LSJAC,ERRREL,NN,ITMAX,XIGUESS,XI,FNORM)
        DO 98 K=1,NN
         XSCALE(K)=1.0
         FSCALE(K)=1.0
 98      CONTINUE
       CALL DN4QBJ(IPARAM,RPARAM)
       IPARAM(1)=0
C        WRITE(*,*) IPARAM(3),RPARAM(1),RPARAM(2)
       IPARAM(3)=500
       RPARAM(1)=0.0D0
       RPARAM(2)=0.0D0
       CALL DNEQBJ(FCNIAS,LSJAC,NN,XIGUESS
    &          ,XSCALE,FSCALE,IPARAM,RPARAM,XI,FVEC)
C        CALL DNEQBF(FCNIAS,NN,XIGUESS
C     &          ,XSCALE,FSCALE,IPARAM,RPARAM,XI,FVEC)
C
C          WRITE(*,*) JJ,J,(XI(K),K=1,NN)
C
```

```
      DO 103 K=1,NN
      QD(JJ,K,J)=XI(K)
      CD(JJ,K,J)=C0(JJ,K)-XMC(JJ,J)/V(JJ,J)*XI(K)
 103  CONTINUE
C
C       QG=Q(JJ,2,J)*MW(2)
C       QDG=QD(JJ,2,J)*MW(2)
C
C ebcm1
C       F(I)=DABS(DLOG(CES(JJ,2,J))-DLOG(CD(JJ,2,J)))
C    &      +DABS(DLOG( Q(JJ,2,J))-DLOG(QD(JJ,2,J)))
C
C ebcm3
C       F(I)=DLOG(CES(JJ,2,J))-DLOG(CD(JJ,2,J))
C ebcm4
C       F(I)=(CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J)**0.5*10
C ebcm5
C       F(I)=CES(JJ,2,J)-CD(JJ,2,J)
C ebcm6
C       F(I)=(CES(JJ,2,J)-CD(JJ,2,J))
C    &       /(DLOG(C0(JJ,2)/CES(JJ,2,J)))**0.5
C ebcm7
C       F(I)=(CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J)
C ebcm8
C       F(I)=DSQRT(DABS(CES(JJ,2,J)-CD(JJ,2,J)))
C ebcm9
C       F(I)=(DABS((CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J)))
C    &      +(DABS(( Q(JJ,2,J)-QD(JJ,2,J))/ Q(JJ,2,J)))
C ebcm10
C       F(I)=DABS(CES(JJ,2,J)-CD(JJ,2,J))
C    &      *(1.0D0/CES(JJ,2,J)+1.0D0/CMEAN)
C ebcm11
C       F(I)=DSQRT( (DLOG(CES(JJ,2,J))-DLOG(CD(JJ,2,J)))**2
C    &          +(DLOG( Q(JJ,2,J))-DLOG(QD(JJ,2,J)))**2 )
C ebcm12
C       F(I)=DSQRT( ((CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J))**2
C    &          + (( Q(JJ,2,J)-QD(JJ,2,J))/ Q(JJ,2,J))**2)
C ebcm13
C       F(I)=DSQRT( (CES(JJ,2,J)-CD(JJ,2,J))**2
C    &          *(1.0D0/CES(JJ,2,J)**2+1.0D0/CMEAN**2) )
C ebcm14
      F(I)=DSQRT(DABS(CES(JJ,2,J)-CD(JJ,2,J))
     &          *(1.0D0/CES(JJ,2,J)+1.0D0/CMEAN) )
C ebcm15
C       F(I)=DSQRT(DABS((CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J)))
C ebcm16
C       F(I)=DSQRT(DABS(DLOG(CES(JJ,2,J))-DLOG(CD(JJ,2,J))))
C ebcm17
C       F(I)=DSQRT(DABS(DLOG(CES(JJ,2,J))-DLOG(CD(JJ,2,J)))
C    &       + DABS(DLOG( Q(JJ,2,J))-DLOG(QD(JJ,2,J))) )
C ebcm18
C       F(I)=DSQRT(DABS((CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J))
C    &       + DABS(( Q(JJ,2,J)-QD(JJ,2,J))/ Q(JJ,2,J)) )
C ebcm19
```

```
C       F(I)=DSQRT( DABS(CES(JJ,2,J)-CD(JJ,2,J))
C   &            *(1.0D0/CES(JJ,2,J)+1.0D0/CMEAN)
C   &           +DABS((Q(JJ,2,J)-QD(JJ,2,J))/Q(JJ,2,J)) )
C ebcm20
C       F(I)=DABS( (Q(JJ,2,J)-QD(JJ,2,J))/Q(JJ,2,J) )
C ebcm21
C        F(I)=DABS( Q(JJ,2,J)-QD(JJ,2,J) )
C
C       WRITE(*,*) JJ,J,QG,QDG
C       WRITE(*,*) JJ,J,I,F(I)
 110  CONTINUE
 115 CONTINUE
C
      SSQ=0
      DO 120 K=1,M
       IF (DABS(F(K)).GT.1.0D-30) THEN
         IF (DABS(F(K)).LT.1.0D30) THEN
           SSQ=SSQ+F(K)**2.0D0
         ENDIF
       ENDIF
 120 CONTINUE
      SSQ=SSQ/M
C
      WRITE (*,1009) ICALL, SSQ
 1009 FORMAT(1X,'Iteration No.:',I5,4X,'Error sum of sq. = ',E14.6)
C
      RETURN
      END
C-----------------------------------------------------------------
C *****************************************************************
C  This set up the equations that will be solved by the
C  subroutine DNEQNF
C  The equation is derived from IAST plus Freundlich equations
C  for a target compound and a background compound
C *****************************************************************
C     SUBROUTINE FCNIAS(X,F,N)
      SUBROUTINE FCNIAS(N,X,F)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      REAL*8 MW(10),XMC(10,50)
C
      COMMON PAR(50),Q(10,3,50),CES(10,3,50),
     &     XK(10),XN(10),C0(10,10),
     &     XMC,V(10,50),ND(10),NC(10),SSQ,IPS(4),MW,NDSETS
C
     COMMON /BLOCK1/JJ,J,KK
C
      DIMENSION X(N),F(N)
C
      QS=X(1)+X(2)
      QNS=XN(1)*X(1)+XN(2)*X(2)
C
      DO 1000 I=1,N
       F(I)=C0(JJ,I)-X(I)*XMC(JJ,J)/V(JJ,J)
     &     -X(I)/QS*(QNS/XN(I)/XK(I))**XN(I)
```

```
C     WRITE(*,*) JJ,I,J,X(I),F(I),'F'
 1000 CONTINUE
C
      RETURN
      END
C-----------------------------------------------------------
C ******************************************************************
C  This set up the equations that will be solved by the
C  subroutine DNEQNF
C  The equation is derived from IAST plus Freundlich equations
C  for a target compound and a background compound
C ******************************************************************
C     SUBROUTINE LSJAC(N,X,FJAC)
      SUBROUTINE LSJAC(N,X,FJAC,LDFJAC)
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      REAL*8 MW(10),XMC(10,50)
      INTEGER N,I,J
C
C     DIMENSION X(N),FJAC(N,N)
      DIMENSION X(N),FJAC(LDFJAC,*)
C
      COMMON PAR(50),Q(10,3,50),CES(10,3,50),
     &      XK(10),XN(10),C0(10,10),
     &      XMC,V(10,50),ND(10),NC(10),SSQ,IPS(4),MW,NDSETS
C
     COMMON /BLOCK1/JJ,J,KK
C
      QS=X(1)+X(2)
      QNS=XN(1)*X(1)+XN(2)*X(2)
C
      DO 1000 I=1,N
       XNI=XN(I)
       XKI=XK(I)
       XI=X(I)
       DO 1100 K=1,N
       IF(I.NE.K) THEN
         FJAC(I,K)=XI/QS**2*(QNS/XNI/XKI)**XNI
     &      -(XI*XNI*XN(K)/QS)
     &      *QNS**(XNI-1.0)/(XNI*XKI)**XNI
         ELSE
         FJAC(I,K)=-XMC(JJ,J)/V(JJ,J)
     &      -1.0/QS*(QNS/XNI/XKI)**XNI
     &      +(XI/QS**2)*(QNS/XNI/XKI)**XNI
     &      -(XI*XNI**2/QS)
     &      *QNS**(XNI-1.0)/(XNI*XKI)**XNI
         ENDIF
C         WRITE(*,*) I,J,FJAC(I,K),'JAC'
C          FJAC(I,K)=FJAC(I,K)*0.5
 1100  CONTINUE
 1000 CONTINUE
C
      RETURN
      END
```

```
C----------------------------------------------------------------
C *****************************************************************
      REAL*8 FUNCTION FS(X)
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      INTEGER JJ,J,KK
      REAL*8 MW(10),XMC(10,50)
C
      COMMON PAR(50),Q(10,3,50),CES(10,3,50),
     &      XK(10),XN(10),C0(10,10),
     &      XMC,V(10,50),ND(10),NC(10),SSQ,IPS(4),MW,NDSETS
C
      COMMON /BLOCK1/JJ,J,KK
C
      FS=C0(JJ,KK)-X*XMC(JJ,J)/V(JJ,J)
     &      -(X/XK(KK))**XN(KK)
C       WRITE(*,*) JJ,J,FS,' FSINGL'
C
      RETURN
      END
```

IAST: EQUILIBRIUM EQUATION SOLVING COMPUTER PROGRAM

```
C     IAST PREDICTION
C    'IASTM.FOR'
C
C    This program solves the Freundlich-type ideal adsorbed solution
C    theory for a closed multi-solute equilibrium system, given the
C    single solute isotherm constants, the carbon dosage, the
C    solution volume.
C*******************************************************************
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      INTEGER ITMAX, N, MAXFN
      REAL*8  ERRREL
      REAL*8 LSJAC, X(10), XGUESS(10),XG1(10),XG2(10)
C
      EXTERNAL FCNIAS,LSJAC,DNEQNJ,F
C
      INTEGER NC,ND,I
      DIMENSION Q(10,50),C(10,50)
      REAL*8 MW(10),M(50),K(10),V(50),CO(10),XN(10)
C
      DIMENSION IPARAM(6), RPARAM(5)
     &     , XSCALE(2), FSCALE(2), FVEC(2)
      REAL*8 QQD(2),FF(2)
C
      CHARACTER CHAR(10)*80
      COMMON PAR(50)
      COMMON /B1/I
C
C    Open files and read input data
C
      OPEN (9, FILE = 'DATA.IN', STATUS = 'OLD')
      OPEN (10, FILE ='DATA.OUT', STATUS = 'OLD')
      READ (9,*) NC, ND
      DO 15 I = 1, ND
        READ (9,*) M(I), V(I)
        M(I) = M(I)/1000.0D0
        V(I) = V(I)/1000.0D0
15    CONTINUE
      DO 20 I = 1,NC
        READ (9,16) CHAR(I)
16      FORMAT (A10)
        READ (9,*) K(I), XN(I), CO(I), MW(I)
        WRITE (*,*) K(I),XN(I),CO(I),MW(I)
        K(I)=K(I)*(1000.0/MW(I))*MW(I)**XN(I)
        CO(I) = CO(I)/MW(I)
        XN(I) = 1/XN(I)
20    CONTINUE
C
C    Solve each dosage individually
C
```

```
      DO 100 J = 1, ND
C    Put 'DATA.IN' into a one dimensional array
C
      IF (J.EQ.1) THEN
        DO 25 I =1,NC
          PAR(I) = K(I)
          PAR(10+I) =XN(I)
          PAR(20+I) =CO(I)
25       CONTINUE
      ENDIF
      PAR(30) =M(J)
      PAR(40) =V(J)
C
C       Calculate initial guesses on surface loadings
C
        DO 30 I = 1, NC
            QMAX2 = K(I)*CO(I)**(1.0/XN(I))
            IF(M(J).GT.0) THEN
              QMAX1 = CO(I)*V(J)/M(J)
              ELSE
              QMAX1 = QMAX2
            ENDIF
          IF(QMAX1.LE.QMAX2) THEN
           QMAX=QMAX1
           ELSE
           QMAX=QMAX2
          END IF
          QEST=QMAX+1.1
          QMIN = 0
          EABS=0
          EREL=0.002
          MAXFN=100
            F1=F(QMIN)
            F2=F(QEST)
C             WRITE(*,*) J,I,F1,F2
          CALL DZBREN(F,EABS,EREL,QMIN,QEST,MAXFN)
          Q(I,J)=QEST
30       CONTINUE
C
          KMAX=1000
          PD=1.1
          MR=1
C
          FMIN1=1.0D99
          NFLG=0
          DO 202 K2=1,KMAX
            QQD(2)=Q(2,J)/PD**(K2-1)
            FABS=1.0D99
            DO 203 K1=1,KMAX
              QQD(1)=Q(1,J)/PD**(K1-1)
              CALL FCNIAS(NC,QQD,FF)
              FABSB=FABS
C               FABS=DABS(FF(1))/CO(1)+DABS(FF(2))/CO(2)
              FABS=(FF(1)/CO(1))**2+(FF(2)/CO(2))**2
```

```
C           FABS=DABS(FF(1))+DABS(FF(2))
C           FABS=(FF(1))**2+(FF(2))**2
          IF(FABS.LT.FMIN1) THEN
           FMIN1=FABS
           XG1(1)=QQD(1)
           XG1(2)=QQD(2)
           K22=K2
           K11=K1
           NFLG=1
          ELSE
           IF(FABS.GT.FABSB) GO TO 205
          ENDIF
203       CONTINUE
205       IF(K2-K22.GE.MR.AND.NFLG.EQ.1) GO TO 204
202      CONTINUE
204      CONTINUE
C
C        GO TO 304
      FMIN2=1.0D99
      NFLG=0
      DO 302 K1=1,KMAX
        QQD(1)=Q(1,J)/PD**(K1-1)
        FABS=1.0D99
        DO 303 K2=1,KMAX
          QQD(2)=Q(2,J)/PD**(K2-1)
          CALL FCNIAS(NC,QQD,FF)
          FABSB=FABS
C           FABS=DABS(FF(1))/CO(1)+DABS(FF(2))/CO(2)
          FABS=(FF(1)/CO(1))**2+(FF(2)/CO(2))**2
C           FABS=DABS(FF(1))+DABS(FF(2))
C           FABS=(FF(1))**2+(FF(2))**2
          IF(FABS.LT.FMIN2) THEN
           FMIN2=FABS
           XG2(1)=QQD(1)
           XG2(2)=QQD(2)
           K11=K1
           K22=K2
           NFLG=1
          ELSE
           IF(FABS.GT.FABSB) GO TO 305
          ENDIF
303       CONTINUE
305       IF(K1-K11.GE.MR.AND.NFLG.EQ.1) GO TO 304
302      CONTINUE
304      CONTINUE
C
      IF(FMIN1.LT.FMIN2) THEN
       XGUESS(1)=XG1(1)
       XGUESS(2)=XG1(2)
       ELSE
       XGUESS(1)=XG2(1)
       XGUESS(2)=XG2(2)
      END IF
C
```

