

**TREATMENT OF THE HUDSON RIVER TO SUPPLY POTABLE WATER:  
FATE OF SELECT TRACE ORGANICS**

Draft of Final Report to the Hudson River Foundation  
January 1996

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Suite 1901  
New York, New York 10168

Published by the Hudson River Foundation

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## FOREWORD

The overall goal of the Hudson River Fund is to provide leadership and support for an integrated program of research, monitoring, modeling, synthesis and education related to the management of the aquatic resources of the Hudson River.

Under the terms of the Settlement Agreement that established the Hudson River Fund, support is given to:

scientific, ecological, and related public policy research on issues and matters of concern to the Hudson River, its tributaries and its drainage basin, with emphasis given, but not limited, to mitigating fishery impacts caused by power plants, providing information needed to manage the fishery resources of the Hudson River, understanding the factors related to the abundance and structure of fish populations, and gaining knowledge of the Hudson River ecosystem.

In its program of scientific research, the Foundation seeks to elucidate the dynamic interactions among the physical, chemical, and biological processes that are important to the Hudson River ecosystem. Major areas of interest include scientific research on resource species, dynamics of Hudson River trophic webs, toxic substances, and hydrodynamics and sediment transport.

For this project, a broad spectrum of potentially toxic organic compounds in the Hudson River were investigated, partly in response to a chemical spill of 1,1,1-trichloroethane on the Hudson River, which contaminated drinking water at Waterford, NY in 1985. At Waterford, the spill resulted in improved reporting procedures between institutions that are responsible for water quality in the Hudson River, as well as improved monitoring for synthetic organic chemicals at the intake for drinking water. However, there was also a perceived need to understand the variability of synthetic organic chemicals in the Hudson River, and the feasibility of their removal from drinking water.



## ACKNOWLEDGMENTS

A number of persons made contributions to this project that were greatly appreciated. The activated carbon pilot column experiments were conducted at Waterford Water Works with the cooperation of Harold Berger and John D. Farrar. Field samples were collected from the Latham Water District with the cooperation of Gary Mostert, Bud Van Dyke and Jack Halstuch. At the Wadsworth Center, the analysis of sample extracts by gas chromatography-mass spectrometry was facilitated by Ken Aldous, with John Snow providing technical assistance. The support of the Hudson River Foundation, and the patient assistance of Dennis Suszkowski as Science Director are also gratefully acknowledged.



## EXECUTIVE SUMMARY

This project represents an experimental investigation of synthetic organic chemicals in the Hudson River and methods for drinking water purification. The primary objectives of this project were:

1. to determine the ability of granular activated carbon (GAC) pilot columns to remove simulated spills of organic chemicals from drinking water at Waterford Water Works
2. to assess the variability of background organic chemicals in drinking water, at different points in conventional treatment, and before and after exposure to GAC: frequencies of detection, average concentrations and standard deviations with respect to analytical quantitation limits
3. to evaluate strategies to detect simulated spills, by analysis of water and activated carbon samples collected weekly

Results were obtained for several groups of organic compounds, classified primarily by different methods of sample preparation and analysis: 7 volatile halogenated organics; 6 volatile aromatic organics; 73 semivolatile base-neutral organics. A subset of these compounds was used in simulated spill experiments.

## EXPERIMENTAL METHODS

Granular activated carbon adsorption of the target compounds was studied by conducting pilot column experiments for 30 weeks at Waterford Water Works. The pilot columns were nominally 15 cm in diameter, packed to contain 117 cm of 12 x 40 mesh Calgon F400 (9.3 Kg), and operated with an average empty-bed contact time of 17 min. One pilot column was exposed to four one-week simulated spills. Two other pilot columns were operated in parallel as controls receiving only background natural organic matter and the byproducts of disinfection at Waterford Water Works. Compounds added during the simulated spills included 7 volatile halogenated organics (chloroform, bromodichloromethane, dibromochloromethane, bromoform, carbon tetrachloride, tri- and tetrachloroethylene), 4 volatile aromatic organics (benzene, toluene, o-xylene and chlorobenzene), and 9 semivolatile base-neutral organics (1,3,5-trimethylbenzene; 1,2,3,4-tetramethylbenzene; naphthalene; biphenyl; dibutylphthalate; 1,2,3-trichlorobenzene; caffeine; atrazine; tributylphosphate). Average contaminant levels during the spills were 180, 90, and 5  $\mu\text{g/L}$  (1.1, 0.9, 0.026  $\mu\text{mol/L}$ ) for the volatile halogenated, volatile aromatic and semivolatile base-neutral organic compounds, respectively.

Concentrations of the target compounds were monitored in raw water and after various stages of conventional treatment (coagulation-flocculation-sedimentation, prechlorination,

filtration), as well as in influent and effluent samples from the pilot columns. Solvent extraction-gas chromatography with electron capture detection was used to analyze for the volatile halogenated organics between 8 and 250  $\mu\text{g/L}$ . Purge-and-trap gas chromatography with photoionization detection was used to screen for the volatile aromatic organics, between 0.1 and 0.8  $\mu\text{g/L}$  for background levels, but between 2 and 100  $\mu\text{g/L}$  during the simulated spills. Resin extraction followed by gas chromatography and mass spectrometric analysis was used to monitor the semivolatile base-neutral organic compounds between 0.2 and 0.8  $\mu\text{g/L}$ . It was also found possible to monitor the volatile halogenated organics within the pilot column, by methanol extraction of GAC samples, gas chromatography and electron capture detection of contaminants at levels between 30 to 810  $\mu\text{g/g}$  GAC.

## **GAC ADSORPTION OF SIMULATED SPILLS**

### **Volatile Halogenated Organic Contaminants**

The most complete set of results was obtained for the volatile halogenated organic contaminants. Analyses of influent and effluent samples provided the data to assess breakthrough. Analyses of GAC samples documented adsorption within the pilot column and the approach to saturation. For the volatile halogenated organics, distributions as a function of time and position within the pilot column were consistent with observations of breakthrough.

Breakthrough of the trihalomethanes occurred during the third and fourth spills, which were conducted just before and just after background chloroform was at complete breakthrough. All remaining compounds were completely removed by GAC adsorption during all four simulated spills.

Results for chloroform adsorption parallel its initial breakthrough at 100 days and complete breakthrough after 180 days. Chloroform moved through the pilot column and began adsorbing on GAC at the bottom in 100 days, reaching maximum uptake (1.5 mg/g) in 175 days.

The remaining trihalomethanes lagged behind chloroform, reaching breakthrough only during the third and fourth spills. Bromodichloromethane began adsorbing at the bottom of the pilot column at 140 days, during the third spill. Chlorodibromomethane was detected at the bottom of the pilot column at 160 days, after the third spill. Bromoform just reached the bottom of the pilot column at 212 days, after the fourth spill. Similar differences were seen in distributions of the brominated trihalomethanes at saturation. By the end of the experiment, bromodichloromethane appeared near saturation on the entire column, whereas chlorodibromomethane had only reached saturation on the top 75 cm of GAC, and bromoform had only reached saturation on the top 55 cm of GAC.

Compounds which did not reach breakthrough (carbon tetrachloride, tri- and tetrachloroethylene) were also found only on the top 55 to 75 cm of the GAC bed.

Although breakthrough of the trihalomethanes was evident during the third and fourth spills, the level was low. Conversely, attenuation of the spills was high, ranging from 82 to 100 percent during the third spill, and from 69 to 97 percent in the fourth spill. The decrease in attenuation between the third and fourth spills is attributed to increased adsorption of background trihalomethanes (and background natural organic matter) between spills. As might be expected, attenuation was greatest for the trihalomethanes farthest from complete breakthrough: bromoform > chlorodibromomethane > bromodichloromethane > chloroform. Attenuation of the brominated trihalomethanes exceeded 90 percent during the third and fourth spills; attenuation of chloroform averaged 75 percent. Perhaps the most remarkable result was that chloroform could be 75 percent attenuated during the spills, although at its background level, chloroform had reached complete breakthrough and was no longer being adsorbed. At least for chloroform, a pilot column at saturation with background organics can shift to a higher capacity during a spill, in keeping with the fundamental properties of adsorption equilibria.

Very little evidence was obtained for post-spill desorption of the contaminants, even those that had reached partial breakthrough during the last two spills. For chloroform, concentrations decreased steadily after the third and fourth spills, in this case returning to the level of breakthrough defined by background chloroform. Post-spill effluent concentrations of the other contaminants were either below the quantitation threshold (volatile halogenated compounds), or at background levels (volatile aromatic compounds; semivolatile base-neutral organic compounds). Since no large pulses of desorbed contaminants were found in post-spill effluent samples, contaminant desorption is hypothesized to be slow, when initiated by a chromatographic decrease in influent concentration.

Mass balances were calculated for the volatile halogenated organics, using both the water and GAC data to determine the cumulative mass input and mass adsorbed. Results from the water data were biased approximately 67 percent high, which is attributed to the time of collecting water samples, just after flows were reset to maintain contaminant levels in the simulated spills.

Competition between the spill constituents and with background natural organic matter is expected to have limited the pilot-column capacity for individual compounds. For all of the volatile halogenated organics, there was a significant increase in pilot column capacities with increasing bed depth. Moreover, capacities achieved on the pilot column were well below values expected from single-solute adsorption isotherms reported in the literature (Speth and Miltner 1990). Pilot-column capacities for chloroform were only a factor of five below the single-solute capacities; for the other volatile halogenated compounds, pilot-column capacities were low by a factor of 20 to 120.

## **Volatile Aromatic Organic Contaminants**

No evidence was obtained for breakthrough of any of the volatile aromatic compounds from the GAC pilot column. All were completely removed to sub- $\mu\text{g/L}$  levels by GAC adsorption during all four simulated spills. Relative to samples collected after various stages of conventional treatment, effluent samples from the pilot columns were found to have the lowest frequency of positives for volatile halogenated organics. Among samples found positive, average contaminant concentrations were also lowest in effluent from the pilot columns.

## **BACKGROUND CONCENTRATIONS OF ORGANIC CONTAMINANTS**

### **Volatile Halogenated Organic Contaminants**

The occurrence of chloroform as a disinfection byproduct of conventional treatment was readily apparent. Chloroform concentrations increased through successive stages of conventional treatment, and background concentrations increased in parallel with the seasonal increase in water temperature. Other volatile halogenated organic compounds of interest were consistently below the lower limit of quantitation by the method being used for water samples.

### **Volatile Aromatic Organic Contaminants**

Volatile aromatic organics were found at sub- $\mu\text{g/L}$  levels in samples collected to represent raw water quality and the effects of conventional treatment. Therefore, results for the volatile aromatic organic compounds preface results to be discussed for the semivolatile base-neutral organics, which were also monitored at sub- $\mu\text{g/L}$  levels in background samples. At the time of this project, the ability to monitor organic contaminants at sub- $\mu\text{g/L}$  levels was still an emerging technology, being developed for very hydrophobic compounds. The effect of conventional treatment or GAC adsorption on sub- $\mu\text{g/L}$  contaminant levels was also little understood.

Interpretation of these data requires an evaluation of statistical significance: results for individual compounds are summarized in terms of frequencies of occurrence, average concentrations in positive samples, and their standard deviations. In general, average contaminant concentrations in samples representing conventional treatment were greater than average concentrations in laboratory blanks, as well as method detection limits for analysis of the volatile aromatic compounds at sub- $\mu\text{g/L}$  levels. Only effluent samples from the GAC pilot columns had contaminant levels as low as the laboratory blanks or method detection limits.



A comparison of results at different sites suggested that analytical recoveries were approximately 25 percent lower for volatile aromatics purged from raw water samples than from treated water samples. Relative to untreated water, contaminants were found with increased frequency and at higher average concentrations after initial stages of treatment: after coagulation-flocculation-sedimentation, just before filtration, and in water pumped from the clearwell as influent to the pilot columns.

The frequency of occurrence ranged from an average of 29 percent for ethyl benzene to 90 percent for toluene. Background composition at sub- $\mu\text{g/L}$  concentrations was also highly variable: relative standard deviations in positive samples ranged from an average of 66 percent for o-xylene to 132 percent for benzene. Benzene, toluene and p-xylene had comparatively high values for the frequency of occurrence, average concentration, and standard deviation. Low values were typical of ethyl benzene, o-xylene and chlorobenzene.

## **DETECTION OF CHEMICAL SPILLS**

No spills of volatile halogenated or aromatic compounds were detected in background samples that were collected during this project, other than those that were created for the pilot column experiments

The one-week simulated spills were unfailingly detected in water samples routinely collected to monitor influent water quality to the GAC pilot column. Analyses of GAC samples for volatile halogenated organics also demonstrated an ability to detect the simulated spills. Efforts to extend this capability to the volatile aromatic organics were not successful, in part because the photoionization detector was not stable to methanol extracts of GAC samples; new high-sensitivity detectors, such as the ion trap mass spectrometer, may be a satisfactory alternative.

## **CONCLUSIONS AND RECOMMENDATIONS**

Granular activated carbon adsorption is a feasible means of removing spills of neutral volatile and semivolatile organic contaminants from Hudson River water. The capacity of granular activated carbon is limited by competitive interactions between organic compounds that are being adsorbed: to understand these limitations, information is needed on the kinetic as well as thermodynamic properties of adsorption for individual compounds.

Granular activated carbon also removes background contaminants at sub- $\mu\text{g/L}$  levels which are highly variable. This capability remains primarily of research interest, since drinking water regulations generally apply to contaminants above  $\mu\text{g/L}$  levels. Current interest in GAC focuses on its use to control natural organic matter which is the precursor to disinfection byproducts.



## CHAPTER 1

### PROJECT OBJECTIVES AND BACKGROUND

This project was initiated partly in response to a chemical spill of 1,1,1-trichloroethane on the Hudson River, which contaminated drinking water at Waterford, NY (Figure 1.1). At Waterford, the spill resulted in improved reporting procedures between institutions that are responsible for water quality in the Hudson River, as well as improved monitoring for synthetic organic chemicals at the intake for drinking water. However, there was also a perceived need to understand changes in the concentrations of synthetic organic chemicals in the Hudson River, and the feasibility of their removal from drinking water. The Hudson River is used to supply drinking water to Queensbury, Waterford, Poughkeepsie, and in times of drought, as a supplement to reservoirs for New York City. The Hudson River also receives discharges from approximately 22 municipalities and 161 industries (Rohmann et al. 1985).

Multiple approaches are generally used to control surface water quality, particularly as a resource for drinking water, in order to minimize substances that have either acute or long-term impacts on human health. Discharges are regulated through the State and Federal Pollutant Discharge Elimination System (NYS 1973; US EPA 1983). Computer-based water quality models, developed to predict the fate and transport of chemicals in aquatic systems, can help in setting discharge permits. A number of models of this type are available on Internet, from the US EPA Center for Exposure Assessment ([earth1.epa.gov](http://earth1.epa.gov)). QUAL2EU 3.21 and WASP 5.1 can be used to evaluate the impact of point-source municipal and industrial discharges on river-water quality (Brown and Barnwell 1987; Ambrose et al 1988). Similarly, PRZM2 2.0 and SWMM 4.3 can be used to assess the effect of nonpoint-source inputs such as agricultural and stormwater runoff (Mullins et al. 1994; Baker et al. 1994). Chemical analyses are an equally essential tool, whether to verify compliance with discharge permits, to check for nonpoint-source contaminants, or to validate the predictions of computer-based models. For synthetic organic chemicals in rivers, chemical analyses can accurately determine frequencies of occurrence, average concentrations and the magnitude of variations. However chemical analyses based on grab samples collected at discrete points in time have a limited ability to detect spills which occur randomly.

At present, notification procedures, computer models and chemical analyses are used interactively to schedule the closing of intakes for drinking water until the bulk of contaminants in a spill has passed downstream. Examples include the relatively large pesticide spill on the Rhine River and the fuel oil spill on the Monongahela and Ohio Rivers (Capel et al. 1988; Wanner et al. 1989; Clark et al. 1990). In these cases, storage capacity and alternate resources were adequate to maintain a supply of drinking water.

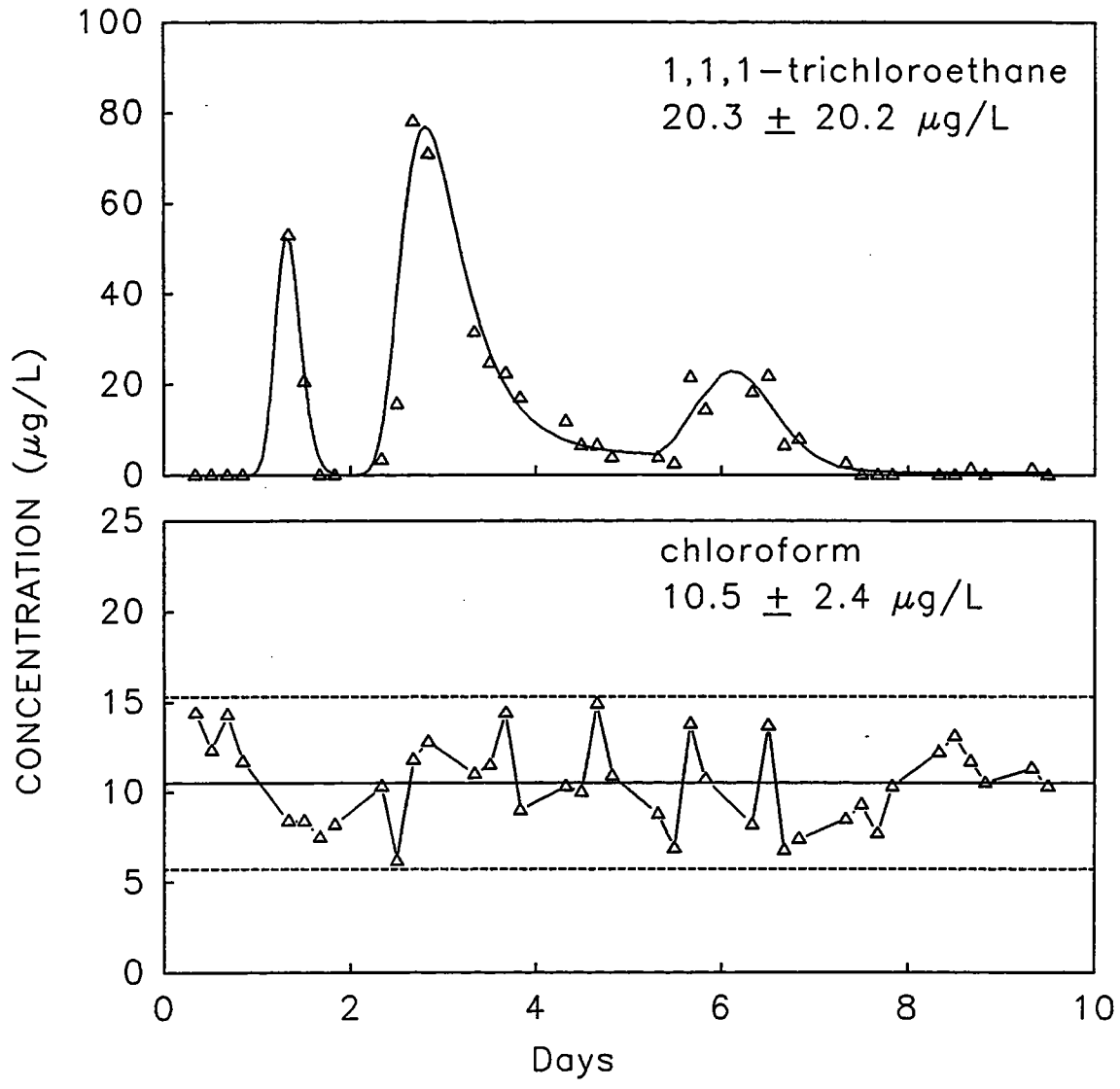


Figure 1.1 Concentrations of 1,1,1-trichloroethane during the spill on the Hudson River at Waterford, NY, compared to chloroform as a disinfection by-product, for February 10th through February 19th, 1985 (Alben et al. 1985).

In general, conventional physical-chemical treatment processes (coagulation-flocculation-sedimentation, filtration, disinfection) are not considered effective as a barrier against chemical spills. Granular activated carbon (GAC) adsorption is a relatively well known process, if not widely practiced, for removal of synthetic organic chemicals from drinking water. GAC consists of porous particles, 1 to 2 mm in diameter: the large internal surface area, on the order of 1000 m<sup>2</sup>/g, is carbonaceous and predominantly neutral. Since many synthetic organic contaminants are nonpolar and hydrophobic, with cross sections less than 10<sup>-18</sup> m<sup>2</sup>/molecule, they are favorably adsorbed by the GAC surface. At present, GAC adsorption is recognized as a best available treatment technology for 52 synthetic organic contaminants in drinking water (Appendix A; US EPA 1989a, 1990). This designation is based on the ability of GAC to remove synthetic organic contaminants below µg/L levels that are of concern in drinking water.

Full-scale applications of GAC for drinking water purification are in part based on the experiences of utilities in heavily developed European cities. In the United States, GAC has been used to some extent in filter-adsorbers, to control unknown sources of taste and odor, often related to the growth of microorganisms (Graese et al. 1987); however, suspensions of powdered activated carbon are more commonly used for this purpose than fixed beds of GAC. Full-scale contactors recently installed at the Cincinnati Water Works on the Ohio River represent a shift in the use of GAC, toward control of varying synthetic organic contaminants as well as precursors to disinfection byproducts (Miller and Westerhoff 1992). More specific uses of GAC for drinking water treatment are becoming possible, because of advances in analytical instrumentation in the last 20 years, particularly the development of highly sensitive and specific methods of detection, and the use of computers for control and automation.

This project was intended to be an experimental investigation of synthetic organic chemicals in the Hudson River and methods for drinking water purification. The primary objectives of this project were:

1. to determine the ability of granular activated carbon pilot columns to remove simulated spills of organic chemicals from drinking water at Waterford Water Works;
2. to evaluate strategies to detect simulated spills, by analysis of water and activated carbon samples collected weekly;
3. to assess the variability of background organic chemicals in drinking water, at different points in conventional treatment, and before and after exposure to GAC: frequencies of detection, average concentrations and standard deviations with respect to analytical quantitation limits.

The remainder of this chapter summarizes aspects of GAC adsorption relevant to treatment of chemical spills, and properties of the model compounds whose removal from drinking water is to be studied.

## CHARACTERISTICS OF CHEMICAL SPILLS AND GAC ADSORPTION

Proposed drinking-water regulations, summarized in Table A.1 for 56 synthetic organic contaminants, provide a relatively clear basis for utilities to evaluate water quality, the need for additional treatment, and the economic impact of best available treatment technologies (US EPA 1989a, 1990). Although these regulations are the product of a great deal of fundamental and applied research, use of GAC to treat chemical spills has not been extensively investigated.

Chemical spills represent extreme dynamic changes in water quality, with concentration changes over one to two orders of magnitude in a relatively short time period (days; weeks) compared to the long time period (year) for seasonal variations to occur. However, chemical spills are but one example of the overall problem of varying chemical concentrations. Synthetic organics in surface waters continually undergo changes in concentration, due to fluctuations in the composition of industrial and municipal effluents. Pesticides and herbicides can also appear in a surface water in a manner similar to a chemical spill, following seasonal applications and increased runoff triggered by storm events (Miltner et al. 1988; Thurman et al. 1991). Disinfection byproducts of natural organics in surface waters undergo seasonal variations in concentration, since their kinetics of formation is regulated by the temperature cycle: chloroform concentrations in the summer are nearly a factor of three greater than in the winter (Alben et al. 1992). However, the uncertain nature of random fluctuations in synthetic organic chemicals, particularly chemical spills, presents a greater challenge to methods of monitoring and treatment than seasonal changes in concentration which are predictable.

The performance of GAC in a fixed bed contactor is generally determined from the shape of a breakthrough curve for a specific organic contaminant, shown schematically in Figure 1.2. If a contaminant is input continuously at a concentration  $C_{inf}$ , the contaminant will be adsorbed for a period of time until breakthrough is reached: the effluent concentration  $C_{eff}$  will gradually increase until it equals the influent concentration. When breakthrough is complete,  $C_{eff} = C_{inf}$ , and the contaminant is no longer being adsorbed from water:  $Q$ , the contaminant's concentration on the GAC, reaches a maximum; in effect, the GAC is saturated (Figure 1.2). At this point, the GAC must be taken out of service and regenerated.

The time interval  $\Delta t$  between 10 and 90 percent breakthrough is determined by matching contactor design and operating conditions (particle size, contact time, bed depth) to a specific compound's rate of adsorption to surfaces within individual GAC particles. The time lapse  $t$  to reach a given percent of breakthrough is determined by a bed's adsorptive capacity.

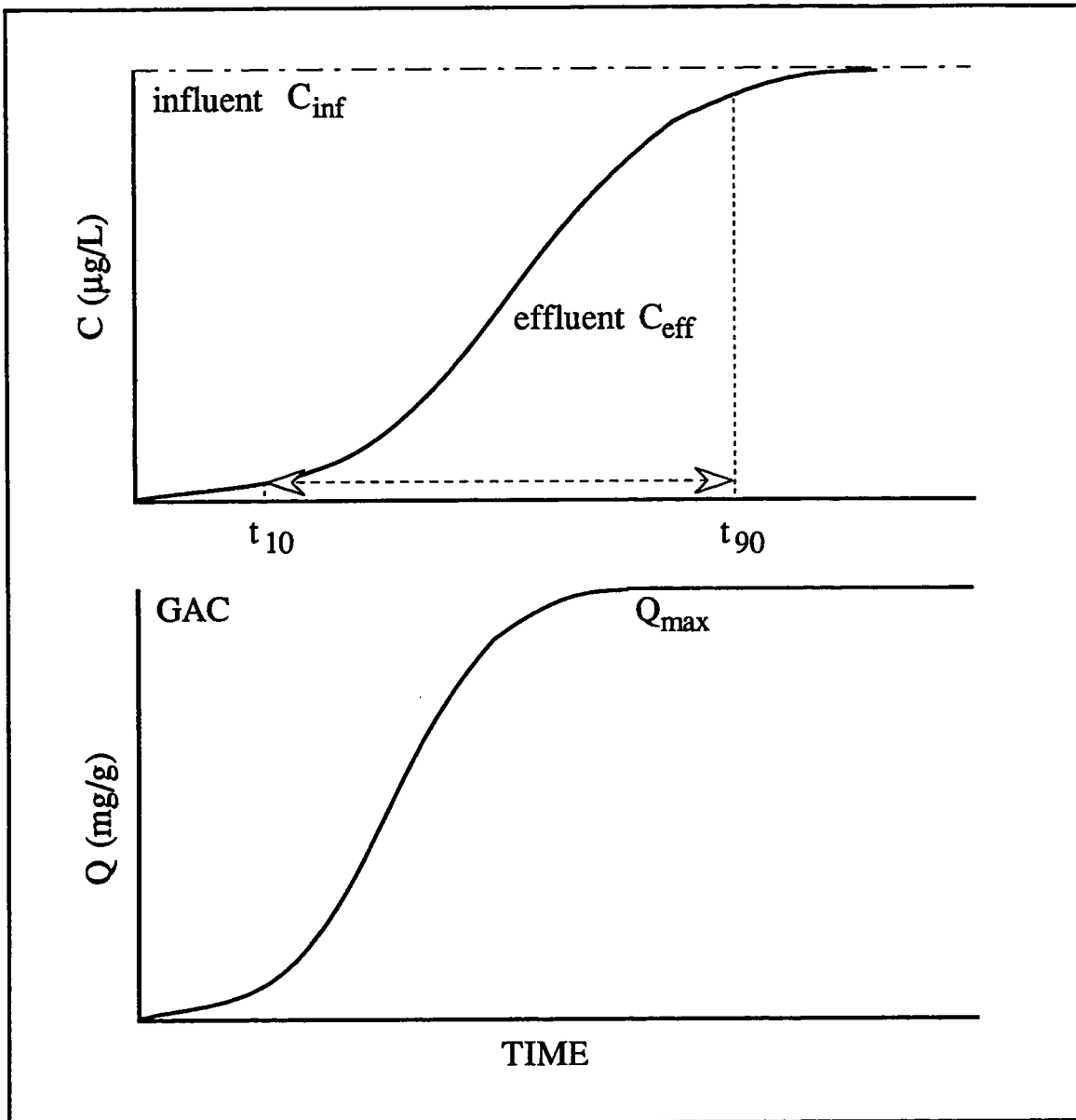


Figure 1.2 Schematic of concentration profiles for a contaminant reaching breakthrough (top - concentrations in water) and saturation (bottom - concentrations on the adsorbent), as a function of service time, on a GAC fixed-bed adsorber

In general, adsorption isotherms are the basis for describing the capacity of GAC for individual organic compounds in water. An adsorption isotherm is basically a mathematical function relating the concentration of a compound in water,  $C$  ( $\mu\text{g/L}$ ), to its concentration on the GAC,  $Q$  ( $\text{mg/g}$ ). Freundlich isotherms are often used to describe GAC adsorption of synthetic organic chemicals:

$$Q = K_F C^{1/n} \quad (1.1)$$

$Q$	adsorbed concentration of a compound at equilibrium, $\text{mg/g}$
$C$	aqueous phase concentration of a compound at equilibrium, $\mu\text{g/L}$
$K_F$	Freundlich coefficient, obtained as the intercept, $\log K_F$ , in a plot of $\log Q$ versus $\log C$ , $(\text{mg/g})(\text{L}/\mu\text{g})^{1/n}$
$1/n$	Freundlich coefficient, obtained as the slope, $1/n$ , in a plot of $\log Q$ versus $\log C$

In principle, an adsorption isotherm describes the distribution of a compound at equilibrium between water and GAC, but it is often difficult to establish true equilibrium in adsorption experiments.

Figure 1.3 shows the concentration relationship of a typical isotherm, while at the same time revealing a potential problem in the treatment of chemical spills. Since adsorption is a partitioning process between the aqueous phase and adsorbent phase, variations in aqueous concentrations are, in principle, directly associated with changes in GAC capacities. Increases in concentration correspond to increased GAC capacities and conversely. Therefore, while adsorption of a spill is favored by an increase in concentration  $C_{\text{inf}}$ , desorption after a spill is possible, in response to a decrease in concentration  $C_{\text{inf}}$ . However, the rate of desorption is not necessarily the same as for adsorption: not only can it be questioned whether equilibrium is reached, but also whether the process of adsorption is reversible, or subject to kinetic limitations.

Figure 1.4 shows two possible effluent profiles for a chemical spill being treated in a fixed-bed GAC contactor. In the first case (Figure 1.4, left), the contaminant reaches complete breakthrough during the spill: following the spill, effluent concentrations decay to zero; decay is rapid if residual, nonadsorbed contaminant is only being washed from the GAC pores, and there is little desorption of adsorbed contaminant from the GAC surface. Behavior of this type has been demonstrated for trichloroethylene (TCE) in pilot-scale GAC columns: only 17 percent of TCE was desorbed in the 60 days following a 43-day simulated spill (Alben et al. 1995). In the second case (Figure 1.4, right), the contaminant does not reach breakthrough: immediately after the spill, effluent concentrations still show no evidence of breakthrough; somewhat later, a pulse



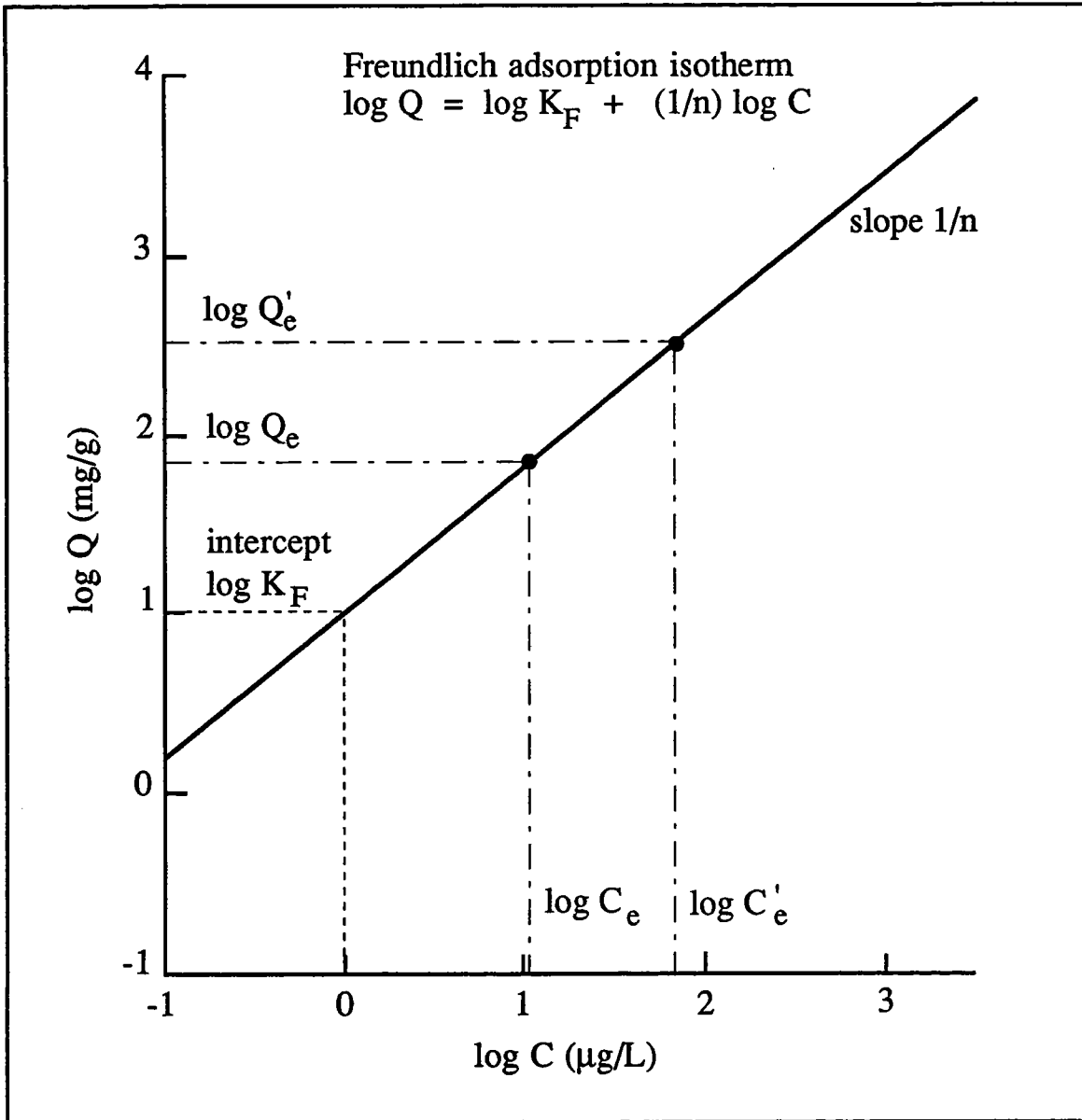


Figure 1.3 Freundlich adsorption isotherm relating contaminant concentrations in water ( $C_e$ ) and on granular activated carbon ( $Q_e$ ) at equilibrium

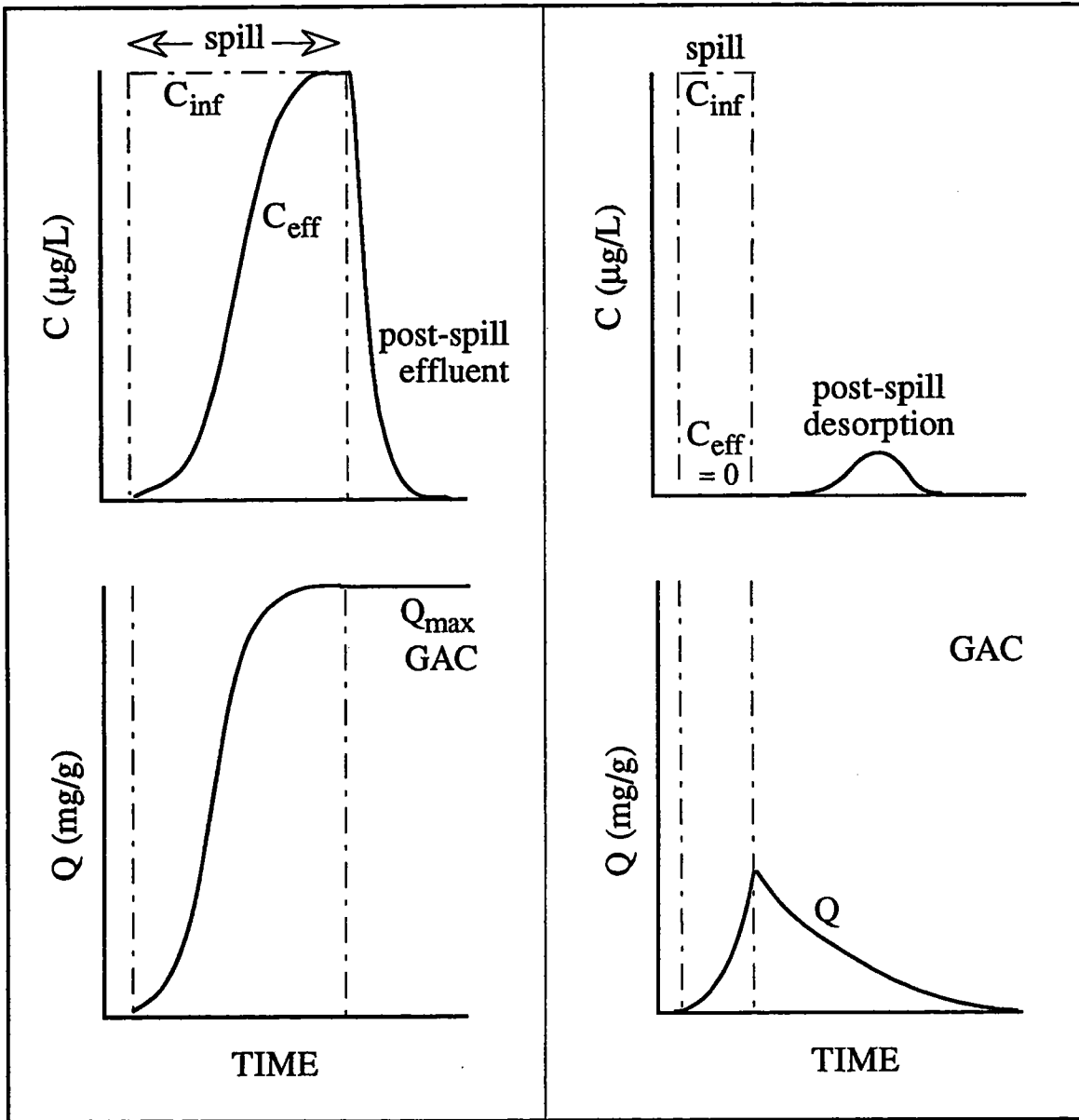


Figure 1.4 Schematic of post-spill effluent profiles and desorption from a fixed-bed GAC adsorber: left, concentrations for GAC reaching saturation during spill; right, concentrations for GAC not reaching saturation during spill.

of contaminant is washed from the GAC bed. Effluent profiles of this type represent complete adsorption of a contaminant during a spill: the contaminant is adsorbed-desorbed to successive bed depths after the spill, until it reaches the end of the bed and is desorbed into the effluent. Results of this type have been obtained for TCE in short, bench-scale minicolumn experiments: TCE desorption data were used to quantify spill attenuation, from the ratio of the maximum concentration of desorbed TCE to the original concentration during the spill (Namuduri and Summers 1991). Because the amount of attenuation increases with increasing bed depth, it is expected to be difficult to observe small pulses of contaminants that would be desorbed from a pilot-scale, fixed-bed contactor.

A related problem is that adsorption of a chemical spill can initiate desorption or displacement of other pre-loaded synthetic organic compounds, adsorbed at trace levels before the spill. Pilot-column data for a broad spectrum of organics were interpreted as evidence that displacement can occur if a GAC contactor is at the point of exhaustion with background organic compounds when it is used to treat a spill (Suffet et al. 1980; Neukrug et al. 1984).

In full-scale systems, there are several non-ideal conditions that generally decrease the GAC capacity for adsorption of chemical spills. Real spills, and discharges in general, often contain a mixture of chemicals: multiple organic compounds compete for the GAC surface, ultimately occupying less surface area than in the absence of competition. Mathematical methods have been developed by Crittenden and Hand to describe partitioning of the GAC surface for mixtures of synthetic organic chemicals (Crittenden et al. 1985). These models for competitive adsorption have also been applied to the removal of complex mixtures of synthetic organic chemicals by GAC pilot columns (Kuennen et al. 1989; Alben et al. 1995). Surface waters such as rivers also contain background natural organic matter: an average of  $4.3 \pm 0.7$  mg/L dissolved organic carbon in the Hudson River at Waterford is similar to values reported for many rivers (Thurman 1985; Wang 1994). Background natural organics adsorb to GAC and reduce the capacity for synthetic organics: Najm and Snoeyink have developed methods to account for the competitive effects of background organic matter on adsorption of synthetic organics such as 2,4,6-trichlorophenol (Najm et al. 1991). A related problem is that a GAC contactor is often in service for a significant length of time, several months to a year, and background natural organic matter may be near breakthrough before a chemical spill. A number of studies have demonstrated that preloading of background natural organic matter can reduce the GAC capacity for TCE (Hand et al. 1989; Summers et al. 1989; Zimmer et al. 1989; Munz et al. 1990; Wilmanski and van Breemen 1990; Alben et al. 1995). For this project, the primary objective is to acquire benchmark data for the ability of GAC pilot columns to treat simulated spills in Hudson River water, while recognizing that results may be affected by specific mechanisms for adsorption and desorption.