```
C        QS=Q(1,J)+Q(2,J)
C        QNS=PAR(11)*Q(1,J)+PAR(12)*Q(2,J)
C
C      DO 40 I=1,NC
C        Q(I,J)=CO(I)
C   &    /(M(J)/V(J)+(QNS/PAR(I)/PAR(10+I))**PAR(10+I)/QS)
C        XGUESS(I)=Q(I,J)
C        WRITE(*,*) QMAX,QEST
C40     CONTINUE
C
C   Enter the rest of parameters for  DNEQNF
C
      IF (J.EQ.1) THEN
      READ (9,*) ITMAX, ERRREL
      ENDIF
      N = NC
C
C   Call DNEQNJ to solve the system of equations
C
C    WRITE(*,*) J,(Q(I,J),I=1,NC)
C    WRITE(*,*) FMIN1,(XG1(I),I=1,NC)
C    WRITE(*,*) FMIN2,(XG2(I),I=1,NC)
      WRITE(*,*) J,(XGUESS(I),I=1,NC)
C
C    CALL DNEQNJ (FCNIAS, LSJAC, ERRREL, N, ITMAX, XGUESS, X, FNORM)
      IPARAM(1)=0
      IPARAM(3)=500
      DO 201 I=1,N
      XSCALE(I)=1
      FSCALE(I)=1
  201 CONTINUE
      CALL DNEQBJ (FCNIAS, LSJAC, N, XGUESS
     &        , XSCALE, FSCALE, IPARAM, RPARAM, X, FVEC)
C    CALL DNEQNF (FCNIAS, ERRREL, N, ITMAX, XGUESS, X, FNORM)
C
C   Store the calculated surface loadings back to Q(I,J)
      QS=0.0
      QNS=0.0
      DO 50 I = 1,NC
        Q(I,J) = X(I)
        QS=QS+X(I)
        QNS=QNS+PAR(10+I)*X(I)
50   CONTINUE
      XMJ=M(J)*1000.0D0
      WRITE(*,*) J,XMJ,'  a.c. dose'
      WRITE(*,*) J,(X(I),I=1,NC)
C
C   Calculate the liquid phase concentrations
C
      DO 60 I = 1, NC
        CD     = CO(I)-M(J)/V(J)*Q(I,J)
        C(I,J) = Q(I,J)/QS*(QNS/PAR(I)/PAR(10+I))**PAR(10+I)
C       WRITE(*,*) CD,C(I,J)
60   CONTINUE
```

```
100  CONTINUE
C
C   change units for printing
C
     DO 120 J =1, ND
       DO 110 I=1,NC
         Q(I,J) = Q(I,J)*MW(I)/1000.D0
         C(I,J) = C(I,J)*MW(I)
110      CONTINUE
120  CONTINUE
C
C
C   Print out results
C
     WRITE (10, 200)
200  FORMAT (//,8X,'PROPERTIES of COMPONENTS')
     WRITE (10,210)
210  FORMAT (/,'COMPONENT',T15,'K (mg/g)(ug/L)**-1/n',T38,'1/n',T45,
    &'CO (ug/l)',3X,'MW(dalton)'/)
     DO 300 I =1,NC
       XN(I) = 1.0D0/XN(I)
       CO(I) = CO(I)*MW(I)
       K(I)=K(I)/
    &     ((1000.0/MW(I))*MW(I)**XN(I))
       WRITE (10,250) CHAR(I),K(I),XN(I),CO(I),MW(I)
250      FORMAT (1X,A10,T20,G11.5,T31,G11.5,T43,G11.5,T55,F10.3/)
300  CONTINUE
     WRITE (10,310)
310  FORMAT (//10X,'IAST PREDICTION')
     WRITE (10,320) CHAR(1), CHAR(2), CHAR(3)
320  FORMAT (///,1X,'DOSAGE',T20,A10,T42,A10,T65,A10)
     WRITE (10,330)
330  FORMAT (/2X,'(mg/l)',T14,'C ug/l',T24,'q mg/g',T35,'C ug/l',T45,
    &'q mg/g',T56,'C ug/l',T66,'q mg/g',/)
     DO 340 J =1,ND
       M(J) = M(J)/V(J)*1000.0D0
       WRITE (10,360) M(J),C(1,J),Q(1,J),C(2,J),Q(2,J)
340  CONTINUE
     IF (NC.GT.2) THEN
     WRITE (10,320) CHAR(4), CHAR(5), CHAR(6)
     WRITE (10,330)
     DO  350 J =1,ND
       WRITE (10,360) M(J),C(3,J),Q(3,J),C(4,J),Q(4,J)
350  CONTINUE
     ENDIF
     IF (NC.GT.6) THEN
     WRITE (10,320) CHAR(7), CHAR(8), CHAR(9)
     WRITE (10,330)
     DO  355 J =1,ND
     WRITE (10,360) M(J),C(7,J),Q(7,J),C(8,J),Q(8,J),C(9,J),
    &Q(9,J)
355  CONTINUE
     ENDIF
360  FORMAT (F6.2,T10,G10.3,T21,G10.3,T32,F10.5,T44,F10.5,T54,F10.5,
```

```
     &T65,F9.4,/)
C
C
C
      do 400 I =1,N
      write (*,*) PAR(I), PAR(I+10), PAR(I+20),PAR(30),PAR(40)
400   continue
      STOP
      END
C
C************
C     subroutine FCNIAS
C     This subroutine will set up the equations that will be solved
C     by the subroutine DNEQNF
C
C      SUBROUTINE FCNIAS(X,F,N)
      SUBROUTINE FCNIAS(N,X,F)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      INTEGER N,I
      REAL*8 X(N),F(N),CC
      COMMON PAR(50)
      CC = PAR(30)/PAR(40)
      QS =0.0D0
      QNS =0.0D0
      DO 1000 I=1,N
        IF(X(I).LT.0) X(I)=0
        QS =QS+X(I)
        QNS =QNS+PAR(10+I)*X(I)
1000  CONTINUE
      DO 1200 I =1,N
C      WRITE(*,*) I,X(I),PAR(I),PAR(10+I),PAR(20+I),CC,QS,QNS
      F(I) = PAR(20+I)-CC*X(I)-X(I)/QS*(QNS/PAR(10+I)/
     &      PAR(I))**PAR(10+I)
C      WRITE(*,*) I,F(I)
1200  CONTINUE
      RETURN
      END
C
C      SUBROUTINE LSJAC(N,X,FJAC)
      SUBROUTINE LSJAC(N,X,FJAC,LDFJAC)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      INTEGER N,I,J
C      REAL*8 X(N),FJAC(N,N),CC
      REAL*8 X(N),FJAC(LDFJAC,*),CC
      COMMON PAR(50)
      CC = PAR(30)/PAR(40)
      QS = 0.0
      QNS= 0.0
      DO 1000 I=1,N
       IF(X(I).LT.0) X(I)=0
       QS=QS+X(I)
       QNS=QNS+PAR(10+I)*X(I)
 1000 CONTINUE
      DO 1200 I=1,N
```

```
        DO 1300 J=1,N
C          WRITE(*,*) I,J
         IF(I.NE.J) THEN
          FJAC(I,J)=X(I)/QS**2*(QNS/PAR(10+I)/PAR(I))**PAR(10+I)
     &         -(X(I)*PAR(10+I)*PAR(10+J)/QS)
     &         *QNS**(PAR(10+I)-1.0)/(PAR(10+I)*PAR(I))**PAR(10+I)
         ELSE
          FJAC(I,J)=-CC
     &         -1.0/QS*(QNS/PAR(10+I)/PAR(I))**PAR(10+I)
     &         +(X(I)/QS**2)*(QNS/PAR(10+I)/PAR(I))**PAR(10+I)
     &         -(X(I)*PAR(10+I)**2/QS)
     &         *QNS**(PAR(10+I)-1.0)/(PAR(10+I)*PAR(I))**PAR(10+I)
         END IF
C          WRITE(*,*) I,J,FJAC(I,J)
C           FJAC(I,J)=FJAC(I,J)*10.0
 1300   CONTINUE
 1200 CONTINUE
      RETURN
      END
C
      REAL*8 FUNCTION F(X)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      INTEGER I
      COMMON PAR(50)
      COMMON /B1/I
      CC = PAR(30)/PAR(40)
      F=PAR(20+I)-CC*X-(X/PAR(I))**PAR(10+I)
C       WRITE(*,*) I,X,F,PAR(20+I)
      RETURN
      END
```

SEARCH: BATCH KINETIC PARAMETER SEARCH COMPUTER PROGRAM

```
PROGRAM SEARCH
C ***************************************************************************
C  * This FORTRAN program is used to simultaneously search for the optimum*
C  * set of kinetic parameters and/or equilibrium parameters that would   *
C  * best fit the HSDM to the experimental batch adsorption data. The IMSL*
C  * optimization subroutine DUNLSF coupled with the subroutine HSDM      *
C  * (same as <HSDM.FOR> program) will be used to determine the optimum   *
C  * parameter values.                                                    *
C  *                                                                      *
C  * The control input file <SEARCH.IN> will identify the name of the     *
C  * experimental data input file, the name of the output file, and the   *
C  * parameters to be searched.                                           *
C  *                                                                      *
C  * The experimental data input file <SEARCH.DAT> needs to be filled with*
C  * the appropriate data, including an initial guess for Ds and kf. Then,*
C  * the program is run to evaluate the Ds and kf values that result in   *
C  * the best fit for the experimental data. If the error for the obtained*
C  * result is high, a different initial guess should be used. The output *
C  * of the search program is contained in the file <SEARCH.OUT>. All     *
C  * other files are intermediate files containing control parameters that*
C  * do not need to be changed.                                           *
C  *                                                                      *
C  *           Department of Civil Engineering                            *
C  *        UNIVERSITY OF ILLINOIS, URBANA-CHAMPAIGN                      *
C  *                                                                      *
C ***************************************************************************
C
   IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
   COMMON /PAR1/ C0V(10),CCONCV(10),RADPV(10),RHOPV(10),
  &          PARV(4,10),NDPV(10),NDSET,IPS(4),ISCALE(4),
  &          TM(50,10),YM(50,5,10),IDREP(10),NDPSV(10),
  &          YF(50,10)
C
   CHARACTER*80 IFNAME(10)
C
   DIMENSION X(4),F(500),XGUESS(4),XSCALE(4),FSCALE(500),
  &       IPARAM(6),RPARAM(7),FVEC(500),FJAC(500,4)
C
   EXTERNAL FIND
C
   OPEN(1,FILE='SEARCH.IN',STATUS='OLD')
C
   K=1
 123 CONTINUE
   READ(1,1000) IFNAME(K)
   IF(IFNAME(K) .NE. 'null') THEN
C *****************************************************************
```

```
C  Read in the name(s) of the data file(s)
C  ****************************************************************
        NDSET=K
        K=K+1
        GO TO 123
      ELSE
C  ****************************************************************
C  Name of output file
C  ****************************************************************
        READ(1,1000) IFNAME(K)
      END IF
C
      READ(1,*) (IPS(I),I=1,4)
C
      WRITE(*,*) ' YOUR INPUT ',NDSET, ' DATA FILE(S):'
      DO 1 K=1,NDSET
        WRITE(*,*) IFNAME(K)
    1 CONTINUE
C
      WRITE(*,*) ' YOUR OUTPUT DATA FILE IS:'
      WRITE(*,*) IFNAME(NDSET+1)
C
      IPSSUM=0
      DO 2 K=1,4
        IF(IPS(K) .EQ. 1) THEN
          IPSSUM=IPSSUM+1
        END IF
    2 CONTINUE
C
      DO 11 K=1,NDSET
        OPEN(K,FILE=IFNAME(K),STATUS='OLD')
        REWIND(K)
        READ(K,*) NDPV(K),C0V(K),IDREP(K)
        DO 22 IP=1,NDPV(K)
          READ(K,*) TM(IP,K),(YM(IP,I,K),I=1,IDREP(K))
   22   CONTINUE
        READ(K,*) CCONCV(K)
        READ(K,*) RADPV(K)
        READ(K,*) RHOPV(K)
        READ(K,*) PARV(3,K)
        READ(K,*) PARV(4,K)
        PARV(3,K)=PARV(3,K)*(1000.0D0**PARV(4,K))
        READ(K,*) PARV(1,K)
        READ(K,*) PARV(2,K)
   11 CONTINUE
C  ****************************************************************
C  Count total number of data points
C  ****************************************************************
      DO 95 II=1,NDSET
        NDPSV(II)=0
        DO 94 IJ=1,NDPV(II)
          DO 93 JJ=1,IDREP(II)
          IF(YM(IJ,JJ,II) .LE. 1.1D0) THEN
            NDPSV(II)=NDPSV(II)+1
```

```
        END IF
  93     CONTINUE
  94   CONTINUE
  95 CONTINUE
C
     M1=0
     DO 211 KK=1,NDSET
       M1=M1+NDPV(KK)
 211 CONTINUE
C
     M=0
     DO 21 KK=1,NDSET
       M=M+NDPSV(KK)
  21 CONTINUE
C
     WRITE(*,*) ' TOTAL OBSERVATION TIMES :',M1
     WRITE(*,*) ' TOTAL DATA POINTS :',M
     WRITE(*,*) ' YOU ARE SEARCHING FOR ',IPSSUM ,' PARAMETERS'
C
     K=1
     IF(IPS(1) .EQ. 1) THEN
       SCALE=DLOG10(PARV(1,1))
       IF(SCALE .GT. 0.0D0) THEN
         ISCALE(K)=DINT(SCALE)+1
       ELSE
         ISCALE(K)=DINT(SCALE)
       END IF
       XGUESS(K)=PARV(1,1)/(10.0D0**ISCALE(K))
       XXX=XGUESS(K)*10.0D0**ISCALE(K)
       WRITE(*,*) ' PARAMETER # ',K,' == kf',' ; IG: ',XXX
       K=K+1
     END IF
C
     IF(IPS(2) .EQ. 1) THEN
       SCALE=DLOG10(PARV(2,1))
       IF(SCALE .GT. 0.0D0) THEN
         ISCALE(K)=DINT(SCALE)+1
       ELSE
         ISCALE(K)=DINT(SCALE)
       END IF
       XGUESS(K)=PARV(2,1)/(10.0D0**ISCALE(K))
       XXX=XGUESS(K)*10.0D0**ISCALE(K)
       WRITE(*,*) ' PARAMETER # ',K,' == Ds',' ; IG: ',XXX
       K=K+1
     END IF
C
     IF(IPS(3) .EQ. 1) THEN
       SCALE=DLOG10(PARV(3,1))
       IF(SCALE .GT. 0) THEN
         ISCALE(K)=DINT(SCALE)+1
       ELSE
         ISCALE(K)=DINT(SCALE)
       END IF
       XGUESS(K)=PARV(3,1)/(10.0D0**ISCALE(K))
```

```
         XXX=XGUESS(K)*10.0D0**ISCALE(K)
         WRITE(*,*) ' PARAMETER # ',K,' == K',' ; IG: ',XXX
         K=K+1
        END IF
C
        IF(IPS(4) .EQ. 1) THEN
         SCALE=DLOG10(PARV(4,1))
         IF(SCALE .GT. 0) THEN
           ISCALE(K)=DINT(SCALE)+1
         ELSE
           ISCALE(K)=DINT(SCALE)
         END IF
         XGUESS(K)=PARV(4,1)/(10.0D0**ISCALE(K))
         XXX=XGUESS(K)*10.0D0**ISCALE(K)
         WRITE(*,*) ' PARAMETER # ',K,' == n',' ; IG: ',XXX
        END IF
C ****************************************************************
C Call to the search routine
C ****************************************************************
        OPEN(NDSET+1,FILE=IFNAME(NDSET+1),STATUS='OLD')
C
        N=IPSSUM
        DO 150 I=1,N
         XSCALE(I)=1.0D0
  150 CONTINUE
        DO 160 J=1,M
         FSCALE(J)=1.0D0
  160 CONTINUE
        IPARAM(1)=0
        LDFJAC=M
C
        CALL DUNLSF(FIND,M,N,XGUESS,XSCALE,FSCALE,IPARAM,RPARAM,
       &           X,FVEC,FJAC,LDFJAC)
C ****************************************************************
C Send results to output file
C ****************************************************************
        DO 111 K=1,NDSET
         DO 222 IP=1,NDPV(K)
           WRITE(NDSET+1,1001) TM(IP,K),(YM(IP,II,K),II=1,IDREP(K)),
       &        YF(IP,K)
 222   CONTINUE
  111 CONTINUE
C
 1000 FORMAT(A)
 1001 FORMAT(2X,6E16.6)
C
        STOP ' all done'
        END
C-----------------------------------------------------------
C ****************************************************************
C This subroutine evaluates the function that defines the least
C squares problem
C ****************************************************************
        SUBROUTINE FIND(M,N,X,F)
```

```
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /PAR1/ C0V(10),CCONCV(10),RADPV(10),RHOPV(10),
     &          PARV(4,10),NDPV(10),NDSET,IPS(4),ISCALE(4),
     &          TM(50,10),YM(50,5,10),IDREP(10),NDPSV(10),
     &          YF(50,10)
C
      DIMENSION X(4),F(500)
      DIMENSION TT(50),YY(50)
      DIMENSION SSQV(10),XXV(4),YYM(50,5)
C
      DATA ICALL /0/
C
      ICALL=ICALL+1
C ****************************************************************
C If trouble, limit the parameters to the smallest value of 10D-30
C ****************************************************************
      DO 1 KK=1,N
       X(KK)=DMAX1(X(KK),1.0D-30)
    1 CONTINUE
C
      WRITE(*,1000) ICALL,(X(KK)*10.0D0**ISCALE(KK),KK=1,N)
      WRITE(NDSET+1,1000) ICALL,(X(KK)*10.0D0**ISCALE(KK),KK=1,N)
C
      LL=1
      DO 111 K=1,NDSET
C ****************************************************************
C  LOAD TIME VECTOR FOR THE K'S DATA SET
C ****************************************************************
       DO 2 L=1,NDPV(K)
         TT(L)=TM(L,K)
         DO 229 KI=1,IDREP(K)
           YYM(L,KI) = YM(L,KI,K)
  229      CONTINUE
    2  CONTINUE
C
       LLL=0
       DO 9 II=1,4
         IF(IPS(II) .EQ. 1) THEN
           LLL=LLL+1
           XXV(II)=X(LLL)*10.0D0**ISCALE(LLL)
         ELSE
           XXV(II)=PARV(II,K)
         END IF
    9  CONTINUE
C
       CALL HSDM(C0V(K),CCONCV(K),RADPV(K),RHOPV(K),XXV(1),XXV(2),
     &         XXV(3),XXV(4),TT,YY,NDPV(K),YYM,IDREP(K))
C ****************************************************************
C  Set up the residual vector F
C ****************************************************************
       SSQV(K)=0.0D0
       DO 3 L=1,NDPV(K)
```

```
        YF(L,K)=YY(L)
        DO 4 ID=1,IDREP(K)
          IF(YM(L,ID,K) .LE. 1.1D0) THEN
            F(LL)=(YM(L,ID,K)-YY(L))/YM(L,ID,K)
CC            WRITE(*,*) LL,F(LL)
            SSQV(K)=SSQV(K)+F(LL)*F(LL)
            LL=LL+1
          END IF
    4   CONTINUE
    3  CONTINUE
  111 CONTINUE
C
      WRITE(*,1000) ICALL,(SSQV(I),I=1,NDSET)
      WRITE(NDSET+1,1000) ICALL,(SSQV(I),I=1,NDSET)
 1000 FORMAT(1X,I5,6E16.6)
C
      RETURN
      END
C-----------------------------------------------------------------
C *****************************************************************
C This subroutine numerically solves the HSDM
C *****************************************************************
      SUBROUTINE HSDM(C01,CCONC1,RADP1,RHOP1,XKF1,DS1,XK1,XN1,
     &               TT,YY,NDP,YYM,IDREP1)
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
      COMMON /COL/  NCP,WP(14),BP(14,14)
      COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
     &             XK,XN,RADP,RHOP,BIOT,CD,TFAC
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
      COMMON /VAR/  Y(15),NTOT
C
      DIMENSION TT(1),YY(1),YYM(1,1)
C
      DATA ICALL /0/
C
      OPEN(31,FILE='PART.C',STATUS='OLD')
      OPEN(32,FILE='HSDM.RAW',STATUS='OLD')
C
      IF(ICALL .EQ. 0) THEN
C
      CALL INPUT
C
      CALL INCOL
C
      ICALL=1
      END IF
C
      C0=C01
      CCONC=CCONC1
      RADP=RADP1
      RHOP=RHOP1
```

```
      XK=XK1
      XN=XN1
      XKF=XKF1
      DS=DS1
C
      CALL INIT
C
      CALL CALCC(TT,YY,NDP,YYM,IDREP1)
C
      RETURN
C
      END
C-------------------------------------------------------
      SUBROUTINE INPUT
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
      COMMON /COL/  NCP,WP(14),BP(14,14)
      COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
     &              XK,XN,RADP,RHOP,BIOT,CD,TFAC
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
      COMMON /VAR/  Y(15),NTOT
C
      OPEN(30,FILE='HSDM.C',STATUS='OLD')
      REWIND (30)
      READ(30,*) IPRC,IPRI,IPRO
C ******************************************************************
C Control Parameters
C ******************************************************************
      READ(30,*) NCP
      READ(30,*) TOL,METH,MITER
      READ(30,*) DTINIT
C
      CLOSE (30)
C
      RETURN
      END
C-------------------------------------------------------------
      SUBROUTINE INCOL
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
      COMMON /COL/  NCP,WP(14),BP(14,14)
      COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
     &              XK,XN,RADP,RHOP,BIOT,CD,TFAC
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
      COMMON /VAR/  Y(15),NTOT
C
      DIMENSION DUMMY(14)
C
      IFL1=0
      IFL2=0
```

```
C
 10 CONTINUE
C
    READ(31,*) ID
    IF(ID .EQ. 999) THEN
C ********************************************************************
C SOMETHING IS WRONG
C ********************************************************************
     WRITE(*,*) ' REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE'
     STOP ' ERROR - all done '
    END IF
C
    IF(ID .EQ. NCP) THEN
     IFL1=1
    END IF
C ********************************************************************
C READ IN AND DISTRIBUTE
C ********************************************************************
    IF(IFL1 .NE. 0) THEN
     READ(31,1001) (WP(I),I=1,ID)
     DO 2 I=1,ID
       READ(31,1001) (BP(I,J),J=1,ID)
  2  CONTINUE
C
     IF(IFL1 .EQ. 0) GO TO 10
     IF(IFL1 .EQ. 1) GO TO 11
C
    END IF
C
    IF(IFL1 .EQ. 0) THEN
     READ(31,1001) (DUMMY(I),I=1,ID)
     DO 6 I=1,ID
       READ(31,1001) (DUMMY(J),J=1,ID)
  6  CONTINUE
     GO TO 10
    END IF
C
 11 CONTINUE
C ********************************************************************
C WRITE THE MATRICES
C ********************************************************************
    IF(IPRC .EQ. 1) THEN
     WRITE(*,*) ' WEIGHTS  '
     WRITE(*,1001) (WP(I),I=1,NCP)
     WRITE(*,*) ' COLLOCATION MATRIX (B)'
     DO 13 I=1,NCP
       WRITE(*,1001) (BP(I,J),J=1,NCP)
 13  CONTINUE
    END IF
C
1001 FORMAT(4D20.12)
C
    RETURN
    END
```

```
C--------------------------------------------------------------
   SUBROUTINE INIT
C
   IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
   COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
   COMMON /COL/  NCP,WP(14),BP(14,14)
   COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
  &           XK,XN,RADP,RHOP,BIOT,CD,TFAC
   COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
   COMMON /VAR/  Y(15),NTOT
C
   NTOT=NCP+1
C ****************************************************************
C INITIAL CONDITION FOR SOLID PHASE
C ****************************************************************
   DO 11 I=1,NTOT-1
    Y(I)=0.0D0
 11 CONTINUE
C ****************************************************************
C LIQUID PHASE
C ****************************************************************
   Y(NTOT)=1.0D0
C ****************************************************************
C COMPUTE DEPENDENT PARAMETERS
C ****************************************************************
   Q0=XK*C0**XN
C
   CD=CCONC*Q0/C0
C
   B1=XKF*RADP*C0
   B2=DS*RHOP*Q0*1000.0D0
   BIOT=B1/B2
C
   TFAC=DS/(RADP*RADP)
C
   IF(IPRI .EQ. 1) THEN
    WRITE(32,1001) C0,CCONC,CD
    WRITE(32,1004) DS
    WRITE(32,1005) XKF
    WRITE(32,1006) BIOT
    WRITE(32,1007) RADP
    WRITE(32,1008) RHOP
    WRITE(32,1009) XK
    WRITE(32,1010) XN
    WRITE(32,1011) TFAC
C ****************************************************************
C CONTROL PARAMETER
C ****************************************************************
    WRITE(32,1013) NTOT,TOL,METH,MITER,DTINIT,DTOUT,TFINAL
   END IF
C ****************************************************************
C FORMAT STATEMENTS
C ****************************************************************
```

```
 1001 FORMAT(2X,'C0    = ',E12.6,/,
   &      2X,'CCONC = ',E12.6,/,
   &      2X,'CD    = ',E12.6,/)
C
 1004 FORMAT(1X,'DS    = ',E12.5)
 1005 FORMAT(1X,'XKF   = ',E12.5)
 1006 FORMAT(1X,'BIOT  = ',E12.5)
 1007 FORMAT(1X,'RADP  = ',E12.5)
 1008 FORMAT(1X,'RHOP  = ',E12.5)
 1009 FORMAT(1X,'XK    = ',E12.5)
 1010 FORMAT(1X,'XN    = ',E12.5)
 1011 FORMAT(1X,'TFAC  = ',E12.5)
C
 1013 FORMAT(1X,'NTOT =',I4,/,
   &      1X,'TOL   =',E16.6,/,
   &      1X,'METH  =',I4,/,
   &      1X,'MITER =',I4,/,
   &      1X,'DTINIT =',E16.6,/,
   &      1X,'DTOUT =',E16.6,/,
   &      1X,'TFINAL =',E16.6,/,
   &      1X,'NULL')
C
    RETURN
    END
C-------------------------------------------------------------
    SUBROUTINE CALCC(TT,YY,NDP,YYM,IDREP1)
C
    IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
    COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
    COMMON /COL/  NCP,WP(14),BP(14,14)
    COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
   &              XK,XN,RADP,RHOP,BIOT,CD,TFAC
    COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
    COMMON /VAR/  Y(15),NTOT
C
    DIMENSION TT(1),YY(1),YYM(1,1)
C
    DIMENSION A(1,1),PARAM(50)
C
    EXTERNAL FCN,FCNJ
C
    N=NTOT
    IDO=1
    DO 50 I=1,50
     PARAM(I)=0.0D0
  50 CONTINUE
    PARAM(1)=DTINIT
    PARAM(12)=METH
    PARAM(13)=MITER
C
    T=0.0D0
C
    ITRY=0
```

```
      ITRYT=0
      TPHYS=0.0D0
      ITER=0
C
      DO 100 IP=1,NDP
C
        ITER=ITER+1
        TEND=TT(IP)*TFAC
C
        IF(TT(IP) .LE. 0.01) THEN
           YY(IP)=1.0D0
           GO TO 100
        END IF
C
        ITRY=0
C
        CALL DIVPAG(IDO,N,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
C
        ITRYT=ITRYT+ITRY
        T=TEND
        TPHYS=T/TFAC
C
        WRITE(*,1000) TPHYS,(YYM(IP,KKI),KKI=1,IDREP1),Y(NTOT)
 1000    FORMAT(1X,5E16.6)
C
        YY(IP)=Y(NTOT)
C
  100 CONTINUE
C
      IDO=3
      CALL DIVPAG(IDO,N,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
C
      RETURN
      END
C------------------------------------------------------------
      SUBROUTINE FCNJ(N,T,Y,PD)
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      DIMENSION Y(N),PD(N,N)
C
      RETURN
      END
C------------------------------------------------------------
      SUBROUTINE FCN(N,T,Y,YPRIME)
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
      COMMON /COL/  NCP,WP(14),BP(14,14)
      COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
     &               XK,XN,RADP,RHOP,BIOT,CD,TFAC
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
C
```