## MODEL COMPOUNDS

It was of interest to study compounds with a wide range of physical-chemical properties, which would differ in their affinity for GAC. At the time of experimental work for this project, maximum contaminant levels and methods of analysis were still in the process of being defined for synthetic organic chemicals in drinking water (US EPA 1987, 1989a,b, 1990, 1991). Therefore a list of 86 target compounds was derived from analytical experiences with procedures to extract organic contaminants from drinking water samples, combined with different types of instrumentation for compound identification and quantitation. Detailed methods of analysis for the target organic compounds are given in Appendix C. In general, these methods are considered suitable for the analysis of relatively nonpolar, hydrophobic organic compounds.

Figure 1.5 shows that the target compounds span an intermediate range of hydrophobicities; as expected, octanol-water partition coefficients tend to decrease as aqueous solubilities increase. Most of the target compounds have octanol-water partition coefficients,  $\log K_{OW}$ , between 1 and 4, with solubilities ranging from  $10^{-1}$  to  $10^{-4}$  mol/L, respectively. Only one target compound is very weakly hydrophobic (caffeine), with  $\log K_{OW}$  less than 1, but several target compounds are considered extremely hydrophobic (several C4 and C5-substituted alkyl benzenes; diphenyl ether; dibutyl and dioctyl phthalate), with  $\log K_{OW}$  greater than 4. The 52 synthetic organic compounds for which GAC is designated a best available treatment technology have similar octanol-water partition coefficients and solubilities: only a few of the regulated compounds are very weakly hydrophobic (aldicarb sulfone; dalapon; picloram); however, a large number of the regulated compounds are extremely hydrophobic (polycyclic aromatic hydrocarbons; the phthalates; chlordane; endrin; heptachlor and heptachlor epoxide; hexachlorobenzene; methoxychlor; polychlorinated biphenyls; pentachlorophenol; tetrachlorodibenzodioxin) (Appendix A).

As shown in Table 1.1, the target list of compounds includes seven halogenated aliphatic organic compounds that can be analyzed by solvent-extraction gas chromatography with electron-capture detection and seven volatile aromatic organic compounds that can be determined using purge-and-trap gas chromatography with photoionization detection. Most of the volatile organic compounds were to be used in simulated spills, as well as for background monitoring, during the field experiments.

Tables 1.2 through 1.4 list the 72 semivolatile organic compounds that were resin-extracted and analyzed by capillary gas chromatography-mass spectrometry. The semivolatile target compounds include several major subgroups that can be differentiated according to composition and structure: 20 aromatic hydrocarbons and a number of heteroatomic organic compounds with various substituents: 30 oxygen-substituted; 15 chlorine-substituted; 7 nitrogen-substituted; two

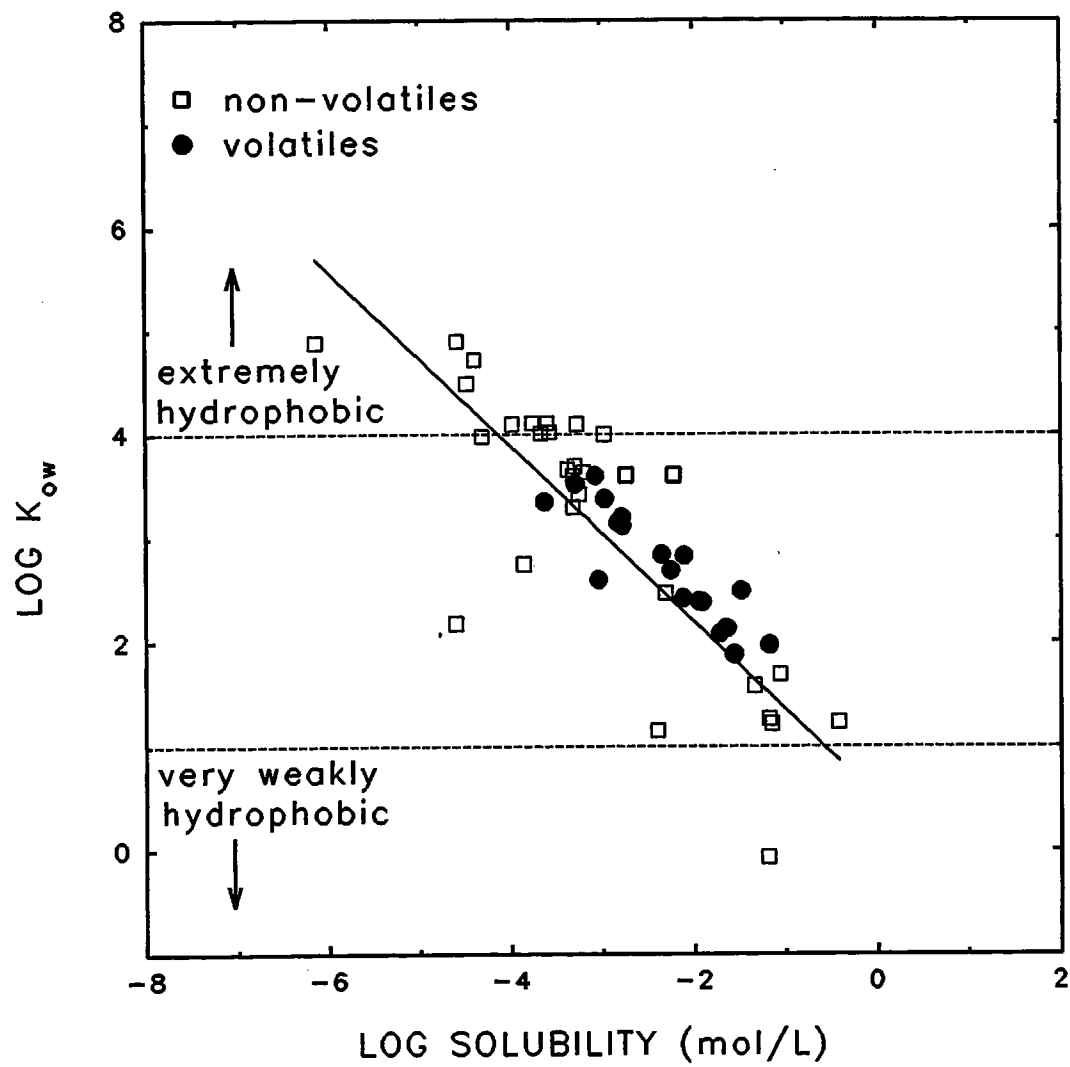


Figure 1.5 Physical-chemical properties of volatile (filled circles) and semivolatile (open squares) compounds selected for Hudson River Foundation project

Table 1.1

Volatile synthetic organic compounds selected for the Hudson River Foundation project

Volatile organic compounds		Mol. wt. (g/mol)	Solubility S (mg/L) <sup>†</sup>	log S (mol/L)	log K <sub>ow</sub> <sup>‡</sup>
<i>7 halogenated aliphatics</i>					
* chloroform	CHCl <sub>3</sub>	119.4	8000	- 1.17	1.97
* bromodichloromethane	CHBrCl <sub>2</sub>	163.8	4500	- 1.56	1.88
* chlorodibromomethane	CHBr <sub>2</sub> Cl	208.3	4000	- 1.72	2.08
* bromoform	CHBr <sub>3</sub>	252.7	3010	- 1.92	2.30
* carbon tetrachloride	CCl <sub>4</sub>	153.8	800	- 2.28	2.83
* trichloroethylene	C <sub>2</sub> HCl <sub>3</sub>	131.4	1100	- 2.08	2.53
* tetrachloroethylene	C <sub>2</sub> Cl <sub>4</sub>	165.8	150	- 3.04	2.60
<i>7 aromatics</i>					
* benzene	C <sub>6</sub> H <sub>6</sub>	78.1	1780	- 1.64	2.13
* toluene	C <sub>7</sub> H <sub>8</sub>	92.1	515	- 2.25	2.65
* chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	112.6	500	- 2.35	2.84
ethylbenzene	C <sub>8</sub> H <sub>10</sub>	106.1	152	- 2.84	3.13
m-xylene	C <sub>8</sub> H <sub>10</sub>	106.1	173	- 2.79	3.20
p-xylene	C <sub>8</sub> H <sub>10</sub>	106.1	156	- 2.87	3.15
* o-xylene	C <sub>8</sub> H <sub>10</sub>	106.1	175	- 2.78	3.12

\* Included in simulated spills.

† An effort is made to give representative values for solubilities at 20 to 25 °C; there is also considerable variation among the references used: Howard et al. (1990); Kenaga and Goring (1980); Mackay et al. (1980); Miller et al. (1985); Montgomery and Welkom (1990); Verscheuren (1983).

‡ Values taken from: Kenaga and Goring (1980); Montgomery and Welkom (1990); Howard et al. (1990).

Table 1.2

Semivolatile synthetic organic hydrocarbons selected for the Hudson River Foundation project

20 semivolatile organic hydrocarbons (CH)		Mol. wt. (g/mol)	Solubility S (mg/L) <sup>†</sup>	log S (mol/L)	log K <sub>ow</sub> <sup>‡</sup>
<i>C3-substituted</i>					
1,2,4-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	120.2	57.0	- 3.32	3.30
1,2,3-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	120.2	65.5	- 3.26	3.60
* mesitylene (1,3,5-trimethylbenzene)	C <sub>9</sub> H <sub>12</sub>	120.2	48.9	- 3.39	3.42
2-ethyltoluene	C <sub>9</sub> H <sub>12</sub>	120.2	93.0	- 3.11	3.53
4-ethyltoluene	C <sub>9</sub> H <sub>12</sub>	120.2	94.8	- 3.10	3.63
cumene (isopropylbenzene)	C <sub>9</sub> H <sub>12</sub>	120.2	50.0	- 3.38	3.66
n-propylbenzene	C <sub>9</sub> H <sub>12</sub>	120.2	55.0	- 3.34	3.69
<i>C4-substituted</i>					
1,2,4,5-tetramethylbenzene	C <sub>10</sub> H <sub>14</sub>	134.2	13.9	- 3.98	4.10
1,2,3,5-tetramethylbenzene	C <sub>10</sub> H <sub>14</sub>	134.2	-	-	4.10
* 1,2,3,4-tetramethylbenzene	C <sub>10</sub> H <sub>14</sub>	134.2	-	-	4.00
1,2-diethylbenzene	C <sub>10</sub> H <sub>14</sub>	134.2	70.4	- 3.28	4.10
1,3-diethylbenzene	C <sub>10</sub> H <sub>14</sub>	134.2	-	-	4.44
1,4-diethylbenzene	C <sub>10</sub> H <sub>14</sub>	134.2	25.0	- 3.73	4.45
sec-butylbenzene	C <sub>10</sub> H <sub>14</sub>	134.2	24.4	- 3.74	4.44
isobutylbenzene	C <sub>10</sub> H <sub>14</sub>	134.2	28.7	- 3.67	4.01
t-butylbenzene	C <sub>10</sub> H <sub>14</sub>	134.2	33.7	- 3.60	4.11
<i>C5-substituted</i>					
t-butyltoluene	C <sub>11</sub> H <sub>16</sub>	148.2	-	-	-
4-amylbenzene	C <sub>11</sub> H <sub>16</sub>	148.2	7.8	- 4.28	4.90
<i>Polycyclic</i>					
* naphthalene	C <sub>10</sub> H <sub>8</sub>	128.2	30.0	- 3.63	3.23
* biphenyl	C <sub>12</sub> H <sub>10</sub>	154.2	8.1	- 4.31	3.98

\* Included in simulated spills.

† An effort is made to give representative values for solubilities at 20 to 25 °C; there is also considerable variation among the references used: Howard et al. (1989, 1990); Kenaga and Goring (1980); Mackay et al. (1980); Miller et al. (1985); Montgomery and Welkom (1990); Nirmalakhandan and Speece (1988); Okouchi et al. (1992); Sikkema et al. (1994); Tewari et al. (1982); Wakita et al. (1986); Wasik et al. (1984); Wilf and Ben-Naim (1979); Verscheuren (1983).

‡ Values taken from: Abraham et al. (1994); Bodor et al. (1989); Bodor and Huang (1992); Doucette and Andren (1988); Howard et al. (1989, 1990); Kenaga and Goring (1980); Mackay et al. (1980); Miller et al. (1985); Montgomery and Welkom (1990); Sherblom and Eganhouse (1988); Tewari et al. (1982).

Table 1.3

Semivolatile oxygen-substituted organic compounds selected for the Hudson River Foundation project

30 semivolatile organic hydrocarbons (CHO)		Mol. wt. (g/mol)	Solubility S (mg/L)	log S (mol/L)	log K <sub>ow</sub>
<i>24 aromatics</i>					
cyclohexanol	C <sub>6</sub> H <sub>12</sub> O	100.2	38000	- 0.42	1.23
acetophenone	C <sub>8</sub> H <sub>8</sub> O	120.1	5500	- 1.34	1.58
2,4-dimethylbenzaldehyde	C <sub>9</sub> H <sub>10</sub> O	134.2	-	-	-
2,5-dimethylbenzaldehyde	C <sub>9</sub> H <sub>10</sub> O	134.2	-	-	-
4-ethylbenzaldehyde	C <sub>9</sub> H <sub>10</sub> O	134.2	-	-	2.47
2'-methylacetophenone	C <sub>9</sub> H <sub>10</sub> O	134.2	-	-	-
3'-methylacetophenone	C <sub>9</sub> H <sub>10</sub> O	134.2	-	-	2.15
4'-methylacetophenone	C <sub>9</sub> H <sub>10</sub> O	134.2	-	-	2.19
isophorone	C <sub>9</sub> H <sub>14</sub> O	138.2	12000	- 1.06	1.69
mesitylaldehyde	C <sub>10</sub> H <sub>12</sub> O	148.2	-	-	-
4-isopropylbenzaldehyde	C <sub>10</sub> H <sub>12</sub> O	148.2	-	-	2.98
3',4'-dimethylacetophenone	C <sub>10</sub> H <sub>12</sub> O	148.2	-	-	-
3'-ethylacetophenone	C <sub>10</sub> H <sub>12</sub> O	148.2	-	-	-
4'-ethylacetophenone	C <sub>10</sub> H <sub>12</sub> O	148.2	-	-	-
diphenylether	C <sub>12</sub> H <sub>10</sub> O	170.2	18.2	- 3.97	4.21
3'-hydroxyacetophenone	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	136.2	-	-	1.39
4'-hydroxyacetophenone	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	136.2	-	-	1.35
phthalic anhydride	C <sub>8</sub> H <sub>4</sub> O <sub>3</sub>	148.1	-	-	1.51
vanillin	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	152.2	10060	- 1.18	1.26
3,4-dimethoxybenzaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	166.2	11600	- 1.16	1.22
dimethylphthalate	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	194.2	4000	- 1.69	1.56
diethylphthalate	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	222.2	1080	- 2.31	2.47
* dibutylphthalate	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	278.3	11.2	- 4.40	4.72
dioctylphthalate	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	390.5	0.285	- 6.14	7.05
<i>6 mono- and bicyclic terpene derivatives</i>					
camphor	C <sub>9</sub> H <sub>16</sub> O	152.2	1237	- 2.09	-
verbenone	C <sub>10</sub> H <sub>14</sub> O	150.2	-	-	-
fenchone	C <sub>10</sub> H <sub>16</sub> O	152.2	-	-	-
fenchyl alcohol	C <sub>10</sub> H <sub>18</sub> O	154.2	-	-	-
isoborneol	C <sub>10</sub> H <sub>18</sub> O	154.2	740	- 2.32	3.26
menthol	C <sub>10</sub> H <sub>20</sub> O	156.3	421	- 2.57	3.20

\* Included in simulated spills.

† Values taken from: Howard et al. (1990); Kenaga and Goring (1980); Mackay et al. (1980); Miller et al. (1985); Montgomery and Welkom (1990); Okouchi et al. (1992); Verscheuren (1983); Wakita et al. (1986).

‡ Values taken from: Abraham et al. (1994); Babich et al. (1991); Bazaco and Coca (1989); Bodor et al. 1989; Bodor and Huang (1992); Breyer et al. (1991); Dunn et al. (1983); Howard et al. (1989, 1990); Kenaga and Goring (1980); McCoy et al. (1990); Montgomery and Welkom (1990); Schultz et al. (1988).



**Table 1.4**

Semivolatile chlorine-, nitrogen-, phosphorus-, and silicon-substituted organic compounds selected for the Hudson River Foundation project

23 heteroatomic semivolatile organic compounds		Mol. wt. (g/mol)	Solubility S (mg/L)	log S (mol/L)	log K <sub>ow</sub>
<i>15 chlorinated (CHOCl)</i>					
* 1,2,3-trichlorobenzene	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	181.4	31.5	- 3.76	4.11
1,2,4-trichlorobenzene	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	181.4	48.8	- 3.57	4.02
1,3,5-trichlorobenzene	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	181.4	6.01	- 4.48	4.49
2,3-dichlorobenzaldehyde	C <sub>7</sub> H <sub>4</sub> OCl <sub>2</sub>	175.0	-	-	-
2,4-dichlorobenzaldehyde	C <sub>7</sub> H <sub>4</sub> OCl <sub>2</sub>	175.0	-	-	-
2,6-dichlorobenzaldehyde	C <sub>7</sub> H <sub>4</sub> OCl <sub>2</sub>	175.0	-	-	-
3,4-dichlorobenzaldehyde	C <sub>7</sub> H <sub>4</sub> OCl <sub>2</sub>	175.0	-	-	-
3,5-dichlorobenzaldehyde	C <sub>7</sub> H <sub>4</sub> OCl <sub>2</sub>	175.0	-	-	-
4,4'-dichlorobenzophenone	C <sub>13</sub> H <sub>8</sub> Cl <sub>2</sub> O	251.1	-	-	-
<i>5 nitrogen-substituted (CHONCl)</i>					
N-ethylmethylmaleimide	C <sub>7</sub> H <sub>9</sub> O <sub>2</sub> N	139.0	-	-	-
phthalimide	C <sub>8</sub> H <sub>5</sub> O <sub>2</sub> N	147.1	586	- 2.40	1.15
* caffeine	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> N <sub>4</sub>	212.1	13500	- 1.20	- 0.02
simazine	C <sub>7</sub> H <sub>12</sub> N <sub>5</sub> Cl	201.7	5	- 5.61	1.51
* atrazine	C <sub>8</sub> H <sub>14</sub> N <sub>5</sub> Cl	215.7	30	- 3.86	2.68
<i>2 phosphorus-substituted (CHOP)</i>					
tripropylphosphate	C <sub>9</sub> H <sub>21</sub> PO <sub>4</sub>	224.2	-	-	1.95
* tributylphosphate	C <sub>12</sub> H <sub>27</sub> PO <sub>4</sub>	266.3	280	- 2.98	4.00
<i>1 silicon-substituted (CHOSi)</i>					
octamethylcyclotetrasiloxane	C <sub>8</sub> H <sub>24</sub> O <sub>4</sub> Si <sub>4</sub>	296.6	0.05	- 6.77	-

\* Included in simulated spills.

† Values taken from: Briggs (1981); Hayes (1982); Hefter (1992); Howard et al. (1990); Kenaga and Goring (1980); Mackay et al. (1980); Miller et al. (1985); Montgomery and Welkom (1990); Nirmalakhandan and Speece (1988); Saeger et al. (1979); Verscheuren (1983); Wakita et al. (1986).

‡ Values taken from: Abraham et al. (1994); Berthod et al. (1992); Bodor et al. (1989); Bodor and Huang (1992); Briggs (1981); Doucette and Andren (1988); Howard et al. (1989); Kenaga and Goring (1980); McCoy et al. (1990); Montgomery and Welkom (1990); Saeger et al. (1979); Valko and Slegel (1991); Yoshioka et al. (1986).

phosphorus-substituted; one silicon-substituted. As shown in Figure 1.5, some of these compounds have more extreme partitioning coefficients and solubilities than the volatile target compounds. Therefore, pilot-scale experiments with these compounds were considered more exploratory than with the volatile organic compounds, and only nine of the semivolatile organic compounds were to be used in simulated spills (indicated by \* in Tables 1.2 through 1.5).

The remaining 63 compounds were of interest for background monitoring: not all compounds were expected to be found in sample extracts; in many cases, particularly for the isomers that have the same chemical composition, similar compounds were chosen to show that some are not present in treated Hudson River water. For example, there are many C3- to C5-substituted alkyl benzenes, in fact more than listed in Table 1.2, because not all possible isomers could be purchased. These alkyl benzenes are often found at low levels in surface waters, as the residue of various, widely-used petroleum products. Therefore, it was expected to be necessary to screen for a number of alkyl benzenes, even if not all could be conclusively identified. Table 1.3 shows that identification is further complicated by the number of alkyl-substituted benzaldehydes and acetophenones that have the same apparent molecular weight as the alkyl benzenes. At the time of this project, it was not known if some of these oxygenated organics could also be present, whether as the result of industrial discharges or as byproducts of microbial metabolism in Hudson River water. However, it was expected that gas chromatography-mass spectrometry should help to resolve which of these compounds are present in river-water samples. It is also of interest to note that the alkyl-substituted benzaldehydes and acetophenones tend to have lower log  $K_{OW}$  values and higher solubilities than the alkyl benzenes: therefore, the fate and transport and the frequency of occurrence should be different for compounds in the three groups.

The chlorine-substituted compounds, phthalimide and the trialkyl phosphates in Table 1.4 are possible constituents of industrial waste, whereas caffeine would be expected in municipal waste. Atrazine, and to some extent simazine, are common herbicides. N-ethylmethyleimide and octamethylcyclotetrasiloxane have been tentatively identified in extracts of surface water samples, previously analyzed by gas chromatography-mass spectrometry at the New York State Department of Health: they were included in this study to be either confirmed or ruled out.

It was beyond the scope of this project to include acidic organic compounds, although several are of interest: fatty acids, natural products of biodegradation; 2,4-D, a widely-used herbicide; monochloro-, dichloro- and trichloroacetic acids, common byproducts of drinking-water chlorination.

## CHAPTER 2 EXPERIMENTAL METHODS

### OVERALL DESIGN OF EXPERIMENTS

The overall plan for pilot column experiments to meet the project objectives is shown in Figure 2.1. The treatability of chemical spills was to be investigated by running a GAC pilot column (I), which would receive four one-week pulses of synthetic organic chemicals (SOCs) at six-week intervals, and a continuous input of background organics (DOC;  $\text{CHCl}_3$ ). A second pilot column (II) was to be run as a control, receiving only background organics for 210 days. A third pilot column (III) was also run as a control, except that the influent was dechlorinated using sulfur dioxide, to examine the effect on GAC adsorption of background organics.

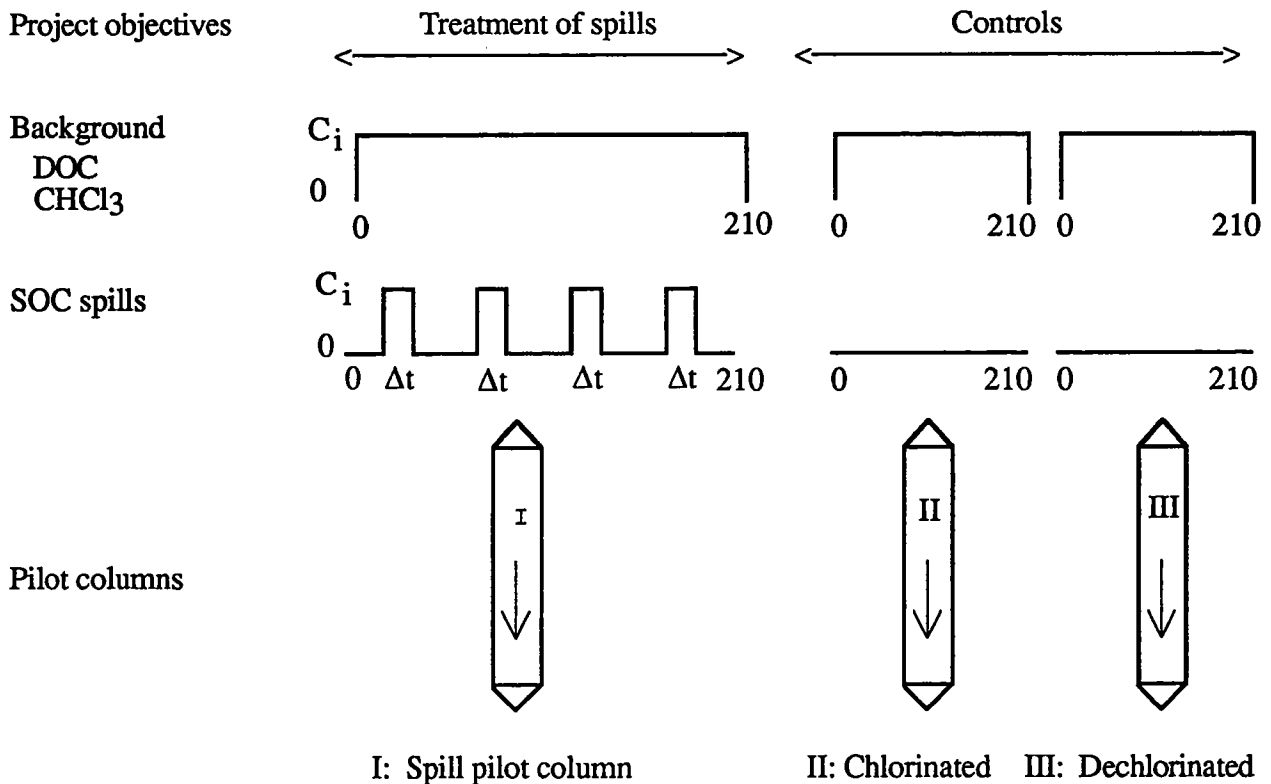


Figure 2.1 Schematic of influents and pilot columns for experiments to meet project objectives.

## **WATERFORD WATER WORKS: CONVENTIONAL FULL-SCALE TREATMENT**

GAC pilot-column experiments were conducted at the Waterford Water Works for 30 weeks (February 12, 1987 to September 11, 1987). A schematic of the Waterford Water Works is given in Figure 2.2. The physical-chemical treatment process to supply potable water includes:

1. aeration to convert dissolved iron to insoluble oxides
2. coagulation with alum to remove suspended particulates
3. addition of activated silica to improve coagulation and flocculation
4. addition of powdered activated carbon to adsorb substances causing taste and odor
5. prechlorination for disinfection and further oxidation of dissolved iron, manganese, and natural organics
5. sedimentation for removal of floc and powdered activated carbon
7. rapid mixed-media filtration (anthracite, sand) for removal of fine particulates and microorganisms
8. addition of soda ash to control the pH and minimize corrosion in the distribution system
9. addition of fluoride to provide a residual in the finished drinking water
10. postchlorination to maintain a chlorine residual for disinfection of the distribution system

Typical operating conditions, chemical feed concentrations, and water quality for the Waterford Water Works are given in Table 2.1.

During this project, additional water samples were collected at Latham Water Works, which uses the Mohawk River. These samples were intended primarily as controls, to cross-check methods of analysis being used for synthetic organic chemicals. The treatment process and operating conditions at Latham Water Works are described in Appendix B.

### **GAC PILOT COLUMNS: DESIGN AND OPERATING CONDITIONS**

Figures 2.3 and 2.4 give a schematic of the water supply to the three pilot columns operated in parallels, and the location of valves for flow control and sampling. Figure 2.5 shows the actual pilot column system during a simulated spill.

#### **Pilot-Column Water Supply**

Water to the three GAC pilot columns was taken after the point of entry to the distribution

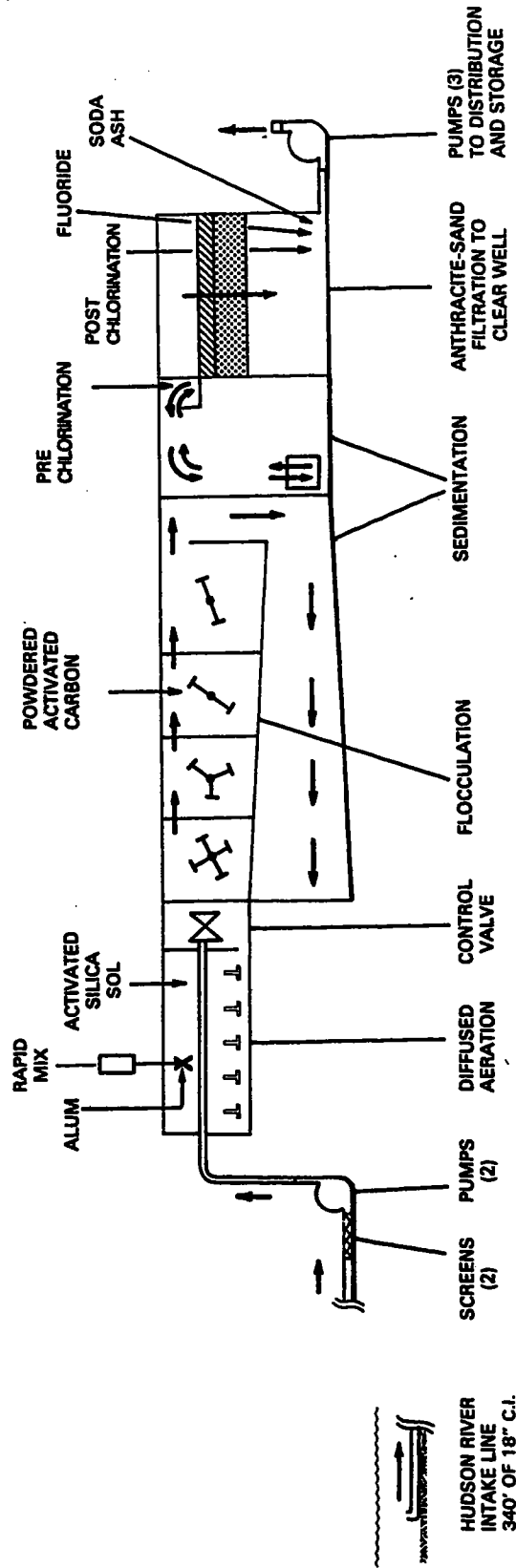
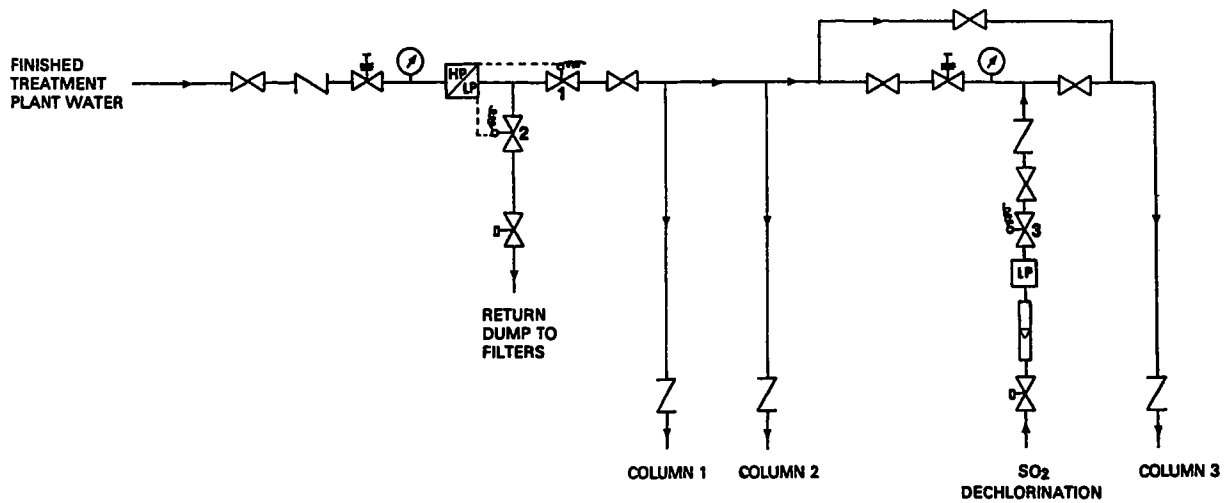


Figure 2.2 Schematic of the Waterford Water Works (Alben et al. 1995)

**Table 2.1**

Typical operating conditions, chemical feed concentrations, and water quality for the Waterford Water Works, based on analysis of 1985 data base (Alben et al. 1992)

Operation		Average	±	Standard deviation	Relative standard deviation (%)
Hudson River flow	ft <sup>3</sup> /s	5621	±	3590	64
	MGD	3625	±	2315	64
Waterford Water Works production	MGD	1.51	±	0.19	12
Alum	mg/L	37.5	±	6.93	18
Activated silica	mg/L	3.61	±	0.78	22
Powdered activated carbon	mg/L	4.24	±	0.93	22
Pre-chlorine dose	mg/L	3.19	±	0.81	25
Post-chlorine dose	mg/L	1.84	±	0.59	32
Soda ash	mg/L	34.0	±	7.56	22
Fluoride	mg/L	1.73	±	0.17	10
<u>Water quality</u>					
Raw water turbidity	NTU	5.8	±	8.12	140
Finished water turbidity	NTU	0.28	±	0.10	36
Raw water pH	-	7.4	±	0.23	3
Finished water pH	-	7.3	±	0.12	2
Prechlorine residual	mg/L	0.90	±	0.12	13
Postchlorine residual	mg/L	0.91	±	0.13	14
Temperature	°C	13.2	±	8.17	62
Chloroform	µg/L	20.3	±	8.3	41



	ACCUMULATOR		HIGH AND LOW PRESSURE SWITCH		CHECK VALVE		SOLENOID VALVE
	FLOWMETER		LOW PRESSURE SWITCH		GATE VALVE (SHUTOFF)		FLOW REGULATOR
	PRESSURE GAUGE		PRESSURE REGULATOR		SAMPLING VALVE		

Figure 2.3 Schematic of the water supply to the GAC pilot columns at Waterford, NY, February 12 - September 11, 1987

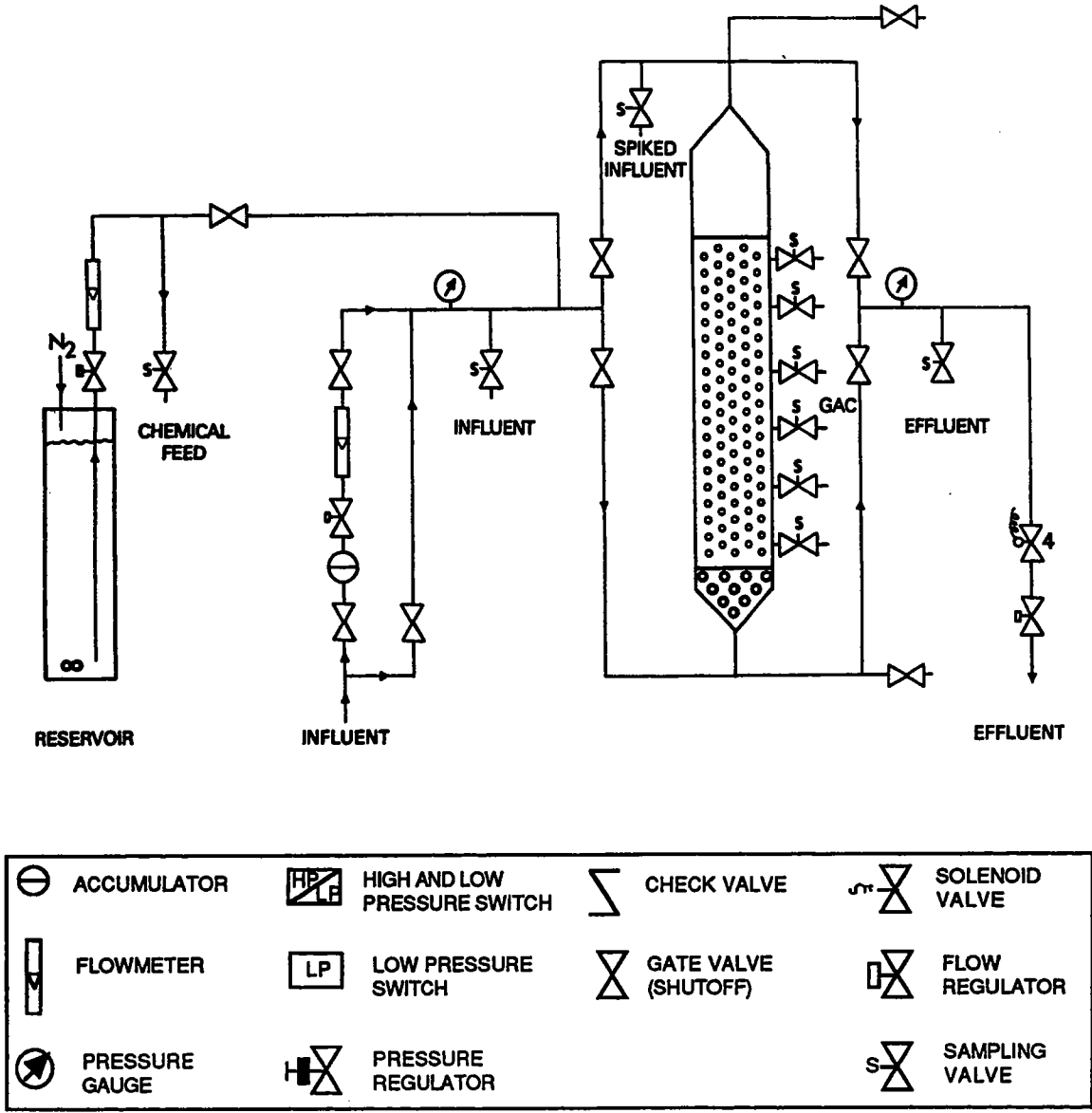


Figure 2.4 Schematic of flow control and sampling ports to the GAC pilot columns at Waterford, NY



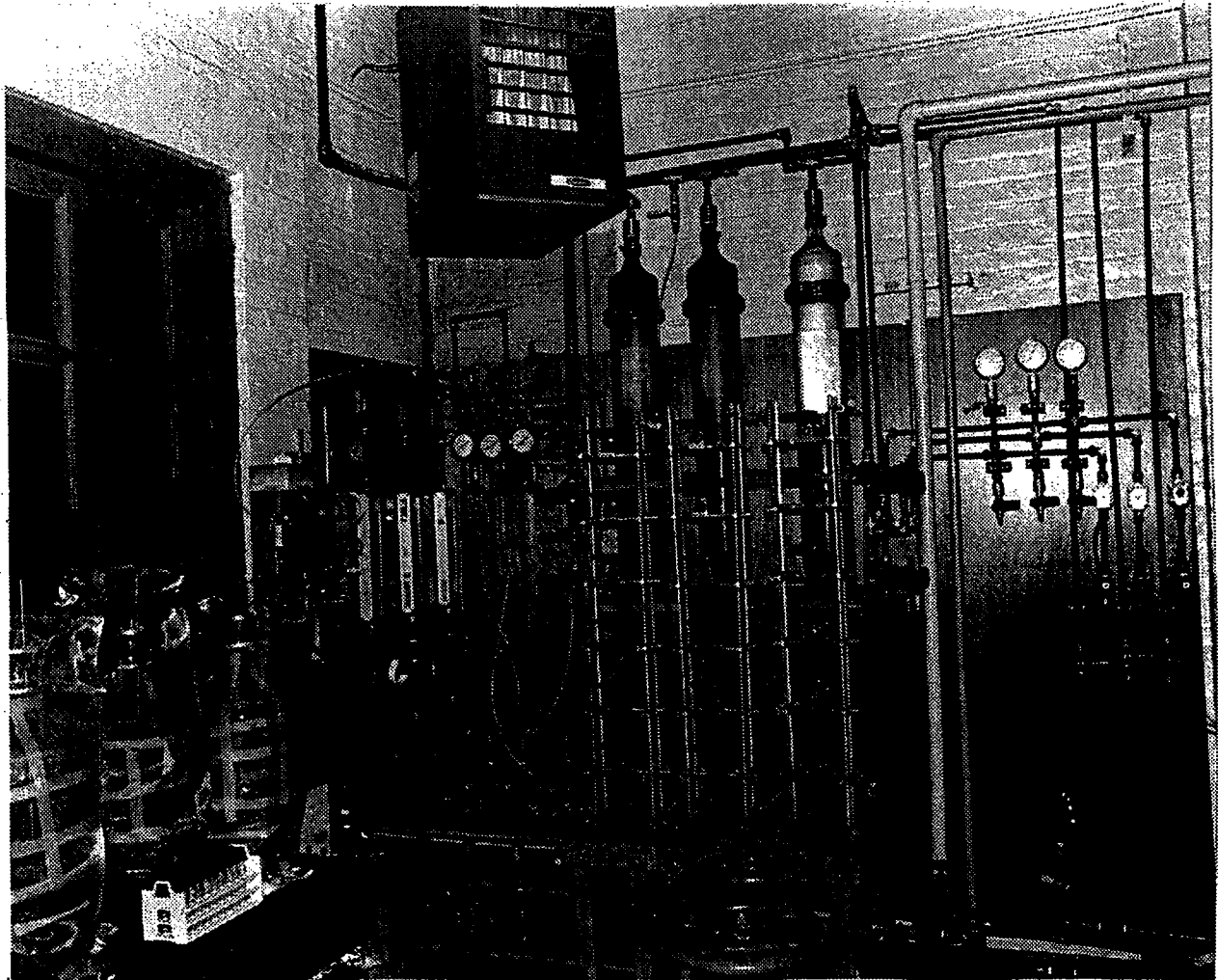


Figure 2.5 GAC pilot columns at Waterford, NY during the Hudson River Foundation project to study treatment of chemical spills: pilot columns from left to right are II (control), I (simulated spills), and III (SO<sub>2</sub>-dechlorinated influent)

system. Thus influent to the pilot columns represents Waterford drinking water after all stages of treatment, and results of chemical analysis of influent water samples correspond to the finished water entering the distribution system. This mode of operation is somewhat different from the use of GAC in full scale drinking water treatment plants, or in other pilot columns that we have run at Waterford (Alben et al. 1995). GAC to be used as a filter-adsorber is placed after coagulation-flocculation-sedimentation; GAC which serves as an adsorber only is placed after the filters (adsorber; post-filter contactor; post contactor). Therefore influent to the pilot columns for this project was initially at pH 7.3, closer to neutral conditions than when the influent is taken after coagulation at pH 6.4. Influent to the pilot columns had also received both the initial and final dose of chlorine for disinfection, with a somewhat longer time for formation of disinfection by-products (approximately 3 hours) than at an earlier stage of treatment.