```
      DIMENSION Y(N),YPRIME(N)
      DIMENSION BB(14)
C
      ITRY=ITRY+1
C
      NTOT=N
      KK=0
      II=0
C
      NICP=NCP-1
C
      DO 30 J=1,NICP
       BB(J)=0.0D0
   30 CONTINUE
C
      WW=0.0D0
C
      DO 50 I=1,NICP
       II=II+1
       LL=0
C
       DO 40 J=1,NCP
         LL=LL+1
         BB(I)=BB(I)+BP(I,J)*Y(LL)
   40   CONTINUE
C *****************************************************************
C  MASS BALANCE INSIDE PARTICLE (EXCEPT BOUNDARY)
C *****************************************************************
       YPRIME(II)=BB(I)
       WW=WW+WP(I)*YPRIME(II)
   50 CONTINUE
C *****************************************************************
C  SOLID-LIQUID INTERFACE (HEAT EQ. AT INTERFACE
C *****************************************************************
      II=II+1
      BSUM=0.0D0
C
      DO 11 KKK=1,NCP
       BSUM=BSUM+BP(NCP,KKK)*Y(KKK)
   11 CONTINUE
C
      IF(Y(II) .LT. 0.0D0) THEN
       YPRIME(II) = (((BIOT*(Y(NTOT)-0.0D0)-WW)/WP(NCP))+BSUM)*0.5D0
      ELSE
       YPRIME(II) = (((BIOT*(Y(NTOT)-(Y(II)**(1.0D0/XN)))-WW)/
     &           WP(NCP))+BSUM)*0.5D0
      END IF
C *****************************************************************
C  LIQUID PHASE MASS BALANCE
C *****************************************************************
      YPRIME(NTOT)=-3.0D0*CD*(WW+(YPRIME(II)*WP(NCP)))
C
      RETURN
      END
```

HSDM: BATCH KINETIC EQUATION SOLVING COMPUTER PROGRAM

```
PROGRAM HSDM
C
C   ********************************************************************
C   *                                                   *
C   * This FORTRAN program <HSDM.FOR> solves the HSDM system of partial*
C   * differential equations for a closed batch reactor or a plug flow *
C   * reactor using the orthogonal collocation technique. The IMSL    *
C   * subroutine DIVPAG is used to solve for the bulk concentration    *
C   * profile versus time.                              *
C   *                                                   *
C   * The input file is <HSDM.IN> requires the user to enter the      *
C   * parameters Co, Ds, kf, K, 1/n, apparent density, and final time. *
C   * The other control terms do not need to be changed. After running *
C   * the program, the output file <HSDM.OUT> will contain the bulk    *
C   * concentration profile as a function of time            *
C   *                                                   *
C   *         Department of Civil Engineering               *
C   *      UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN            *
C   ********************************************************************
   IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
   COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
   COMMON /COL/  NCP,WP(14),BP(14,14)
   COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
  &           XK,XN,RADP,RHOP,BIOT,CD,TFAC
   COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
   COMMON /VAR/  Y(15),NTOT
C
C
   OPEN(30,FILE='HSDM.IN',STATUS='OLD')
   OPEN(31,FILE='PART.C',STATUS='OLD')
   OPEN(32,FILE='HSDM.OUT',STATUS='OLD')
C
   CALL INPUT
C
   CALL INCOL
C
   CALL INIT
C
   CALL CALCC
C
   STOP '        all done'
C
   END
C-----------------------------------------------------------
C ******************************************************************
C This subroutine reads the data from the input file HSDM.IN
C ******************************************************************
```

```
      SUBROUTINE INPUT
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
      COMMON /COL/  NCP,WP(14),BP(14,14)
      COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
     &          XK,XN,RADP,RHOP,BIOT,CD,TFAC
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
      COMMON /VAR/  Y(15),NTOT
C
      READ(30,*) IPRC,IPRI,IPRO
C ******************************************************************
C Physical parameters
C ******************************************************************
      READ(30,*) C0
      READ(30,*) CCONC
      READ(30,*) DS
      READ(30,*) XKF
      READ(30,*) XK
      READ(30,*) XN
      XK = XK*1000.0D0**XN
      READ(30,*) RADP
      READ(30,*) RHOP
C ******************************************************************
C  Control parameters
C ******************************************************************
      READ(30,*) NCP
      READ(30,*) TOL,METH,MITER
      READ(30,*) DTINIT
      READ(30,*) DTOUT
      READ(30,*) TFINAL
      READ(30,*) ITMAX
C
      RETURN
      END
C------------------------------------------------------------------
C ******************************************************************
C This subroutine determines the weights and collocation matrix
C ******************************************************************
      SUBROUTINE INCOL
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
      COMMON /COL/  NCP,WP(14),BP(14,14)
      COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
     &          XK,XN,RADP,RHOP,BIOT,CD,TFAC
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
      COMMON /VAR/  Y(15),NTOT
C
      DIMENSION DUMMY(14)
C
      IFL1=0
```

```
      IFL2=0
C
   10 CONTINUE
C
      READ(31,*) ID
      IF(ID .EQ. 999) THEN
C   SOMETHING IS WRONG
       WRITE(*,*) ' REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE'
       STOP ' ERROR - all done '
      END IF
C
      IF(ID .EQ. NCP) THEN
       IFL1=1
      END IF
C ****************************************************************
C  Read weights into array WP and collocation matrix into array BP
C ****************************************************************
      IF(IFL1 .NE. 0) THEN
       READ(31,1001) (WP(I),I=1,ID)
       DO 2 I=1,ID
         READ(31,1001) (BP(I,J),J=1,ID)
    2  CONTINUE
       IF(IFL1 .EQ. 0) GO TO 10
       IF(IFL1 .EQ. 1) GO TO 11
      END IF
C
      IF(IFL1 .EQ. 0) THEN
       READ(31,1001) (DUMMY(I),I=1,ID)
       DO 6 I=1,ID
         READ(31,1001) (DUMMY(J),J=1,ID)
    6  CONTINUE
       GO TO 10
      END IF
C
   11 CONTINUE
C ****************************************************************
C   Write the arrays to the screen if desired
C ****************************************************************
      IF(IPRC .EQ. 1) THEN
       WRITE(*,*) ' WEIGHTS  '
       WRITE(*,1001) (WP(I),I=1,NCP)
       WRITE(*,*) ' COLLOCATION MATRIX (B)'
       DO 13 I=1,NCP
         WRITE(*,1001) (BP(I,J),J=1,NCP)
   13  CONTINUE
      END IF
C
 1001 FORMAT(4D20.12)
C
      RETURN
      END
C-------------------------------------------------------------
C ****************************************************************
C  This subroutine writes initial data to the output file HSDM.OUT
```

```
C ******************************************************************
      SUBROUTINE INIT
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
      COMMON /COL/  NCP,WP(14),BP(14,14)
      COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
     &             XK,XN,RADP,RHOP,BIOT,CD,TFAC
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
      COMMON /VAR/  Y(15),NTOT
C
      NTOT=NCP+1
C ******************************************************************
C  Initial conditions for the solid phase
C ******************************************************************
      DO 11 I=1,NTOT-1
       Y(I)=0.0D0
   11 CONTINUE
C ******************************************************************
C  Initial condition for the liquid phase
C ******************************************************************
      Y(NTOT)=1.0D0
C ******************************************************************
C  Compute dependent parameters
C ******************************************************************
      Q0=XK*C0**XN
C
      CD=CCONC*Q0/C0
C
      B1=XKF*RADP*C0
      B2=DS*RHOP*Q0*1000.0D0
      BIOT=B1/B2
C
      TFAC=DS/(RADP*RADP)
C
      IF(IPRI .EQ. 1) THEN
       WRITE(32,1001) C0,CCONC,CD
       WRITE(32,1004) DS
       WRITE(32,1005) XKF
       WRITE(32,1006) BIOT
       WRITE(32,1007) RADP
       WRITE(32,1008) RHOP
       WRITE(32,1009) XK
       WRITE(32,1010) XN
       WRITE(32,1011) TFAC
       WRITE(32,1013) NTOT,TOL,METH,MITER,DTINIT,DTOUT,TFINAL
      END IF
C ******************************************************************
C  FORMAT STATEMENTS
C ******************************************************************
 1001 FORMAT(2X,'C0    = ',E12.6,/,
     &       2X,'CCONC = ',E12.6,/,
     &       2X,'CD    = ',E12.6,/)
```

```
C
 1004 FORMAT(1X,'DS    = ',E12.5)
 1005 FORMAT(1X,'XKF   = ',E12.5)
 1006 FORMAT(1X,'BIOT  = ',E12.5)
 1007 FORMAT(1X,'RADP  = ',E12.5)
 1008 FORMAT(1X,'RHOP  = ',E12.5)
 1009 FORMAT(1X,'XK    = ',E12.5)
 1010 FORMAT(1X,'XN    = ',E12.5)
 1011 FORMAT(1X,'TFAC  = ',E12.5)
C
 1013 FORMAT(1X,'NTOT =',I4,/,
     &      1X,'TOL  =',E16.6,/,
     &      1X,'METH =',I4,/,
     &      1X,'MITER =',I4,/,
     &      1X,'DTINIT =',E16.6,/,
     &      1X,'DTOUT =',E16.6,/,
     &      1X,'TFINAL =',E16.6,/,
     &      1X,'NULL')
C
      RETURN
      END
C-----------------------------------------------------------
C *****************************************************************
C This subroutine solves the differential equation
C *****************************************************************
      SUBROUTINE CALCC
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
      COMMON /COL/  NCP,WP(14),BP(14,14)
      COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
     &              XK,XN,RADP,RHOP,BIOT,CD,TFAC
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
      COMMON /VAR/  Y(15),NTOT
C
      DIMENSION A(1,1),PARAM(50)
C
      EXTERNAL FCN,FCNJ
C *****************************************************************
C Set parameters for IMSL subroutine DIVPAG
C *****************************************************************
      N=NTOT
      IDO=1
      DO 50 I=1,50
       PARAM(I)=0
   50 CONTINUE
      PARAM(1)=DTINIT
      PARAM(12)=METH
      PARAM(13)=MITER
C
      T=0.0D0
C
      ITRY=0
```

```
      ITRYT=0
      TPHYS=0.0D0
      ITER=0
C
      WRITE(*,*) TPHYS,Y(NTOT)
      WRITE(32,1500) TPHYS,Y(NTOT)
C
  100 CONTINUE
C
      ITER=ITER+1
      TEND=T+DTOUT*TFAC
C
      ITRY=0
      CALL DIVPAG(IDO,N,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
C
      ITRYT=ITRYT+ITRY
      T=TEND
      TPHYS=T/TFAC
C
      WRITE(*,*) TPHYS,Y(NTOT)
      WRITE(32,1500) TPHYS,Y(NTOT)
C
 1500 FORMAT(1X,F8.2,T10,F10.6)
C
      IF (T/TFAC .LT. TFINAL)  GO TO 100
C
      WRITE(*,*) 'ITRYT = ',ITRYT
      WRITE(32,*) ' 999  999  999  999  999  999  999'
      RETURN
      END
C--------------------------------------------------------------
C ***************************************************************
C  This is a dummy subroutine that is required by DIVPAG
C ***************************************************************
      SUBROUTINE FCNJ(N,T,Y,PD)
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      DIMENSION Y(N),PD(N,N)
C
      RETURN
      END
C--------------------------------------------------------------
C ***************************************************************
C  This subroutine calculates the Jacobian required by DIVPAG
C ***************************************************************
      SUBROUTINE FCN(N,T,Y,YPRIME)
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
      COMMON /COL/  NCP,WP(14),BP(14,14)
      COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
     &          XK,XN,RADP,RHOP,BIOT,CD,TFAC
```

```
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
C
      DIMENSION Y(N),YPRIME(N)
      DIMENSION BB(14)
C
      ITRY=ITRY+1
C
      NTOT=N
      KK=0
      II=0
C
      NICP=NCP-1
C
      DO 30 J=1,NICP
       BB(J)=0.0D0
   30 CONTINUE
C
      WW=0.0D0
C
      DO 50 I=1,NICP
       II=II+1
       LL=0
C
       DO 40 J=1,NCP
        LL=LL+1
        BB(I)=BB(I)+BP(I,J)*Y(LL)
   40   CONTINUE
C *****************************************************************
C  Mass balance inside particle (except boundary)
C *****************************************************************
       YPRIME(II)=BB(I)
C
       WW=WW+WP(I)*YPRIME(II)
   50 CONTINUE
C *****************************************************************
C  Solid-liquid interface (heat eq. at interface)
C *****************************************************************
      II=II+1
      BSUM=0.0D0
C
      DO 11 LLL=1,NCP
       BSUM=BSUM+BP(NCP,LLL)*Y(LLL)
   11 CONTINUE
C
      IF(Y(II) .LT. 0.0D0) THEN
       YPRIME(II) = (((BIOT*(Y(NTOT)-0.0D0)-WW)/WP(NCP))+BSUM)
     &           *0.5D0
C
      ELSE
       YPRIME(II) = (((BIOT*(Y(NTOT)-(Y(II)**(1.0D0/XN)))-WW)/
     &           WP(NCP))+BSUM)*0.5D0
      END IF
C *****************************************************************
C  Liquid phase mass balance
```

```
C ****************************************************************
      YPRIME(NTOT)=-3.0D0*CD*(WW+(YPRIME(II)*WP(NCP)))
C
      RETURN
      END
```

CSTR: EQUATION SOLVING COMPUTER PROGRAM

```
      PROGRAM CSTR
C
C   *******************************************************************
C   *                                        *
C   * This FORTRAN program is used to solve for the steady-state    *
c   * performance of PAC in a CSTR with or without solids residence *
C   * time distribution. The program uses the secant method to solve *
C   * the nonlinear equation (i.e the CSTR model). The convergence  *
C   * criterion for the infinite series is a relative error of <.1%. *
C   *                                        *
C   * The input file <CSTR.IN> should be used to enter the parameters*
C   * R, Ds, K, N, Cin, Ccin, and final time. The other parameters  *
C   * are the first and second guesses for the value of Ceff in ug/l *
C   * which do not need to be changed. Finally the tolerable error is*
C   * set to 1.0e-04; it can be increased to 1.0e-03 depending on   *
C   * the sensitivity of the required data.              *
C   *                                        *
C   * The output file <CSTR.OUT> contains the input parameters as   *
C   * well as the list of the steady-state effluent concentrations  *
C   * as a function of solids residence time.             *
C   *                                        *
C   *          Department of Civil Engineering            *
C   *       UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN          *
C   *******************************************************************
C
C   The following are the input variables to the program:
C
C     R  = radius of carbon particle, cm
C    Ds  = surface diffusion coefficient, cm2/min
C     K  = Freundlich coeff, (mg/g)(ug/L)^-1/n
C     N  = Freundlich constant n, (inverse of 1/n)
C    Cin = influent adsorbate concentration, ug/L
C   CCin = influent PAC dose, mg/L
C  TFINAL = final desired time,min
C     A  = first guess for the value of Ceff, ug/L
C     B  = second guess for the value of Ceff, ug/l
C     E  = tolerable error
C
      IMPLICIT REAL(A-H,N-Z)
C
C
      DATA INP,IOUT/5,6/
      OPEN(INP,FILE='CSTR.IN',STATUS='OLD')
      OPEN(IOUT,FILE='CSTR.OUT',STATUS='OLD')
C
C
      READ(INP,*) R
      READ(INP,*) DS
      READ(INP,*) FRK
      READ(INP,*) N
```

```
      READ(INP,*) CIN
      READ(INP,*) CCIN
      READ(INP,*) A,B,E
      READ(INP,*) TFINAL
      WRITE(*,*) 'Is This Completely Mixed Reactor:'
      WRITE(*,*) '(1) WITH a Solids Age Distribution, or'
      WRITE(*,*) '(2) WITHOUT a Solids Age Distribution ?'
      READ(*,*) FLAG
C
C
      WRITE(IOUT,20) R
      WRITE(IOUT,25) DS
      WRITE(IOUT,30) FRK
      WRITE(IOUT,35) N
      WRITE(IOUT,50) CIN
      WRITE(IOUT,55) CCIN
      WRITE(IOUT,*)
C
      IF(FLAG .EQ. 1) THEN
       WRITE(IOUT,*)'** THIS IS A CSTR WITH PAC AGE DISTRIBUTION **'
      ELSE
       WRITE(IOUT,*)'** THIS IS A CSTR WITHOUT PAC AGE DISTRIBUTION **'
      END IF
      WRITE(IOUT,*)
C
   20 FORMAT(1X,'PARTICLE RADIUS, R =',F10.4,' cm')
   25 FORMAT(1X,'DIFFUSION COEFFICIENT, Ds =',E10.2,' cm2/min')
   30 FORMAT(1X,'FREUNDLICH CONSTANT, K =',F10.4,' (mg/g-ug/L)')
   35 FORMAT(1X,'FREUNDLICH CONSTANT, N =',F10.4)
   50 FORMAT(1X,'INFLUENT ADSORBATE CONCENTRATION =',F10.4,' ug/L')
   55 FORMAT(1X,'INFLUENT PAC CONCENTRATION =',F10.4,' mg/L')
C
      ZZ=0
      WRITE(IOUT,90) ZZ,CIN/CIN
      WRITE(*,90) ZZ,CIN/CIN
      XII=0.0
   13 IF(XII .LT. 4.95) THEN
       XII=XII+1.0
      ELSE
       XII=XII+5.0
      END IF
      THS = XII
      PI = 3.141590
C
C
      IF(FLAG .EQ. 2) THEN
       CALL XSUM(R,THS,DS,PI,S)
      ELSE
       CALL SUM(R,THS,DS,PI,S)
      END IF
C
C
      COEF = CCIN*FRK*(1-(6*S/PI**2))
C
```

```
C
      CALL ITER(CIN,CONC,COEF,N,A,B,E)
C
C
C
C
      CONCNON = CONC/CIN
      WRITE(IOUT,90) THS/60,CONCNON
      WRITE(*,90) THS/60,CONCNON
   90 FORMAT(1X,F10.4,T20,F10.4)
      IF(XII .LT. TFINAL) GOTO 13
C
      STOP
      END
C
C=====================================================================
C
      SUBROUTINE SUM(R,THS,DS,PI,S)
      IMPLICIT REAL(A-H,N-Z)
C
C
      CKAPPA = R**2/THS/DS/PI**2
      S = 0
      DO 15 I=1,100
       SP = S
       S = S + (1/(I**2*(1+I**2/CKAPPA)))
       IF(((S-SP)/S) .LT. 0.001) GOTO 77
   15 CONTINUE
   77 RETURN
      END
C
C=====================================================================
C
      SUBROUTINE ITER(CIN,X,COEF,N,A,B,E)
      IMPLICIT REAL(A-H,N-Z)
C
C
   40 X = A
      CALL FUNCT(Y,CIN,X,COEF,N)
      U = Y
      X = B
      CALL FUNCT(Y,CIN,X,COEF,N)
      V = Y
      CE = (B*U-A*V)/(U-V)
      X = CE
      CALL FUNCT(Y,CIN,X,COEF,N)
      IF(ABS(Y) .GT. E) THEN
      A = B
      B = CE
      GOTO 40
      END IF
      RETURN
      END
C
```

```
C--------------------------------------------------------------
C
      SUBROUTINE FUNCT(Y,CIN,X,COEF,N)
      IMPLICIT REAL(A-H,N-Z)
C
C
      Y = CIN - X - COEF*X**(1/N)
      RETURN
      END
C
C--------------------------------------------------------------
C
      SUBROUTINE XSUM(R,THS,DS,PI,S)
      IMPLICIT REAL(A-H,N-Z)
      CKAPPA=R**2/THS/DS/PI**2
      S=0
      DO 185 I=1,100
       SP=S
       FACT=(EXP(-1.0*I**2/CKAPPA))/I**2
       S=SP+FACT
       IF((FACT/S) .LT. 0.001) GOTO 187
  185 CONTINUE
  187 CONTINUE
      RETURN
      END
```

FS-SI: FIXED-BED ADSORPTION KINETIC PARAMETER SEARCH COMPUTER PROGRAM

```
C   FS-SI.FOR

C

C   FIXED BED ADSORPTION, FS MODEL

C   MAIN PROGRAM
C
    IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
    DIMENSION X(2),XGUESS(2),XSCALE(2),FSCALE(100)
   *     ,IPARAM(6),RPARAM(7),FVEC(100),FJAC(100,2),FDUMY(100)
C
    DIMENSION CB(21),CCB(21)
   *     ,Q(21,21),QQ(21,21)
   *     ,SOLUTE(18)
   *     ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
C
    DIMENSION CDI(200),TDATAI(200)
    COMMON /BLOCKC/ FMIN,TP(4000),CP(4000)
   *         ,TD(200),CD(200),CINT(200),RES(200),NDATA
C
    COMMON /BL1/CB,Q,QSD,F,FD
   *    /BL2/CCB,QQ
   *    /BLS/S1,S2,S3,S4
   *    /BLDATA/SOLUTE,ISO,A,B,C0,Q0,IR0
   *        ,U,DIA,RS,RB,AKF,DS,DB
   *        ,DELT,DELTMX,TEND,DELZ,ZEND,DTUBE
   *        ,IITM
C
    EXTERNAL FCN,DU4LSF
C
    OPEN(5,FILE='FS.IN')
    OPEN(6,FILE='FS-SI.OUT')
C
    READ(5,1001) SOLUTE
    ISO=2
    READ(5,*) A
    READ(5,*) B
    READ(5,*) C00
    READ(5,*) IR0
C
    READ(5,*,END=500) U
    READ(5,*,END=500) DIA
    READ(5,*,END=500) RS
    READ(5,*,END=500) RB
    READ(5,*,END=500) AKF
    READ(5,*,END=500) DS
```

```
      READ(5,*,END=500) DB
      READ(5,*) DELT
      READ(5,*) DELTMX
      READ(5,*) TEND
      READ(5,*) DELZ
      READ(5,*) ZEND
      READ(5,*) DTUBE
C
      READ(5,*) IITM
C
      C0=C00/1000.0
      Q0=A*C00**B
C
      WRITE(6,1008) SOLUTE,A,B,C00,Q0,IR0
     *         ,U,DIA,RS,RB,AKF,DS,DB
     *         ,DELT,DELTMX,TEND,DELZ,ZEND,DTUBE
      WRITE(*,1008) SOLUTE,A,B,C00,Q0,IR0
     *         ,U,DIA,RS,RB,AKF,DS,DB
     *         ,DELT,DELTMX,TEND,DELZ,ZEND,DTUBE
 1001 FORMAT(18A4)
 1002 FORMAT(I10,3F10.0,I10)
C 1003 FORMAT(F10.0)
C 1007 FORMAT(I10)
 1008 FORMAT(1H ,'FIXED BED ADSORPTION, FS MODEL'/
     *     1H ,'SOLUTE = ',5X,18A4/
     *     1H ,'A,B,C0,Q0,IR0 = ',/1H ,1P4E16.5,I10/
     *     1H ,'U,DIA,RS,RB,AKF,DS,DB ='/1H ,1P7E16.5/
     *     1H ,'DELT.DELTMX,TEND,DELZ,ZEND,DTUBE ='/1H ,1P6E16.5/)
C
      READ(5,*) NDATA
      IF (NDATA.LE.0) STOP
      DO 10 I=1,NDATA
      READ(5,*) TDATAI(I),CDI(I)
      CD(I)=CDI(I)/C0/1000.0
      TD(I)=TDATAI(I)/60.0
   10 CONTINUE
C
      A=A*1000.0**B
C
      U=U*60.
      RS=RS*1000.
      RB=RB*1000.
C     AKF=AKF*3600.
C     DS=DS*3600.
      DB=DB*3600.
C
C     searching for Kf and Ds
      N=2
      M=NDATA
      LDFJAC=M
      XGUESS(1)=AKF
      XGUESS(2)=DS*1.0E10
      DO 50 I=1,N
      XSCALE(I)=1.0
```

```
   50 CONTINUE
      DO 51 I=1,M
      FSCALE(I)=1.0
   51 CONTINUE
C
      CALL DU4LSF(IPARAM,RPARAM)
      IPARAM(3)=400
      IPARAM(4)=2500
C
      WRITE(*,*) 'start searching'
C
      CALL DUNLSF(FCN,M,N,XGUESS,XSCALE,FSCALE,
     &          IPARAM,RPARAM,X,FVEC,FJAC,LDFJAC)
C
      CALL FCN(M,N,X,FDUMY)
C
      AKF=DABS(X(1))
      DS=DABS(X(2)/1.0E10)
      WRITE(*,120) AKF,DS,FMIN
      WRITE(6,120) AKF,DS,FMIN
  120 FORMAT(1X,'OPTIMUM'/
     &     'KF=',1PG15.7,4X,'DS=',G15.7/
     &     ' ',19X,'ERROR=',G15.7)
      WRITE(6,*)
     & ' TIME(hr)    C/Co(obs)    C/Co(cal)     error(%)'
      DO 11 I=1,NDATA
      WRITE(6,121) TD(I),CD(I),CINT(I),RES(I)
   11 CONTINUE
  121 FORMAT(1X,4(1PG15.5))
C
  500 CONTINUE
      STOP  ' ALL DONE '
      END
C
C
      SUBROUTINE FCN(MS,NS,XX,FF)
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      DIMENSION XX(NS),FF(MS)
C
      DIMENSION CB(21),CCB(21),QT(21),Z(21)
     *      ,Q(21,21),QQ(21,21),CS(21),CCS(21)
     *      ,N(21),NR(21),INDEX(21),IR(21),F1(21),F2(21)
     *      ,CK(50),QK(50),FDK(50),CKK(25),SOLUTE(18)
     *      ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
     *      ,CBX(25),QTX(25)
C
      COMMON /BLOCKC/ FMIN,TP(4000),CP(4000)
     *           ,TD(200),CD(200),CINT(200),RES(200),NDATA
C
      COMMON /BL1/CB,Q,QSD,F,FD
     *      /BL2/CCB,QQ
     *      /BLS/S1,S2,S3,S4
```

```
     *    /BLDATA/SOLUTE,ISO,A,B,C0,Q0,IR0
     *        ,U,DIA,RS,RB,AKF,DS,DB
     *        ,DELTT,DELTMX,TEND,DELZ,ZEND,DTUBE
     *        ,IITM
C
      DELT=DELTT
C
      AKFF=DABS(XX(1))
      DSS=DABS(XX(2)/1.0E10)
      WRITE(*,*) 'Kf & Ds ',AKFF,DSS
      AKF=AKFF*3600.0
      DS=DSS*3600.0
C     WRITE(*,1008) SOLUTE,ISO,A,B,C0,Q0,IR0
C    *          ,U,DIA,RS,RB,AKF,DS,DB
C    *          ,DELT,DELTMX,TEND,DELZ,ZEND,DTUBE
C1008 FORMAT(1H ,'SOLUTE = ',5X,18A4/
C    *    1H ,I10,5X,1P4E16.5,I10/
C    *    1H ,1P7E16.5/
C    *    1H ,1P6E16.5)
C
      NKK=25
      CKK(1)=0.0
      CKK(2)=0.0001
      CKK(3)=0.0002
      CKK(4)=0.0005
      CKK(5)=0.001
      CKK(6)=0.002
      CKK(7)=0.005
      CKK(8)=0.0075
      CKK(9)=0.01
      CKK(10)=0.02
      CKK(11)=0.05
      CKK(12)=0.075
      CKK(13)=0.1
      CKK(14)=0.15
      CKK(15)=0.2
      CKK(16)=0.3
      CKK(17)=0.4
      CKK(18)=0.5
      CKK(19)=0.6
      CKK(20)=0.7
      CKK(21)=0.8
      CKK(22)=0.9
      CKK(23)=1.0
      CKK(24)=1.5
      CKK(25)=2.0
C
      NK=NKK
      DO 120 K=1,NK
      CK(K)=C0*CKK(K)
      IF(ISO.EQ.1) QK(K)=A*B*CK(K)/(1.+B*CK(K))
      IF(ISO.EQ.2) QK(K)=A*CK(K)**B
      IF(ISO.EQ.3) QK(K)=A*CK(K)
      IF(K.EQ.1) GO TO 120
```