### **Materials, Design and Construction**

As shown in Figure 2.5, the pilot columns were constructed from glass process pipe (Kimax, 15 cm id x 152 cm long) joined at each end to straight glass reducers (Kimax, 15 cm id x 3.8 cm id). Glass had the advantage of being resistant to corrosion from wet GAC, in addition to providing a clear view of the GAC bed. Six glass side tubes (Kimax, 1.25 cm id x 4.0 cm long) were attached by a glassblower along the length of the process pipe, to collect GAC samples at 13, 34, 55, 75, 95, and 113 cm bed depths. The modified process pipes were annealed overnight after fabrication.

All glass pieces were purchased with ends finished in standard bead sizes, so that bead-to-bead couplings with Teflon inner seals could be used at glass joints. At the top and bottom, bead-to-bead Teflon couplings (Kimax, 15 cm id) were used to connect the beaded glass reducers to the beaded process pipe. Similarly Teflon bead adaptors with a female pipe thread (Kimax 1.25 cm x 1 1/2" FPT) were used on stainless steel fittings with male pipe threads (1 1/2" MPT), so that metal plumbing could be connected to the beaded glass reducers at the ends of the pilot column. At the sampling ports, bead-to-bead Teflon couplings (Kimax 1.25 cm id) were used to connect beaded glass pieces to 316 stainless steel adaptors (Kimax 1.25 cm id), beaded at one end. The other end of the adaptors was finished with a 1/2" male pipe thread to couple to the valves used for sampling (Whitey B-45F8).

All remaining plumbing for the pilot columns was metal, connected with standard compression fittings and pipe-thread fittings. Tubing for plumbing was copper (1/2" id, 0.040" size L wall thickness; 3/4" id 0.045" size L wall thickness). Compression and pipe thread fittings were brass. Shut-off valves (Jenkins 370 gate valves) were bronze; sampling valves and regulating valves were brass. Valves (Whitey B-45F8) used for collecting GAC samples were

roddable, with a 1.03 cm id; the valves were mounted on aluminum blocks which were rigidly attached to a frame of aluminum rods for support. Tubes used for collecting GAC samples were stainless steel (0.64 cm od x 46 cm long).

Calgon F400 was used as an adsorbent. This granular activated carbon is prepared from bituminous coal and has a particle size distribution which is considered suitable for a post-filter mode of operation (12 x 40 mesh; 1.6 mm average diameter; Calgon 1986) . The intraparticle pore-volume consists of a complex network of macro- (> 50 nm) , meso- (2 - 50 nm), and micropores (< 2 nm): surfaces of the micropores are believed to favor adsorption of synthetic organic chemicals with molecular diameters typically less than 0.5 nm.

The GAC bed was prepared with the top glass reducer (15 cm id x 3.8 cm id) and its Teflon coupling (15 cm ) disconnected. A stainless steel screen (13 cm od), glass beads (3 mm od; approximately 1.8 kg per column), and dry GAC (9.5 kg Calgon F400) were then added. The stainless steel screen lay flat across the narrow diameter (3.8 cm) opening in the bottom glass reducer and supported the glass beads, which filled the bottom glass reducer and the bottom 5 cm of the pilot column. Dry GAC was added after the pilot column had been filled with water in an upflow mode to a depth of approximately 125 cm, well above the top pilot column sampling port. The GAC settled in the water, supported by the glass beads. When the GAC reached the desired bed depth, approximately 110 cm, ideally 2 - 4 cm above the top sampling port, the top glass reducer (15 cm id x 3.8 cm id) and its Teflon coupling (15 cm) were reconnected and flow through the pilot column was switched to a downflow mode

## Operation

Operating conditions for the GAC pilot columns are summarized in Table 2.2. During pilot column operation, the water temperature varied seasonally from 2.5 °C (day 0 February 12), to a maximum of 26.4 °C (day 163 July 25), to 19.5°C (day 212 September 11). Figure 2.6 shows the measured change in water temperatures.

To control flow, the pilot columns were operated as low-pressure contactors. At startup, water was allowed to flow in parallel through the three columns and the column bypass line, and all control valves were fully open: typically, all the water went out the column bypass line, where there was essentially no resistance, rather than through the pilot columns, where there was resistance from the GAC. The valve (Whitey B-18VF8) controlling flow through the column bypass line was gradually closed until incoming water could be seen filling the top of the pilot columns: for normal operation, this occurred with the valve on the column bypass line partially open. The valve (Whitey B-18VF8) on the pilot column effluent was then gradually closed to

Table 2.2

Pilot column operating conditions: February 12, 1987 - September 11, 1987

		Column I Spill column	Column II Control	Column III Dechlorinated
<u>Mass of GAC</u>	kg	9.25	9.35	9.25
Calgon F400 12 x 40 mesh				
<u>Bed dimensions</u>				
diameter	cm	15	15	15
cross sectional area	cm <sup>2</sup>	182	182	182
length (initial)	cm	118	116	118
volume (initial)	L	21.5	21.1	21.5
<u>Flow</u>				
mode		Downflow	Downflow	Downflow
flowmeter	L/min	1.30 ± 0.25	1.43 ± 0.26	1.36 ± 0.22
accumulator	L/min	1.18 ± 0.30	1.24 ± 0.23	1.36 ± 0.23
Total throughput	L	361032	379862	561963
Empty bed contact time	min	18.2	17.0	15.8
Hydraulic loading	gal/min-ft <sup>2</sup>	1.59	1.67	1.83
Linear velocity	m <sup>3</sup> /m <sup>2</sup> -hr	4.01	4.21	4.62
	cm/min	6.48	6.62	7.46
<u>Water Pressures</u>				
Supply (range)	psi	15 - 20	15 - 20	15 - 20
Influent	psi	5.0 ± 1.5	7.5 ± 2.5	4.0 ± 1.7
Effluent	psi	3.2 ± 1.6	4.3 ± 2.5	4.1 ± 1.9
<u>Water temperatures</u>				
Day 0: February 12	°C	2.5	2.5	2.5
Day 163: July 25 (max)	°C	26.4	26.4	26.4
Day 212: September 11	°C	19.5	19.5	19.5
<u>Water pH and chlorine residual</u>				
Influent pH	-	7.2 ± 0.2	7.2 ± 0.3	5.3 ± 0.6
Influent chlorine	mg/L	1.28 ± 0.35	1.24 ± 0.35	0.1 ± 0.1

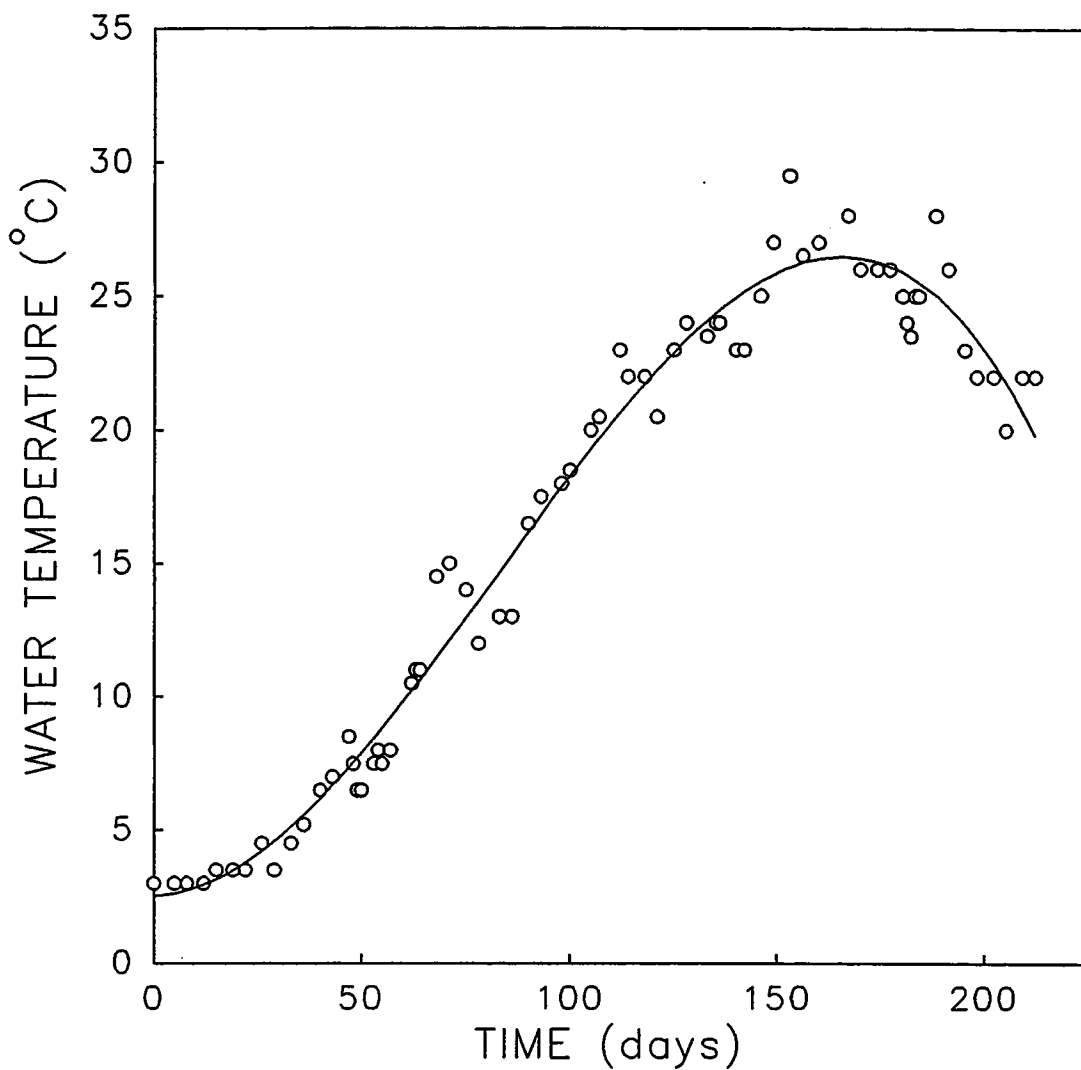


Figure 2.6 Seasonal change in temperature of influent water to the GAC pilot columns at Waterford, NY during the Hudson River Foundation project, February 12 to September 11, 1987.

increase the effluent water pressure to 8 psi and the influent pressure to 15 psi. Thus the valve on the pilot column effluent defined the pilot column operating pressures and provided coarse control of water flow through the GAC. The valve on the pilot column influent was gradually closed to reduce the flow through the GAC to the desired value. Thus the influent valve was used to obtain fine control of flow through the GAC, while reducing the influent pressure to approximately 10 psi and the effluent pressure to approximately 5 psi. In practice, the setting of the influent and effluent valves was iterative, to avoid settings that reduced the influent pressure below 5 psi and the effluent pressure to 0 psi. With 5 psi on the effluent, flow could be obtained through the pilot column and from its effluent sampling valve (Whitey B-44F4).

Valves (Jenkins 901-T Forged Bronze Ball Valve with Teflon seat) on the bleed lines were opened briefly and closed repeatedly until the pilot columns were completely filled with water and no air was visible trapped in the space above the GAC. With the bleed valves open, the column influent pressure dropped to 0 psi and trapped air was vented; with the bleed valves shut, the column influent pressure increased to 5-10 psi, and the pilot columns resumed filling with water in a downflow mode.

Thus, the pilot columns were operated manually. Pilot column influent and effluent pressures and flows were checked weekly, and flow control valves were reset if necessary. Typically, a slight loss in flow through the pilot columns was noted over a period of one week, corresponding to a decrease in effluent pressure: thus the effluent control valve was closed a small amount and/or the influent control valve was opened a bit, increasing the flow and pilot column operating pressure. Since the pilot columns were operating on water that had been treated by coagulation, flocculation, sedimentation and filtration, it was not necessary to backwash the pilot columns during 30 weeks operation: relatively minor changes in flow control valves were sufficient to maintain desired operating pressures and flows. As indicated in Table 2.2, the average flow in pilot columns I, II, and III varied by 25, 28 and 17 percent, respectively, as calculated from the relative standard deviation.

Each pilot column had its own flowmeter (Brooks Model 1307D08E1A1A, R8M-25-4F tube, stainless steel float, 5.3 L/min, 1.4 gpm full scale) and accumulator (Badger Read-o-Matic) in line. Readings from both were recorded weekly. The flowmeter was useful as an indicator of instantaneous flow, particularly when adjusting valve settings; the accumulator (calibrated in  $\text{ft}^3/\text{min} = 28.3 \text{ L}/\text{min}$ ) was useful to measure total flow through the pilot column. Results in Table 2.2 indicate that there is relatively good agreement in values of the average flow when calculated from the two sets of measurements. Readings from the accumulator are used in mass balance calculations.

## Simulated Chemical Spills: Pilot Column I

Four chemical spills were simulated in the influent to pilot column I for periods of one week at 6 to 7 week intervals. Effluent from pilot column I was connected to the waste discharge line from the treatment plant throughout the project.

During a simulated spill, three stock solutions of chemicals were fed to the influent of pilot column I, as shown in Table 2.3: a mixture (Ia) of volatile halogenated organics; a mixture (Ib) of volatile aromatic organics; a mixture (Ic) of semivolatile organics. The chemicals were measured by volume or weight and transferred to the reservoirs (5 gal, 18.9 L Pyrex bottles) half-filled with effluent water from pilot column II. The reservoirs were then filled with water and sealed. During spiking, the contents of the reservoirs were continuously mixed by magnetic stirrers. A positive pressure of 20 psi nitrogen was used to displace the chemical mixtures from the reservoirs into the influent of pilot column I; flowmeters and needle valves in the transfer lines from the reservoirs were used to monitor and control the flow rate.

During the first simulated spill, all chemicals were placed in the same reservoir: this was found unsatisfactory, since an insoluble pool of halogenated volatiles settled to the bottom of the reservoir and in effect extracted other organics from the stock solution. This problem was unexpected, but may have been caused by the low water temperature (7 °C): concentrations of individual compounds in the reservoir were below solubilities reported at 20-25 °C; unfortunately there are insufficient data in the literature to determine the extent to which the aqueous solubilities of these compounds decrease as temperature is lowered. Three separate reservoirs were used in later spills. Thus synthetic organics from the three reservoirs were combined after injection into the pilot column influent, when they had been diluted approximately 500-fold. In addition, water temperatures were also higher for the last three spills than during the first.

As shown in Table 2.3, nominal concentrations of organics were 53 mg/L for volatile organics in reservoirs Ia and Ib, and 5.3 mg/L for semivolatile organics in reservoir Ic. Calculations in Table 2.4 show that flow from the reservoirs was to be injected in a ratio of 1:433 into the influent of pilot column I, to obtain nominal influent concentrations of 122 µg/L for volatile organics and 12 µg/L for semivolatile organics. With flow from the reservoirs at 3 mL/min, the reservoir contents would last 4 days, and the reservoirs would only have to be refilled once during a week long simulated spill. In practice, however, the flowmeters and needle valves used to control flow at 3 mL/min from the reservoirs were larger than the optimum size. Variations in flow were also caused by the changing cross section and increasing headspace in the Pyrex bottles from which the chemicals were being displaced.

In a subsequent project, the system for input of synthetic organic chemicals was redesigned (Alben et al. 1995). The glass bottles were replaced with stainless-steel reservoirs. Flowmeters

**Table 2.3**

Mixtures for spiking into influent of pilot column I during simulated chemical spills

<u>Reservoir Ia: Volatile compounds denser than water</u>				1.00 g/18.9 L = 53 mg/L stock
	Density (g/mL)	Volume (mL) to give 1 g	Solubility (mg/L)	
CHCl <sub>3</sub>	1.492	0.670	800	
CHBrCl <sub>2</sub>	2.006	0.498	4500	
CHBr <sub>2</sub> Cl	2.445	0.408	4000	
CHBr <sub>3</sub>	2.890	0.346	3010	
CCl <sub>4</sub>	1.594	0.627	800	
C <sub>2</sub> HCl <sub>3</sub>	1.462	0.684	1100	
C <sub>2</sub> Cl <sub>4</sub>	1.623	0.616	150	
chlorobenzene	1.1058	0.904	500	
<u>Reservoir Ib: Volatile Compounds Less Dense than Water</u>				1.00 g/18.9 L = 53 mg/L stock
	Density (g/mL)	Volume (mL) to give 1 g	Solubility (mg/L)	
benzene	0.8787	1.138	1780	
toluene	0.8669	1.153	515	
o-xylene	0.8802	1.136	175	
<u>Reservoir Ic: Semivolatile Compounds</u>				0.10 g/18.9 L = 5.3 mg/L stock
	Density (g/mL)	Volume (mL) to give 0.1 g	Weight (g) to give 0.1 g	Solubility (mg/L)
<u>Base-neutral</u>				
mesitylene (1,3,5-trimethylbenzene)	0.864	0.116	-	48.9
1,2,3,4 tetramethylbenzene	0.901	0.111	-	-
1,2,3 trichlorobenzene	1.454	0.069	-	31.5
tributylphosphate	0.979	0.102	-	280
dibutylphthalate	1.043	0.096	-	11.2
naphthalene	-	-	0.100	30.0
biphenyl	-	-	0.100	8.1
atrazine	-	-	0.100	33
caffeine	-	-	0.100	13500



**Table 2.4**

Design flow conditions and nominal influent concentrations for simulated chemical spills to pilot column I

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Dilution factor	=	$\frac{\text{Flow rate - pilot column I influent}}{\text{Flow rate - reservoir for spiking}}$
	=	$\frac{1.3 \text{ L/min}}{3.0 \times 10^{-3} \text{ L/min}}$
	=	433
Nominal influent concentrations	=	$\frac{\text{Reservoir concentration}}{\text{Dilution factor}}$
Reservoirs Ia, Ib	=	$\frac{53 \text{ mg/L}}{433} = 122 \text{ } \mu\text{g/L}$
Reservoir Ic	=	$\frac{5.3 \text{ mg/L}}{433} = 12 \text{ } \mu\text{g/L}$

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were selected in the correct range of flows from the reservoirs. Separate lines were set up to feed chemicals to the pilot columns and to collect samples from the reservoirs and pilot-column influents.

### **Dechlorination : Pilot Column III**

As shown in Figure 2.3, sulfur dioxide (anhydrous; initially a 40 lb cylinder, later a 150 lb cylinder) was used for continuous dechlorination of the influent to pilot column III. Sulfur dioxide is commonly used in treatment plants for dechlorination; sulfur dioxide was also calculated to cost less and require less time to maintain in operation than alternative methods of dechlorination eg continuous feed of solutions of sodium sulfite or sodium thiosulfate.

For this project, the regulator (Matheson 13-660) to the sulfur dioxide tank was set up with a purge valve (401 V) connected to a tank of high purity nitrogen (Grade 5; size 200 cylinder). When the sulfur dioxide tank was changed, a valve in the transfer line to the influent of pilot column III was closed, and a valve was opened to a line outside the treatment plant to vent residual sulfur dioxide in the regulator.

Nitrogen was also used to test the transfer line for injection of SO<sub>2</sub> into the influent of pilot column III, by manually closing the SO<sub>2</sub> tank, opening the SO<sub>2</sub> regulator and purge valve, and

opening the N<sub>2</sub> tank and valves on its regulator. The N<sub>2</sub> pressure regulator was set at 40 psi, and the SO<sub>2</sub> regulator was set at 20 psi. The pressure switch (ASCO SB20A TE 20A32) in the transfer line was then set and checked: as the N<sub>2</sub> pressure dropped below the set point, several solenoids closed: the solenoid (Fluorocarbon DV2-122 NCA2) in the SO<sub>2</sub> transfer line; all solenoids in the water supply line; solenoids in the pilot-column effluent lines. When the SO<sub>2</sub> tank was opened later, the regulator and transfer line were again leak checked, using a Kimwipe tissue moistened with a solution of household ammonia: white vapors were seen from the reaction of ammonia and SO<sub>2</sub> at fittings where there was an SO<sub>2</sub> leak.

Since the SO<sub>2</sub> was liquefied, the maximum tank pressure was approximately 37 psi at 20 °C and less at lower temperatures. To maintain positive pressure for injection of SO<sub>2</sub>, a pressure reducer (Watts U5LP) was used to set the water pressure to 10 psi at the point of injection of SO<sub>2</sub>, and the SO<sub>2</sub> pressure regulator was set at 18 to 20 psi.

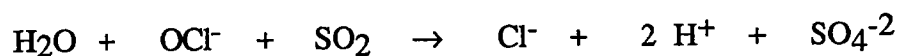
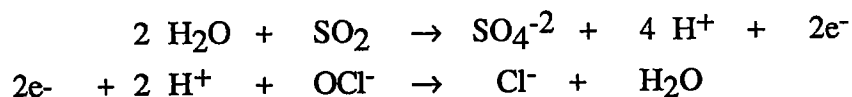
Teflon was used for the SO<sub>2</sub> transfer line tubing and the solenoid valve. A Teflon membrane (Fluorocarbon GPC-142-S) isolated the pressure switch; the cavity between the Teflon membrane and the pressure switch was filled with silicone fluid. Stainless steel tubing (1/8" od 24" long) was used to inject the SO<sub>2</sub> into the water stream. Initially, copper tubing was used for the water line where SO<sub>2</sub> was injected. However, after 10 weeks operation, a pin-hole leak would develop in the copper tubing at the point where the SO<sub>2</sub> was injected, because of the high local concentration of sulfuric and hydrochloric acid. Later the copper tubing was changed to glass. It was interesting to observe the injection of SO<sub>2</sub>. If the gas pressure was high, the glass tube would fill with gas (N<sub>2</sub> or SO<sub>2</sub>) and water would stream down the walls.; if the gas pressure was low, the glass tube would fill with water and gas bubbles could be seen coming from the tip of the stainless steel injector.

The flow of SO<sub>2</sub> was metered to 10% of full scale on a flowmeter (15 of 150 units, Brooks Model 1355CB1G1BAA R-2-15 AAA ), corresponding to 3.2 mL/min; this was essentially the minimum that could be reliably achieved with mechanical flow control. As shown by the reactions and calculations in Table 2.5, SO<sub>2</sub> was in a stoichiometric excess by a factor of approximately 3.7. Since this amount of SO<sub>2</sub> corresponds to  $1.8 \times 10^{-4}$  moles SO<sub>2</sub>/min, the use rate of SO<sub>2</sub> is calculated in Table 2.6 to be 0.26 lb/wk: thus a 40 lb cylinder is estimated to last for 156 weeks, which is longer than the duration of the experiment. Results in Table 2.2 indicate that this flow rate was sufficient to remove 1.26 mg/L residual chlorine from the influent to pilot column III. A lowering of the pH to 3.1 is also predicted in Table 2.5 from the reaction of SO<sub>2</sub> with residual chlorine; results in Table 2.2 indicate that in fact the pH was only lowered from 7.2 to 5.3, which suggests that the hydrogen ions combined with natural organic acids rather than remaining free in solution. Some of the SO<sub>2</sub> was also consumed by the reduction of MnO<sub>2</sub> to Mn<sup>2+</sup> rather than by the reduction of residual chlorine. During the pilot column experiment, MnO<sub>2</sub> became visible as a

**Table 2.5**

Dose of SO<sub>2</sub> gas for continuous dechlorination and effect on pH of pilot column III influent

Reaction of residual free chlorine and SO<sub>2</sub>:



Chlorine residual in influent: ~ 1.26 mg/L  
 ~ 3.6 x 10<sup>-5</sup> moles/L

Flow rate through GAC column: ~ 1.36 L/min  
 ~ 1.37 x 10<sup>4</sup> L/wk

Chlorine flow rate: ~ 4.9 x 10<sup>-5</sup> moles/min

Sulfur dioxide flow rate needed:  $\frac{dV}{dt} = \frac{dn}{dt} \frac{RT}{P}$

P = SO<sub>2</sub> tank pressure 20 psi = 1.36 atm  
 R = 82 mL-atm/mole-deg K  
 T = 273 + 23 = 296 °K  
 $\frac{dn}{dt} = 4.9 \times 10^{-5}$  moles/min  
 $\frac{dV}{dt} = 0.87$  mL/min for 1:1 dose of moles SO<sub>2</sub> : moles HOCl

Flow of SO<sub>2</sub> (Brooks flow meter Model 1355CB1G1BAA R2-15AAA)

$$\text{Max flow SO}_2 \approx \left( \frac{\text{specific gravity N}_2}{\text{specific gravity SO}_2} \right)^{1/2} * \text{Maximum flow of air}$$

$$\approx (1.251/2.927)^{1/2} (49 \text{ mL/min})$$

$$\approx 32 \text{ mL/min SO}_2 \text{ at full scale}$$

Flow of SO<sub>2</sub> at 10% of full scale: ≈ 3.2 mL/min SO<sub>2</sub>

Stoichiometric excess of SO<sub>2</sub>: ≈  $\frac{3.2 \text{ cc/min}}{0.87 \text{ cc/min}} \approx 3.7$

Effect of dechlorination on pH: 2 x (4.9 x 10<sup>-5</sup> moles/min) / 1.18 L/min  
 8.3 x 10<sup>-5</sup> moles H<sup>+</sup>/L for a 1:1 dose ie pH 4.1  
 3.1 x 10<sup>-4</sup> moles H<sup>+</sup>/L for a 3.7:1 dose ie pH 3.5

**Table 2.6**

Calculated use rate of SO<sub>2</sub> cylinder for continuous dechlorination of influent to pilot column III

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Rate of cylinder depletion for a 1:1 dose:	$4.9 \times 10^{-5}$ moles/min x 64 g/mole / (454 g/lb) $6.9 \times 10^{-6}$ lb/min 0.069 lb/wk
Therefore a 40 lb cylinder will last:	580 weeks for a 1:1 dose 156 weeks for a 3.7:1 dose

---

brown deposit in the plumbing to pilot columns I and II, whereas the plumbing to pilot column III remained clean (Figure 2.5).

Initially, a needle valve (Brooks Line IV Size Low) was used in the SO<sub>2</sub> flowmeter which caused sawtoothing: SO<sub>2</sub> flow rates dropped significantly after each day in operation until the needle valve was manually reset. When the needle valve was changed to a Brooks Model 8503 NRS Size1, sawtoothing was effectively eliminated, and the SO<sub>2</sub> flow was stable for periods greater than one week.

#### **Fault Detection: Standby**

As shown in Figures 2.3 and 2.4, additional solenoid valves were placed in the pilot column system, so that the main water supply, the SO<sub>2</sub> supply, and flow of water through the pilot columns could be shut off by throwing a switch in a control box and cutting electrical power to the solenoids. A wiring diagram for the control box is given in Figure 2.7. The control box was designed for convenience as well as safety, so that the experiment could be placed in standby with minimum effort when necessary.

Since "normally closed" solenoids were used in the flow path, the experiment could be automatically switched to standby if the treatment plant lost electrical power. Occasionally the experiment was placed in standby for periods of several hours, during maintenance on the treatment plant (pumps, filters, valves, settling basins). Several additional conditions could also result in an automatic shutdown of the experiment. A pressure reducer (Watts U5LP) in the main water supply line was used to reduce the influent pressure from approximately 70 psi to 20 psi. A dual pressure switch (ASCO SC10B TE10A32) placed in the main water supply line could shut off the experiment if the water pressure exceeded 30 psi or fell below 5 psi: above 30 psi, the 6" bead-to-bead couplings on the pilot column inlets would start to leak; below 5 psi, flow could not be maintained through the GAC beds but would go through the column bypass line. In either case, a

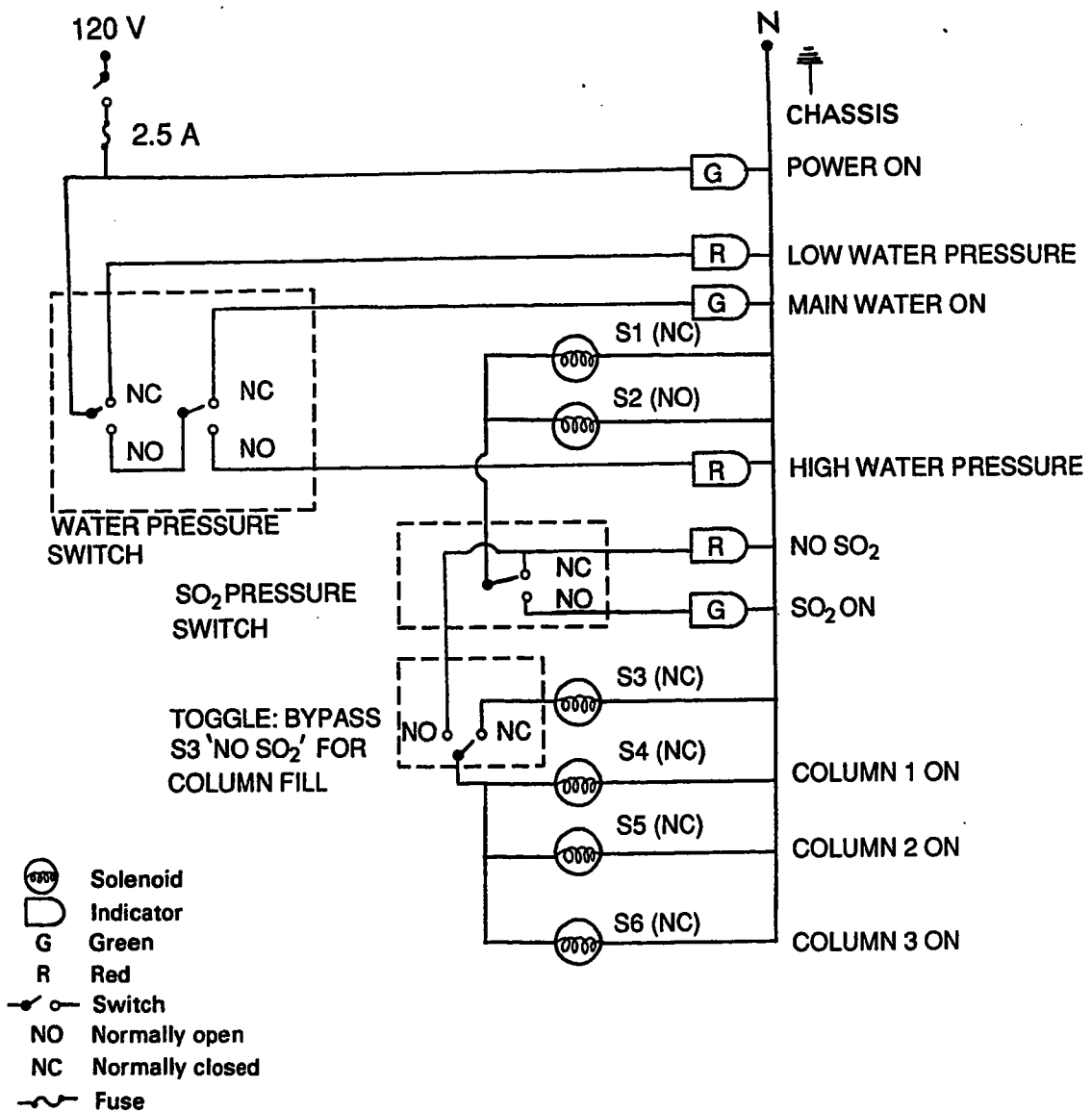


Figure 2.7 Schematic of the pressure switches and relays to solenoids controlling flow through the GAC pilot columns at Waterford, NY

solenoid valve (ASCO 8210 D95 NC, 0 - 100 psi) would close, shutting off flow to the columns, and a solenoid (ASCO 8210 C13 NO 5-250 psi) on a tee connection would open, diverting flow to the filters. To prevent the pilot columns from draining, solenoids (ASCO 8210 C94 NO) on the effluent lines would also close simultaneously. An additional pressure switch (ASCO SB20A TE-20A32) was placed in the SO<sub>2</sub> line, to detect an abnormally low pressure (less than 14 psi), for example if the SO<sub>2</sub> tank was empty. This switch could close a solenoid (Fluorocarbon DV2-122NC A2) in the SO<sub>2</sub> line, as well as the solenoids controlling flow to the columns. However, a switch to override "no SO<sub>2</sub>" was also included in the control box, so that the columns could be filled with water at the start of the experiment, when the SO<sub>2</sub> tank was manually shut off.

## SAMPLE COLLECTION

As shown in Table 2.7, water samples were collected from several points in the treatment plant at Waterford, and from the GAC pilot columns. Raw and finished water samples were also collected weekly at Latham Water Works (Mohawk View Plant) on the Mohawk River, to obtain additional information on background organics in river-water samples. Operating conditions at Latham Water Works are summarized in Appendix B.

In general, water samples were collected twice weekly. However, during a one-week simulated spill, influent and effluent samples were collected daily from pilot column I. Volumes of water collected were: 27 mL for volatile halogenated organics, in disposable glass culture tubes containing 50 mg Na<sub>2</sub>SO<sub>3</sub> for dechlorination and sealed with screw caps lined with aluminum foil; 27 mL for volatile aromatic organics, in screw-cap disposable glass culture tubes lined with aluminum foil; 10 L for semivolatile base-neutral organics, in glass Pyrex bottles sealed with a rubber stopper lined with aluminum foil.

In addition, GAC samples were also collected weekly at specific bed depths from each of the GAC pilot columns. The GAC samples, approximately 2.5 g each, were placed while wet in screw cap disposable glass culture tubes lined with aluminum foil.

All water and GAC samples were stored at 4 °C until analysis.

Methods of instrumental analysis are described in Appendix C for the organic compounds of interest.

**Table 2.7**

Summary of locations for collecting samples at the Waterford and Latham Water Works and codes for sample identification: mdd = month day; n = week of operation

Sequential treatment processes	Sample identification			
	Waterford Water			Latham Water
1. Raw water intake		mddA		mddF
2. Aeration		-		-
3. Coagulation		-		-
Flocculation		-		-
4. Powdered activated carbon		-		-
5. Pre-chlorination		-		-
6. Sedimentation		mddB		-
7. Filtration		mddC		-
8. Post-chlorination		-		-
9. pH adjustment		-		-
10. Fluoridation		-		-
Pilot columns	Column I	Column II	Column III	
11. Influent	mddD2	mddD1	mddD3	mddG
12. GAC-bed depth (cm)				
13	W5-6-n	W4-6-n	W6-6-n	-
34	W5-5-n	W4-5-n	W6-5-n	-
55	W5-4-n	W4-4-n	W6-4-n	-
75	W5-3-n	W4-3-n	W6-3-n	-
95	W5-2-n	W4-2-n	W6-2-n	-
113	W5-1-n	W4-1-n	W6-1-n	-
13. Effluents	mddE2	mddE1	mddE3	-





## CHAPTER 3

### VOLATILE HALOGENATED ORGANICS: RESULTS AND DISCUSSION

#### CONVENTIONAL PHYSICAL-CHEMICAL TREATMENT AND BACKGROUND CONCENTRATIONS OF TARGET COMPOUNDS

During the pilot column experiments, background concentrations of volatile halogenated organic compounds were monitored at a number of sites at Waterford and Latham Water Works. Except for chloroform, concentrations of these compounds were below the low quantitation limit established for analysis of hexane extracts by gas chromatography with electron capture detection (generally 6.4 to 8.0  $\mu\text{g/L}$ , but 1.6  $\mu\text{g/L}$  for carbon tetrachloride; Table C.1, Appendix C).

Concentrations of chloroform are shown in Figure 3.1 and summarized in Table 3.1. The occurrence of chloroform as a disinfection byproduct is readily apparent. At both Waterford and Latham Water Works, chloroform concentrations are significantly higher in the treated water than in the raw water: at the intake, the number of positive samples is low and chloroform concentrations are generally less than the lower quantitation limit. The results at Waterford show a steady increase in chloroform concentrations through successive stages of treatment, with increasing time for contact between chlorine and background natural organic matter. In Figure 3.1, it can also be seen that background concentrations of chloroform increased during the project period, from initial values of 5 to 10  $\mu\text{g/L}$  to final values of about 25  $\mu\text{g/L}$ , resulting in a large standard deviation relative to the average: this behavior parallels the seasonal increase in water temperature which accelerates the rate of chloroform formation (Figure 2.6; Table 2.2).

**Table 3.1**

Concentrations of chloroform during various stages of conventional treatment: average of positives ( $\text{avg}_{\text{pos}}$ ), standard deviation (st dev), number of positives ( $N_{\text{pos}}$ ) and total ( $N_{\text{tot}}$ )

		<b>Waterford</b>					<b>Latham</b>		
		<b>A</b>	<b>B</b>	<b>C</b>	<b>D1</b>	<b>D3</b>	<b>F</b>	<b>G</b>	
		raw	coag.- flocc.- sed.	filtration	influent pilot II	influent pilot III	raw	finished	
<b>CHCl<sub>3</sub></b>	$\text{avg}_{\text{pos}}$ $\mu\text{g/L}$	5.3	9.9	11.1	14.0	13.5	5.5	17.1	
	st dev $\mu\text{g/L}$	$\pm 3.6$	$\pm 5.0$	$\pm 13.5$	$\pm 8.9$	$\pm 8.7$	$\pm 3.0$	$\pm 8.1$	
	$N_{\text{pos}}$	-	22	52	53	54	52	13	47
	$N_{\text{tot}}$	-	56	56	56	57	54	52	47

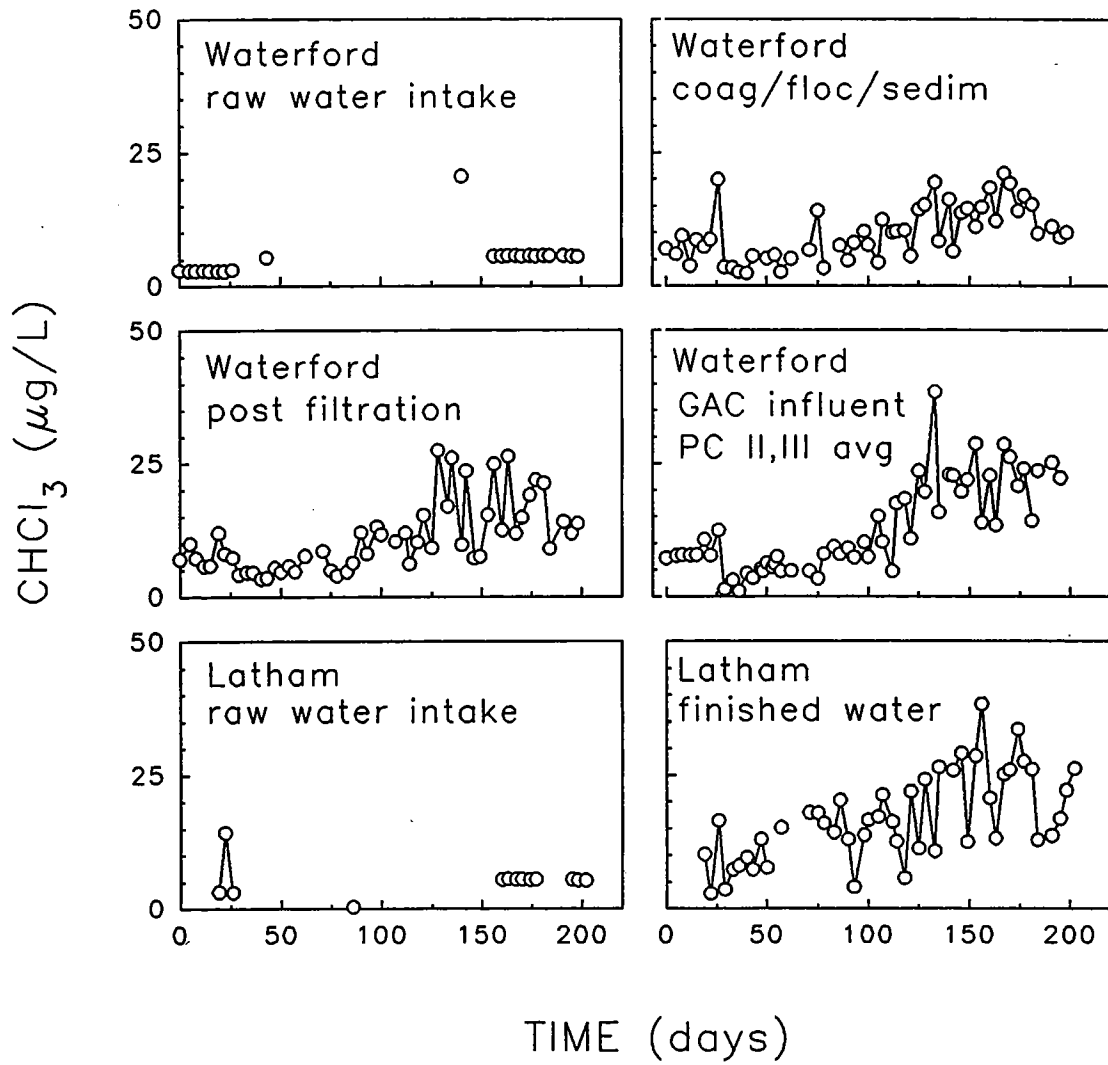


Figure 3.1 Concentrations of chloroform at sites used for background monitoring.