```
      FDK(K)=(CK(K)-CK(K-1))/(QK(K)-QK(K-1))
  120 CONTINUE
      Q0=QK(23)
C
      RADIUS=DIA/2.
      NR0=20*2**IR0
C     NR0=5*2**IR0
      DELR=RADIUS/DFLOAT(NR0)
      AV=3.*RB/RS/RADIUS
      EB=1.-RB/RS
      COEF=DTUBE**2*3.14/4.*U/1000.
      F10=DELR**2/DS/DELT
      F20=AKF/RS/DS/RADIUS*DELR*(RADIUS+DELR)
      IF(DB.EQ.0.) FY=-AKF*AV/U
      IF(DB.NE.0.) FY=(U-DSQRT(U**2+4.*AKF*AV*EB*DB))/2./EB/DB
      F3=U/AKF/AV/DELZ
      F4=DEXP(FY*DELZ)
      F5=AKF*AV*DELT/2./RB
    6 DO 130 I=1,21
      ZX=DELZ*DFLOAT(I-1)
      IF(ZX.GE.ZEND) GO TO 7
      CX=DEXP(FY*ZX)
      IF(CX.LT.0.001) M=I-1
      IF(CX.LT.0.001) M1=I
      IF(CX.LT.0.001) GO TO 8
  130 CONTINUE
      DELZ=2.*DELZ
      F3=U/AKF/AV/DELZ
      F4=DEXP(FY*DELZ)
      GO TO 6
    7 M=20
      M1=21
      DELZ=ZEND/20.
      F3=U/AKF/AV/DELZ
      F4=DEXP(FY*DELZ)
      F3M1=F3
      F4M1=F4
    8 DO 150 I=1,M1
      Z(I)=DFLOAT(I-1)*DELZ
      CB(I)=DEXP(FY*Z(I))*C0
      CBX(I)=CB(I)/C0
      CCB(I)=CB(I)
      CS(I)=0.
      CCS(I)=0.
      QT(I)=0.
      IR(I)=IR0
      NR(I)=NR0
      F1(I)=F10
      F2(I)=F20
      N(I)=11
      INDEX(I)=0
      DO 140 J=1,21
      Q(I,J)=0.
      QQ(I,J)=0.
```

```
  140 CONTINUE
  150 CONTINUE
      T=0.
C
      IIT=0
      IITT=0
C
      KW=0
      KC=0
      KXY=0
      NPT=0
      KWH=10
      KCH=100
      KXYH=10
C     WRITE(*,1010) T
C     WRITE(*,1011) (Z(I),I=1,M1)
C     WRITE(*,1012) (CBX(I),I=1,M1)
C
C     WRITE(6,1010) T
C     WRITE(*,1010) T
C
   10 T=T+DELT
C
      IIT=IIT+1
C
      KXY=KXY+1
      KW=KW+1
      KC=KC+1
      DO 200 I=1,M1
   20 QSD=QQ(I,21)
      DO 210 K=2,NK
      IF(QSD.LT.QK(K)) GO TO 21
  210 CONTINUE
   21 FD=FDK(K)
      F=FDK(K)*(QSD-QK(K-1))+CK(K-1)
      IF(I.NE.1) X=CCS(I-1)
      IF(I.NE.1) Y=CCB(I-1)
      IF(Z(I).NE.ZEND) F3I=F3
      IF(Z(I).NE.ZEND) F4I=F4
      IF(Z(I).EQ.ZEND) F3I=F3M1
      IF(Z(I).EQ.ZEND) F4I=F4M1
      CALL KEISU(I, N(I), NR(I), INDEX(I), IR(I)
     *        ,F1(I), F2(I), F3I, F4I, X, Y, CS(I))
      CALL GAUSS(I, N(I))
      IF(ISO.EQ.3) GO TO 22
      ERR=(QQ(I,21)-QSD)/QQ(I,21)
      IF(ABS(ERR).GT.1.E-4) GO TO 20
   22 CCS(I)=F
      CUTQ=QQ(I,21)*0.01
      IF(QQ(I,N(I)).LT.CUTQ) GO TO 200
      IF(N(I).EQ.1) GO TO 23
      N(I)=N(I)-1
      GO TO 20
   23 IF(IR(I).EQ.0) GO TO 200
```

```
      IR(I)=IR(I)-1
      NR(I)=NR(I)/2
      DELR=RADIUS/DFLOAT(NR(I))
      F1(I)=DELR**2/DS/DELT
      F2(I)=AKF/RS/DS/RADIUS*DELR*(RADIUS+DELR)
      N(I)=10
      INDEX(I)=0
      DO 220 J=21,11,-1
      JJ=2*J-21
      Q(I,J)=Q(I,JJ)
      QQ(I,J)=QQ(I,JJ)
  220 CONTINUE
      DO 230 J=1,10
      Q(I,J)=0.
      QQ(I,J)=0.
  230 CONTINUE
      GO TO 20
  200 CONTINUE
      DO 240 I=1,M1
      QT(I)=F5*(CCB(I)+CB(I)-CCS(I)-CS(I))+QT(I)
      CB(I)=CCB(I)
      CS(I)=CCS(I)
      DO 240 J=1,21
      Q(I,J)=QQ(I,J)
  240 CONTINUE
      IF(Z(M1).LT.ZEND) GO TO 30
C     IF(Z(M1).LT.ZEND*0.9999) GO TO 30
      IF(KXY.LT.KXYH) GO TO 30
      NPT=NPT+1
C     TW(NPT)=T
      CWNPT=CB(M1)/C0
C     VOL(NPT)=T*COEF
      KXY=0
   30 IF(KW.LT.KWH) GO TO 40
      DO 300 I=1,M1
      CBX(I)=CB(I)/C0
      QTX(I)=QT(I)/Q0
  300 CONTINUE
C
      IF(IIT.GE.IITM) IIT=0
C
      IF(IIT.EQ.0) THEN
        IITT=IITT+1
C       WRITE(6,*) M1,M
C       WRITE(6,1010) T,CWNPT
C       WRITE(*,1010) T,CWNPT
        TP(IITT)=T
        CP(IITT)=CWNPT
        ELSE
      ENDIF
C     WRITE(6,1011) (Z(I),I=1,M1)
C     WRITE(6,1012) (CBX(I),I=1,M1)
C     WRITE(6,1013) (QTX(I),I=1,M1)
 1010 FORMAT(1H ,'T=',1PE10.3,'(HR)',5X,'CB/C0=',1PE11.4)
```

```
 1011 FORMAT(1H ,'    Z=',1P11E11.4/1H ,7X,1P11E11.4)
 1012 FORMAT(1H ,' C/C0=',1P11E11.4/1H ,7X,1P11E11.4)
 1013 FORMAT(1H ,' Q/Q0=',1P11E11.4/1H ,7X,1P11E11.4)
      KW=0
      KXY=0
      IF(CB(M1)/C0.GE.0.98) GO TO 50
      IF(T.GE.TEND) GO TO 50
      IF(KC.LT.KCH) GO TO 40
      KC=0
      KCH=90
      IF(10.*DELT.GE.DELTMX) KWH=10
      IF(10.*DELT.GE.DELTMX) GO TO 40
      DELT=10.*DELT
      F10=F10/10.
      F5=F5*10.
      DO 310 I=1,M1
      F1(I)=F1(I)/10.
      INDEX(I)=0
  310 CONTINUE
   40 IF(QT(2)/Q0.LT.0.999) GO TO 45
      IF(M.EQ.1) GO TO 50
      M=M-1
      M1=M1-1
      DO 400 I=1,M1
      II=I+1
      Z(I)=Z(II)
      CB(I)=CB(II)
      CCB(I)=CCB(II)
      CS(I)=CS(II)
      CCS(I)=CCS(II)
      QT(I)=QT(II)
      IR(I)=IR(II)
      NR(I)=NR(II)
      F1(I)=F1(II)
      F2(I)=F2(II)
      N(I)=N(II)
      INDEX(I)=INDEX(II)
      DO 400 J=1,21
      Q(I,J)=Q(II,J)
      QQ(I,J)=QQ(II,J)
      S1(I,J)=S1(II,J)
      S2(I,J)=S2(II,J)
      S3(I,J)=S3(II,J)
  400 CONTINUE
      CB(1)=C0
      CCB(1)=C0
   45 IF(CB(M1)/C0.LT.0.001) GO TO 10
      IF(Z(M1).GE.ZEND) GO TO 10
C     IF(Z(M1).GE.ZEND*0.99999) GO TO 10
      IF(M1.EQ.21) GO TO 46
      M=M+1
      M1=M1+1
      GO TO 47
   46 DELZ=2.*DELZ
```

```
      F3=U/AKF/AV/DELZ
      F4=DEXP(FY*DELZ)
      DO 410 I=2,11
      II=2*I-1
      Z(I)=Z(II)
      CB(I)=CB(II)
      CCB(I)=CCB(II)
      CS(I)=CS(II)
      CCS(I)=CCS(II)
      QT(I)=QT(II)
      IR(I)=IR(II)
      NR(I)=NR(II)
      F1(I)=F1(II)
      F2(I)=F2(II)
      N(I)=N(II)
      INDEX(I)=INDEX(II)
      DO 410 J=1,21
      Q(I,J)=Q(II,J)
      QQ(I,J)=QQ(II,J)
      S1(I,J)=S1(II,J)
      S2(I,J)=S2(II,J)
      S3(I,J)=S3(II,J)
  410 CONTINUE
      M=11
      M1=12
C     M=10
C     M1=11
   47 Z(M1)=Z(M)+DELZ
      CB(M1)=CB(M)*F4+CS(M)*(F3-F4-F3*F4)
      IF(Z(M1).LT.ZEND) GO TO 48
      DELZM1=ZEND-Z(M)
      F3M1=U/AKF/AV/DELZM1
      F4M1=DEXP(FY*DELZM1)
      Z(M1)=ZEND
      CB(M1)=CB(M)*F4M1+CS(M)*(F3M1-F4M1-F3M1*F4M1)
   48 CCB(M1)=CB(M1)
      CS(M1)=0.
      CCS(M1)=0.
      QT(M1)=0.
      IR(M1)=IR0
      NR(M1)=NR0
      F1(M1)=F10
      F2(M1)=F20
      N(M1)=11
      INDEX(M1)=0
      DO 420 J=1,21
      Q(M1,J)=0.
      QQ(M1,J)=0.
  420 CONTINUE
      GO TO 10
   50 CONTINUE
C
C     WRITE(*,*) 'END OF N TH SEARCH'
      NP=IITT
```

```
      CALL OBJFUN ( NP )
      DO 81 J=1,NDATA
       RES(J) = ((CINT(J) - CD(J))/CD(J))*100.0
       FF(J)=DABS(RES(J))
C        WRITE(*,*) CD(J),CINT(J)
   81 CONTINUE
      WRITE(*,112) NDATA,FMIN
  112 FORMAT(5X,'FMIN BASED ON',I4,2X,'DATA POINTS:',
     &      3X,'FMIN = ',G15.8)
C
      RETURN
      END
C
C
      SUBROUTINE OBJFUN ( NP )
C
C ************************************************************
C  * This subroutine calculates the standard deviation between  *
C  * the predicted concentrations and experimental data, if any  *
C  * is given.  If no data is given this subroutine is ignored.  *
C ************************************************************
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/BLOCKC/ FMIN,TP(4000),CP(4000)
     *           ,TD(200),CD(200),CINT(200),RES(200),NDATA
        FMIN = 0.0D0
        NP1 = NP - 1
        DO 10 J = 1,NDATA
          DO 5 I = 1,NP1
            IF( TD(J) .LT. TP(I) .OR. TD(J) .GT. TP(I+1) ) GO TO 5
            CAP = CP(I) + ((TD(J)-TP(I))/(TP(I+1)-TP(I)))*
     &            (CP(I+1)-CP(I))
            CINT(J) = CAP
            FMIN = FMIN + ((CAP-CD(J))/CD(J))**2
            GO TO 10
    5     CONTINUE
   10   CONTINUE
        FMIN = SQRT(FMIN/FLOAT(NDATA-1))*100.0D0
      RETURN
      END
C
C
C   SUBROUTINE KEISU
      SUBROUTINE KEISU(I,N,NR,INDEX,IR,F1,F2,F3,F4,X,Y,CS)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION CB(21),Q(21,21)
     *      ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
      COMMON /BL1/CB,Q,QSD,F,FD
     *    /BLS/S1,S2,S3,S4
      IF(INDEX.NE.0) GO TO 10
      DO 100 J=1,20
      EJ=NR-21+J
      IF(EJ.EQ.0.) GO TO 100
      S1(I,J)=-(EJ-1.)/2./EJ
```

```
      S2(I,J)=F1+1.
      S3(I,J)=-(EJ+1.)/2./EJ
  100 CONTINUE
      IF(IR.EQ.0) S2(I,1)=F1+3.
      IF(IR.EQ.0) S3(I,1)=-3.
      S1(I,21)=-1.
      S3(I,21)=-F2
      S2(I,22)=1.
      INDEX=1
   10 DO 110 J=N,20
      IF(J.EQ.1.AND.IR.EQ.0) S4(I,1)=3.*(Q(I,2)-Q(I,1))+F1*Q(I,1)
      IF(J.EQ.1.AND.IR.NE.0) S4(I,1)=(F1-1.)*Q(I,1)-S3(I,1)*Q(I,2)
      IF(J.NE.1) S4(I,J)=-S1(I,J)*Q(I,J-1)+(F1-1.)*Q(I,J)
     *              -S3(I,J)*Q(I,J+1)
  110 CONTINUE
      S2(I,21)=1.+F1+F2*FD
      S4(I,21)=Q(I,20)-F2*(CS+F-FD*QSD)+(F1-1.)*Q(I,21)+F2*CB(I)
      IF(I.NE.1) S1(I,22)=(-1.+F3-F3*F4)*FD
      IF(I.NE.1) S4(I,22)=(1.-F3+F3*F4)*(F-FD*QSD)+(F3-F4-F3*F4)*X+F4*Y
      RETURN
      END
C
C     SUBROUTINE GAUSS-SEIDEL
      SUBROUTINE GAUSS(I,N)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION CCB(21),QQ(21,21),QG(21)
     *       ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
      COMMON /BL2/CCB,QQ
     *      /BLS/S1,S2,S3,S4
    1 DO 100 J=1,21
      QG(J)=QQ(I,J)
  100 CONTINUE
      CBG=CCB(I)
      IF(I.EQ.1) GO TO 10
      CCB(I)=(S4(I,22)-S1(I,22)*QG(21))/S2(I,22)
   10 QQ(I,21)=(S4(I,21)-S1(I,21)*QG(20)-S3(I,21)*CCB(I))/S2(I,21)
      DO 110 J=20,N,-1
      IF(J.EQ.1) QQ(I,1)=(S4(I,1)-S3(I,1)*QQ(I,2))/S2(I,1)
      IF(J.NE.1) QQ(I,J)=(S4(I,J)-S1(I,J)*QG(J-1)-S3(I,J)*QQ(I,J+1))
     *              /S2(I,J)
  110 CONTINUE
      IF(I.EQ.1) GO TO 20
      ERR=(CCB(I)-CBG)/CCB(I)
      IF(ABS(ERR).GT.1.E-4) GO TO 1
   20 DO 120 J=21,N,-1
      IF(QQ(I,J).EQ.0.) GO TO 120
      ERR=(QQ(I,J)-QG(J))/QQ(I,J)
      IF(ABS(ERR).GT.1.E-4) GO TO 1
  120 CONTINUE
      RETURN
      END
```

FS: FIXED-BED ADSORPTION EQUATION SOLVING COMPUTER PROGRAM

```
C   FS.FOR

C

C   FIXED BED ADSORPTION, FS MODEL

C   MAIN PROGRAM
C
    IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
    DIMENSION CB(21),CCB(21),QT(21),Z(21)
   *     ,Q(21,21),QQ(21,21),CS(21),CCS(21)
   *     ,N(21),NR(21),INDEX(21),IR(21),F1(21),F2(21)
   *     ,CK(50),QK(50),FDK(50),CKK(25),SOLUTE(18)
   *     ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
   *     ,CBX(25),QTX(25)
C  *      ,TW(10000),CW(10000),VOL(10000)
    COMMON /BL1/CB,Q,QSD,F,FD
   *    /BL2/CCB,QQ
   *    /BLS/S1,S2,S3,S4
C  *    /BLXY/TW,CW,VOL
C  *    /BLDATA/SOLUTE,ISO,A,B,C0,Q0,IR0
C  *         ,U,DIA,RS,RB,AKF,DS,DB
C  *         ,DELT,DELTMX,TEND,DELZ,ZEND,DTUBE
C   DATA NKK/22/
C  *  ,CKK/0., 0.001, 0.002, 0.005, 0.0075, 0.01, 0.02
C  *     ,0.05, 0.075, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5
C  *     ,0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0/
    DATA NKK/25/
   *  ,CKK/0.,0.0001,0.0002, 0.0005
   *     ,0.001   ,0.002 , 0.005, 0.0075, 0.01, 0.02
   *     ,0.05, 0.075, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5
   *     ,0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0/
C
    OPEN(5,FILE='FS.IN')
    OPEN(6,FILE='FS.OUT')
C
    READ(5,1001) SOLUTE
    ISO=2
    READ(5,*) AA
    READ(5,*) B
    READ(5,*) C00
    READ(5,*) IR0
C
    C0=C00/1000.0
    IF(ISO.EQ.2) A=AA*1000.0**B
C
1001 FORMAT(18A4)
```

```
C      1002 FORMAT(I10,3F10.0,I10)
 1004 FORMAT(1H1/////1H ,'SOLUTE = ',18A4///)
 1005 FORMAT(1H ,'CK (MG/L)'/(1H ,1P10E12.3))
 1006 FORMAT(1H ,'QK (MG/G)'/(1H ,1P10E12.3))
C      1007 FORMAT(7I10)
    2 NK=NKK
      DO 120 K=1,NK
      CK(K)=C0*CKK(K)
      IF(ISO.EQ.1) QK(K)=A*B*CK(K)/(1.+B*CK(K))
      IF(ISO.EQ.2) QK(K)=A*CK(K)**B
      IF(ISO.EQ.3) QK(K)=A*CK(K)
      IF(K.EQ.1) GO TO 120
      FDK(K)=(CK(K)-CK(K-1))/(QK(K)-QK(K-1))
  120 CONTINUE
      Q0=QK(23)
    3 CONTINUE
C
    5 CONTINUE
      READ(5,*,END=500) U
      READ(5,*,END=500) DIA
      READ(5,*,END=500) RS
      READ(5,*,END=500) RB
      READ(5,*,END=500) AKF
      READ(5,*,END=500) DS
      READ(5,*,END=500) DB
      READ(5,*) DELT
      READ(5,*) DELTMX
      READ(5,*) TEND
      READ(5,*) DELZ
      READ(5,*) ZEND
      READ(5,*) DTUBE
C
      READ(5,*) IITM
C
      WRITE(6,1008) SOLUTE,AA,B,C00,Q0,IR0
     *           ,U,DIA,RS,RB,AKF,DS,DB
     *           ,DELT,DELTMX,TEND,DELZ,ZEND,DTUBE
      WRITE(*,1008) SOLUTE,AA,B,C00,Q0,IR0
     *           ,U,DIA,RS,RB,AKF,DS,DB
     *           ,DELT,DELTMX,TEND,DELZ,ZEND,DTUBE
 1008 FORMAT(1H ,'FIXED BED ADSORPTION, FS MODEL'/
     *      1H ,'SOLUTE = ',5X,18A4/
     *      1H ,'A,B,C0,Q0,IR0 = '/1H ,1P4E16.5,I10/
     *      1H ,'U,DIA,RS,RB,AKF,DS,DB ='/1H ,1P7E16.5/
     *      1H ,'DELT,DELTMX,TEND,DELZ,ZEND,DTUBE ='/1H ,1P6E16.5/)
      U=U*60.
      RS=RS*1000.
      RB=RB*1000.
      AKF=AKF*3600.
      DS=DS*3600.
      DB=DB*3600.
      RADIUS=DIA/2.
      NR0=20*2**IR0
C     NR0=5*2**IR0
```

```
      DELR=RADIUS/DFLOAT(NR0)
      AV=3.*RB/RS/RADIUS
      EB=1.-RB/RS
      COEF=DTUBE**2*3.14/4.*U/1000.
      F10=DELR**2/DS/DELT
      F20=AKF/RS/DS/RADIUS*DELR*(RADIUS+DELR)
      IF(DB.EQ.0.) FY=-AKF*AV/U
      IF(DB.NE.0.) FY=(U-DSQRT(U**2+4.*AKF*AV*EB*DB))/2./EB/DB
      F3=U/AKF/AV/DELZ
      F4=DEXP(FY*DELZ)
      F5=AKF*AV*DELT/2./RB
    6 DO 130 I=1,21
      ZX=DELZ*DFLOAT(I-1)
      IF(ZX.GE.ZEND) GO TO 7
      CX=DEXP(FY*ZX)
      IF(CX.LT.0.001) M=I-1
      IF(CX.LT.0.001) M1=I
      IF(CX.LT.0.001) GO TO 8
  130 CONTINUE
      DELZ=2.*DELZ
      F3=U/AKF/AV/DELZ
      F4=DEXP(FY*DELZ)
      GO TO 6
    7 M=20
      M1=21
      DELZ=ZEND/20.
      F3=U/AKF/AV/DELZ
      F4=DEXP(FY*DELZ)
      F3M1=F3
      F4M1=F4
    8 DO 150 I=1,M1
      Z(I)=DFLOAT(I-1)*DELZ
      CB(I)=DEXP(FY*Z(I))*C0
      CBX(I)=CB(I)/C0
      CCB(I)=CB(I)
      CS(I)=0.
      CCS(I)=0.
      QT(I)=0.
      IR(I)=IR0
      NR(I)=NR0
      F1(I)=F10
      F2(I)=F20
      N(I)=11
      INDEX(I)=0
      DO 140 J=1,21
      Q(I,J)=0.
      QQ(I,J)=0.
  140 CONTINUE
  150 CONTINUE
      T=0.
C
      IIT=0
C
      KW=0
```

```
      KC=0
      KXY=0
      NPT=0
      KWH=10
      KCH=100
      KXYH=10
      WRITE(*,1010) T
      WRITE(*,1011) (Z(I),I=1,M1)
      WRITE(*,1012) (CBX(I),I=1,M1)
C
      WRITE(6,1010) T
      WRITE(*,1010) T
C
   10 T=T+DELT
C
      IIT=IIT+1
C
      KXY=KXY+1
      KW=KW+1
      KC=KC+1
      DO 200 I=1,M1
   20 QSD=QQ(I,21)
      DO 210 K=2,NK
      IF(QSD.LT.QK(K)) GO TO 21
  210 CONTINUE
   21 FD=FDK(K)
      F=FDK(K)*(QSD-QK(K-1))+CK(K-1)
      IF(I.NE.1) X=CCS(I-1)
      IF(I.NE.1) Y=CCB(I-1)
      IF(Z(I).NE.ZEND) F3I=F3
      IF(Z(I).NE.ZEND) F4I=F4
      IF(Z(I).EQ.ZEND) F3I=F3M1
      IF(Z(I).EQ.ZEND) F4I=F4M1
      CALL KEISU(I, N(I), NR(I), INDEX(I), IR(I)
     *        ,F1(I), F2(I), F3I, F4I, X, Y, CS(I))
      CALL GAUSS(I, N(I))
      IF(ISO.EQ.3) GO TO 22
      ERR=(QQ(I,21)-QSD)/QQ(I,21)
      IF(ABS(ERR).GT.1.E-4) GO TO 20
   22 CCS(I)=F
      CUTQ=QQ(I,21)*0.01
      IF(QQ(I,N(I)).LT.CUTQ) GO TO 200
      IF(N(I).EQ.1) GO TO 23
      N(I)=N(I)-1
      GO TO 20
   23 IF(IR(I).EQ.0) GO TO 200
      IR(I)=IR(I)-1
      NR(I)=NR(I)/2
      DELR=RADIUS/DFLOAT(NR(I))
      F1(I)=DELR**2/DS/DELT
      F2(I)=AKF/RS/DS/RADIUS*DELR*(RADIUS+DELR)
      N(I)=10
      INDEX(I)=0
      DO 220 J=21,11,-1
```

```
      JJ=2*J-21
      Q(I,J)=Q(I,JJ)
      QQ(I,J)=QQ(I,JJ)
  220 CONTINUE
      DO 230 J=1,10
      Q(I,J)=0.
      QQ(I,J)=0.
  230 CONTINUE
      GO TO 20
  200 CONTINUE
      DO 240 I=1,M1
      QT(I)=F5*(CCB(I)+CB(I)-CCS(I)-CS(I))+QT(I)
      CB(I)=CCB(I)
      CS(I)=CCS(I)
      DO 240 J=1,21
      Q(I,J)=QQ(I,J)
  240 CONTINUE
      IF(Z(M1).LT.ZEND) GO TO 30
C     IF(Z(M1).LT.ZEND*0.99999999) GO TO 30
      IF(KXY.LT.KXYH) GO TO 30
      NPT=NPT+1
C     TW(NPT)=T
      CWNPT=CB(M1)/C0
C     VOL(NPT)=T*COEF
      KXY=0
   30 IF(KW.LT.KWH) GO TO 40
      DO 300 I=1,M1
      CBX(I)=CB(I)/C0
      QTX(I)=QT(I)/Q0
  300 CONTINUE
C
      IF(IIT.GE.IITM) IIT=0
C
      IF(IIT.EQ.0) WRITE(6,1010) T,CWNPT
C    WRITE(6,*) M1,M
      IF(IIT.EQ.0) WRITE(*,1010) T,CWNPT,DELT
C    WRITE(6,1011) (Z(I),I=1,M1)
C    WRITE(6,1012) (CBX(I),I=1,M1)
C    WRITE(6,1013) (QTX(I),I=1,M1)
 1010 FORMAT(1H ,'T=',1PE10.3,'(HR)',5X,'CB/C0=',1PE11.4,3X,1PE9.2)
 1011 FORMAT(1H ,'    Z=',1P11E11.4/1H ,7X,1P11E11.4)
 1012 FORMAT(1H ,' C/C0=',1P11E11.4/1H ,7X,1P11E11.4)
 1013 FORMAT(1H ,' Q/Q0=',1P11E11.4/1H ,7X,1P11E11.4)
      KW=0
      KXY=0
      IF(CB(M1)/C0.GE.0.98) GO TO 50
      IF(T.GE.TEND) GO TO 50
      IF(KC.LT.KCH) GO TO 40
      KC=0
      KCH=90
      IF(10.*DELT.GE.DELTMX) KWH=10
      IF(10.*DELT.GE.DELTMX) GO TO 40
      DELT=10.*DELT
      F10=F10/10.
```

```
   F5=F5*10.
   DO 310 I=1,M1
   F1(I)=F1(I)/10.
   INDEX(I)=0
310 CONTINUE
 40 IF(QT(2)/Q0.LT.0.999) GO TO 45
   IF(M.EQ.1) GO TO 50
   M=M-1
   M1=M1-1
   DO 400 I=1,M1
   II=I+1
   Z(I)=Z(II)
   CB(I)=CB(II)
   CCB(I)=CCB(II)
   CS(I)=CS(II)
   CCS(I)=CCS(II)
   QT(I)=QT(II)
   IR(I)=IR(II)
   NR(I)=NR(II)
   F1(I)=F1(II)
   F2(I)=F2(II)
   N(I)=N(II)
   INDEX(I)=INDEX(II)
   DO 400 J=1,21
   Q(I,J)=Q(II,J)
   QQ(I,J)=QQ(II,J)
   S1(I,J)=S1(II,J)
   S2(I,J)=S2(II,J)
   S3(I,J)=S3(II,J)
400 CONTINUE
   CB(1)=C0
   CCB(1)=C0
 45 IF(CB(M1)/C0.LT.0.001) GO TO 10
   IF(Z(M1).GE.ZEND) GO TO 10
   IF(M1.EQ.21) GO TO 46
   M=M+1
   M1=M1+1
   GO TO 47
 46 DELZ=2.*DELZ
   F3=U/AKF/AV/DELZ
   F4=DEXP(FY*DELZ)
   DO 410 I=2,11
   II=2*I-1
   Z(I)=Z(II)
   CB(I)=CB(II)
   CCB(I)=CCB(II)
   CS(I)=CS(II)
   CCS(I)=CCS(II)
   QT(I)=QT(II)
   IR(I)=IR(II)
   NR(I)=NR(II)
   F1(I)=F1(II)
   F2(I)=F2(II)
   N(I)=N(II)
```

```
      INDEX(I)=INDEX(II)
      DO 410 J=1,21
      Q(I,J)=Q(II,J)
      QQ(I,J)=QQ(II,J)
      S1(I,J)=S1(II,J)
      S2(I,J)=S2(II,J)
      S3(I,J)=S3(II,J)
  410 CONTINUE
      M=11
      M1=12
C     M=10
C     M1=11
   47 Z(M1)=Z(M)+DELZ
      CB(M1)=CB(M)*F4+CS(M)*(F3-F4-F3*F4)
      IF(Z(M1).LT.ZEND) GO TO 48
      DELZM1=ZEND-Z(M)
      F3M1=U/AKF/AV/DELZM1
      F4M1=DEXP(FY*DELZM1)
      Z(M1)=ZEND
      CB(M1)=CB(M)*F4M1+CS(M)*(F3M1-F4M1-F3M1*F4M1)
   48 CCB(M1)=CB(M1)
      CS(M1)=0.
      CCS(M1)=0.
      QT(M1)=0.
      IR(M1)=IR0
      NR(M1)=NR0
      F1(M1)=F10
      F2(M1)=F20
      N(M1)=11
      INDEX(M1)=0
      DO 420 J=1,21
      Q(M1,J)=0.
      QQ(M1,J)=0.
  420 CONTINUE
      GO TO 10
   50 CONTINUE
C     GO TO 5
  500 CONTINUE
      STOP
      END
C    SUBROUTINE KEISU
      SUBROUTINE KEISU(I,N,NR,INDEX,IR,F1,F2,F3,F4,X,Y,CS)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION CB(21),Q(21,21)
     *      ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
      COMMON /BL1/CB,Q,QSD,F,FD
     *     /BLS/S1,S2,S3,S4
      IF(INDEX.NE.0) GO TO 10
      DO 100 J=1,20
      EJ=NR-21+J
      IF(EJ.EQ.0.) GO TO 100
      S1(I,J)=-(EJ-1.)/2./EJ
      S2(I,J)=F1+1.
      S3(I,J)=-(EJ+1.)/2./EJ
```