## GAC PILOT-COLUMN RESULTS

### Contaminant Concentrations During Simulated Spills

Table 3.2 summarizes the average concentrations of volatile halogenated organics during the simulated spills to pilot column I: clearly influent concentrations during the spills were well above background levels discussed in the previous section. High contaminant concentrations are also evident in the GC-ECD chromatograms for influent samples collected during the simulated spills to pilot column I (Figure 3.2). By comparison, only background levels of trihalomethanes are evident in the GC-ECD chromatograms for influent samples to pilot column II, run as a control (Figure 3.3).

In general, high contaminant concentrations were achieved in the last three simulated spills. As discussed in Chapter 2, contaminant concentrations were low during the first spill, because of solubility problems at the low water temperature (7.2 °C), and because of difficulty maintaining the flow of chemicals from the contaminant reservoirs.

Among the contaminants, concentrations tended to be higher for the trihalomethanes (> 100 µg/L overall) than for carbon tetrachloride, tri- and tetrachloroethylene (< 100 µg/L overall).

**Table 3.2**

Average influent concentrations of volatile halogenated organics during simulated chemical spills to pilot column I

		Spill 1	Spill 2	Spill 3	Spill 4	Overall (2,3,4)
Time	week	7	13	20	26	-
Duration	days	7: 48-55	8: 92-100	5: 137-142	4: 180-184	-
Temperature	°C	7.2	17.6	23.0	24.5	16.5
CHCl <sub>3</sub>	µg/L	28	206	438	294	313
CHBrCl <sub>2</sub>	µg/L	0	112	162	188	154
CHBr <sub>2</sub> Cl	µg/L	22	94	436	477	336
CHBr <sub>3</sub>	µg/L	10	136	269	253	219
CCl <sub>4</sub>	µg/L	15	47	76	106	76
C <sub>2</sub> HCl <sub>3</sub>	µg/L	10	62	115	139	105
C <sub>2</sub> Cl <sub>4</sub>	µg/L	0	32	36	34	34

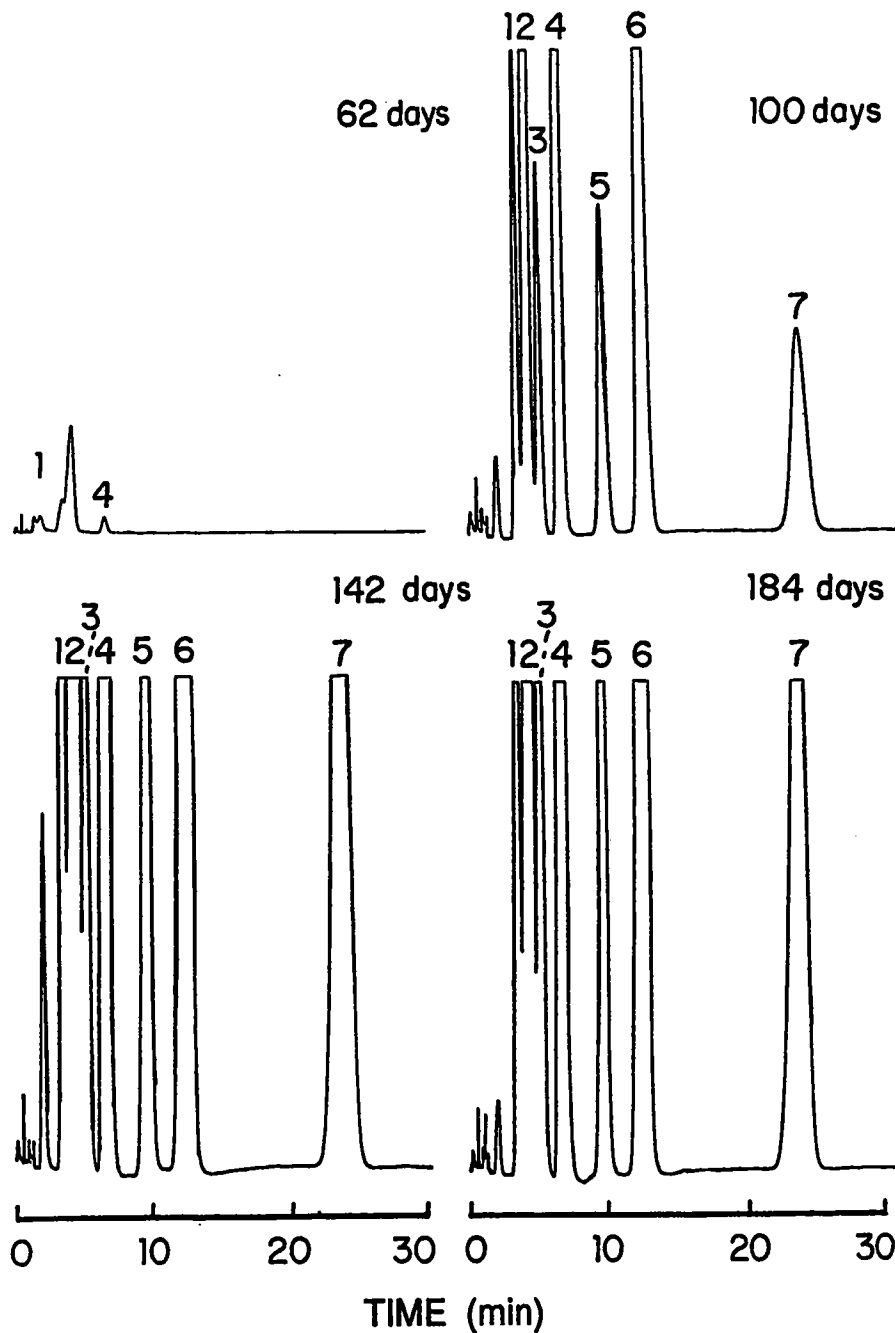


Figure 3.2 Gas chromatogram with electron capture detection of water samples (D2) collected from influent to pilot column I on days 62, 100, 142, and 184, during simulated chemical spills. Peaks are labeled: 1 chloroform; 2 carbon tetrachloride; 3 trichloroethylene; 4 bromodichloromethane; 5 tetrachloroethylene; 6 chlorodibromomethane; 7 bromoform. Hexane contaminant is evident in chromatogram of 62-day sample.

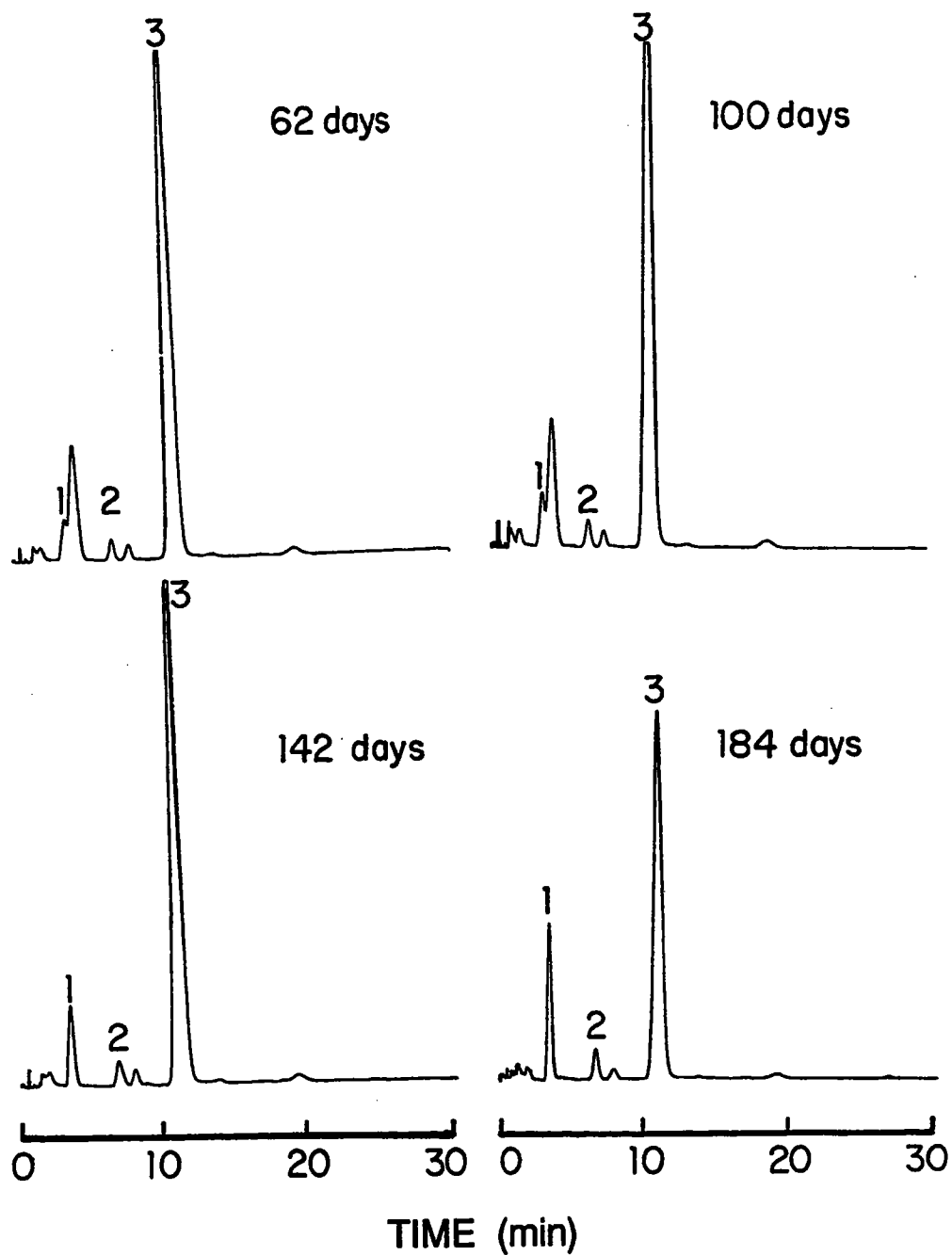


Figure 3.3 Gas chromatogram with electron capture detection of water samples (D1) collected from influent to pilot column II on days 62, 100, 142, and 184. Peaks are labeled: 1 chloroform; 2 bromodichloromethane; 3 2-bromo-1-chloropropane (internal standard). Hexane contaminant is evident in chromatogram of 62 and 100-day samples.

## **Breakthrough: Effluent Concentrations Relative to Influent Concentrations**

The primary question of interest in the pilot column experiments is whether the spill chemicals were removed by the GAC. A preliminary indication of contaminant breakthrough is given by the GC-ECD chromatograms for pilot column effluent samples. All four trihalomethanes are present in the chromatogram of effluent from pilot column I during spill 3 on day 142; in addition to the trihalomethanes, carbon tetrachloride, tri- and tetrachloroethylene are detected during spill 4 on day 184 (Figure 3.4). For the control pilot column (II), chloroform, and perhaps bromodichloromethane, are found in chromatograms for days 142 and 184, but none of the other compounds of interest are detected (Figure 3.5).

Plots of contaminant concentrations as a function of time in provide a quantitative measure of breakthrough, beginning when a compound is detected in the effluent, and reaching completion when effluent concentrations equal influent concentrations. Background chloroform reaches initial and complete breakthrough after 100 and 160 operating days, respectively, for both control pilot columns II and III (Figure 3.6, right). The first two simulated spills to pilot column I were conducted at approximately 50 and 100 days: throughout this period, chloroform is either below or just at the limit of quantitation ( $8 \mu\text{g/L}$ ); therefore chloroform is concluded to have been completely removed during the first two spills (Figure 3.6, left). The third and fourth simulated spills were conducted at approximately 140 and 180 days: in both cases, above-background concentrations of chloroform in the effluent indicated breakthrough from pilot column I. Breakthrough of chloroform during the third and fourth spills is not surprising, since these spills were conducted just before and just after background chloroform was at complete breakthrough.

Similar to chloroform, the brominated trihalomethanes were completely removed during the first two simulated spills (Figures 3.7 - 3.9). Bromodichloromethane and dibromochloromethane were detected in effluent samples from pilot column I during the third and fourth spills, whereas bromoform was detected in only one effluent sample from pilot column I during the fourth spill. Based on the similarity to chloroform, breakthrough of the brominated trihalomethanes during the third and fourth spills to pilot column I suggests that these compounds were nearing breakthrough (at their background levels) just before the spills. This interpretation is supported by results obtained from analyses of GAC samples, presented in the next section.

Removal of carbon tetrachloride, trichloroethylene, and tetrachloroethylene was complete during all four simulated spills to pilot column I. Only influent samples were found positive during the spills (Figure 3.10), relative to quantitation limits given in Appendix C (Table C.1).

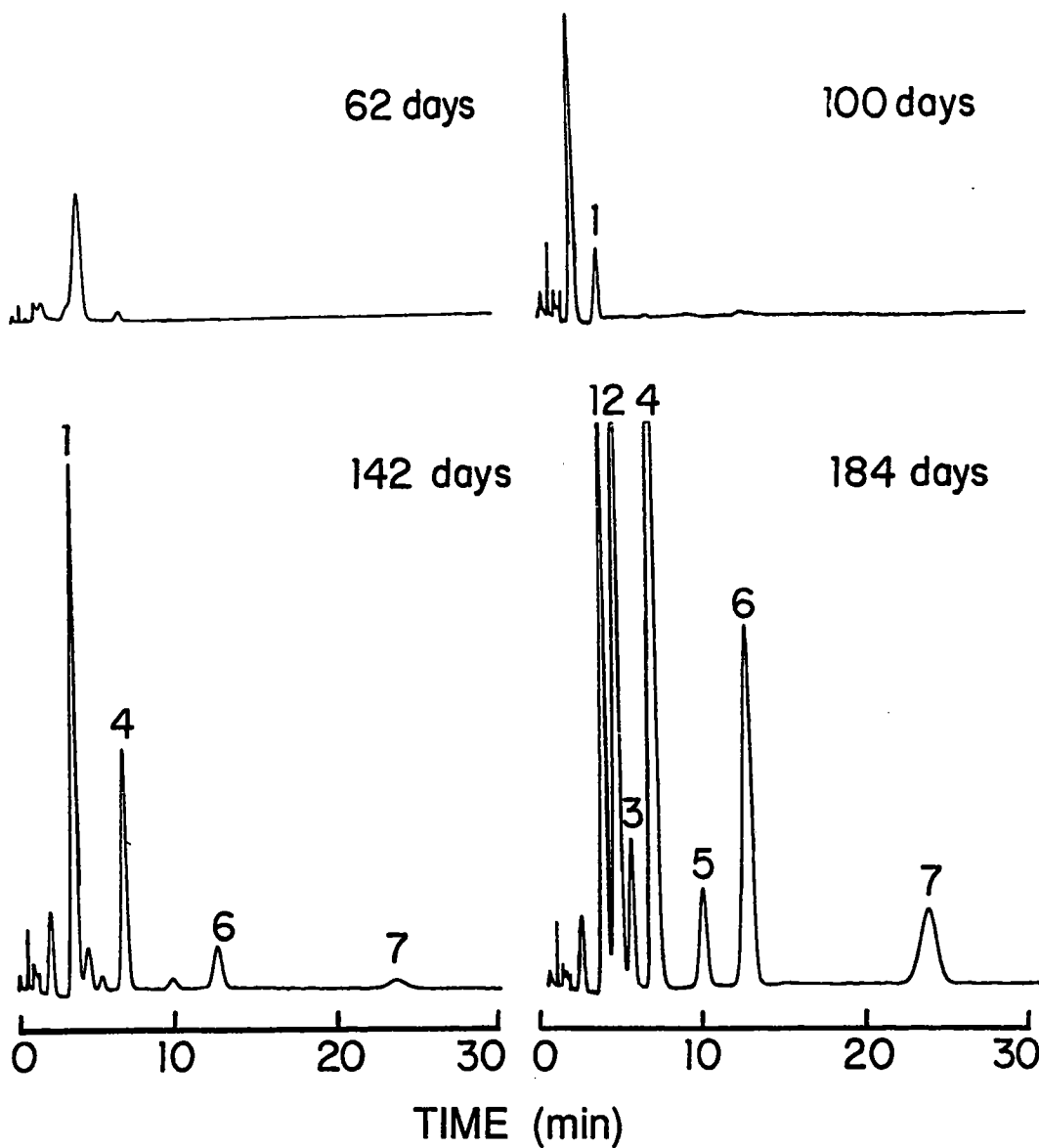


Figure 3.4 Gas chromatogram with electron capture detection of water samples (E2) collected from effluent to pilot column I on days 62, 100, 142, and 184, during simulated chemical spills. Peaks are labeled: 1 chloroform; 2 carbon tetrachloride; 3 trichloroethylene; 4 bromodichloromethane; 5 tetrachloroethylene; 6 chlorodibromomethane; 7 bromoform. Hexane contaminant is evident in chromatogram of 62-day sample.

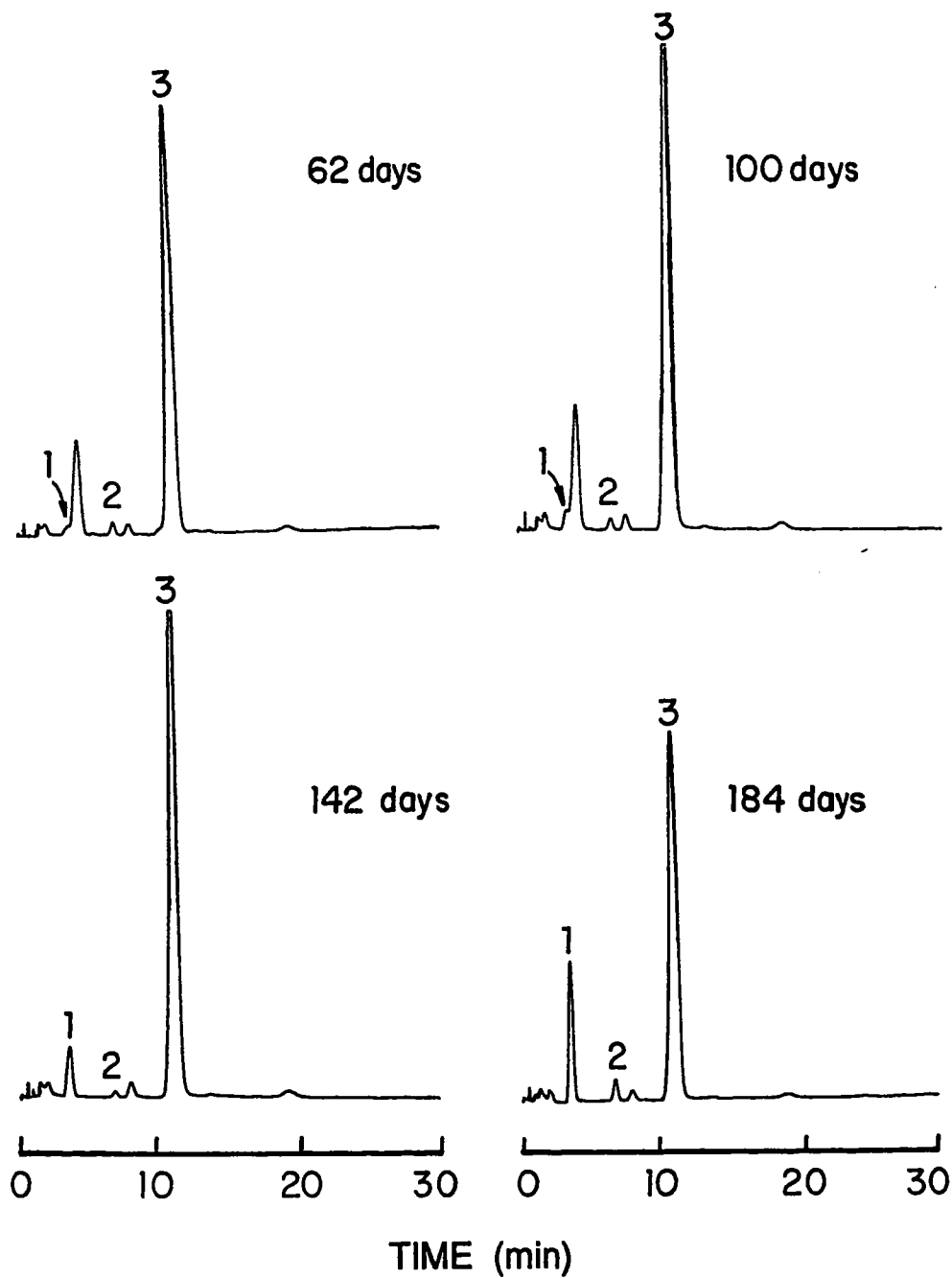


Figure 3.5 Gas chromatogram with electron capture detection of water samples (E1) collected from effluent to pilot column II on days 62, 100, 142, and 184. Peaks are labeled: 1 chloroform; 2 bromodichloromethane; 3 2-bromo-1-chloropropane (internal standard). Hexane contaminant is evident in chromatogram of 62 and 100-day samples.



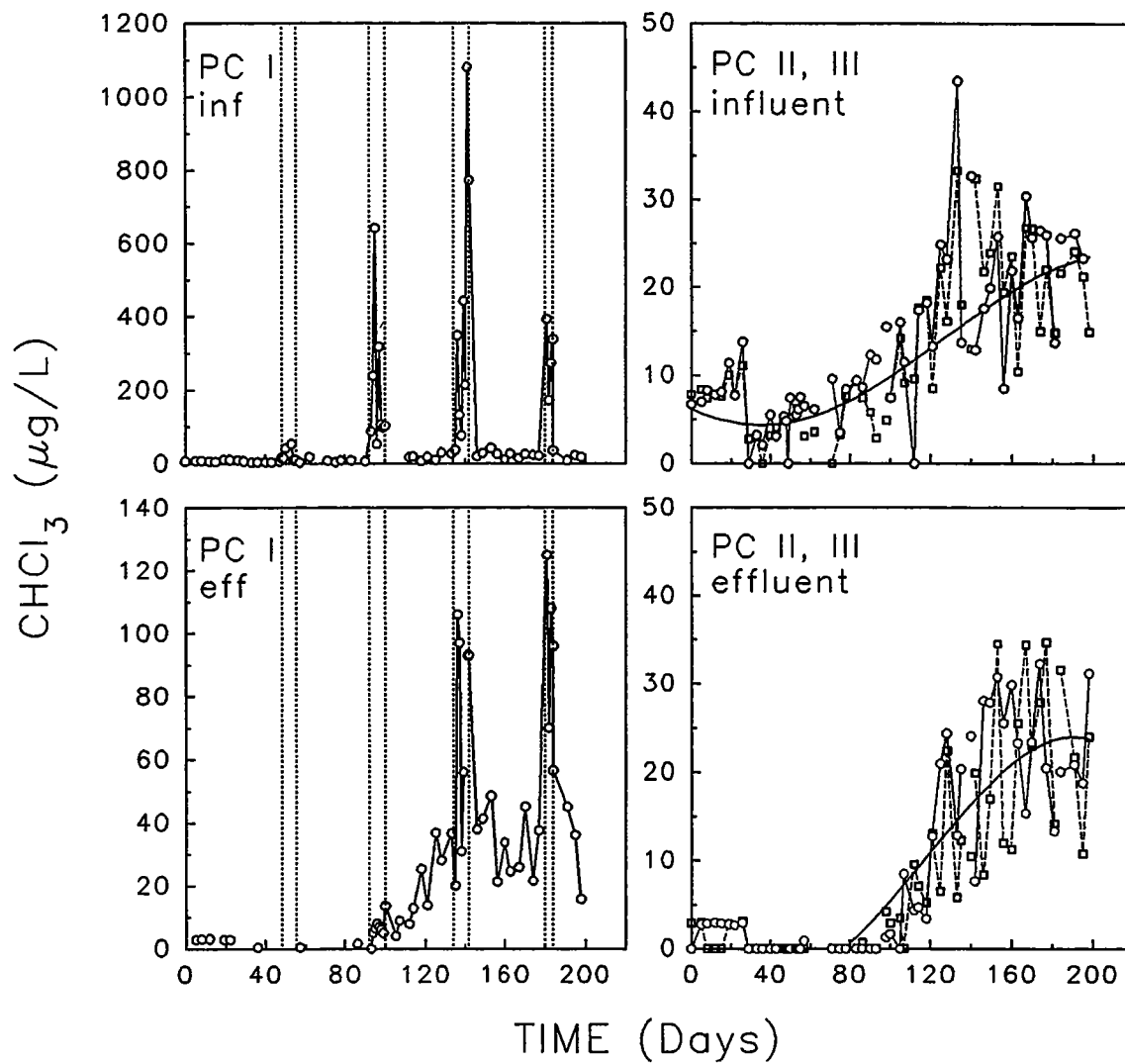


Figure 3.6 Chloroform concentrations in influent (top) and effluent (bottom) water samples from pilot column I (left) and from pilot columns II and III (right). The vertical dotted lines in figures on the left for pilot column I indicate the times of the four simulated spills:  $\text{CHCl}_3$  concentrations are plotted on a large scale in these figures, because  $\text{CHCl}_3$  was added as a spill constituent.

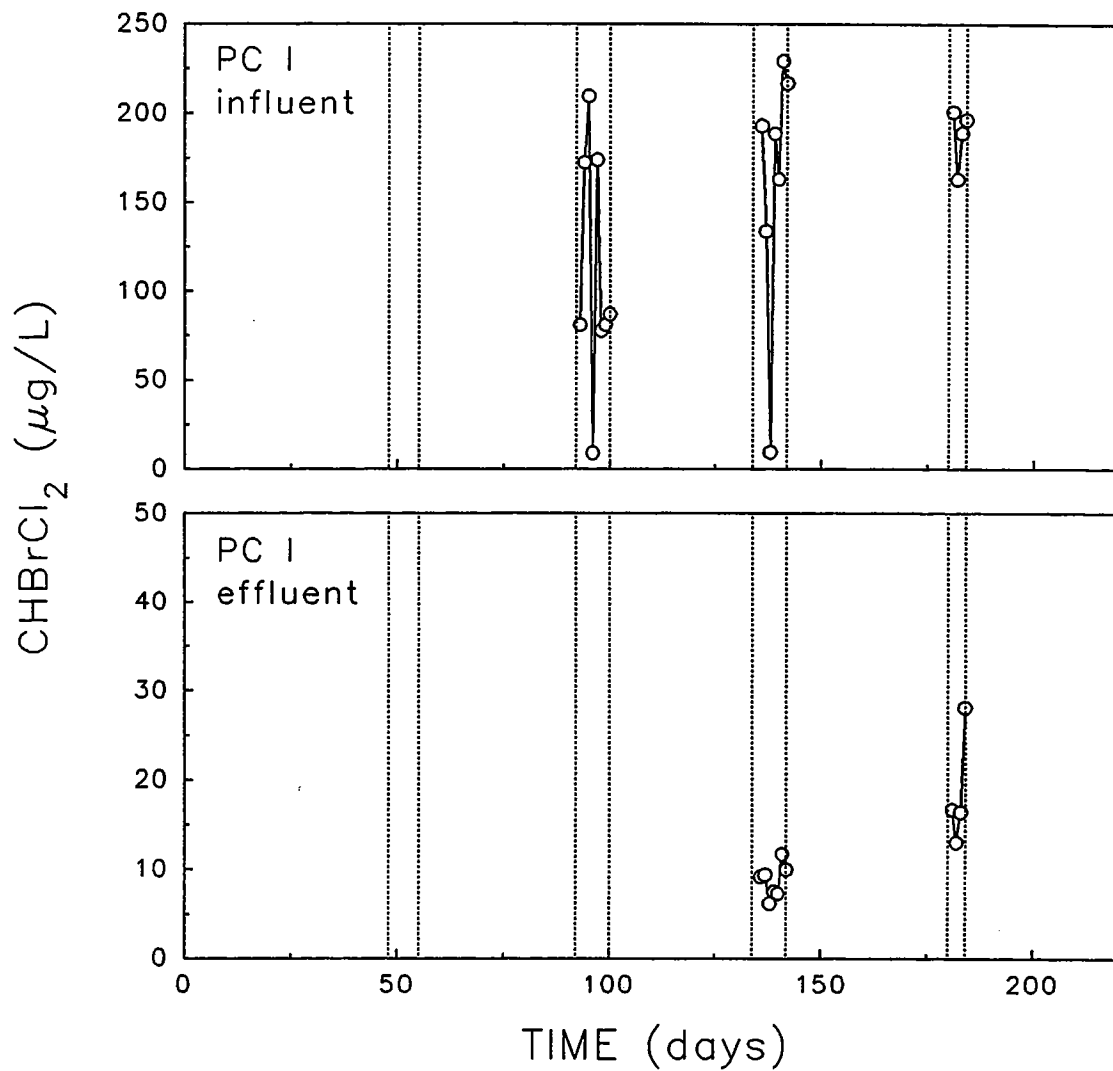


Figure 3.7 Bromodichloromethane concentrations in influent (top) and effluent (bottom) water samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

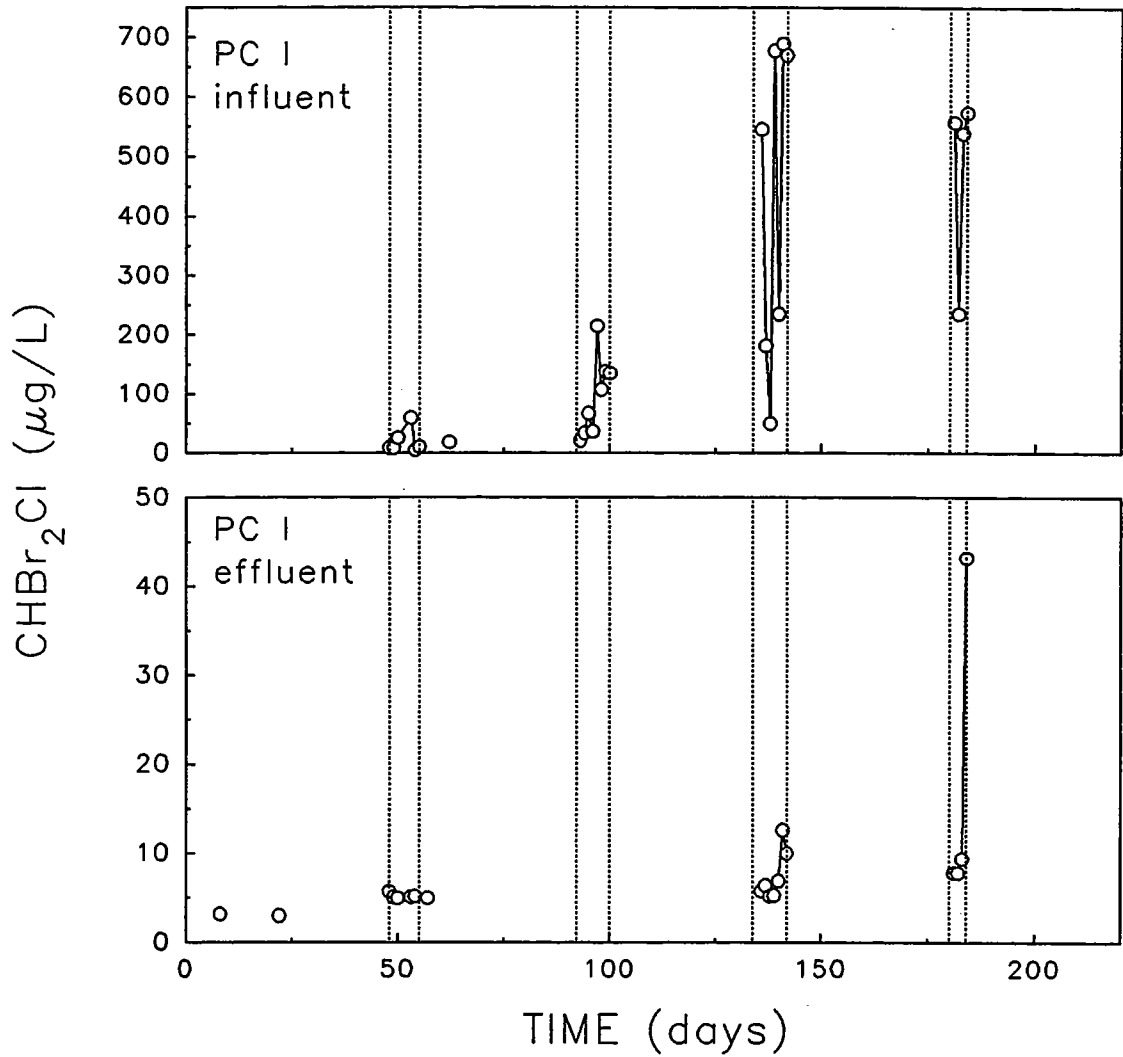


Figure 3.8 Dibromochloromethane concentrations in influent (top) and effluent (bottom) water samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

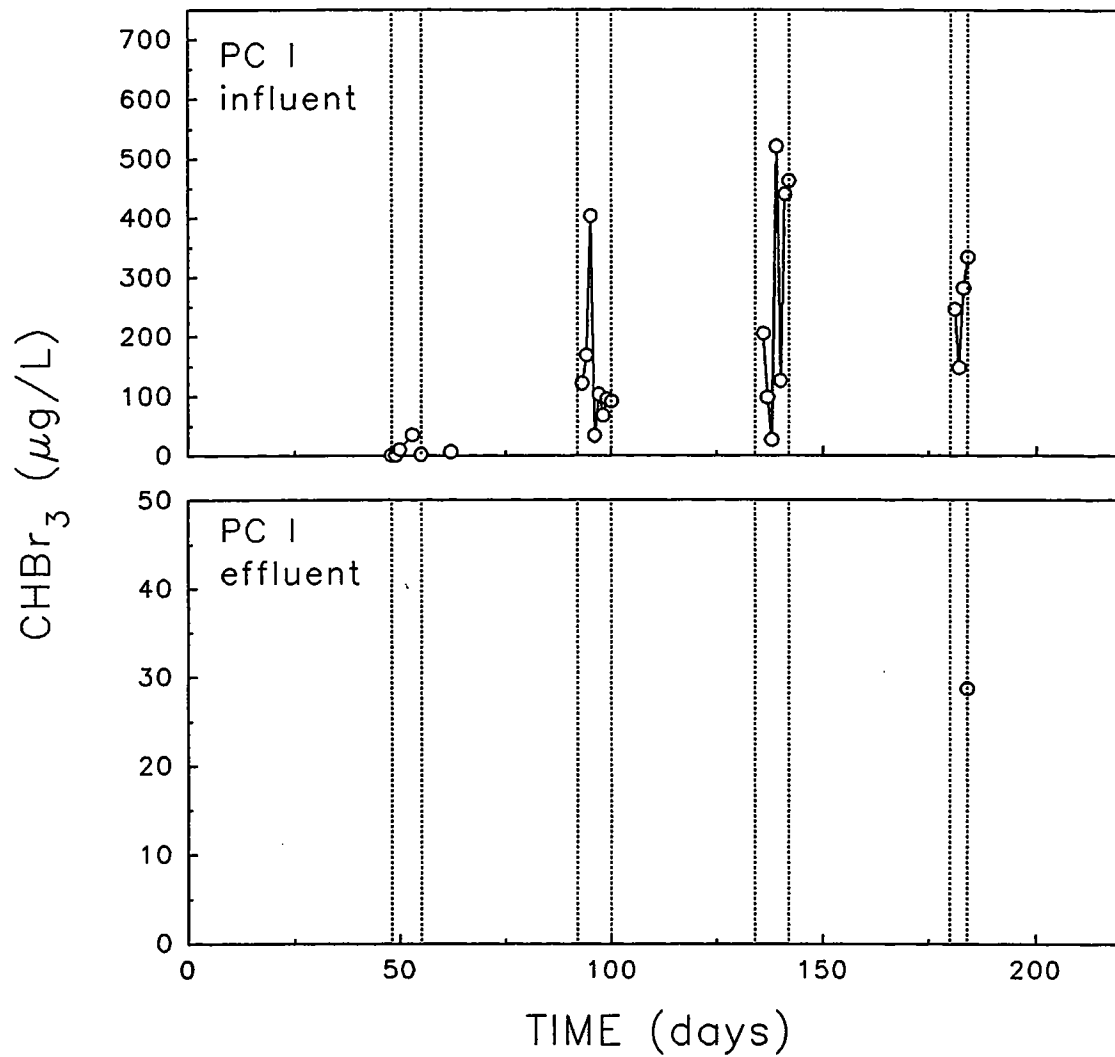


Figure 3.9 Bromoform concentrations in influent (top) and effluent (bottom) water samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

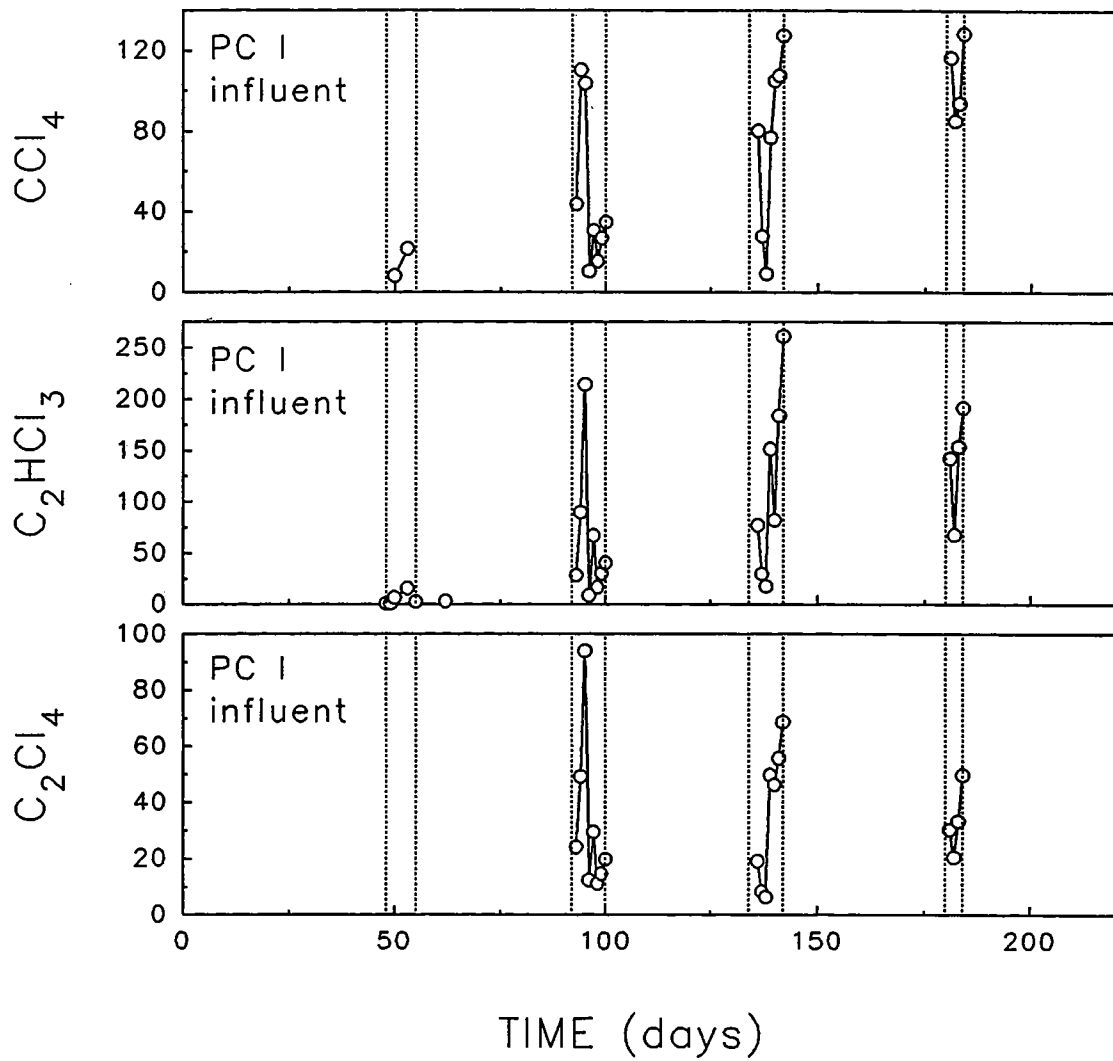


Figure 3.10 Carbon tetrachloride (top), trichlorethylene (middle), and tetrachlorethylene (bottom) concentrations in influent water samples from pilot column I: these compounds were not detected in effluent water samples. The vertical dotted lines indicate the times of the four simulated spills.