```
 100 CONTINUE
      IF(IR.EQ.0) S2(I,1)=F1+3.
      IF(IR.EQ.0) S3(I,1)=-3.
      S1(I,21)=-1.
      S3(I,21)=-F2
      S2(I,22)=1.
      INDEX=1
  10 DO 110 J=N,20
      IF(J.EQ.1.AND.IR.EQ.0) S4(I,1)=3.*(Q(I,2)-Q(I,1))+F1*Q(I,1)
      IF(J.EQ.1.AND.IR.NE.0) S4(I,1)=(F1-1.)*Q(I,1)-S3(I,1)*Q(I,2)
      IF(J.NE.1) S4(I,J)=-S1(I,J)*Q(I,J-1)+(F1-1.)*Q(I,J)
    *              -S3(I,J)*Q(I,J+1)
 110 CONTINUE
      S2(I,21)=1.+F1+F2*FD
      S4(I,21)=Q(I,20)-F2*(CS+F-FD*QSD)+(F1-1.)*Q(I,21)+F2*CB(I)
      IF(I.NE.1) S1(I,22)=(-1.+F3-F3*F4)*FD
      IF(I.NE.1) S4(I,22)=(1.-F3+F3*F4)*(F-FD*QSD)+(F3-F4-F3*F4)*X+F4*Y
      RETURN
      END
C    SUBROUTINE GAUSS-SEIDEL
      SUBROUTINE GAUSS(I,N)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION CCB(21),QQ(21,21),QG(21)
    *       ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
      COMMON /BL2/CCB,QQ
    *      /BLS/S1,S2,S3,S4
   1 DO 100 J=1,21
      QG(J)=QQ(I,J)
 100 CONTINUE
      CBG=CCB(I)
      IF(I.EQ.1) GO TO 10
      CCB(I)=(S4(I,22)-S1(I,22)*QG(21))/S2(I,22)
  10 QQ(I,21)=(S4(I,21)-S1(I,21)*QG(20)-S3(I,21)*CCB(I))/S2(I,21)
      DO 110 J=20,N,-1
      IF(J.EQ.1) QQ(I,1)=(S4(I,1)-S3(I,1)*QQ(I,2))/S2(I,1)
      IF(J.NE.1) QQ(I,J)=(S4(I,J)-S1(I,J)*QG(J-1)-S3(I,J)*QQ(I,J+1))
    *              /S2(I,J)
 110 CONTINUE
      IF(I.EQ.1) GO TO 20
      ERR=(CCB(I)-CBG)/CCB(I)
      IF(ABS(ERR).GT.1.E-4) GO TO 1
  20 DO 120 J=21,N,-1
      IF(QQ(I,J).EQ.0.) GO TO 120
      ERR=(QQ(I,J)-QG(J))/QQ(I,J)
      IF(ABS(ERR).GT.1.E-4) GO TO 1
 120 CONTINUE
      RETURN
      END
```

"In the ordinary business of life, industry can do anything which genius can do, and very many things which it cannot." (Henry Ward Beecher)

Vita

THOMAS EDWARD TOKUO GILLOGLY

PERSONAL INFORMATION

Date of Birth: June 5, 1971
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EDUCATION

University of Illinois, IL

Doctor of Philosophy in Environmental Engineering in Civil Engineering, January 1999

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Advisor: Vernon L. Snoeyink

Master of Science in Civil Engineering, May 1995

Advisor: Vernon L. Snoeyink

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Bachelor of Science in Chemical Engineering and Engineering & Public Policy (with an Environmental Engineering minor), May 1993

EXPERIENCE

12/93 - present	Graduate Research Assistant - Advisor: Vernon L. Snoeyink, Ph.D. *University of Illinois Environmental Engineering Program*, Urbana, IL • Research the theory and basic design of processes used in water treatment • Correlate physical/chemical measurements to adsorption phenomena
9/93 – 12/93	Teaching Assistant - CE342: Water and Wastewater Treatment Unit Operations *University of Illinois, Environmental Engineering Program*, Urbana, IL
6/93 – 9/93	Health Services Officer – Public Health Service (0-1 ensign) *U.S. Environmental Protection Agency (EPA, OSWER, OPM)*, Washington, D.C.

- Analyzed and compiled regional data for Superfund directoral meetings
- Reviewed external reports concerning the Superfund Program
- Wrote internal document consolidating Superfund program information

9/92 – 5/93 Undergraduate Research Assistant - *Advisor: David A. Dzombak, Ph.D., P.E.*
Carnegie Mellon University, Department of Civil and Environmental Engineering, Pittsburgh, PA

- Wrote, "Synthesis of MnO_2 Coated Granular Activated Carbon for the Removal of Heavy Metals From Aqueous Media"
- Developed methodologies to produce various MnO_2 coatings
- Analyzed stability and adsorptive capacity of coatings

6/92 – 9/92 Health Services Officer – Public Health Service (0-1 ensign)
U.S. Environmental Protection Agency (EPA, ORD, SITE Program), Cincinnati, OH

- Analyzed proposed innovative technologies for hazardous waste site remediation
- Orchestrated work on scaling up a dehalogenation process

6/91 – 9/91, Engineering Intern – (GS-4)
12/91 – 1/92 *U.S. Army Toxic and Hazardous Materials Agency,* A.P.G., MD

- Wrote, "The Development of a Soil Sampling Plan for the RDX Manufacturing Area, Newport Army Ammunition Plant"
- Assisted project managers in data analysis/management

PUBLICATIONS AND PRESENTATIONS

Peer Reviewed

Gillogly, T.E.T., V.L. Snoeyink, J. Vogel, C.M. Wilson & E.P. Royal. Determining Remaining GAC Bed Life for Taste and Odor Control. *Journal American Water Works Association* (Submitted 10/98).

Gillogly, T.E.T., V.L. Snoeyink, G. Newcombe & J.R. Elarde. A Simplified Method to Determine the PAC Dose Required to Remove MIB. *Water Science and Technology* (Accepted 4/98).

Gillogly, T.E.T., V.L. Snoeyink, A. Holthouse, C.M. Wilson & E.P. Royal. (1998) Effect of Chlorine on PAC's Ability to Adsorb MIB. *Journal American Water Works Association* 90:2:107.

Gillogly, T.E.T., V.L. Snoeyink, J.R. Elarde, C.M. Wilson & E.P. Royal. (1998) ^{14}C-MIB Adsorption on PAC in Natural Water. *Journal American Water Works Association* 90:1:98.

Conference Proceedings

Gillogly, T.E.T., V.L. Snoeyink, G. Newcombe & J.R. Elarde. A Simplified Method to Determine the PAC Dose Required to Remove MIB. In

Proceedings of the IAWQ - Fifth International Symposium on Off-Flavours in the Aquatic Environment. Paris, France. 12-16 October, 1997.

Gillogly, T.E.T., V.L. Snoeyink, A. Holthouse, C.M. Wilson & E.P. Royal. Effect of Chlorine on 2-Methylisoborneol Adsorption by Activated Carbon. In *Proceedings of the American Water Works Association Annual Conference & Exposition.* Atlanta, Georgia. 15-19 June, 1997.

Gillogly, T.E.T., V.L. Snoeyink, J.R. Elarde, C.M. Wilson & E.P. Royal. Kinetic and Equilibrium Studies of ^{14}C-MIB Adsorption on PAC in Natural Water. In *Proceedings of the American Water Works Association Annual Conference & Exposition.* Toronto, Canada. 23-27 June, 1996.

Snoeyink, V.L., T.E.T. Gillogly, D.R.U. Knappe & J.R. Elarde. Optimal Use of Powdered Activated Carbon for Pesticide and Taste and Odour Removal. In *Proceedings of WaterTech (Australian Water & Wastewater Association).* Sydney, Australia. 27-28 May, 1996.

Invited Lectures

Gillogly, T.E.T., V.L. Snoeyink, J.R. Elarde, & G. Newcombe. Practical and Innovative Use of PAC for Taste and Odor Control. Small Reservoir Management Conference. Rensselaer, New York. 10 June, 1998.

Platform Presentations

Gillogly, T.E.T., V.L. Snoeyink, G. Newcombe & J.R. Elarde. A Simplified Method to Determine the PAC Dose Required to Remove MIB. IAWQ - Fifth International Symposium on Off-Flavours in the Aquatic Environment. Paris, France. 12-16 October, 1997.

Gillogly, T.E.T., V.L. Snoeyink, A. Holthouse, C.M. Wilson & E.P. Royal. Effect of Chlorine on 2-Methylisoborneol Adsorption by Activated Carbon. AWWA Annual Conference. Atlanta, Georgia. 15-19 June, 1997.

Gillogly, T.E.T., V.L. Snoeyink, J.R. Elarde, C.M. Wilson & E.P. Royal. Kinetic and Equilibrium Studies of ^{14}C-MIB Adsorption on PAC in Natural Water. AWWA Annual Conference. Toronto, Canada. 23-27 June, 1996.

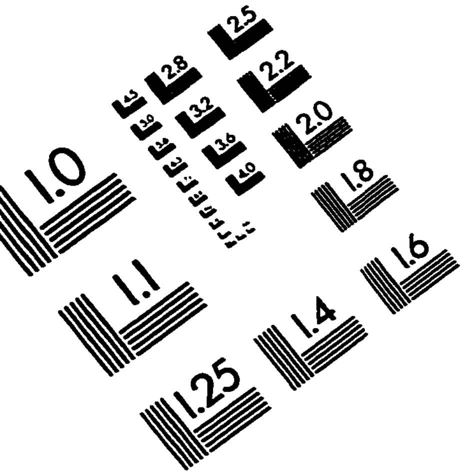
Thurston E. Larson - Best Paper Award. Gillogly, T.E.T., V.L. Snoeyink, J.R. Elarde, C.M. Wilson & E.P. Royal. Taste and Odor Studies: Recent Illinois Problems and Solutions. Illinois Section AWWA 87th Annual Meeting. Rockford, Illinois. 26-29 March, 1996.

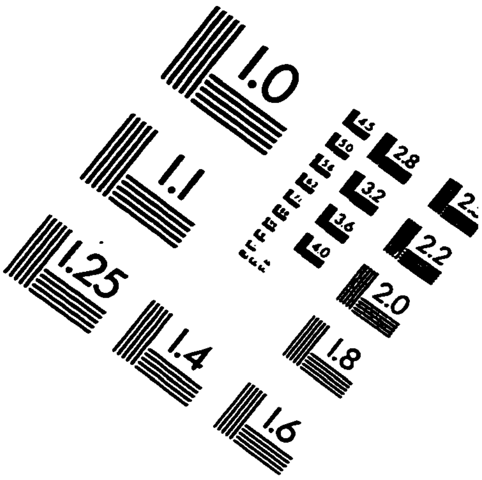
Snoeyink, V.L. & T.E.T. Gillogly. Progress Report Presentation. City of Chicago Department of Water. Chicago, Illinois. 30 November, 1998; 22 July, 1998; 19 December, 1997; 26 February, 1997; 9 October, 1996; 10 January, 1996; 21 July, 1995; 2 December, 1994; 10 June, 1994.

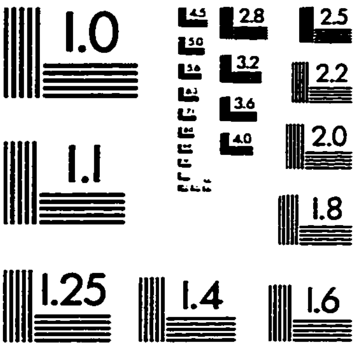
PROFESSIONAL REGISTRATION AND MEMBERSHIP

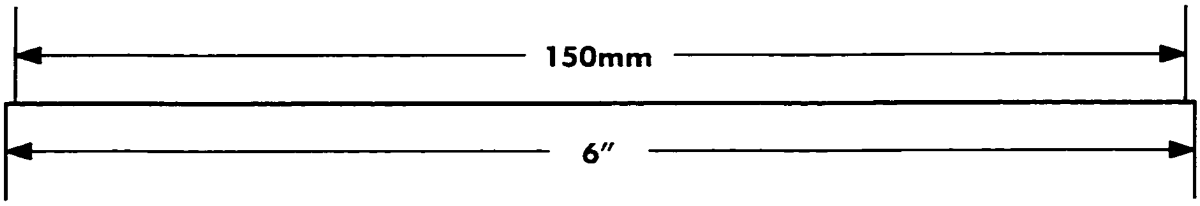
1994	E.I.T. Illinois
1993-present	American Water Works Association
1990-1993	American Institute of Chemical Engineers

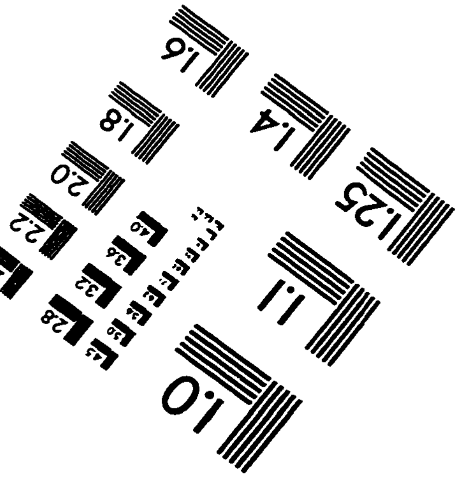
IMAGE EVALUATION
TEST TARGET (QA-3)

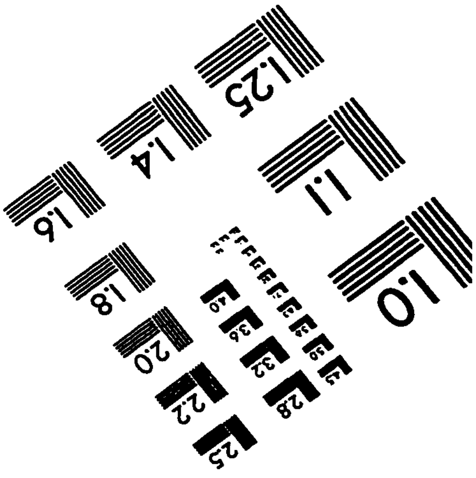












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