## Adsorption and Saturation: Contaminant Concentrations on GAC Samples

Methanol extraction of GAC samples for GC-ECD analysis provided an ability to confirm evidence for breakthrough based on analysis of water samples. In fixed-bed contactors, adsorption at shallow bed depths precedes adsorption at deep bed depths; adsorption through the entire bed is necessary for a compound to break through in the effluent. Measurements of concentrations on GAC samples as a function of time and bed depth should indicate that the trihalomethanes were adsorbed through all of pilot column I, by the time that these compounds reached breakthrough. However carbon tetrachloride, tri- and tetrachloroethylene should be found only on GAC samples at shallow bed depths, since these compounds did not reach breakthrough. In fact, analyses of GAC samples from sequential bed depths provided advance information on the position of all compounds in the pilot column, before any had reached breakthrough.

Chromatograms for methanol extracts of GAC samples gave a preliminary indication of how adsorption was proceeding within each pilot column. Chromatograms of GAC collected from the mid-section of pilot column I indicated that the trihalomethanes were present during all four spills (Figure 3.11). Similarly, carbon tetrachloride was found after the second spill; tri- and tetrachloroethylene were detected after the third spill. Only chloroform and bromodichloromethane were found on GAC samples collected at the same times from the midsection of the control pilot column II (Figure 3.12).

Plots of contaminant concentrations on the GAC as a function of time provided a quantitative description of adsorption within each pilot column. Chloroform moved through pilot column I and began adsorbing on GAC at the bottom (116 cm) in 100 days, reaching a maximum concentration (1.5 mg/g), or saturation, at 175 days (Figure 3.13). Similar results were obtained for the timing of chloroform adsorption on pilot columns II and III, although maximum concentrations did not exceed 1 mg/g (Figures 3.14, 3.15). These data are consistent with evidence for chloroform's initial breakthrough at 100 days and complete breakthrough after 180 days (Figure 3.6).

For the other trihalomethanes, with increasing bromine substitution, the GAC data indicated a progressively slower advance through pilot column I, as expected from differences seen in the breakthrough data. Bromodichloromethane moved through pilot column I and began adsorbing on GAC at the bottom (116 cm) in 150 days, nearing saturation, approximately 0.6 mg/g, at 212 days (Figure 3.16). Chlorodibromomethane reached saturation (0.6 mg/g) on only the top 75 cm of pilot column I; this compound was detected at the bottom of the pilot column at 150 days, but the concentration was still increasing at the end of the experiment (Figure 3.17). Bromoform reached saturation (0.6 mg/g) on only the top 55 cm of pilot column I; by the end of the experiment, at 212 days, bromoform had barely begun adsorbing on the bottom of the pilot

column (Figure 3.18). Therefore, distributions of brominated trihalomethanes within the pilot column are consistent with observations of breakthrough, during spills 3 and 4 for bromodichloromethane and dibromochloromethane, but only during spill 4 for bromoform.

Similar to bromoform, carbon tetrachloride appears to have reached saturation to 75 cm, and was only detected on GAC samples collected from the bottom of pilot column I near the end of the experiment (Figure 3.19). However, trichloroethylene and tetrachloroethylene were not found on the GAC below 55 cm (Figures 3.20, 3.21). These compounds were retained within the pilot column, as expected, since they had not been found in effluent samples.

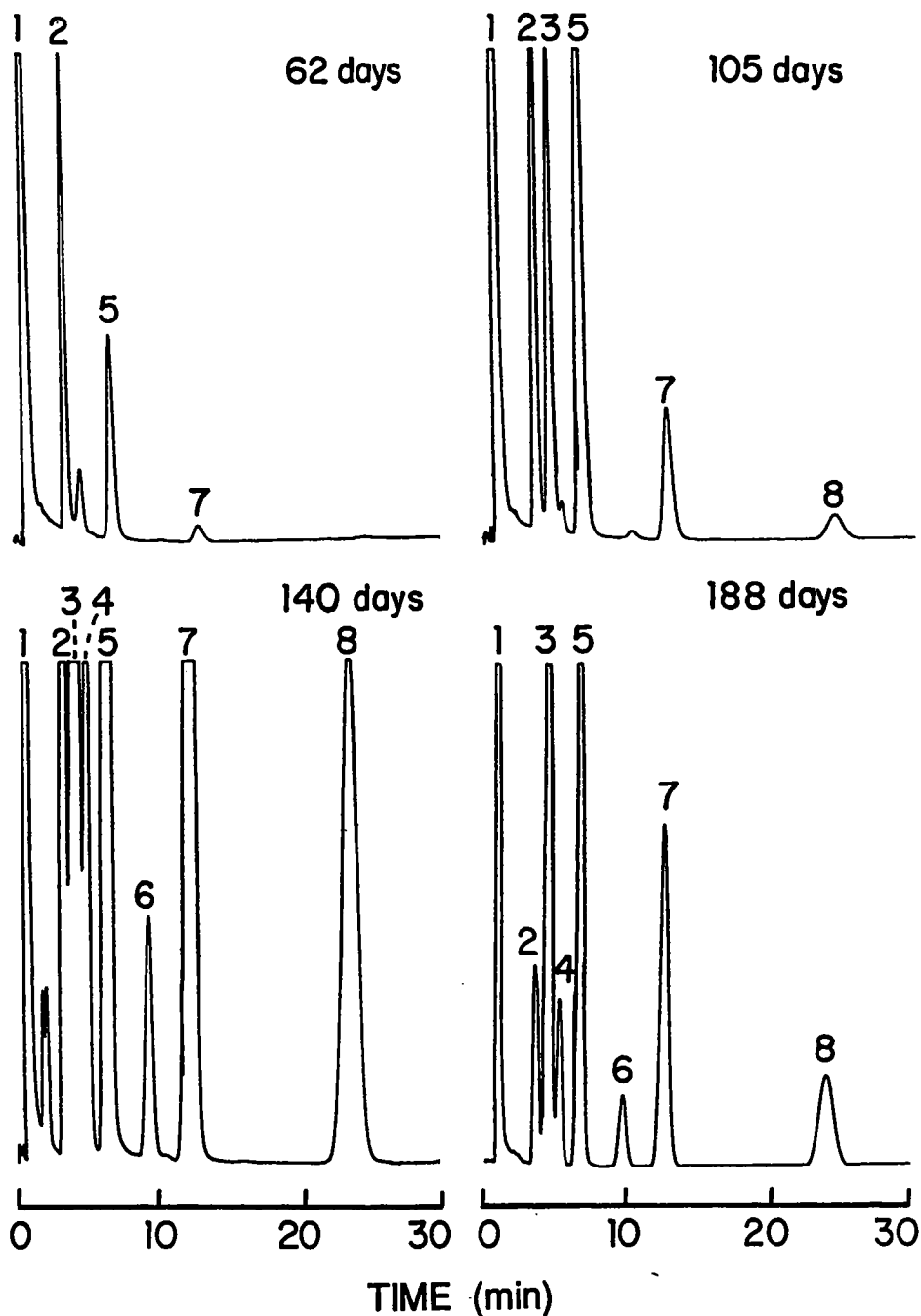


Figure 3.11 Gas chromatogram with electron capture detection of GAC samples collected from pilot column I at 44 cm bed depth on days 62, 105, 140, and 188, during or just following simulated chemical spills. Peaks are labeled: 1 methanol; 2 chloroform; 3 carbon tetrachloride; 4 trichloroethylene; 5 bromodichloromethane; 6 tetrachloroethylene; 7 chlorodibromomethane; 8 bromoform.



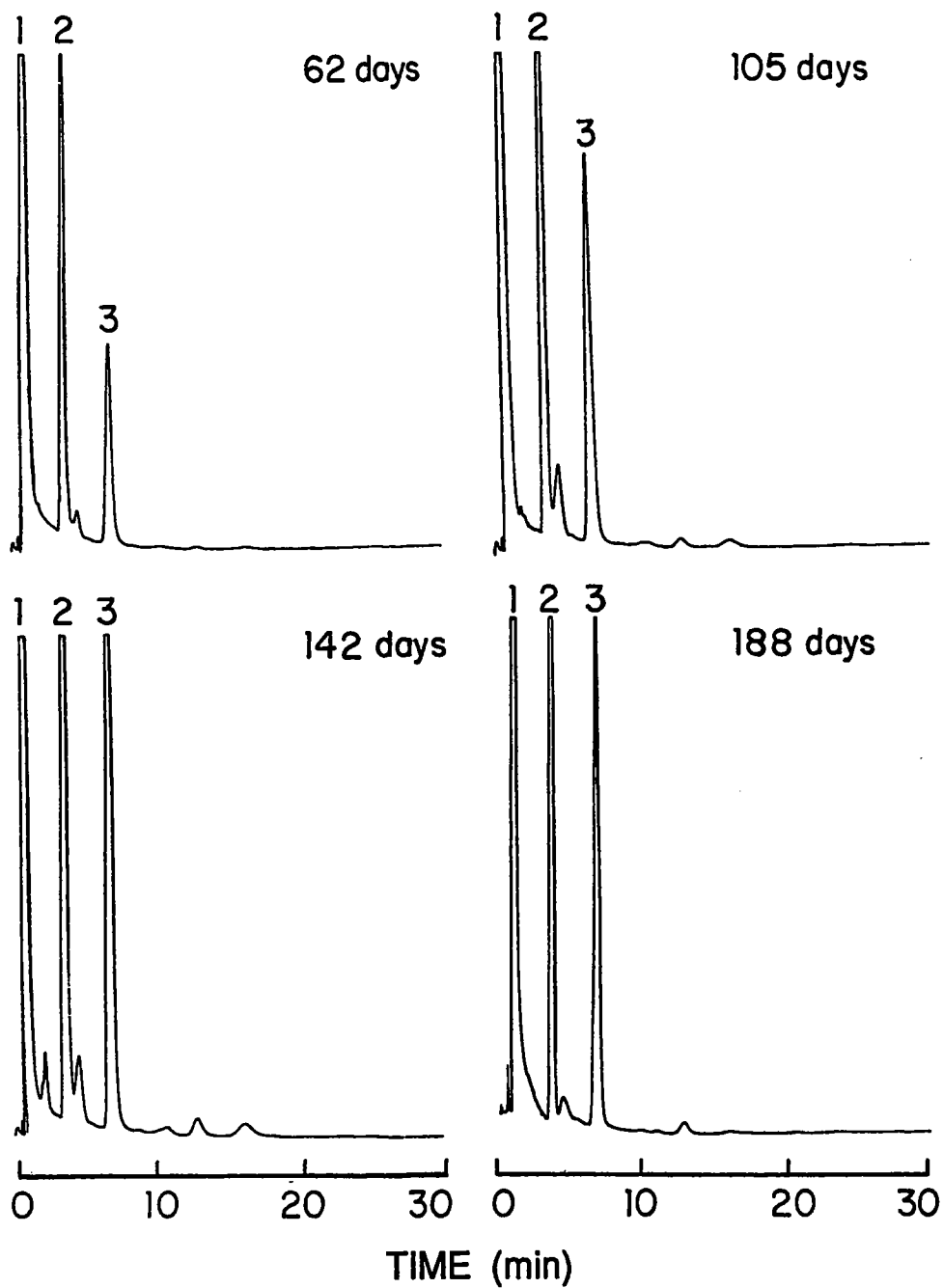


Figure 3.12 Gas chromatogram with electron capture detection of GAC samples collected from pilot column II at 44 cm bed depth on days 62, 105, 140, and 188. Peaks are labeled: 1 methanol; 2 chloroform; 3 bromodichloromethane.

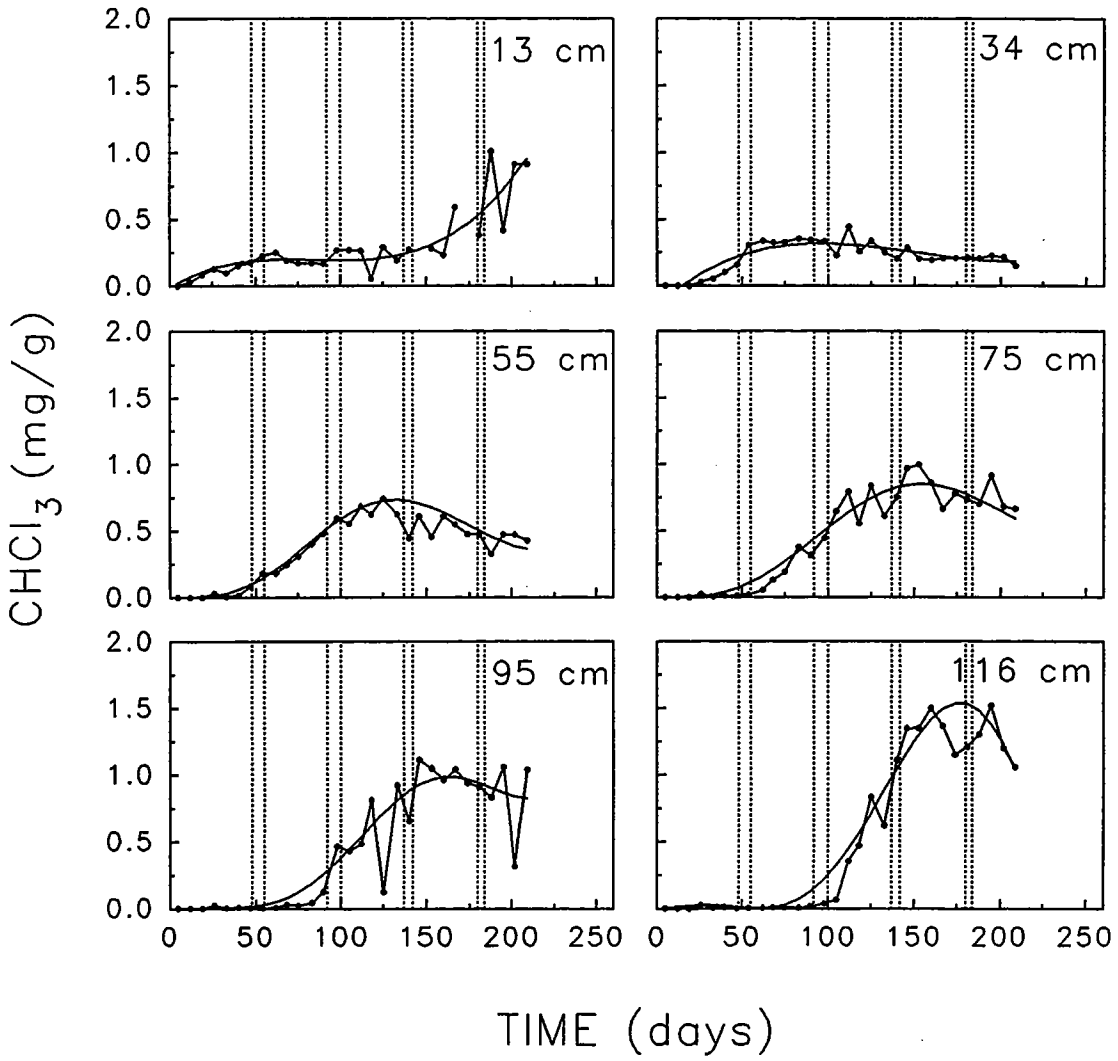


Figure 3.13 Chloroform concentrations in GAC samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

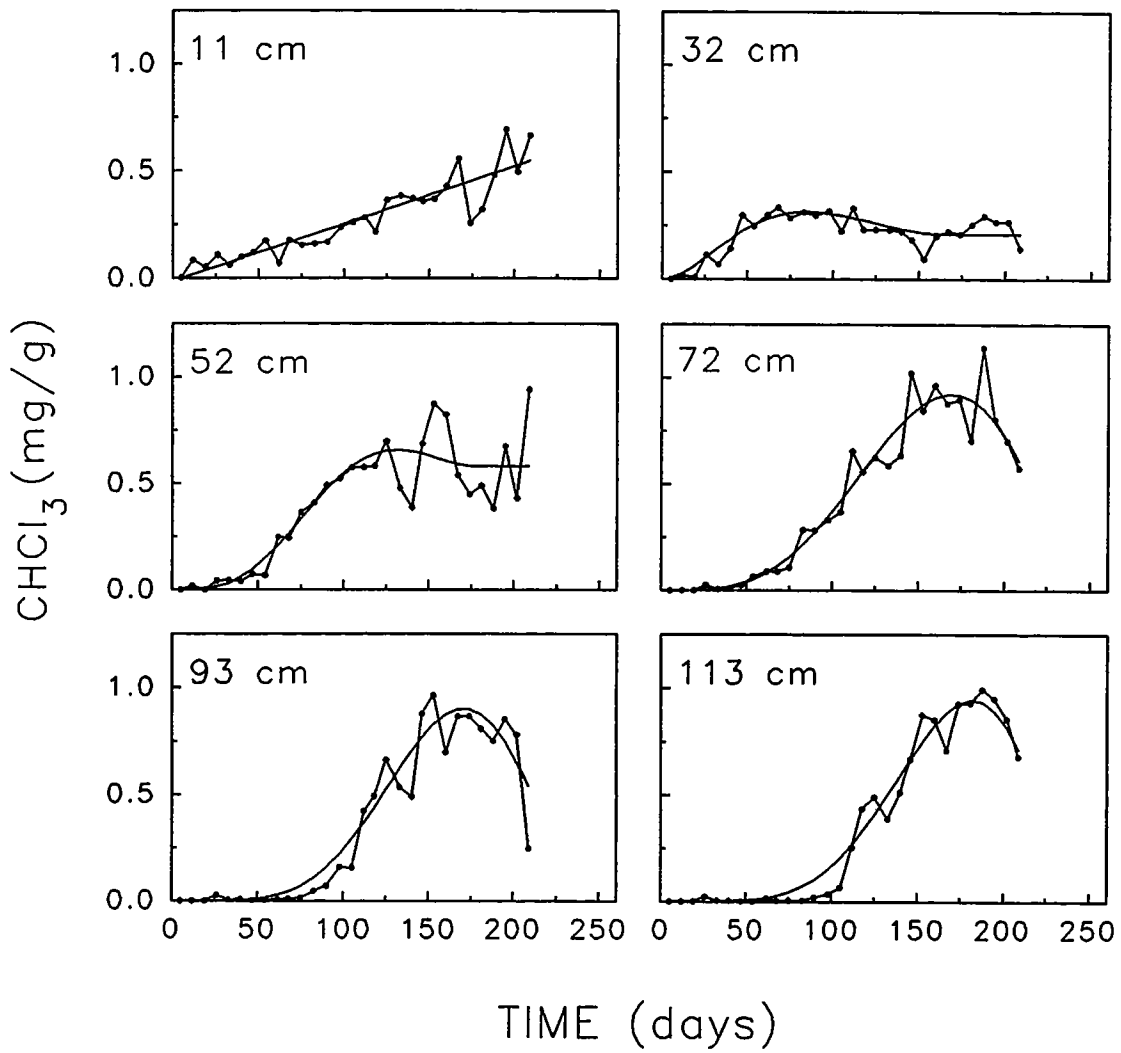


Figure 3.14 Chloroform concentrations in GAC samples from pilot column II.

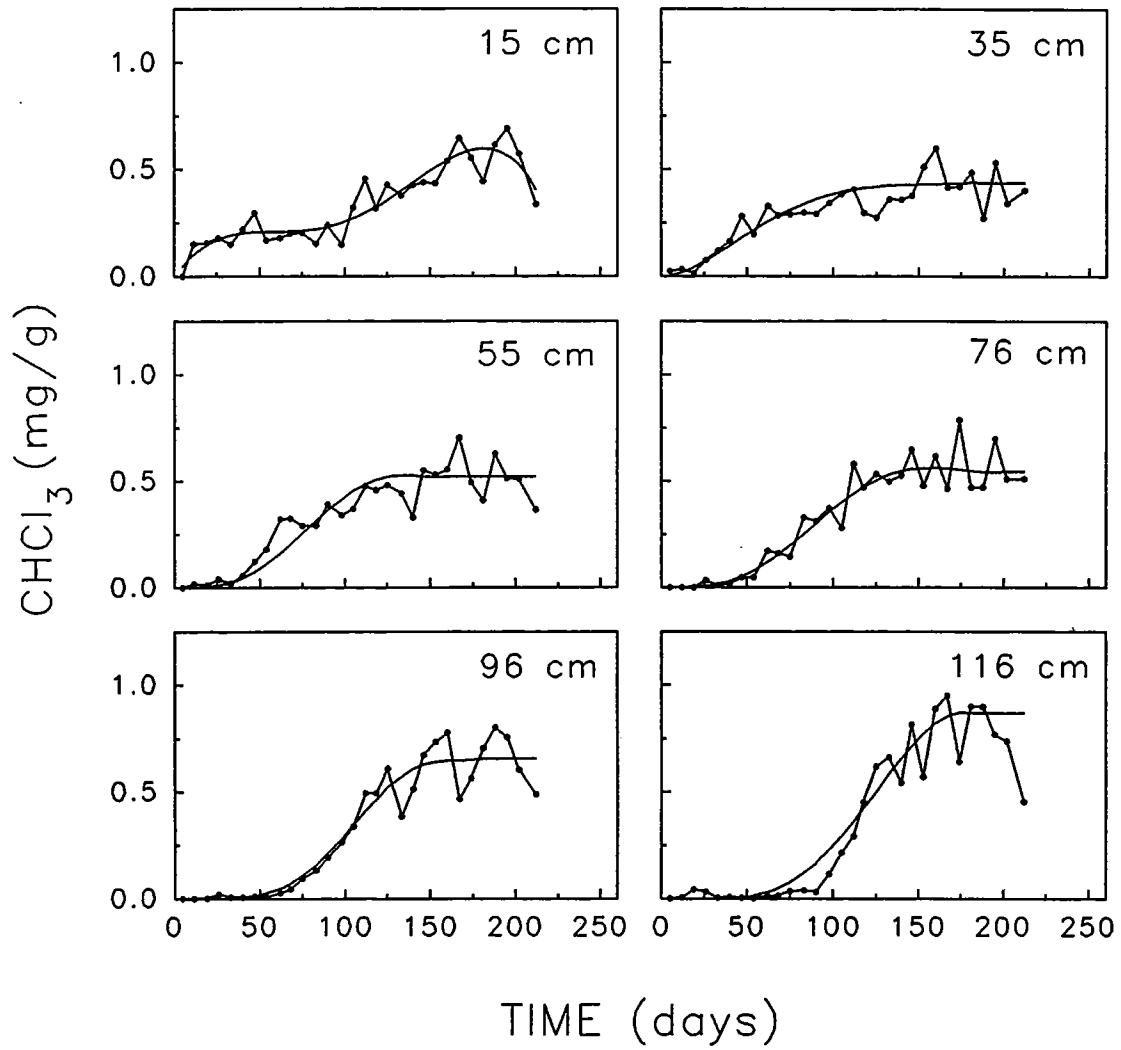


Figure 3.15 Chloroform concentrations in GAC samples from pilot column III.

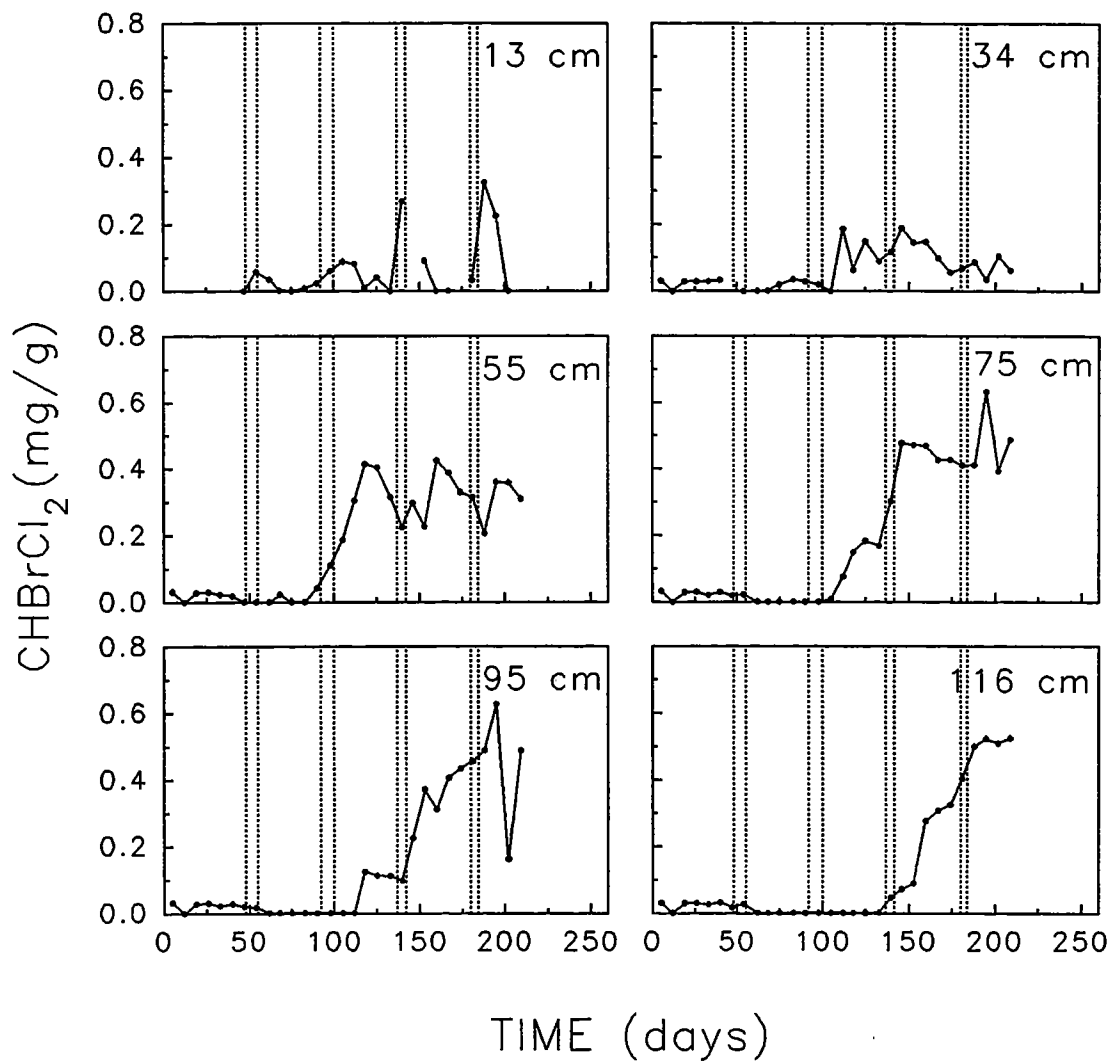


Figure 3.16 Bromodichloromethane concentrations in GAC samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

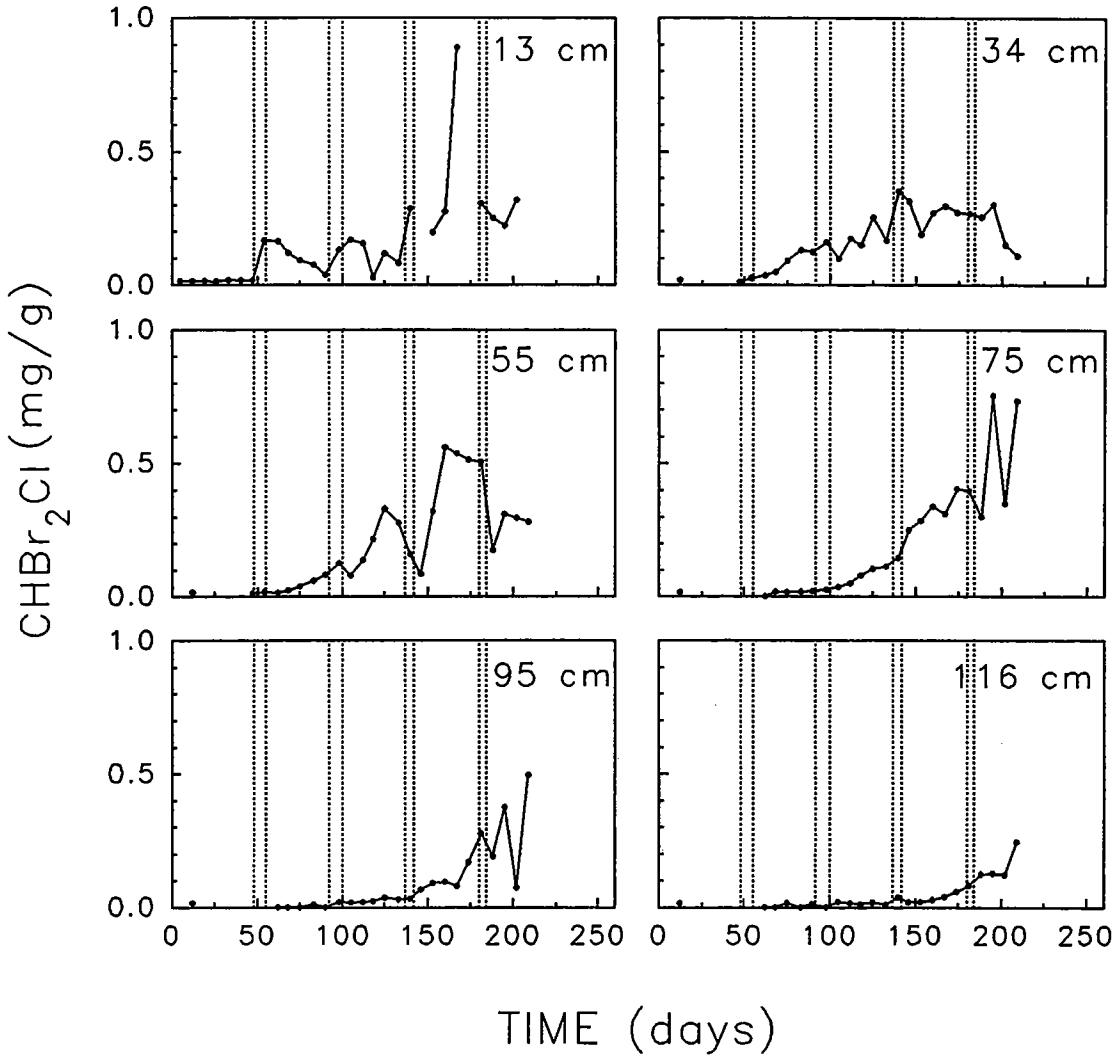


Figure 3.17 Dibromochloromethane concentrations in GAC samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

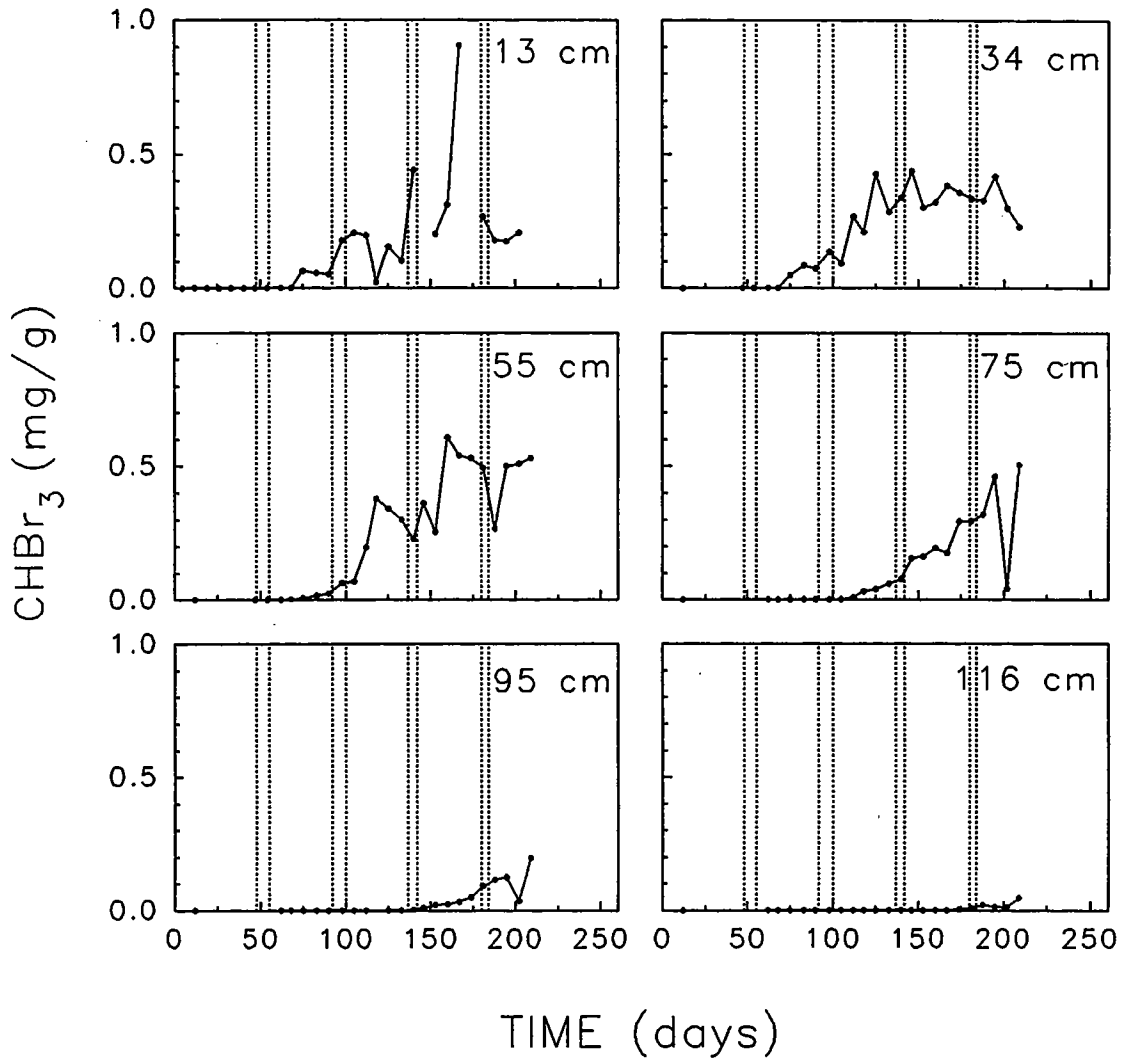


Figure 3.18 Bromoform concentrations in GAC samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

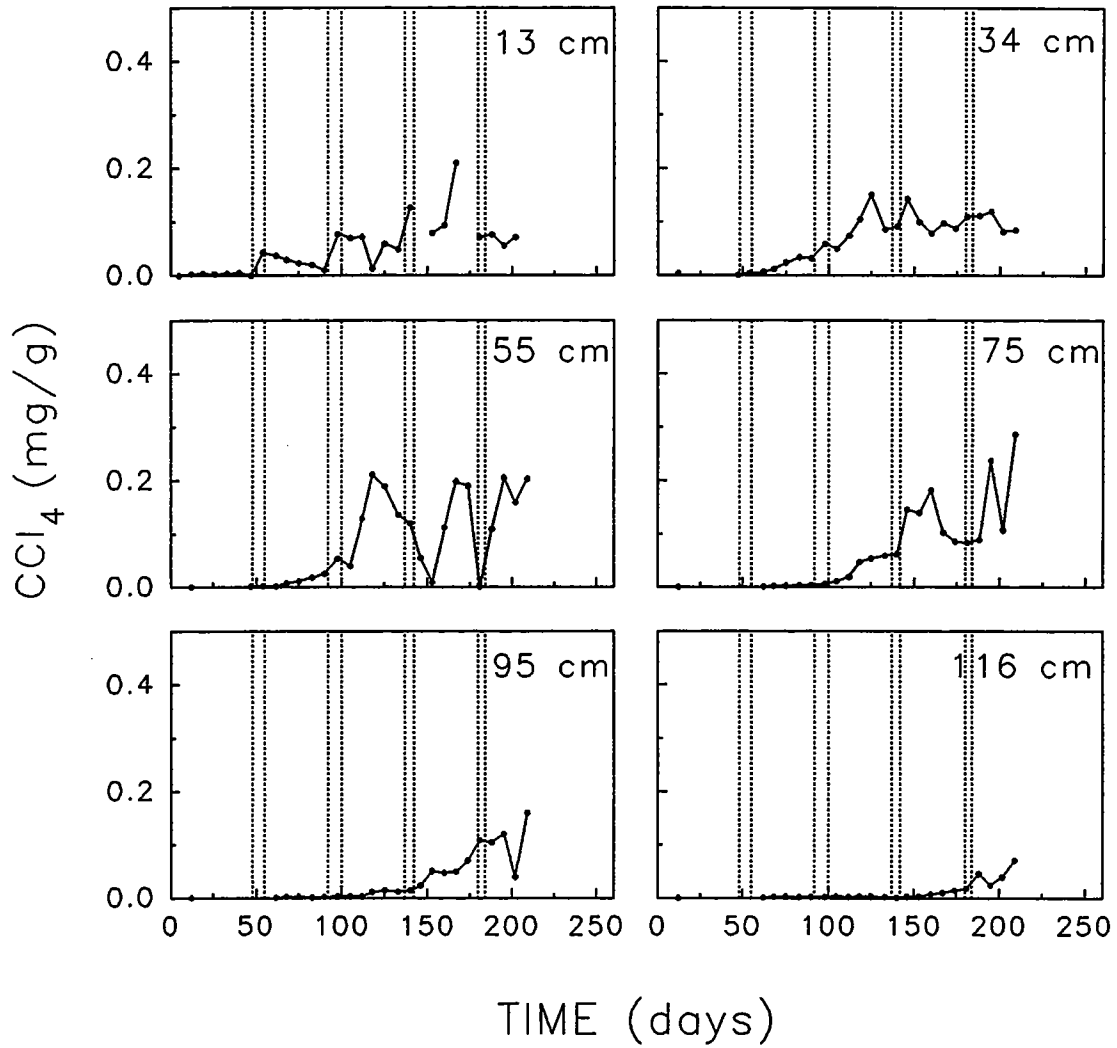


Figure 3.19 Carbon tetrachloride concentrations in GAC samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.



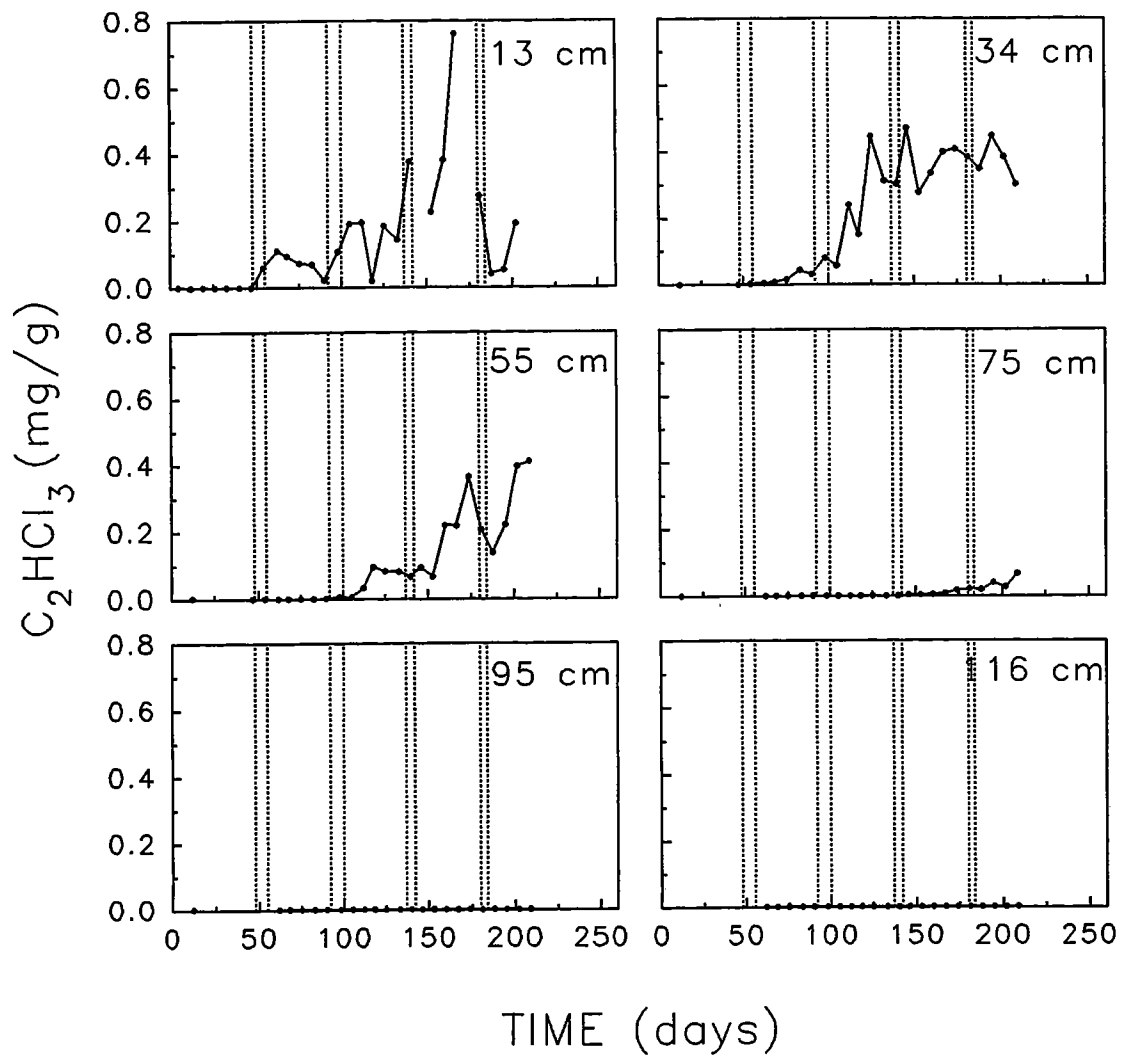


Figure 3.20 Trichloroethylene concentrations in GAC samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

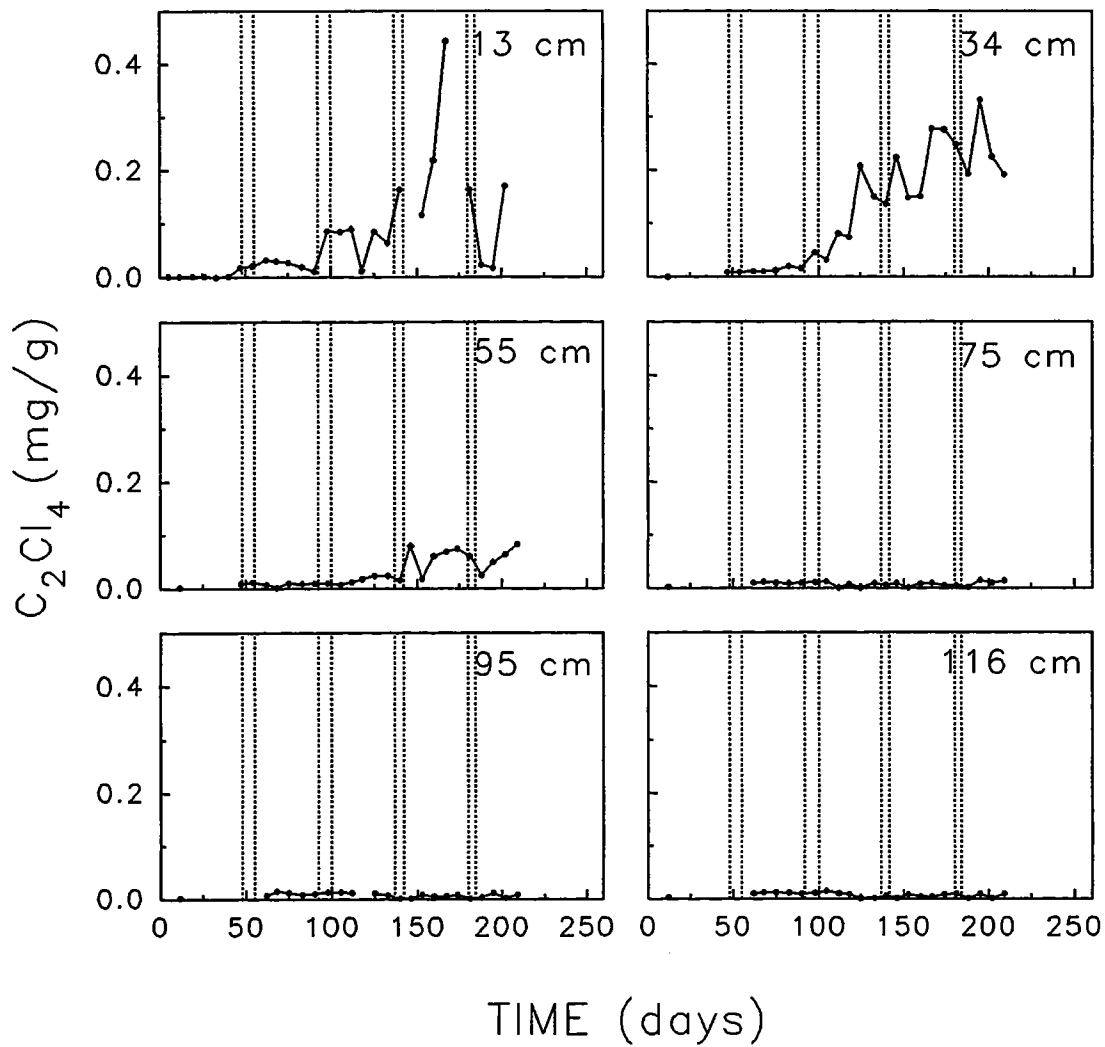


Figure 3.21 Tetrachloroethylene concentrations in GAC samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

## Spill Attenuation

The fact that the trihalomethanes broke through to the effluent during the third and fourth simulated spills does not entirely describe the performance of the GAC pilot column. Table 3.3 summarizes average influent and effluent concentrations for the trihalomethanes during the spills. As expected, average concentrations of chloroform in effluent samples are substantial during the third and fourth spills. For the brominated trihalomethanes, effluent concentrations are at and just above the 8 µg/L threshold for quantitation, in the third and fourth spills, respectively. During the fourth spill, when the pilot column is also at complete breakthrough with background chloroform, the total concentration of trihalomethanes in the effluent exceeds the 100 µg/L maximum contaminant level specified for drinking water (Appendix A).

In general, however, effluent concentrations are well below influent concentrations, for all of the trihalomethanes at breakthrough during the spills. Therefore the spills are attenuated; even

**Table 3.3**

Average performance of pilot column I during simulated chemical spills  
(calculated for more than one positive sample except for bromoform, spill 4)

		Spill 1	Spill 2	Spill 3	Spill 4
week		7	13	20	26
days		48-55	92-100	137-142	180-184
temperature (°C)		7.2	17.6	23.0	24.5
<i>Concentrations</i>					
CHCl <sub>3</sub>	Avg influent µg/L	28	206	438	294
	Avg effluent µg/L	< 8	< 8	79	91
CHBrCl <sub>2</sub>	Avg influent µg/L	0	112	162	188
	Avg effluent µg/L	< 8	< 8	9	19
CHBr <sub>2</sub> Cl	Avg influent µg/L	22	94	436	477
	Avg effluent µg/L	< 8	< 8	8	17
CHBr <sub>3</sub>	Avg influent µg/L	10	136	269	253
	Avg effluent µg/L	< 8	< 8	< 8	29 (N=1)
<i>Attenuation</i>					
CHCl <sub>3</sub>	%	100	100	82	69
CHBrCl <sub>2</sub>	%	100	100	94	90
CHBr <sub>2</sub> Cl	%	100	100	98	96
CHBr <sub>3</sub>	%	100	100	100	> 97

though there is some breakthrough of the spills, it is far from complete. As shown in Table 3.3, attenuation of all four trihalomethanes is somewhat greater in the third spill, 82 to 100 percent, than in the fourth spill, 69 to 97 percent. The decreased attenuation in the fourth spill is attributed to increased loading of background trihalomethanes (and background natural organics) on pilot column I, between spills.

As might be expected, attenuation is greatest for the spill constituents farthest from breakthrough: bromoform > chlorodibromomethane > bromodichloromethane > chloroform. Attenuation of the brominated trihalomethanes exceeds 90 percent; attenuation of chloroform averages 75 percent. This performance is considered somewhat remarkable for a pilot column at saturation with background organics, but demonstrates an ability to shift to a new point of equilibrium, in keeping with the fundamental properties of adsorption, discussed for Figure 1.3.

### **Post-Spill Desorption**

Evidence that GAC in the pilot column can shift to a higher equilibrium capacity for adsorption of a spill raises the question of whether desorption can also occur, following a spill. For chloroform, the third and fourth spills are of the type discussed for a column at saturation (Figure 1.4, left): effluent concentrations are expected to decrease (monotonically) following the spill, approaching pre-spill concentrations of background chloroform. However, the contaminant should not appear as a delayed pulse in the effluent (Figure 1.4, right). Results in Figure 3.6 (lower left, pilot column I effluent) show that, as expected, concentrations of chloroform decrease steadily after the third and fourth spills, in this case returning to the level of breakthrough defined by background chloroform. Results obtained for the GAC samples also indicate very little desorption of chloroform following the simulated spills: in Figure 3.13, concentrations of chloroform on the GAC generally remain constant or continue to increase following successive spills. Mass balance calculations presented in a later section support the argument that very little chloroform was desorbed following the simulated spills in this project. For hydrophobic synthetic organic contaminants in general, the kinetics of desorption from GAC is believed to be slower than the rate of adsorption.

Very little evidence was obtained for post-spill desorption of the other contaminants. As discussed in an earlier section, post-spill effluent concentrations of the other contaminants were consistently below the quantitation threshold. Analyses of GAC samples indicated some post-spill desorption from the top bed depth (13 cm) of pilot column I. At 13 cm, there was a general tendency for concentrations of the contaminants on the GAC to increase during each spill, and to decrease afterward (Figures 3.16 through 3.21). However, the contaminants were retained at deeper bed depths, where concentrations generally increased.

It may be of concern that effluent samples were only collected daily to screen for post-spill desorption. However, in a later experiment, following a 43-day simulated spill of trichloroethylene, samples were collected hourly for four days, and four times per day thereafter, to screen for desorption: trichloroethylene concentrations simply decreased to pre-spill levels, and only 17 percent of trichloroethylene was desorbed in the 60 days following the simulated spill (Alben et al 1995).

Problems are also encountered using GAC samples to screen for post-spill desorption, since the evidence for a specific compound is restricted to only a few samples collected at a particular location and time. Interpretation of the GAC data is hampered by occasional anomalies, where concentrations are unusually low for a contaminant on one GAC sample, whereas concentrations are high on the samples collected before and after. In an effort to eliminate artifacts from the GAC data base, analyses were repeated for 31 of the 178 samples analyzed for pilot column I (17 percent). In the second set of analyses, reasonable concentrations were found for 25 samples, suggesting that low recoveries were obtained in 14 percent of the original analyses. However, unusually low concentrations were confirmed for contaminants in six samples identified in Table 3.4. Low concentrations could not be verified for the remaining nine samples because too little GAC remained for analysis. Therefore, 15 anomalous results remain in the GAC data base,

**Table 3.4**

Location and time of samples from pilot column I with anomalously low concentrations for specific contaminants

Bed depth	Time (days)						
	CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	CCl <sub>4</sub>	C <sub>2</sub> HCl <sub>3</sub>	C <sub>2</sub> Cl <sub>4</sub>
13 cm	118 153 160 167 181 195	118	118	118	118	118	118
		202				188 195	188 195
55 cm			146		153 181 188		153 181 188
	188	188	188	188	188	188	188
75 cm			202	202	202	-	-
95 cm	125 202	202	202	202	202	-	-

which is approximately eight percent of the 178 samples analyzed. None of these low results are considered to be evidence of desorption, because they are not consistently associated with the time of a spill and they are often bracketed by samples with high concentrations.

Other mechanisms than desorption are thought to be responsible for the anomalies in the GAC data base, and may need to be investigated in future studies. In three cases cited in Table 3.4, concentrations of all contaminants were low: for samples from 13 cm on day 118, from 55 cm on day 188, and from 95 cm on day 202. Since these results were confirmed by the analysis of duplicate samples, it is possible that there was an irregular flow through the GAC at these positions, at least temporarily. In other cases, low concentrations were associated with a specific compound. Low concentrations for these samples may also indicate a deviation from plug-flow conditions, but it is not entirely understood why only specific compounds are affected. There is no pattern in Table 3.4 that suggests the unusually low concentrations are an example of displacement, resulting from competitive interactions between adsorbed contaminants.

### Factors Controlling GAC Performance

The data that have been presented indicate the pilot column's performance and the ability to treat chemical spills. In this section, it is of interest to determine if removal of the volatile halogenated contaminants is consistent with knowledge of their influent concentrations and affinities for GAC, or if overall pilot column performance is less than ideal. It is also of interest to check for inconsistencies within the group of compounds, that may provide additional insight into mechanisms controlling GAC adsorption of specific compounds. Molar concentration units are used to compare the adsorption behavior of different compounds, since these units describe interactions on a molecular level, whereas mass concentration units are used only for analytical convenience.

Pilot column performance is indicated by times to breakthrough and saturation, which for the compounds of interest increase in the order shown:

$$\begin{array}{l} \text{Time to} \\ \text{breakthrough,} \\ \text{saturation} \end{array} \quad \underline{\text{CHCl}_3} < \underline{\text{CHBrCl}_2} < \underline{\text{CHBr}_2\text{Cl}} < \text{CCl}_4 < \underline{\text{CHBr}_3} < \text{C}_2\text{HCl}_3 < \text{C}_2\text{Cl}_4 \quad (3.1)$$

In the simplest approximation, times to breakthrough and saturation are inversely related to molar influent concentrations and mass inputs (Table 3.5), which decrease in the order:

$$\begin{array}{l} \text{Influent} \\ \text{concentrations} \\ \text{mass inputs} \end{array} \quad \underline{\text{CHCl}_3} > \underline{\text{CHBr}_2\text{Cl}} > \underline{\text{CHBrCl}_2} > \underline{\text{CHBr}_3} > \text{C}_2\text{HCl}_3 > \text{CCl}_4 > \text{C}_2\text{Cl}_4 \quad (3.2)$$

**Table 3.5**

Influent concentrations in the simulated spills and predicted capacities using Freundlich coefficients for single-solute adsorption of halogenated organics on Calgon F400

	MW g/mole	Average influent		$K_F^*$ (mg/g)(L/ $\mu$ g) <sup>1/n</sup>	1/n* -	Isotherm capacity	
		$\mu$ g/L	$\mu$ mol/L			mg/g	$\mu$ mol/g
CHCl <sub>3</sub>	119.4	313	2.621	0.092	0.669	4.30	36.0
CHBrCl <sub>2</sub>	163.8	154	0.940	0.241	0.655	6.53	39.8
CHBr <sub>2</sub> Cl	208.3	336	1.613	0.585	0.636	23.6	113.6
CHBr <sub>3</sub>	252.7	219	0.867	0.929	0.665	33.4	132.4
CCl <sub>4</sub>	153.8	76	0.494	0.387	0.594	5.07	32.9
C <sub>2</sub> HCl <sub>3</sub>	131.4	105	0.799	2.00	0.482	18.8	143.1
C <sub>2</sub> Cl <sub>4</sub>	165.8	34	0.205	4.05	0.516	25.0	150.8

\* Speth and Miltner 1990

Actual times to breakthrough and saturation (Equation 3.1) increase in nearly in the same order as influent concentrations decrease (Equation 3.2): however, carbon tetrachloride advances through the pilot column somewhat more rapidly than would be expected from its influent concentration alone. This suggests that the pilot-column capacity for CCl<sub>4</sub> may be abnormally low relative to the other compounds.

Expected GAC capacities can be calculated, as shown in Table 3.5 using the Freundlich coefficients for the compounds of interest adsorbed as single compounds on Calgon F400. At the influent concentration of each compound to the pilot column, capacities in molar units are predicted to increase in the order:

GAC capacities, predicted

$$CCl_4 < CHCl_3 < CHBrCl_2 < CHBr_2Cl < CHBr_3 < C_2HCl_3 < C_2Cl_4 \quad (3.3)$$

Based on the Freundlich adsorption isotherms, the highest adsorption capacity is expected for tetrachloroethylene, and the lowest capacity is expected for carbon tetrachloride. Since the time to breakthrough and saturation is directly related to molar adsorption capacities, carbon tetrachloride would be expected to reach breakthrough and saturation ahead of the other compounds. In fact, carbon tetrachloride did not move through the pilot column quite as rapidly as would be expected

from Freundlich adsorption capacities. For the remaining compounds, the observed order of breakthrough is the same as the order of increasing single-solute adsorption capacities.

It is also important to compare actual pilot column capacities to those calculated for single-solute adsorption. Maximum concentrations achieved on the pilot column GAC are given in Table 3.6: values represent an average over the weeks at saturation. In general, capacities increase steadily with increasing bed depth: at the first bed depth, concentrations of  $\text{CHCl}_3$  do not fit this pattern, for reasons that remain under investigation. The primary concern is that actual capacities are generally less than one mg/g, whereas much greater capacities are predicted from the single-solute adsorption isotherms, ranging from 4.3 to 33 mg/g. For all compounds, capacities achieved in the GAC pilot column fall well below values expected under single-solute conditions. Pilot-column capacities for  $\text{CHCl}_3$  are only a factor of five below the isotherm capacity, but for the other compounds, the differences range from a factor of 20 to 100. In general, competition with background natural organic matter, as well as volatile halogenated organics, is believed to limit capacities observed on GAC pilot columns (Crittenden et al. 1985; Kuennen et al 1989; Najm et al. 1991). In molar units, pilot column capacities for the individual compounds increase in the order:

$$\text{GAC capacities, actual, pilot column I} \quad \text{CCl}_4 < \text{C}_2\text{Cl}_4 < \underline{\text{CHBr}_3} < \underline{\text{CHBr}_2\text{Cl}} < \underline{\text{CHBrCl}_2} < \text{C}_2\text{HCl}_3 < \underline{\text{CHCl}_3} \quad (3.4)$$

Comparing Equations 3.4 and 3.3, pilot column capacities are comparatively high for trichloroethylene and low for carbon tetrachloride, as expected. However, pilot column capacities for all of the trihalomethanes rank higher than expected, and increase with decreasing bromine substitution, in reverse to the order in Equation 3.3. The ranking for tetrachloroethylene is lower than expected from Equation 3.3.

In future work, it is of interest to examine how differences in the compounds' rates of adsorption (diffusivities) affect their ability to compete. Adsorption of the trihalomethanes may be favored by a rate of adsorption that is rapid relative to the other compounds, whereas competitive adsorption of tetrachloroethylene may be hindered by a slow rate of adsorption. To fully understand competitive limitations to capacities for removal of chemical spills, information is needed on kinetic as well as thermodynamic differences between the volatile halogenated organic compounds.



**Table 3.6**

Maximum capacities of volatile halogenated compounds achieved on successive bed depths of pilot column I (omitting data from sections considered below saturation)

Bed depth	Concentration (mg/g)						
	CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	CCl <sub>4</sub>	C <sub>2</sub> HCl <sub>3</sub>	C <sub>2</sub> Cl <sub>4</sub>
PC I (spills)							
13 cm	0.215 (0.913)	0.094	0.205	0.254	0.080	0.288	0.124
34	0.313	0.107	0.253	0.344	0.104	0.354	0.250
55	0.612	0.327	0.335	0.497	0.146	0.404	-
75	0.824	0.447	0.534	-	0.154	-	-
95	0.818	0.442	-	-	-	-	-
116	1.257	0.515	-	-	-	-	-
Average							
mg/g	0.790	0.368	0.332	0.365	0.121	0.349	0.187
μmol/g	6.61	2.24	1.59	1.44	0.79	2.65	1.13
PC II (control)							
11 cm	(0.450)	-	-	-	-	-	-
32	0.252	-	-	-	-	-	-
52	0.599	-	-	-	-	-	-
72	0.853	-	-	-	-	-	-
93	0.829	-	-	-	-	-	-
113	0.864	-	-	-	-	-	-
Average							
mg/g	0.641	-	-	-	-	-	-
μmol/g	5.37	-	-	-	-	-	-
PC III (control, dechlorination)							
15 cm	(0.514)	-	-	-	-	-	-
35	0.418	-	-	-	-	-	-
55	0.520	-	-	-	-	-	-
76	0.547	-	-	-	-	-	-
96	0.615	-	-	-	-	-	-
116	0.721	-	-	-	-	-	-
Average							
mg/g	0.556	-	-	-	-	-	-
μmol/g	4.66	-	-	-	-	-	-

## Mass Balances and Correction Factors for Adsorbed Halogenated Organics

Most often, mass balances are calculated using flow data and concentrations in influent and effluent samples to determine the cumulative mass adsorbed as a function of the cumulative mass input. This information provides another measure of pilot column performance: the mass adsorbed increases steadily and equals the mass input until breakthrough begins; then the mass adsorbed levels off to a limiting value, which is the pilot column's total capacity. If there is desorption after breakthrough or after a spill, the cumulative mass adsorbed goes through a maximum and decreases.

Cumulative mass inputs are given in Table 3.7 for organic contaminants in the simulated spills to pilot column I. Values were calculated as a function of time  $t_j$  from:

$$\text{Cumulative Mass Input } (t_j) = \sum_i \text{Influent } (t_j) * \text{Volume } (t_j) \quad (3.5)$$

Influent concentrations were determined for samples collected daily from the top of pilot column I during each simulated spill (average values given in Table 3.2). Corresponding volumes of water input to pilot column I were read daily from an accumulator and cross-checked by a flowmeter (average values given in Table 2.2). As expected, the mass input of chloroform is greater for the spill column (I) than for either of the controls (II, III). Except for chloroform and dibromochloromethane, mass inputs for individual compounds have the same relative order as average influent concentrations.

It was intended to cross-check mass inputs based on analysis of influent samples, by analysis of water samples collected directly from the reservoirs and by measuring the volume of water displaced from the reservoirs each day. Water from the reservoirs was sampled from the transfer lines to the pilot columns. Concentrations of volatile organics in these samples were a factor of ten lower than expected, indicating that the water being collected was diluted by backflow from the pilot column during sampling, and was not only from the reservoir. In subsequent experiments, samples were collected directly from the reservoirs under positive pressure, rather than from the transfer lines: also the reservoirs were momentarily taken off-line, to prevent backflow from the pilot columns (Alben et al. 1995).

**Table 3.7**

Cumulative mass inputs (g) from successive chemical spills to pilot column I

	Spill 1 g	Spill 2 g	Spill 3 g	Spill 4 g
Days	48 - 55	92 - 100	137 - 142	180 - 184
<i>Pilot column I (spills)</i>				
CHCl <sub>3</sub>	1.11	4.89	9.49	13.16
CHBrCl <sub>2</sub>	0.00	1.89	3.21	4.18
CHBr <sub>2</sub> Cl	0.61	1.98	5.47	7.94
CHBr <sub>3</sub>	0.28	2.72	4.89	6.21
CCl <sub>4</sub>	0.13	0.99	1.60	2.15
C <sub>2</sub> HCl <sub>3</sub>	0.14	1.11	2.01	2.73
C <sub>2</sub> Cl <sub>4</sub>	0.00	0.54	0.82	1.00
<i>Pilot column II (control)</i>				
CHCl <sub>3</sub>	0.67	1.37	2.80	4.38
<i>Pilot column III (dechlorination)</i>				
CHCl <sub>3</sub>	0.68	1.13	2.70	4.24

Figures 3.22 through 3.24 show the cumulative mass adsorbed for the compounds of interest as a function of their cumulative mass inputs. Since both water and GAC samples were analyzed for this project, the cumulative mass adsorbed was calculated using both data sets as shown by equations 3.6 and 3.7, respectively.

$$\text{Cumulative Mass Adsorbed from Water (t}_j\text{)} = \sum_i (\text{Influent (t}_j\text{)} - \text{Effluent (t}_j\text{)}) * \text{Volume (t}_j\text{)} \quad (3.6)$$

$$\text{Cumulative Mass Adsorbed on GAC(t}_j\text{)} = \sum_j \text{Conc. on GAC(t}_j\text{,z}_j\text{)} * \text{Amount of GAC(z}_j\text{)} \quad (3.7)$$

Differences should be noted between results obtained from the water and GAC samples. If the water data are used (Equation 3.6), the cumulative mass adsorbed is based on the difference between influent and effluent concentrations, summed for successive days (t<sub>j</sub>) through the entire period of pilot column operation. In this case, fluctuations in concentrations have a small impact

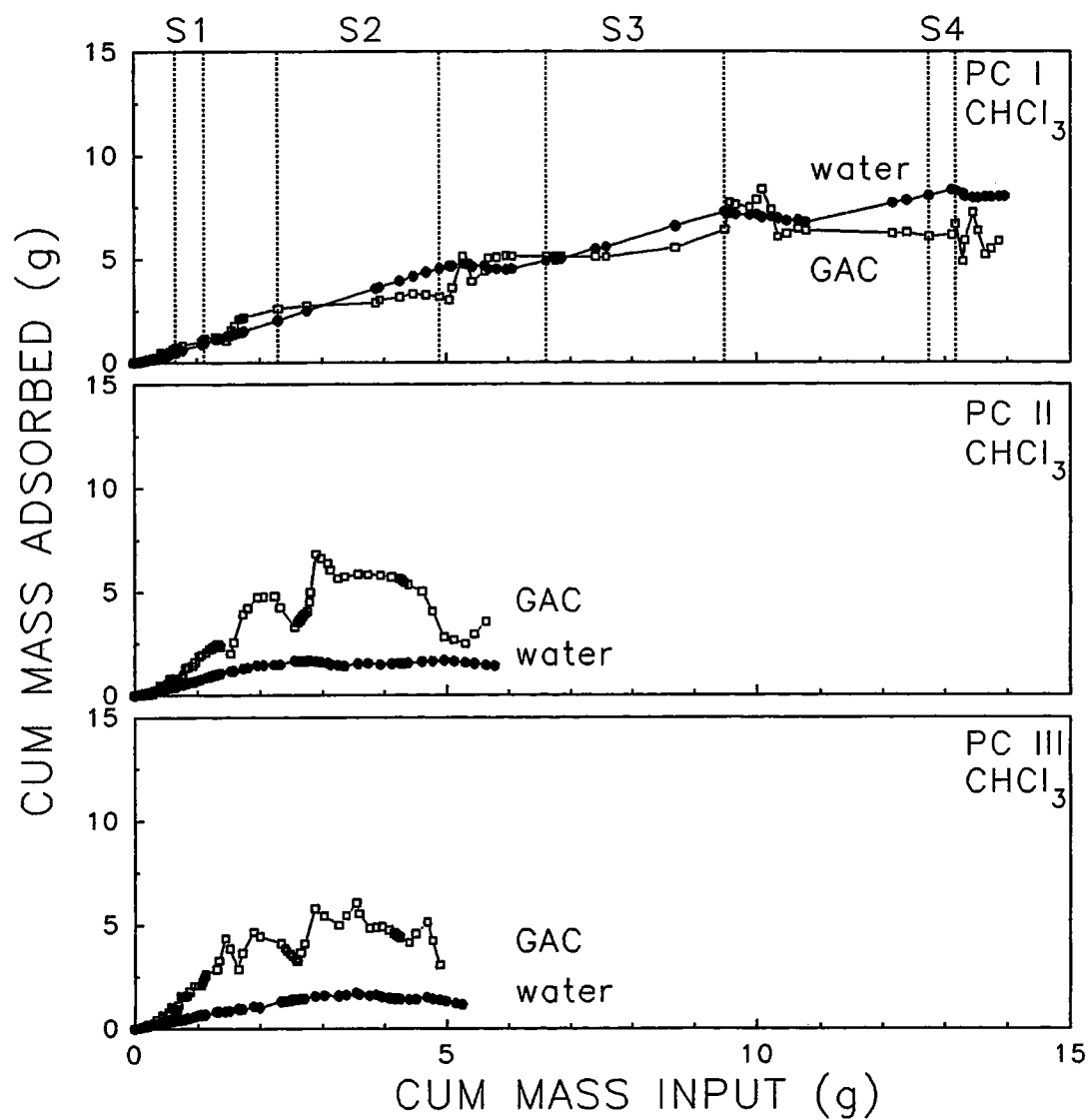


Figure 3.22 Cumulative mass of chloroform adsorbed on pilot columns I, II, and III, as a function of mass inputs: simulated spills to pilot column I are designated S1, S2, S3, and S4.

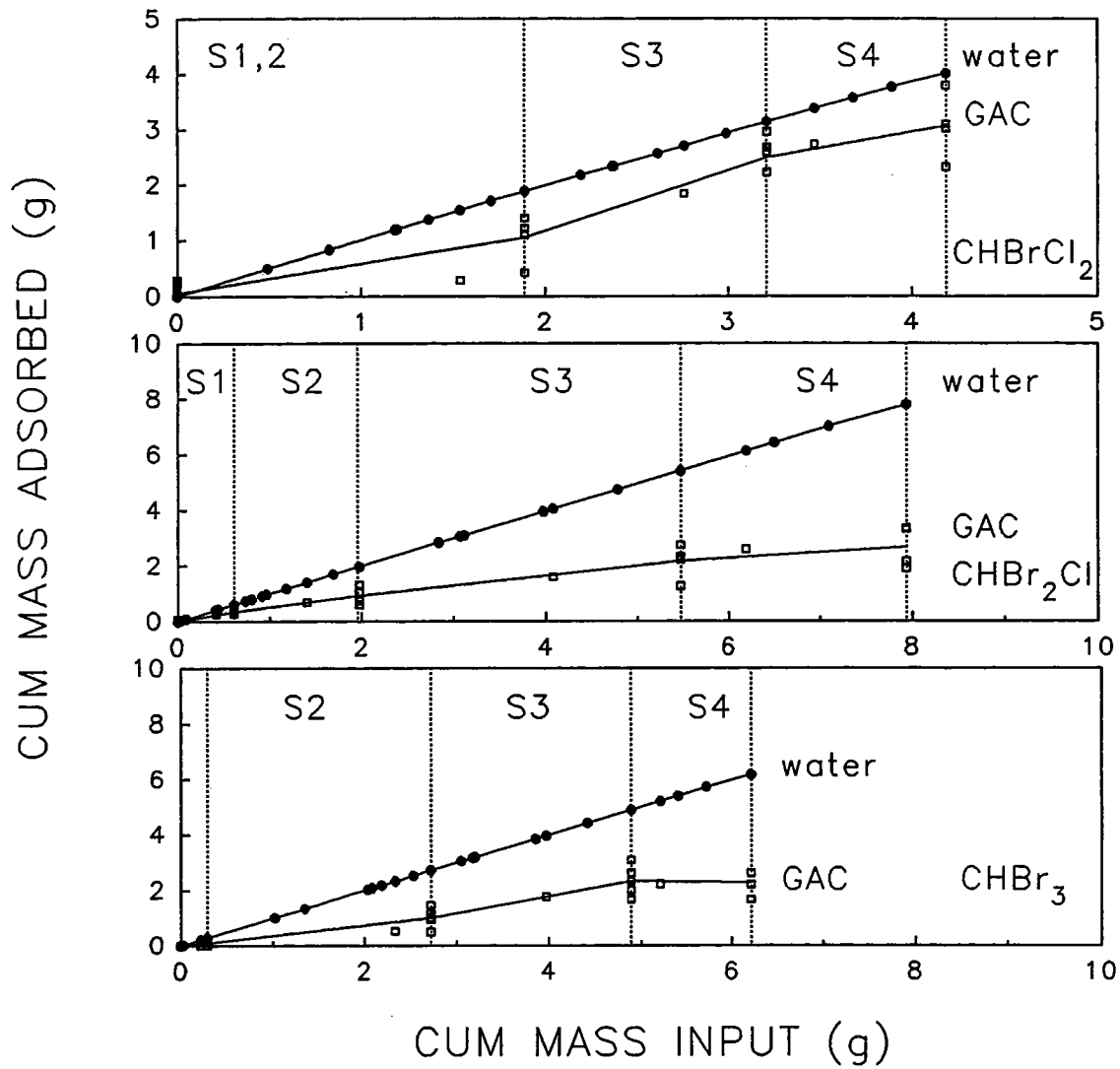


Figure 3.23 Cumulative mass of bromodichloromethane, chlorodibromomethane, and bromoform adsorbed on pilot column I, as a function of mass inputs: simulated spills to pilot column I are designated S1, S2, S3, and S4.

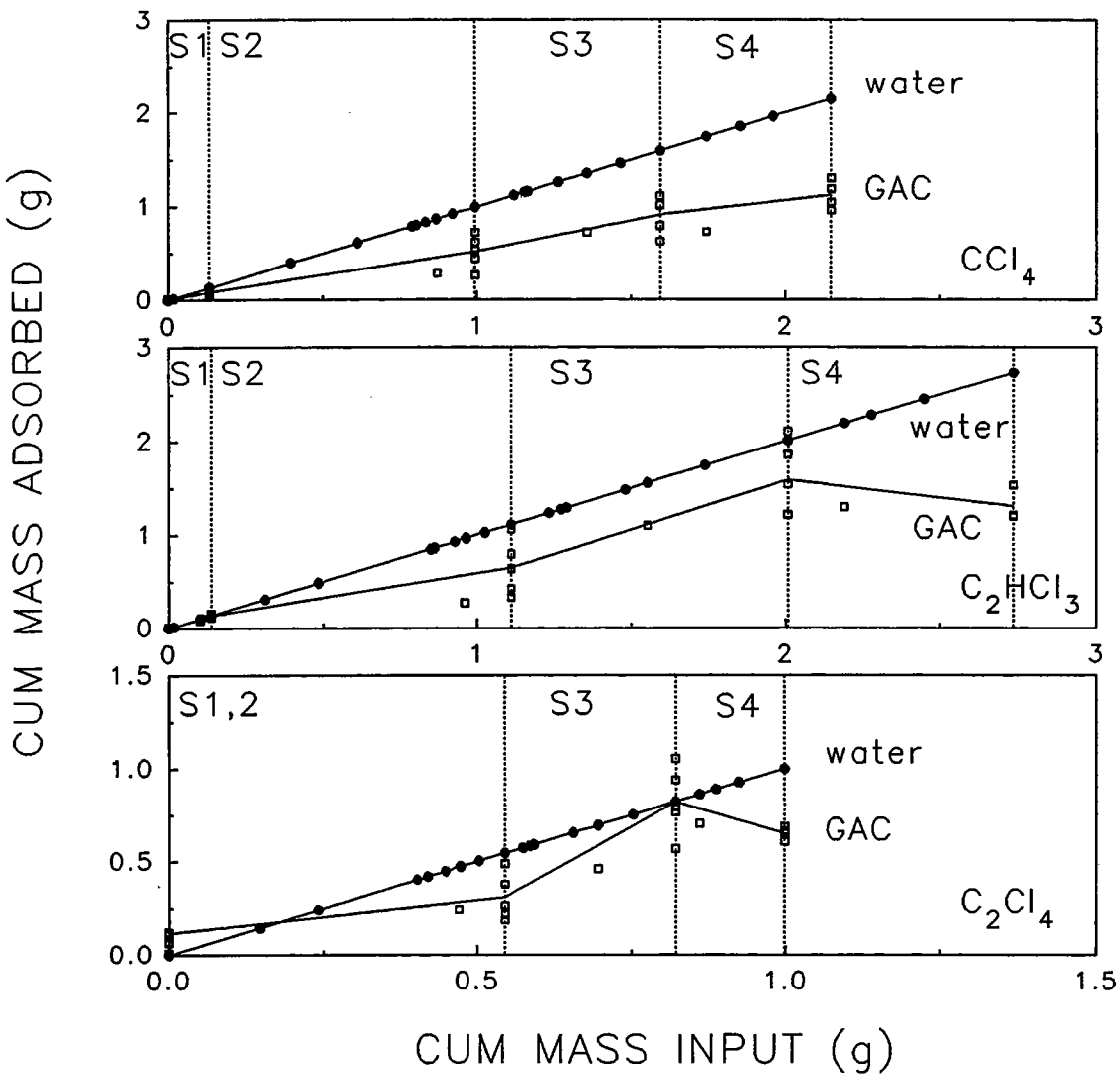


Figure 3.24 Cumulative mass of carbon tetrachloride, trichloroethylene, and tetrachloroethylene adsorbed on pilot column I, as a function of mass inputs: simulated spills to pilot column I are designated S1, S2, S3, and S4.

on the total: the cumulative mass adsorbed increases smoothly with relatively little noise, but errors propagate, such as differences in the recovery of contaminants in influent and effluent samples. If the GAC data are used (Equation 3.7), the cumulative mass adsorbed is based on a sum of amounts found at successive bed depths ( $z_i$ ), but values are not added for successive days. Since the GAC data give an instantaneous measurement of the total mass adsorbed, there is noise in values at successive points in time.

Results for chloroform in Figure 3.22 are easiest to understand after looking at results for the other compounds. For both the brominated trihalomethanes (Figure 3.23), as well as the chlorinated synthetic organics (Figure 3.24), values for the cumulative mass adsorbed based on the water data exceed values obtained using the GAC data. In the case of the water data, values for the cumulative mass adsorbed are identical to the cumulative mass input: there was no breakthrough of the brominated trihalomethanes in the first two spills, and less than 10 percent in the last two spills. Therefore, these compounds were almost completely adsorbed during the entire experiment. The relatively high values based on the water data suggest that influent concentrations may be overestimated for the spill constituents: this is possible, because influent samples were collected when flows from the reservoirs were optimum; generally, flows from the reservoirs decreased and had to be reset each day. By comparison, results based on the GAC data are considered correct, rather than low: in a previous study, quantitative recoveries were found for solvent extraction of the trihalomethanes adsorbed on GAC samples (Alben and Kaczmarczyk 1986).

Table 3.8 gives the ratio of mass balances based on the GAC data to mass balances based on the water data. Assuming the GAC data are accurate, these ratios can be used as correction factors, to calculate actual influent concentrations during the spills from values that were measured but which are thought to be biased high by the time of sampling. These correction factors permit a recalculation of concentrations that are the basis for comparisons in Equations 3.2 and 3.3, but the only effect is to reverse the order of trichloroethylene and bromoform in Equation 3.2.

For chloroform adsorbed on the control columns (II, III), generally more chloroform was found adsorbed on the GAC samples than was accounted for by the water samples, contrary to results for all other compounds. In subsequent pilot column experiments at Waterford, similar inconsistencies have been found, using data for water and GAC samples to calculate the amount of background chloroform that is adsorbed (Alben et al. 1995).

To explain the unusual results for chloroform it is necessary to consider each of the terms in Equation 3.6. Chloroform is the only compound in this project for which mass balances on water samples involve taking differences between influent and effluent concentrations. Influent samples were nearly always positive for chloroform, resulting in a continuous mass input, whereas influent concentrations of the other compounds were only positive during the spills. For the control pilot columns (II, III), effluent concentrations only exceeded the quantitation threshold after 118

**Table 3.8**

Mass balance ratios and corrected concentrations for the volatile halogenated contaminants in Equations 3.2 and 3.3

	CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	CCl <sub>4</sub>	C <sub>2</sub> HCl <sub>3</sub>	C <sub>2</sub> Cl <sub>4</sub>	Avg
<i>Mass balance ratio:</i>								
<u>GAC</u> water	0.59 (0.35)	0.69	0.44	0.40	0.56	0.71	0.74	0.59
<i>Corrected influent</i>								
μg/L	185 (110)	106	148	87.6	42.3	75.0	25.1	-
μmol/L	1.55 (0.92)	0.65	0.71	0.35	0.28	0.57	0.15	-
<i>Corrected Freundlich capacities</i>								
mg/g	3.02 (2.14)	5.11	14.0	18.2	3.58	16.0	21.4	-
μmol/g	25.3 (17.9)	31.2	67.2	72.0	23.3	122.	129.	-

days. Finally, no correction factor was applied to the influent concentrations for incomplete recovery, although previous work indicated a 77 percent recovery of chloroform in solvent extracts of water samples (Alben and Kaczmarczyk 1986). If influent concentrations are underestimated, and effluent concentrations before breakthrough are overestimated, the net effect would be to continually decrease the value obtained for the cumulative mass adsorbed. For the control pilot columns (II, III), it is believed that mass balance calculations using data for water samples underestimate the amount of chloroform that is adsorbed.

For chloroform adsorbed on the spill column (I), however, there is surprisingly good agreement between values for the cumulative mass adsorbed obtained using the water and GAC data. In the case of the spill column (I), results for the other compounds suggest that influent concentrations during the spills are overestimated. The net effect would be to increase the value obtained for the cumulative mass adsorbed: somewhat fortuitously, the overestimate of chloroform concentrations during the spills is just enough to put mass balances for the water data in good agreement with the GAC data. Table 3.8 gives two possible correction factors for chloroform: one factor, 0.59, is the average of correction factors for the other halogenated compounds; the other factor, 0.35, is derived to maintain consistency between CHCl<sub>3</sub> adsorption in the spill column (I) and the control columns (II, III). In either case, if influent concentrations during the



spills are corrected as in Table 3.8, then a mass balance calculation indicates less chloroform is adsorbed from water than is found on the GAC from pilot column I, similar to results discussed above for the control columns.

The corrected concentrations in Table 3.8 should be included in further evaluations of results for this project, for example, those using mechanistic models to interpret competitive adsorption.



## CHAPTER 4

### VOLATILE AROMATIC ORGANICS: RESULTS AND DISCUSSION

#### CONVENTIONAL PHYSICAL-CHEMICAL TREATMENT AND BACKGROUND CONCENTRATIONS OF TARGET COMPOUNDS

Background concentrations of the volatile aromatic organics were determined at a number of sites at Waterford and Latham Water Works, to assist with interpretation of results for the GAC pilot columns. Purge-and-trap gas chromatography with photoionization detection was used to analyze for volatile aromatic organics, rather than solvent-extraction gas chromatography with electron-capture detection which was used for the volatile halogenated organics (Appendix C). With the purge-and-trap instrumentation, conditions could be optimized to screen for contaminants at very low background levels, between 0.1 and 1.0  $\mu\text{g/L}$ . During the simulated spills, conditions were adjusted to analyze influent and effluent samples from pilot column I in a higher concentration range, between 2 and 80  $\mu\text{g/L}$ . Maximum contaminant levels for the targeted aromatic compounds in drinking water are also in a relatively high concentration range, between 5 and 10,000  $\mu\text{g/L}$  in drinking water (Appendix A). It can be anticipated that the discussion of monitoring at background sites will focus on the statistical significance of sub- $\mu\text{g/L}$  concentrations. At the time of this project, the ability to monitor or control organic contaminants at sub- $\mu\text{g/L}$  levels was still an emerging technology, being developed for very hydrophobic organic compounds. Results in this section for background levels of the volatile aromatic contaminants provide an introduction to methods of data interpretation that are also applied to the semivolatile organic contaminants discussed in the next chapter.

Background levels of the volatile aromatic organics are summarized in Table 4.1, for results shown in Figures 4.1 through 4.6. In summarizing the data, it is of interest to look for trends among the sites and among the compounds. In both cases, rankings can be made based on the frequencies of occurrence, contaminant concentrations, and standard deviations. With regard to the different sites, it is of interest to know if background contaminant levels decrease through the successive stages of treatment. For the different compounds, it is of interest to know which are the most abundant as background contaminants. Since the effect of GAC adsorption on sub- $\mu\text{g/L}$  contaminant levels has not been extensively investigated, concentrations in influent and effluent samples from the control pilot columns II and III are compared in Table 4.2.

Table 4.3 gives the overall ranking of the sites, obtained by averaging over the ranking of sites for the six volatile aromatic compounds. In raw water samples (A), the contaminants had an unexpectedly low frequency of occurrence. Relative to untreated water at Waterford, contaminants were found with increased frequency after successive stages of treatment: after coagulation-

**Table 4.1**

Concentrations of volatile aromatic organics during various stages of conventional treatment: average values (avg), standard deviation (st dev), frequency of occurrence (freq)\*, and total number of samples (N<sub>PID</sub>)

			Waterford					Latham	
			A	B	C	D1	D3	F	G
			raw	coag.- flocc.- sed.	filtra- tion	influent pilot II	influent pilot III	raw	finished
benzene	avg	μg/L	0.064	0.094	0.104	0.068	0.054	0.285	0.277
	st dev	μg/L	± 0.114	± 0.112	± 0.084	± 0.053	± 0.033	± 0.508	± 0.447
toluene	avg	μg/L	0.077	0.154	0.174	0.137	0.103	0.107	0.515
	st dev	μg/L	± 0.084	± 0.181	± 0.207	± 0.114	± 0.108	± 0.137	± 0.397
ethyl- benzene	avg	μg/L	0.074	0.084	0.084	0.091	0.080	0.125	0.130
	st dev	μg/L	± 0.066	± 0.050	± 0.050	± 0.053	± 0.035	± 0.049	± 0.216
p-xylene	avg	μg/L	0.095	0.123	0.131	0.127	0.116	0.094	0.248
	st dev	μg/L	± 0.097	± 0.116	± 0.113	± 0.119	± 0.057	± 0.043	± 0.669
o-xylene	avg	μg/L	0.063	0.076	0.087	0.084	0.086	0.078	0.167
	st dev	μg/L	± 0.037	± 0.046	± 0.065	± 0.042	± 0.063	± 0.041	± 0.259
chloro- benzene	avg	μg/L	0.053	0.066	0.075	0.067	0.063	0.095	0.087
	st dev	μg/L	± 0.042	± 0.039	± 0.055	± 0.039	± 0.033	± 0.123	± 0.076
benzene	freq	%	56	89	78	86	72	81	96
toluene	freq	%	73	100	100	88	89	87	96
ethyl- benzene-	freq	%	16	33	31	36	26	6	55
p-xylene	freq	%	36	67	70	78	48	37	88
o-xylene	freq	%	33	44	50	50	37	29	75
chloro- benzene	freq	%	31	75	81	69	56	27	98
N <sub>PID</sub>	total	-	55	55	54	58	54	48	51

\* freq = 100 \* (number positive)/(N<sub>PID</sub> total)

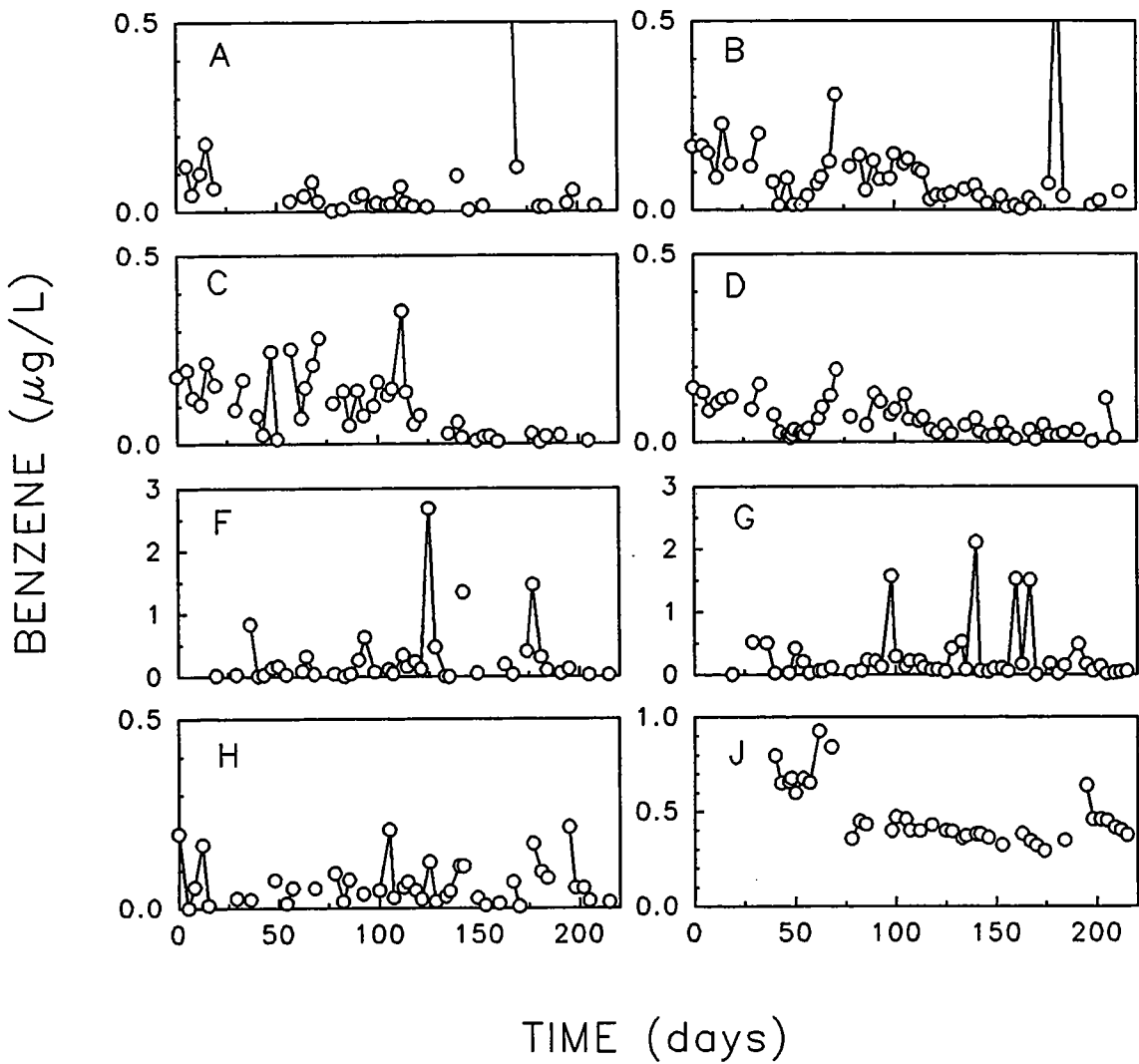


Figure 4.1 Concentrations of benzene at sites used for background monitoring: A, Waterford raw water intake; B, Waterford coagulation, flocculation, sedimentation; C, Waterford, post filtration; D, Waterford GAC influent, pilot columns II and III average; F, Latham raw water intake; G, Latham finished water; H, lab blank; J, spiked lab water.

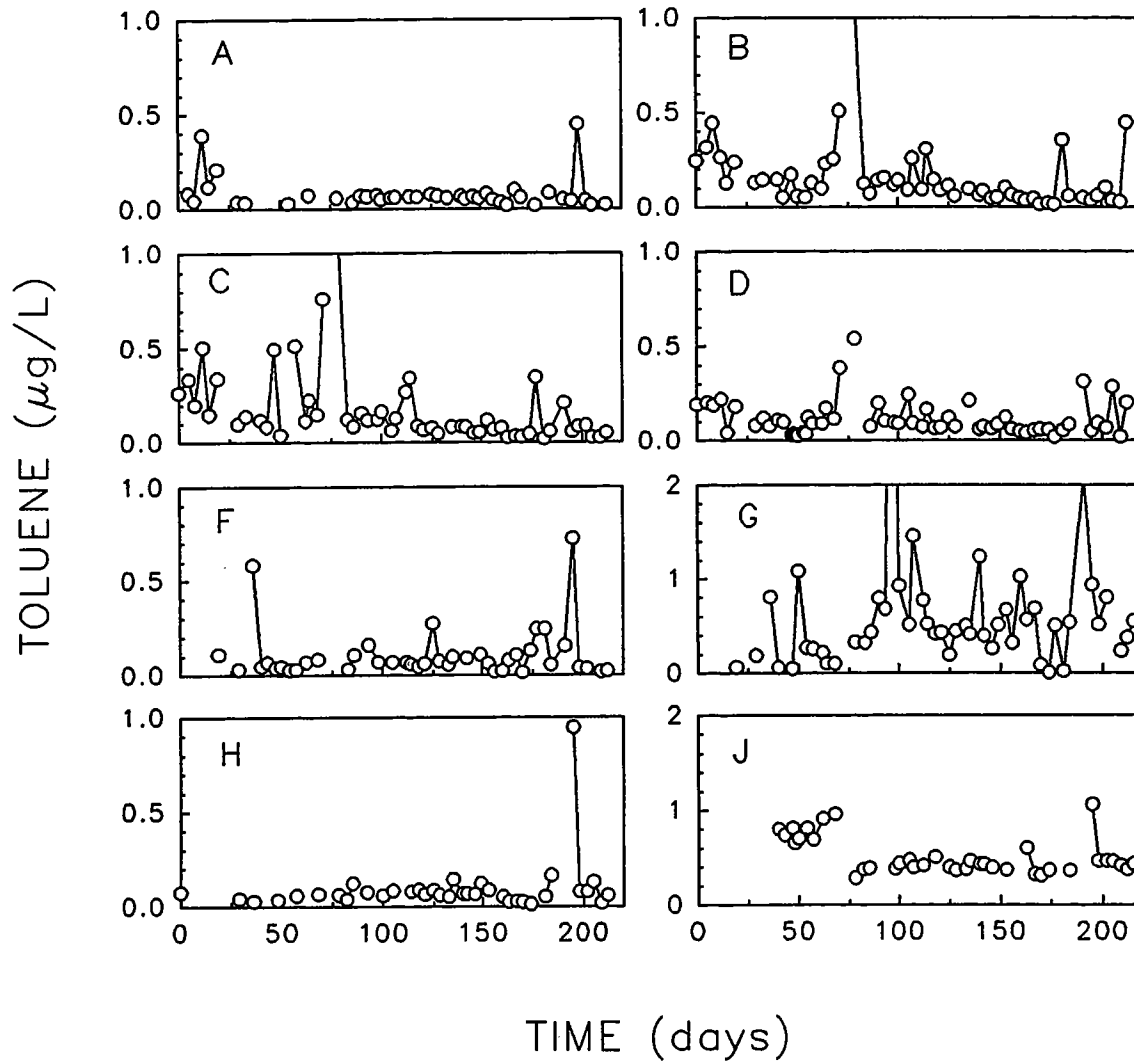


Figure 4.2 Concentrations of toluene at sites used for background monitoring: A, Waterford raw water intake; B, Waterford coagulation, flocculation, sedimentation; C, Waterford, post filtration; D, Waterford GAC influent, pilot columns II and III average; F, Latham raw water intake; G, Latham finished water; H, lab blank; J, spiked lab water.

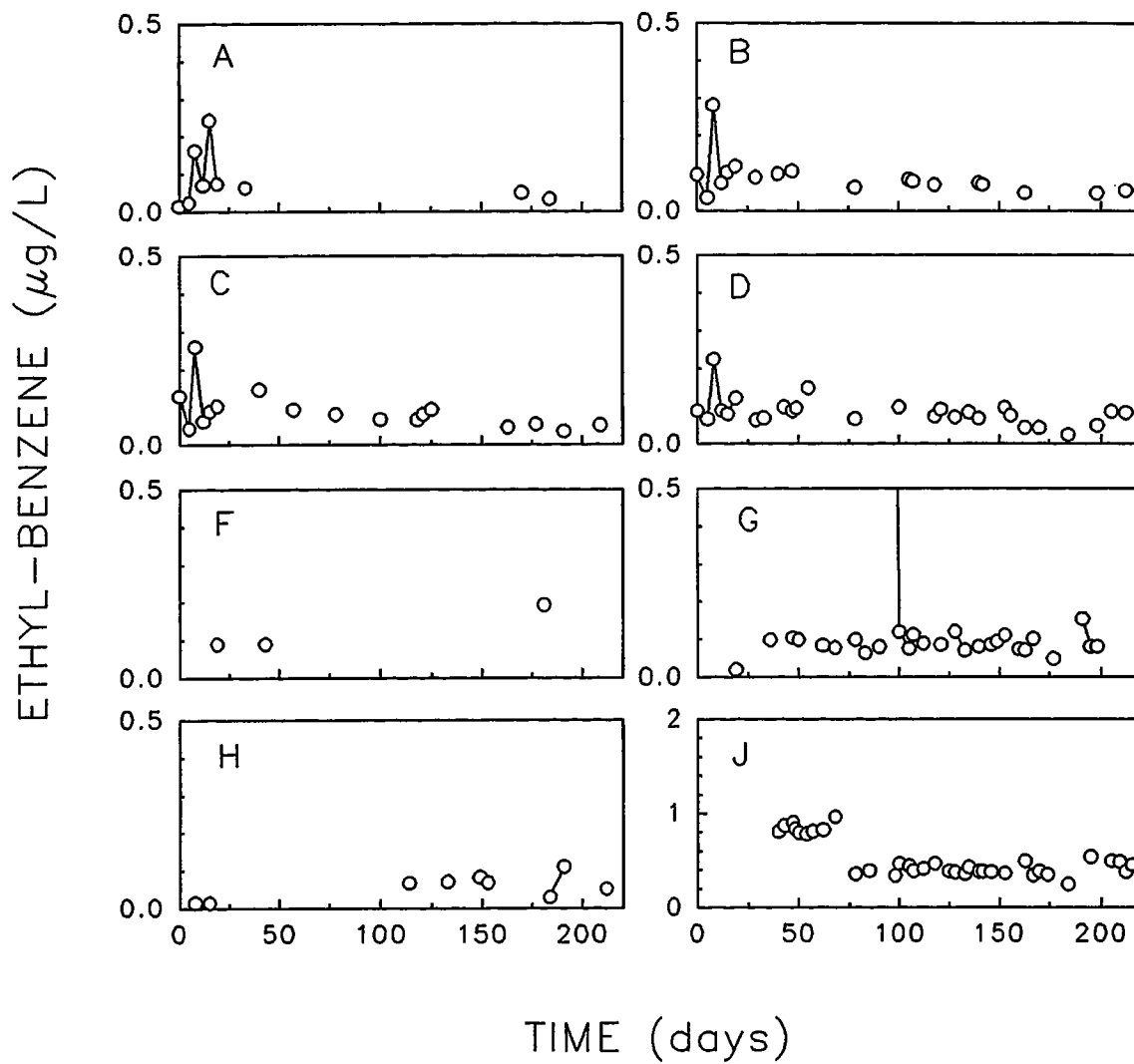


Figure 4.3 Concentrations of ethylbenzene at sites used for background monitoring: A, Waterford raw water intake; B, Waterford coagulation, flocculation, sedimentation; C, Waterford, post filtration; D, Waterford GAC influent, pilot columns II and III average; F, Latham raw water intake; G, Latham finished water; H, lab blank; J, spiked lab water.

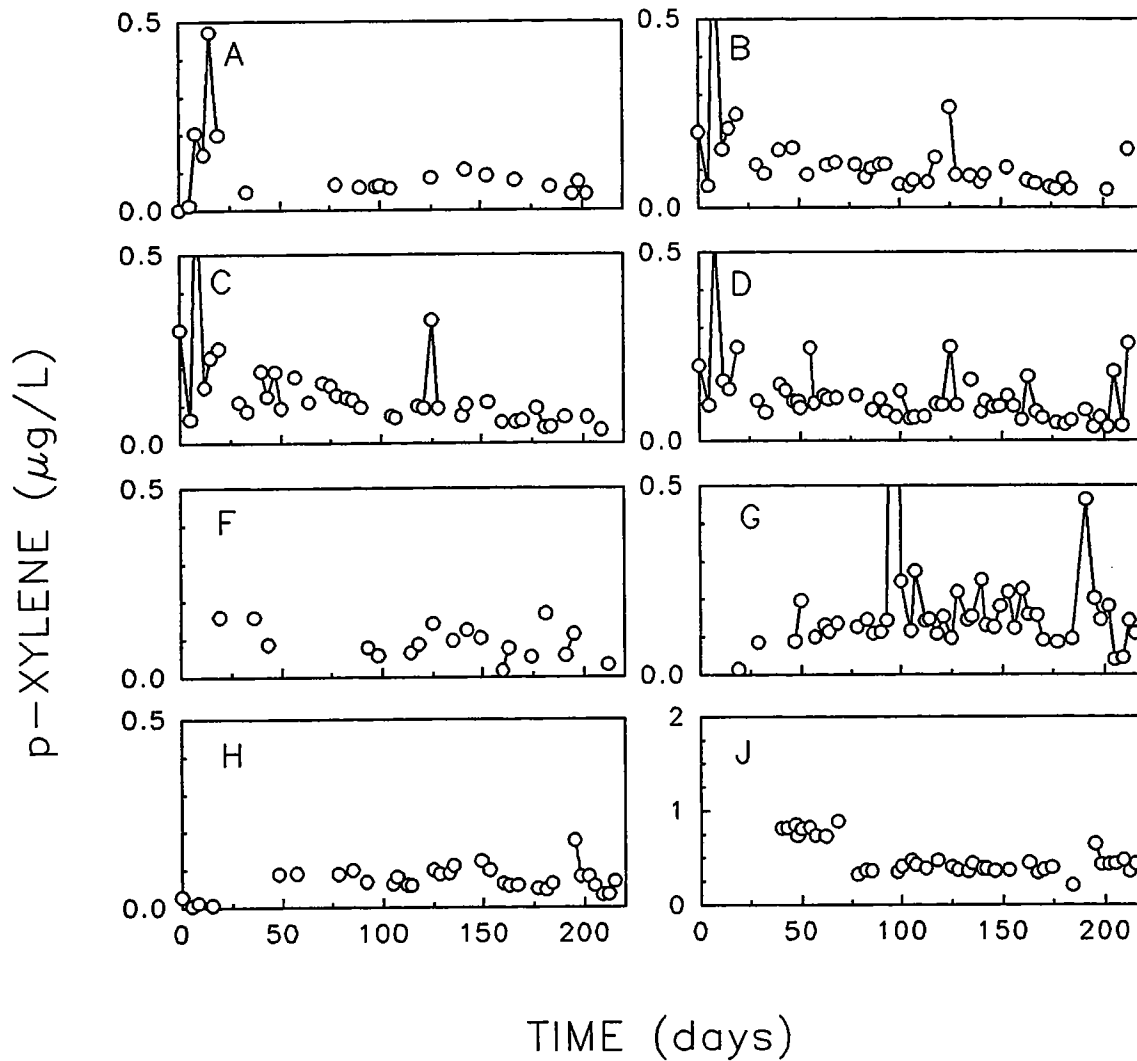


Figure 4.4 Concentrations of p-xylene at sites used for background monitoring: A, Waterford raw water intake; B, Waterford coagulation, flocculation, sedimentation; C, Waterford, post filtration; D, Waterford GAC influent, pilot columns II and III average; F, Latham raw water intake; G, Latham finished water; H, lab blank; J, spiked lab water.



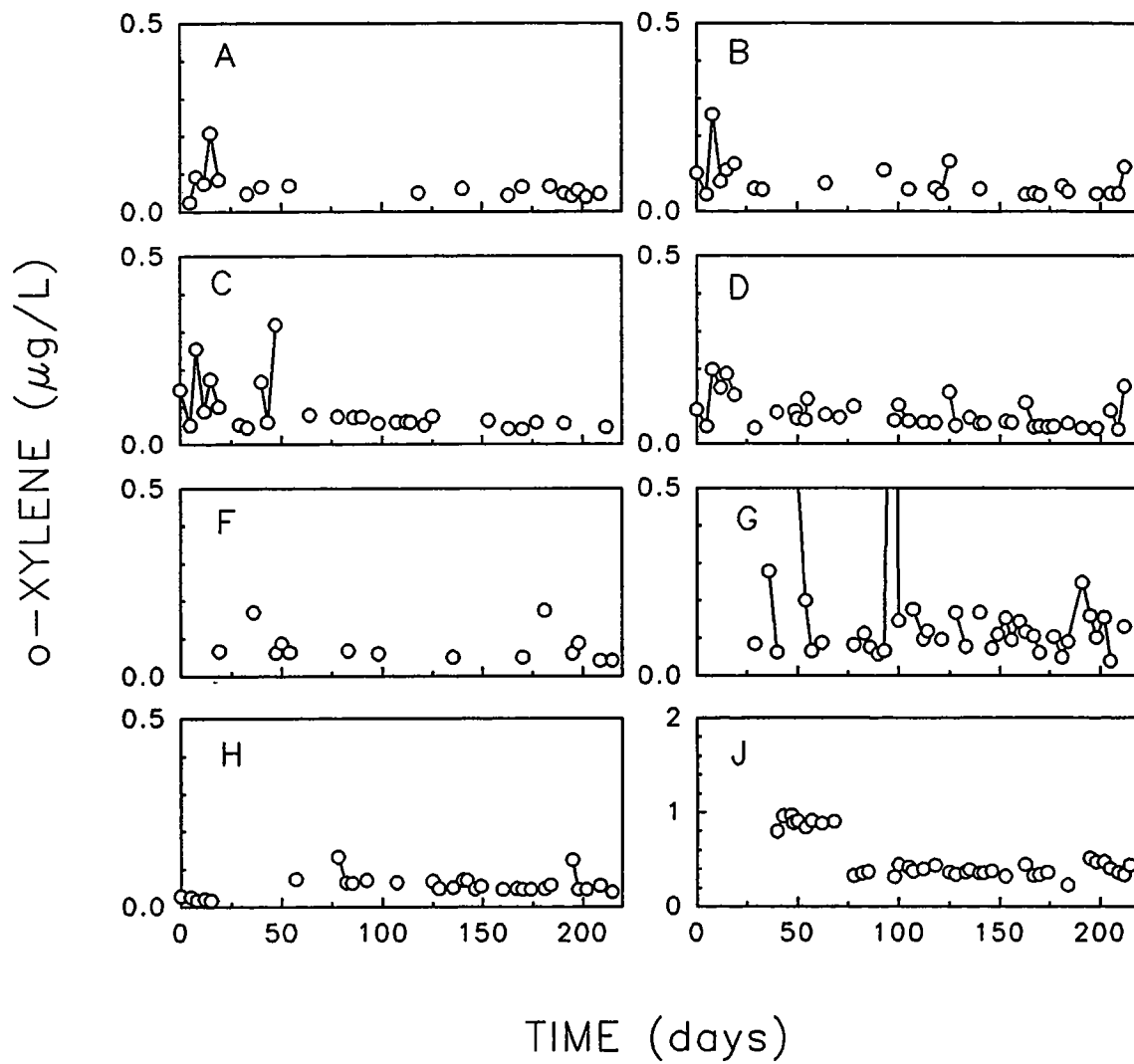


Figure 4.5 Concentrations of o-xylene at sites used for background monitoring: A, Waterford raw water intake; B, Waterford coagulation, flocculation, sedimentation; C, Waterford, post filtration; D, Waterford GAC influent, pilot columns II and III average; F, Latham raw water intake; G, Latham finished water; H, lab blank; J, spiked lab water.

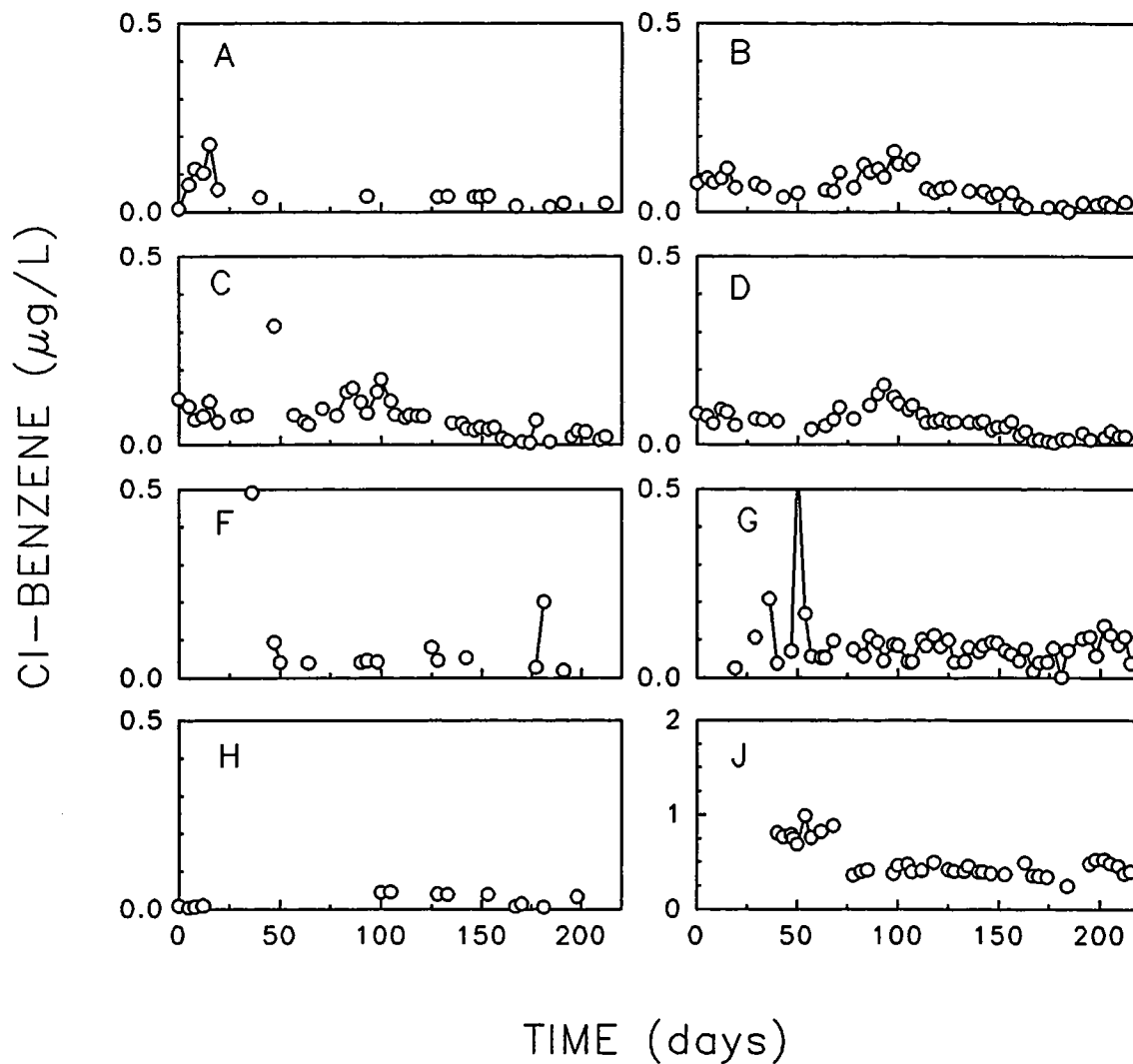


Figure 4.6 Concentrations of chlorobenzene at sites used for background monitoring: A, Waterford raw water intake; B, Waterford coagulation, flocculation, sedimentation; C, Waterford, post filtration; D, Waterford GAC influent, pilot columns II and III average; F, Latham raw water intake; G, Latham finished water; H, lab blank; J, spiked lab water.

**Table 4.2**

Concentrations ( $\mu\text{g/L}$ ) of volatile aromatic organics before and after GAC treatment, for control pilot columns II and III: average values (avg), standard deviation (st dev), frequency of occurrence (freq)\*, and total number of samples ( $N_{\text{PID}}$ )

			<u>pilot column II</u>		<u>pilot column III</u>	
			<u>D1</u>	<u>E1</u>	<u>D3</u>	<u>E3</u>
			<b>influent</b>	<b>effluent</b>	<b>influent</b>	<b>effluent</b>
benzene	avg	$\mu\text{g/L}$	0.068	0.044	0.054	0.054
	st dev	$\mu\text{g/L}$	$\pm 0.053$	$\pm 0.075$	$\pm 0.033$	$\pm 0.088$
toluene	avg	$\mu\text{g/L}$	0.137	0.064	0.103	0.059
	st dev	$\mu\text{g/L}$	$\pm 0.114$	$\pm 0.078$	$\pm 0.108$	$\pm 0.091$
ethylbenzene	avg	$\mu\text{g/L}$	0.091	0.055	0.080	0.052
	st dev	$\mu\text{g/L}$	$\pm 0.053$	$\pm 0.030$	$\pm 0.035$	$\pm 0.023$
p-xylene	avg	$\mu\text{g/L}$	0.127	0.066	0.116	0.060
	st dev	$\mu\text{g/L}$	$\pm 0.119$	$\pm 0.038$	$\pm 0.057$	$\pm 0.036$
o-xylene	avg	$\mu\text{g/L}$	0.084	0.057	0.086	0.055
	st dev	$\mu\text{g/L}$	$\pm 0.042$	$\pm 0.019$	$\pm 0.063$	$\pm 0.020$
chlorobenzene	avg	$\mu\text{g/L}$	0.067	0.030	0.063	0.038
	st dev	$\mu\text{g/L}$	$\pm 0.039$	$\pm 0.020$	$\pm 0.033$	$\pm 0.034$
benzene	freq	%	86	56	72	46
toluene	freq	%	88	75	89	75
ethylbenzene	freq	%	36	19	26	15
p-xylene	freq	%	78	58	48	46
o-xylene	freq	%	50	26	37	40
chlorobenzene	freq	%	69	19	56	17
$N_{\text{PID}}$	total	-	58	57	54	52

\*  $\text{freq} = 100 * (\text{number positive}) / (N_{\text{PID}} \text{ total})$

**Table 4.3**

Ranking of sites based on results for background levels of contaminants in Tables 4.1 and 4.2: scale from 1 to 10 indicates the site with the lowest to highest relative contaminant level, respectively; sites at Waterford are ranked independently from sites at Latham

	Waterford						Latham		
	A raw	B coag.- flocc.- sed.	C filtra- tion	D1 influent pilot II	D3 influent pilot III	E1 effluent pilot II	E3 effluent pilot III	F raw	G finished
relative frequency of occur- rence	<u>2.6</u>	$\overline{7.8}$	$\overline{7.8}$	$\overline{7.8}$	5.0	<u>3.3</u>	<u>2.6</u>	<u>1.0</u>	$\overline{10.0}$
relative concen- tration	4.6	7.4	$\overline{9.6}$	7.8	6.0	<u>2.4</u>	<u>1.8</u>	<u>4.3</u>	$\overline{7.1}$
relative standard deviation	6.4	7.4	$\overline{8.1}$	6.4	4.6	<u>2.4</u>	<u>3.3</u>	<u>4.3</u>	$\overline{7.1}$

flocculation-sedimentation (B), just before filtration (C), and in water pumped from the clearwell as influent to the pilot columns (D1). The raw water at Latham was also distinguished by a lower frequency of occurrence for volatile aromatic contaminants than the finished water. Similarly, the raw water at Waterford and Latham is differentiated from the finished water by low contaminant concentrations and standard deviations. These relationships suggest that the volatile aromatic compounds may be purged less efficiently from raw water samples than from treated water samples, although the source of analytical interference in raw water samples is unknown. It is also possible that the background of volatile aromatic compounds increases in the treatment plant because these compounds are contained in products used to lubricate or seal pumps and valves. Both possibilities need to be investigated before the effect of conventional treatment processes on background volatile aromatic compounds at sub- $\mu\text{g/L}$  levels can be resolved.

Another tendency is for the aromatic contaminants to be found less often in the influent to pilot column III (D3) than in the influent to pilot column II (D1). Since both pilot columns received water from the clearwell, water quality is expected to be the same. At present, it is not clear if volatile aromatic contaminants were being removed in the long path to dechlorinate the influent of pilot column III or during injection of sulfur dioxide at low pH (5.5).

A positive result is that the frequency of occurrence and contaminant concentrations are generally lowest for effluent samples from the pilot columns (Tables 4.2 and 4.3). This implies that, even at sub- $\mu\text{g/L}$  levels, the volatile aromatic compounds are adsorbed by granular activated carbon.

A concern underlying this discussion is whether it is analytically valid to rank the sites according to the frequency and magnitude of background contamination by volatile aromatic compounds. Table 4.4 compares average concentrations after conventional treatment and after GAC adsorption to concentrations in laboratory blanks and to method detection limits. In general, average contaminant concentrations in samples representing conventional treatment (B, C, D1, D3, G) are greater than average concentrations in laboratory blanks, as well as method detection limits determined for analysis of the volatile aromatic compounds at sub- $\mu\text{g/L}$  levels. Only effluent

**Table 4.4**

Concentrations of volatile aromatic organics in water after conventional treatment (average, avg; standard deviation, st dev), compared to GAC-processed Waterford water, GAC-processed laboratory water, and method detection limits (MDL)

		<u>Conventional treatment</u>		<u>GAC</u>	<u>Lab blank</u>	<u>MDL</u>	
		<u>Waterford</u>	<u>Latham</u>	<u>pilot</u>	<u>GAC-</u>		
		<u>coag.-flocc.-</u>	<u>finished</u>	<u>columns</u>	<u>processed</u>		
		<u>sed.-filt.</u>	<u>water</u>	<u>II, III</u>	<u>lab water</u>		
		<u>B,C,D1,D3</u>	<u>G</u>	<u>E1,E3</u>			
benzene	avg	$\mu\text{g/L}$	0.080	0.277	0.048	0.064	0.03
	st dev	$\mu\text{g/L}$	$\pm 0.081$	$\pm 0.447$	$\pm 0.081$	$\pm 0.056$	
toluene	avg	$\mu\text{g/L}$	0.143	0.515	0.061	0.093	0.03
	st dev	$\mu\text{g/L}$	$\pm 0.162$	$\pm 0.397$	$\pm 0.085$	$\pm 0.146$	
ethylbenzene	avg	$\mu\text{g/L}$	0.088	0.130	0.054	0.057	0.07
	st dev	$\mu\text{g/L}$	$\pm 0.049$	$\pm 0.216$	$\pm 0.027$	$\pm 0.031$	
p-xylene	avg	$\mu\text{g/L}$	0.126	0.248	0.063	0.070	0.04
	st dev	$\mu\text{g/L}$	$\pm 0.108$	$\pm 0.669$	$\pm 0.038$	$\pm 0.035$	
o-xylene	avg	$\mu\text{g/L}$	0.085	0.167	0.055	0.056	0.06
	st dev	$\mu\text{g/L}$	$\pm 0.055$	$\pm 0.259$	$\pm 0.020$	$\pm 0.025$	
chloro-benzene	avg	$\mu\text{g/L}$	0.069	0.087	0.034	0.024	0.03
	st dev	$\mu\text{g/L}$	$\pm 0.043$	$\pm 0.076$	$\pm 0.028$	$\pm 0.017$	

samples (E1, E3) from the GAC pilot columns II and III have contaminant levels as low as the laboratory blanks or method detection limits.

Table 4.5 gives the overall ranking of the compounds, obtained by averaging over the ranking of compounds for all nine sites. Toluene stands out as a compound with a high frequency of occurrence, a high average concentration, and large standard deviation (Tables 4.2, 4.5). Benzene and p xylene also rank as compounds with a relatively high frequency of occurrence, average concentration and standard deviation. At the other extreme, ethylbenzene has a low frequency of occurrence, whereas chlorobenzene is distinguished by very low concentrations with a small standard deviation. o-Xylene is similar to these two compounds.

Analytically, it is somewhat surprising that, for the volatile aromatic contaminants, there is a direct correspondence between the magnitude of average concentrations and the magnitude of standard deviations. When a given compound is analyzed over its quantitation range, generally the relative standard deviation is smallest at mid-range concentrations and largest at the extremes of the quantitation range. At sub- $\mu\text{g/L}$  concentrations, which presumably represent background, the

**Table 4.5**

Ranking of compounds based on results for background levels of contaminants in Tables 4.1 and 4.2: scale from 1 to 10 indicates the compound with the smallest to largest relative value, respectively

	benzene	toluene	ethyl benzene	p-xylene	o-xylene	chloro- benzene
relative frequency of occurrence	7.7	$\overline{9.7}$	<u>1.7</u>	7.8	4.0	4.7
relative $\mu\text{g/L}$ concentration	5.5	$\overline{8.8}$	5.2	8.4	4.8	<u>2.2</u>
relative molar concentration	7.7	$\overline{9.4}$	4.7	7.3	4.3	<u>1.8</u>
relative $\mu\text{g/L}$ standard deviation	7.2	$\overline{8.5}$	4.0	7.2	3.3	<u>3.2</u>
relative molar standard deviation	8.4	$\overline{8.5}$	3.8	6.8	3.5	<u>3.0</u>
relative relative standard deviation	$\overline{8.2}$	7.3	<u>3.7</u>	6.0	<u>3.7</u>	4.7

volatile aromatic compounds should collectively be at the low end of their quantitation range, where variability is large. However, the compounds seem divided between one group which is the most abundant and most variable (toluene, benzene, p-xylene) and a second group which is the least abundant and least variable (chlorobenzene, ethylbenzene, o-xylene). This behavior suggests that environmental factors (patterns of use and disposal; prevailing conditions; fate and transport properties), rather than analytical limitations, control the background concentrations being measured for these volatile aromatic compounds.

In future work, it remains of interest to use more advanced statistical methods to screen for differences among the sites and among the compounds that have been studied at background levels. Factor analysis may be able to provide a more accurate interpretation of trends and patterns of behavior than those deduced from average values and standard deviations. Mathematical methods need to be investigated that can simultaneously analyze all of the results (positives and negatives), for all of the compounds, at all of the sites.

## **GAC PILOT-COLUMN RESULTS**

While the previous section has given a preliminary view of pilot column performance for background contaminant levels, the ability to remove the simulated spills is of equal interest.

### **Contaminant Concentrations During Simulated Spills**

High contaminant concentrations of the spill constituents (benzene, toluene, chlorobenzene, o-xylene) are evident in the GC-PID chromatograms of influent samples collected during the simulated spills to pilot column I (Figure 4.7). By comparison, only background levels of the volatile aromatic organics (benzene, toluene, chlorobenzene, p-xylene) are evident in the GC-PID chromatograms for influent samples to pilot column II, run as a control (Figure 4.8). Average concentrations of the four volatile aromatic compounds added during the simulated spills to pilot column I are given in Table 4.6: clearly influent concentrations during the spills were well above sub- $\mu\text{g/L}$  background levels.

In general, high contaminant concentrations were achieved in the last three simulated spills. As discussed in Chapter 2, contaminant concentrations were low during the first spill, because of solubility problems at the low water temperature ( $7.2\text{ }^{\circ}\text{C}$ ), and because of difficulty maintaining the flow of chemicals from the contaminant reservoirs.

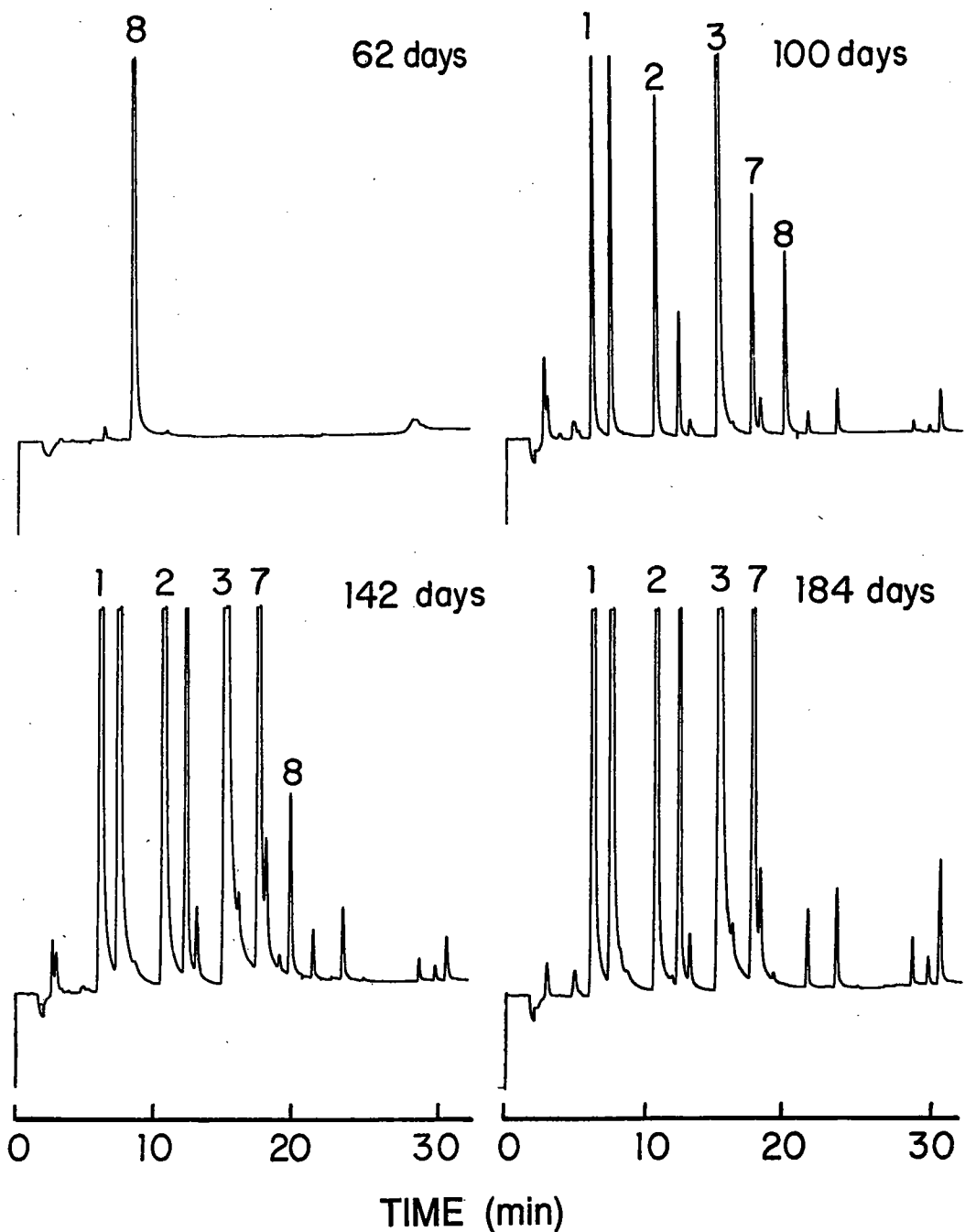


Figure 4.7 Gas chromatogram with photoionization detection of water samples (D2) collected from influent to pilot column I on days 62, 100, 142, and 184, during simulated chemical spills. Peaks are labeled: 1 benzene; 2 toluene; 3 chlorobenzene; 4 ethylbenzene; 5 m-xylene; 6 p-xylene; 7 o-xylene; 8 (internal standard). The internal standard for the day 62 sample was  $\alpha,\alpha,\alpha$ -trifluorotoluene, which elutes at 8.6 min; the internal standard for the day 100, 142, and 184 samples was bromobenzene, which elutes at 19.3 min. Internal standard is missing in chromatogram of day 184 sample.



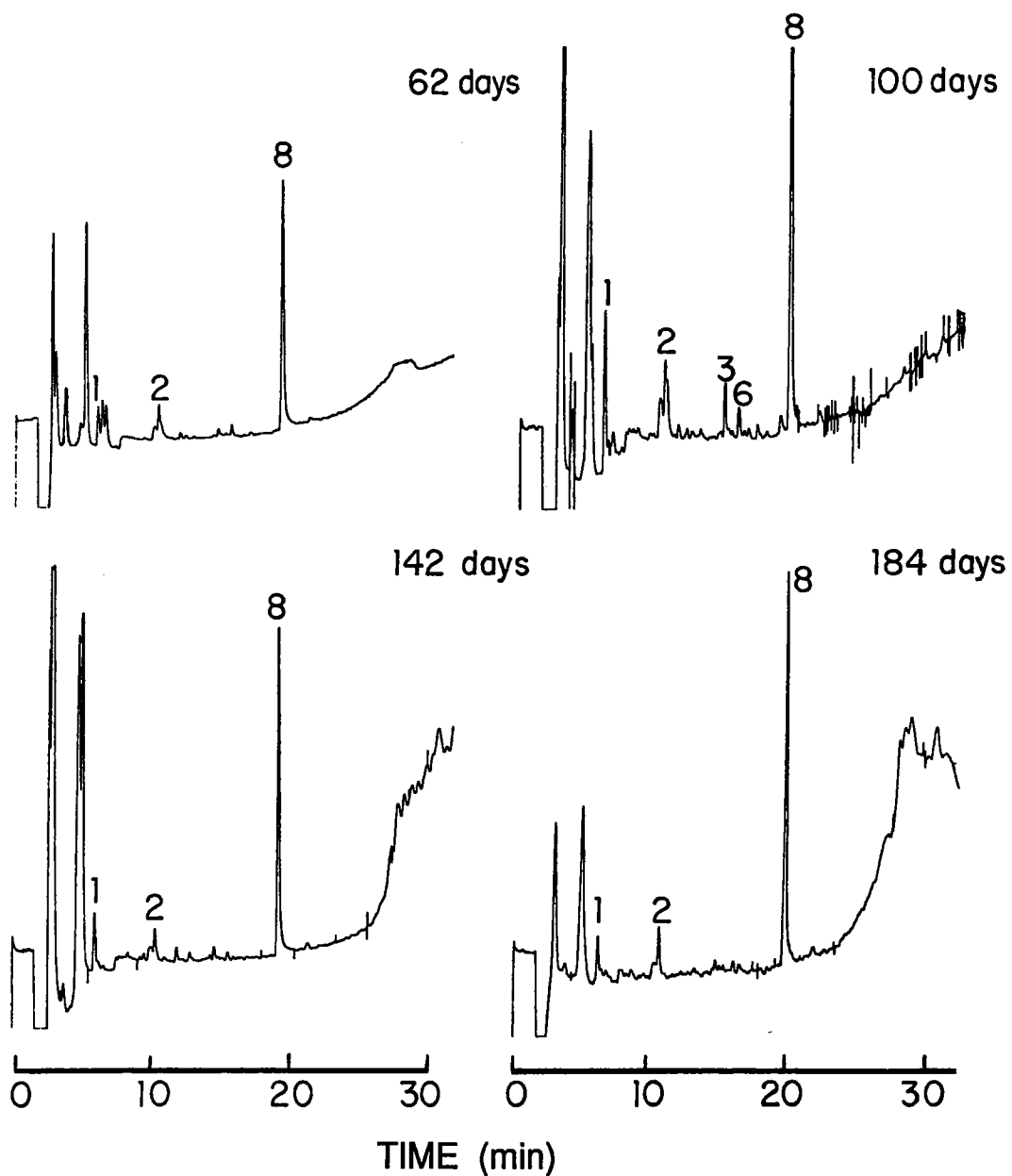


Figure 4.8 Gas chromatogram with photoionization detection of water samples (D1) collected from influent to pilot column II on days 62, 100, 142, and 184. Peaks are labeled: 1 benzene; 2 toluene; 3 chlorobenzene; 4 ethylbenzene; 5 m-xylene; 6 p-xylene; 7 o-xylene; 8 bromobenzene (internal standard).

**Table 4.6**

Average influent concentrations ( $\mu\text{g/L}$ ) of volatile aromatic organics added during simulated chemical spills to pilot column I

		Spill 1	Spill 2	Spill 3	Spill 4	Overall (2,3,4)
Time	week	7	13	20	26	-
Duration	days	7: 48-55	8: 92-100	5: 137-142	4: 180-184	-
Temperature	$^{\circ}\text{C}$	7.2	17.6	23.0	24.5	16.5
benzene		28	66	134	69	90
toluene		11	57	146	54	86
o xylene		4	38	136	53	76
chlorobenzene		11	74	129	107	103

### Breakthrough: Effluent Concentrations Relative to Influent Concentrations

The primary question of interest in the pilot column experiments is whether the spill chemicals were removed by the GAC. The GC-PID chromatograms for effluent samples from pilot column I provide essentially no evidence of breakthrough during the simulated spills: none of the volatile aromatic compounds were detected above  $2 \mu\text{g/L}$ , the lower limit of quantitation in effect for these samples (Figure 4.9). For the control pilot column (II), benzene and toluene were found at background levels in chromatograms for days 100 and 184, but none of the other compounds of interest were detected: for these samples, instrumental conditions were set for the low quantitation range, between  $0.1$  and  $1.0 \mu\text{g/L}$  (Figure 4.10).

Plots of concentration as a function of time show no breakthrough in effluent samples, despite concentrations on the order of  $100 \mu\text{g/L}$  in influent samples during the spills (Figures 4.11 to 4.14). Effluent concentrations were below  $2 \mu\text{g/L}$  during the spills, and below  $1 \mu\text{g/L}$  for the periods between spills. Removal of benzene, toluene, o-xylene and chlorobenzene was complete within the limits of quantitation, better than 98 percent, during all four simulated spills to pilot column I.

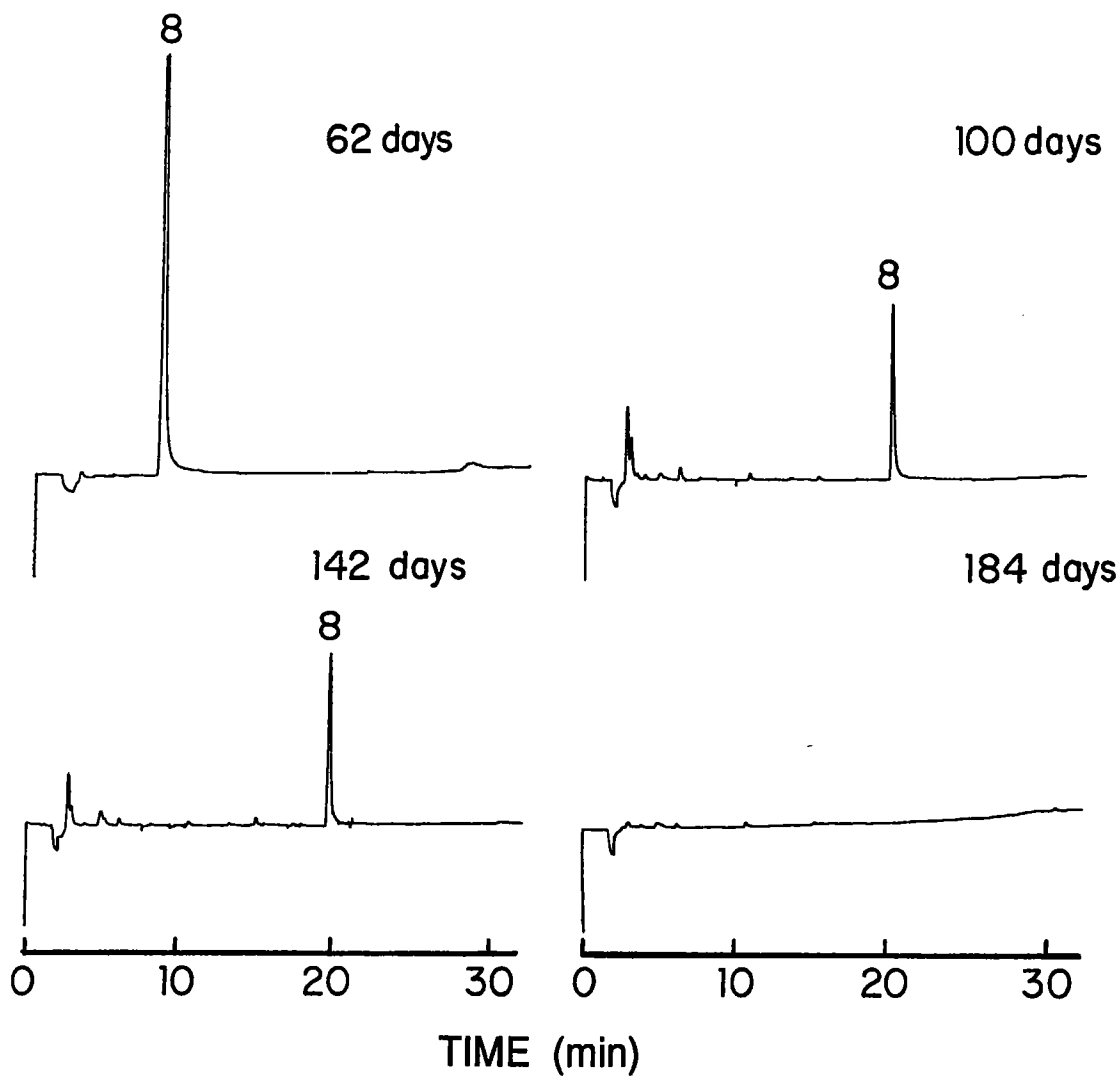


Figure 4.9 Gas chromatogram with photoionization detection of water samples (E2) collected from effluent to pilot column I on days 62, 100, 142, and 184, during simulated chemical spills. Peaks are labeled: 1 benzene; 2 toluene; 3 chlorobenzene; 4 ethylbenzene; 5 m-xylene; 6 p-xylene; 7 o-xylene; 8 (internal standard). The internal standard for the day 62 sample was  $\alpha,\alpha,\alpha$ -trifluorotoluene, which elutes at 8.6 min; the internal standard for the day 100, 142, and 184 samples was bromobenzene, which elutes at 19.3 min. Internal standard is missing in chromatogram of day 184 sample.

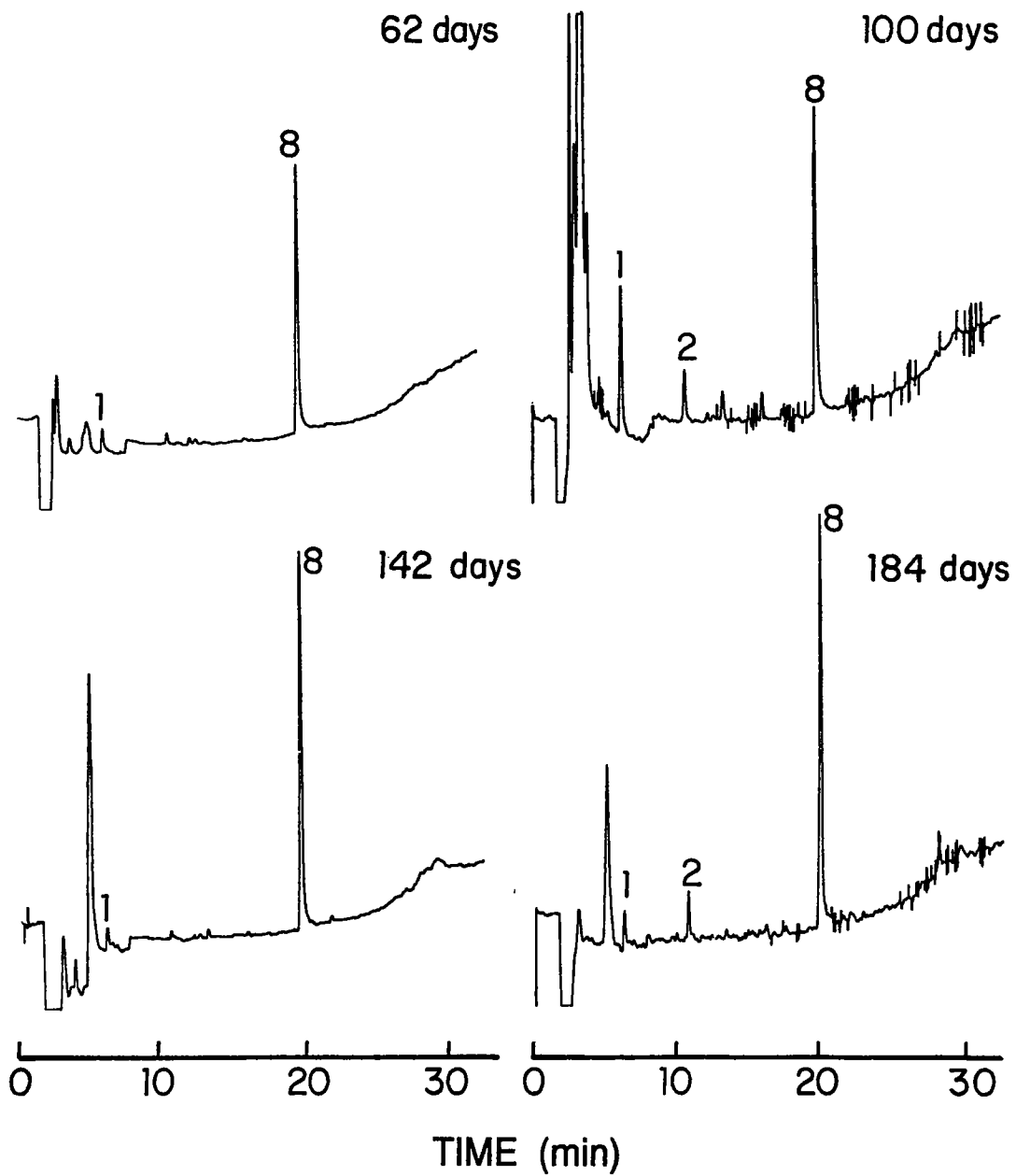


Figure 4.10 Gas chromatogram with photoionization detection of water samples (E1) collected from effluent to pilot column II on days 62, 100, 142, and 184. Peaks are labeled: 1 benzene; 2 toluene; 3 chlorobenzene; 4 ethylbenzene; 5 m-xylene; 6 p-xylene; 7 o-xylene; 8 bromobenzene (internal standard).

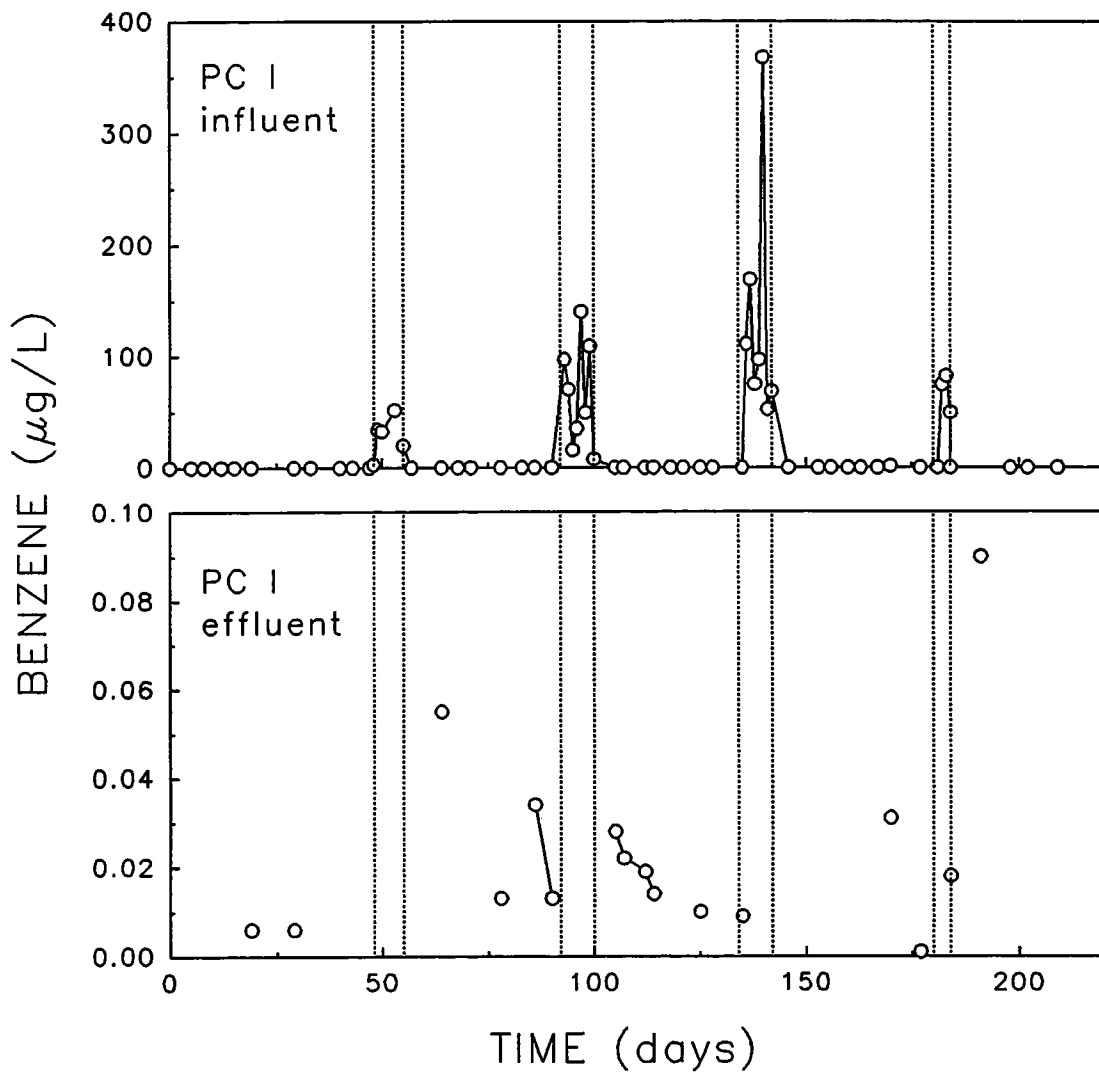


Figure 4.11 Benzene concentrations in influent (top) and effluent (bottom) water samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

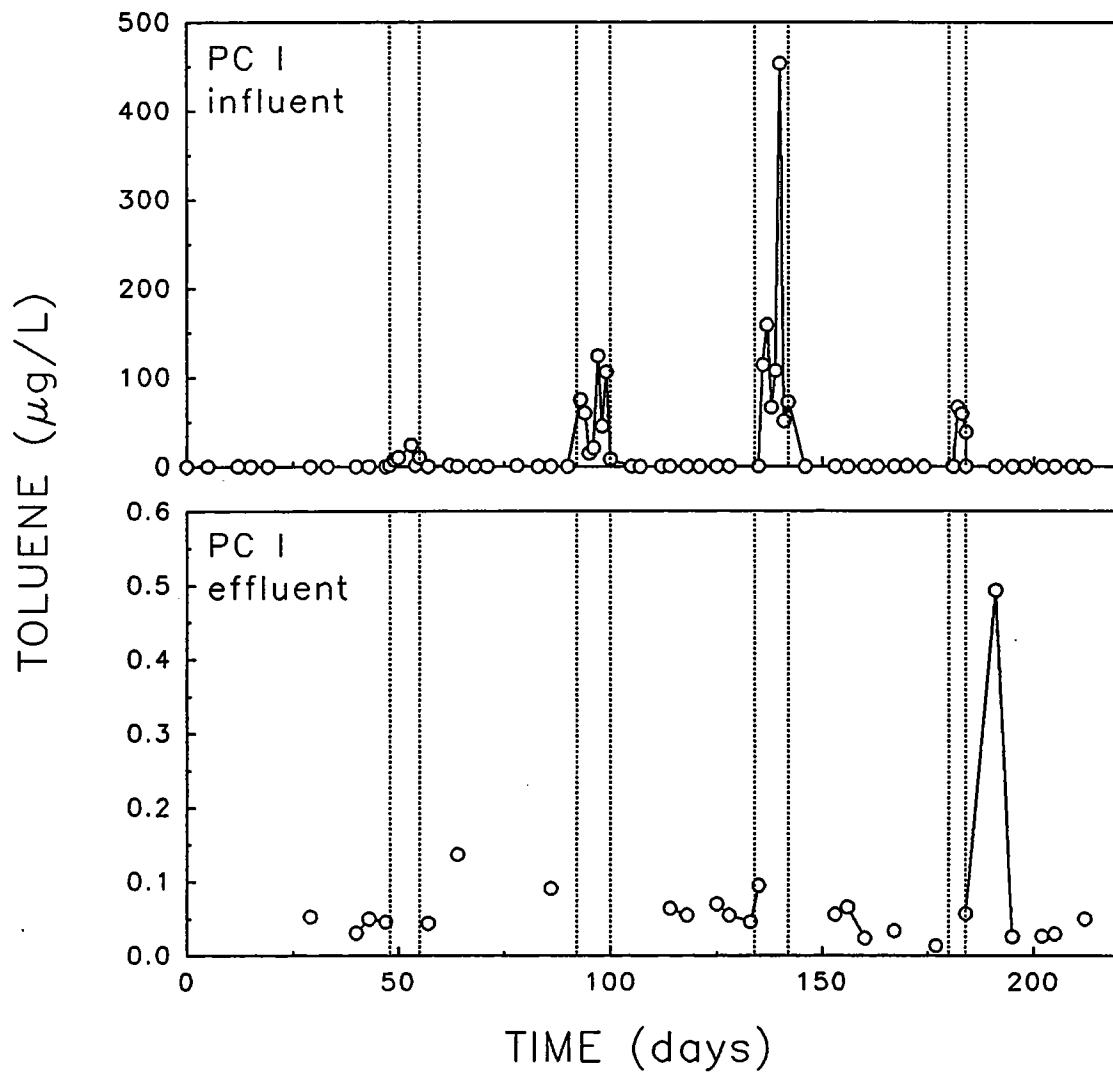


Figure 4.12 Toluene concentrations in influent (top) and effluent (bottom) water samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

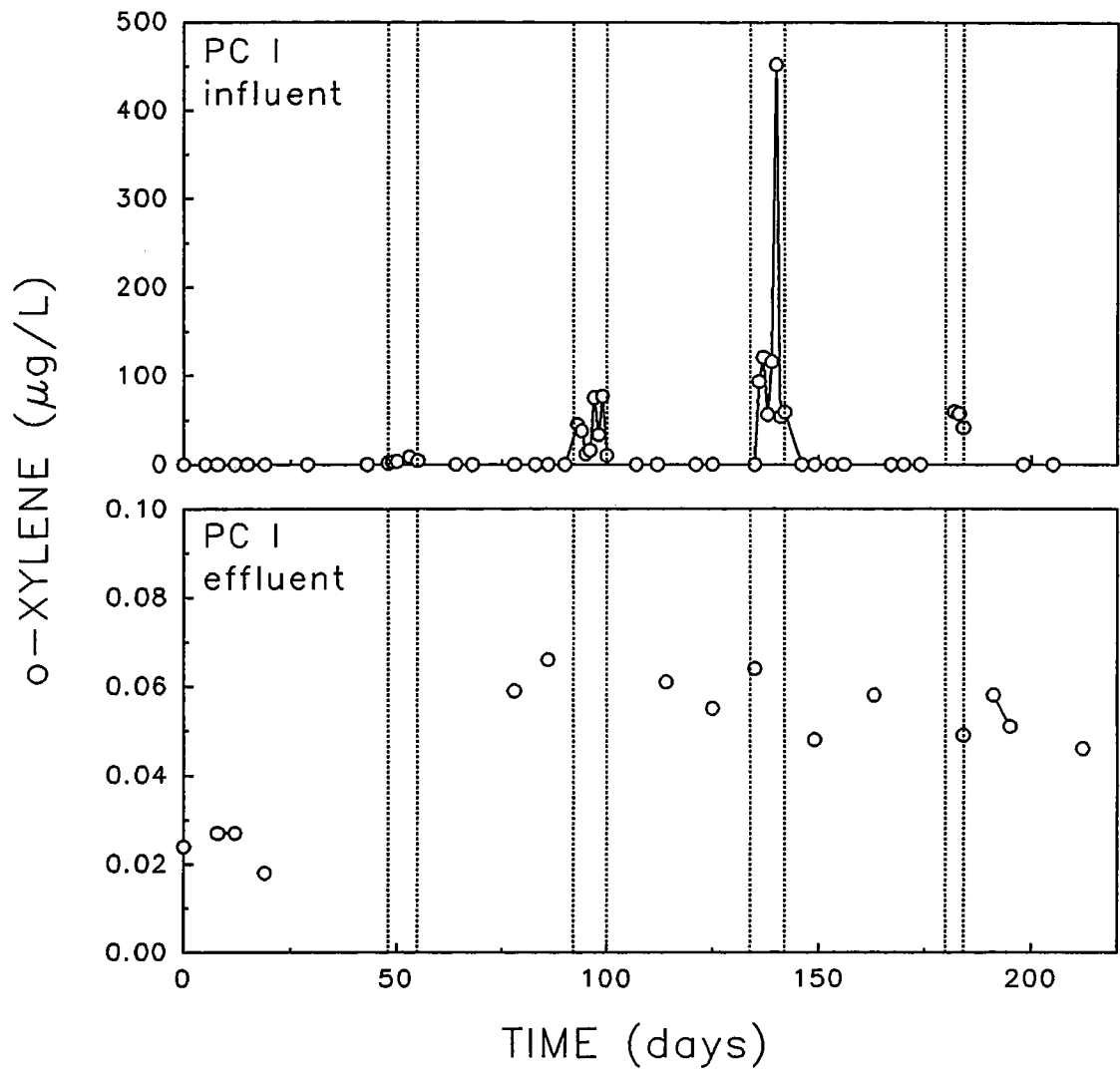


Figure 4.13 o-Xylene concentrations in influent (top) and effluent (bottom) water samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.

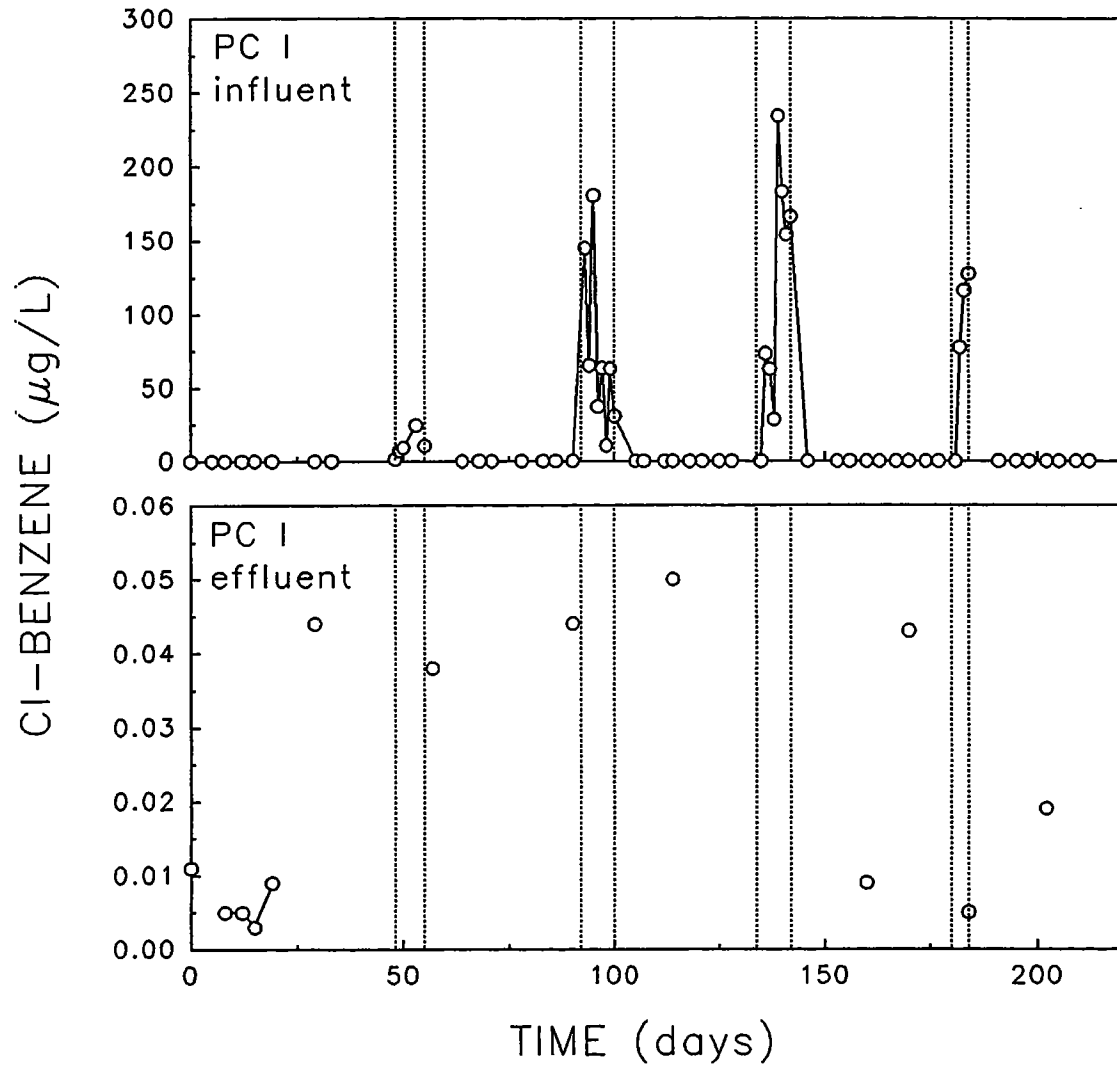


Figure 4.14 Chlorobenzene concentrations in influent (top) and effluent (bottom) water samples from pilot column I. The vertical dotted lines indicate the times of the four simulated spills.



## **Adsorption and Saturation: Contaminant Concentrations on GAC Samples**

During the first few weeks of the pilot column experiment, GAC samples were extracted in methanol for GC-PID analysis of the volatile aromatic compounds. The intent was to confirm results obtained by analysis of water samples, analogous to the analytical approach that was being used for the volatile halogenated compounds. However, only traces of the aromatic contaminants were found in the methanol extracts of GAC samples. The ability of methanol to recover the aromatic compounds of interest from GAC had not been demonstrated. Another concern was that the methanol extracts contained unknown compounds which could pass through the megabore column and foul the PID, even if the compounds were not ionized. For aromatic compounds purged from water samples, the PID response was stable for only a limited time, and periodic cleaning of the window was required to maintain sensitivity. Therefore PID analyses of methanol extracts were discontinued. Although the analyses of water samples indicated no breakthrough of the volatile aromatic compounds, results from the GAC samples would have been useful to determine how far the volatile aromatic compounds had advanced within the pilot column.

### **Spill Attenuation**

Since there was no evidence of breakthrough, attenuation is considered complete for the four volatile aromatic compounds added during the simulated spills: benzene, toluene, o-xylene, and chlorobenzene. As indicated in the previous chapter, attenuation was also complete for carbon tetrachloride, trichloroethylene, and tetrachloroethylene.

### **Post-Spill Desorption**

Monitoring at low levels after the spills provided no evidence of post-spill desorption of the volatile aromatic contaminants (Figures 4.11 to 4.14). For benzene, toluene, o-xylene and chlorobenzene, effluent concentrations were below 2 µg/L during the spills, and below 1 µg/L for the periods between spills.

### **Factors Controlling GAC Performance**

The data that have been presented document the pilot column's performance and ability to treat chemical spills. In this section, it is of interest to determine if removal of the volatile aromatic contaminants is consistent with knowledge of their influent concentrations and affinities for GAC. It is also of interest to compare the results for the volatile aromatic compounds with those presented

in the previous chapter for the volatile halogenated contaminants. Molar concentration units are used to compare the adsorption behavior of different compounds, since these units describe interactions on a molecular level, whereas mass concentration units are used only for analytical convenience.

The lack of evidence for breakthrough of the volatile aromatic contaminants during the spills places their advance through the pilot columns behind the trihalomethanes, approximately between carbon tetrachloride and tetrachloroethylene:

$$\text{Time to breakthrough, saturation} \quad \underline{\text{CHCl}_3} < \underline{\text{CHBrCl}_2} < \underline{\text{CHBr}_2\text{Cl}} < \text{CCl}_4 < \underline{\text{CHBr}_3} < \text{C}_2\text{HCl}_3 < \text{C}_2\text{Cl}_4 \quad (4.1)$$

[benzene, toluene, o xylene, chlorobenzene]

In the simplest approximation, times to breakthrough and saturation are inversely related to molar influent concentrations and mass inputs (Table 4.7). Molar concentrations of the volatile aromatics during the simulated spills range from 0.7 to 1.1  $\mu\text{mol/L}$ , comparable to intermediate values achieved for some of the volatile halogenated organics:

$$\text{Influent concentrations mass inputs} \quad \underline{\text{CHCl}_3} > \underline{\text{CHBr}_2\text{Cl}} > \underline{\text{CHBrCl}_2} > \underline{\text{CHBr}_3} > \text{C}_2\text{HCl}_3 > \text{CCl}_4 > \text{C}_2\text{Cl}_4 \quad (4.2)$$

[benzene > toluene, chlorobenzene > o xylene]

**Table 4.7**

Influent concentrations in the simulated spills and predicted capacities using Freundlich coefficients for single-solute adsorption of aromatic organics on Calgon F400

	MW g/mole	Average influent		$K_F^*$ (mg/g)(L/ $\mu\text{g}$ ) <sup>1/n</sup>	1/n*	Isotherm capacity	
		$\mu\text{g/L}$	$\mu\text{mol/L}$			mg/g	$\mu\text{mol/g}$
benzene	78.1	90	1.152	1.26	0.533	13.9	178
toluene	92.1	86	0.934	5.01	0.429	33.9	368
o xylene	106.1	76	0.716	9.76	0.474	76.0	717
chlorobenzene	112.6	103	0.915	9.17	0.348	46.0	409

\* Speth and Miltner 1990

Expected GAC capacities can be calculated, as shown in Table 4.7 using the Freundlich coefficients for the compounds of interest adsorbed as single compounds on Calgon F400. Very large capacities are predicted for the volatile aromatic contaminants, based on their influent concentrations to the pilot column. Values between 178 and 717  $\mu\text{mol/g}$  are all in excess of the capacity predicted for tetrachloroethylene, 150  $\mu\text{mol/g}$ , which was the largest value in the group of volatile halogenated organics. In molar units, capacities are predicted to increase in the order:

$$\text{GAC capacities, predicted} \quad \text{C}_2\text{Cl}_4 < \text{benzene} < \text{toluene} < \text{chlorobenzene} < \text{o-xylene} \quad (4.3)$$

Based on the Freundlich adsorption isotherms, the volatile aromatic contaminants would be expected to reach breakthrough and saturation after tetrachloroethylene, later than indicated by the comparison of influent concentrations in Equation 4.2.

Unfortunately there are no results from analysis of GAC samples, to be able to compare actual pilot column capacities to those calculated for single-solute adsorption. However, it can be recalled that for the volatile halogenated contaminants, capacities achieved in the GAC pilot column were much below the predicted isotherm capacity. The reduction was worst for tetrachloroethylene, by a factor of 132, or 114 if mass balance data were used to correct the measured influent concentration (Chapter 3). Although tetrachloroethylene had advanced to a bed depth of only 55 cm, it had the second lowest capacity on the pilot column, 1.13  $\mu\text{mol/g}$ . In general, competition with background natural organic matter, as well as volatile halogenated organics, is believed to limit capacities achieved on GAC pilot columns (Crittenden et al. 1985; Kuennen et al 1989; Najm et al. 1991). These problems are also expected to affect adsorption of the volatile aromatic contaminants in the simulated spills. Therefore, in molar units, pilot column capacities for the volatile aromatic contaminants are hypothesized to be comparable to or below values for tetrachloroethylene and carbon tetrachloride:

$$\text{GAC capacities, actual, pilot column I} \quad \text{o-xylene} < \text{chlorobenzene} < \text{toluene} < \text{benzene} < \text{CCl}_4 < \text{C}_2\text{Cl}_4 \quad (4.4)$$

It should also be noted that the predicted order for volatile aromatic contaminants in Equation 4.4 is in reverse to that based on the Freundlich isotherms and given in Equation 4.3.

In future work, it is of interest to verify the hypothesized effect of competition on adsorption capacities for the volatile aromatic compounds, and to examine how differences in the compounds' rates of adsorption affect their ability to compete. To fully understand competitive

limitations to capacities for removal of chemical spills, information is needed on kinetic as well as thermodynamic properties for adsorption of the volatile aromatic and halogenated organic compounds. Diffusivities are expected to be slow for the volatile aromatic contaminants, in water and on the GAC surface, so that they have no kinetic advantage to counteract the effects of competition.

### Mass Balances for Adsorbed Aromatic Organics

Most often, mass balances are calculated using flow data and concentrations in influent and effluent samples to determine the cumulative mass adsorbed as a function of the cumulative mass input. This information provides another measure of pilot column performance: the mass adsorbed increases steadily and equals the mass input until breakthrough begins; then the mass adsorbed levels off to a limiting value, which is the pilot column's total capacity. For the volatile halogenated organics, it was possible to calculate mass balances using both the water and GAC data.

Cumulative mass inputs are given in Table 4.8 for aromatic organic contaminants in the simulated spills to pilot column I. Values were calculated as a function of time  $t_j$  from:

$$\text{Cumulative Mass Input } (t_j) = \sum_i \text{Influent } (t_j) * \text{Volume } (t_j) \quad (4.5)$$

Influent concentrations were determined for samples collected daily from the top of pilot column I during each simulated spill (average values given in Table 4.6). Corresponding volumes of water input to pilot column I were read daily from an accumulator and cross-checked by a flowmeter (average values given in Table 2.2). Mass inputs for individual compounds have the same relative order as average influent concentrations during the spills (Tables 4.6 and 4.8).

It was intended to cross-check mass inputs based on analysis of influent samples, by analysis of water samples collected directly from the reservoirs and by measuring the volume of water displaced from the reservoirs each day. Water from the reservoirs was sampled from the transfer lines to the pilot columns. Concentrations of volatile organics in these samples were a factor of ten lower than expected, indicating that the water being collected was diluted by backflow from the pilot column during sampling, and was not only from the reservoir. In subsequent experiments, the design for sampling from the reservoirs was modified, to prevent backflow from the pilot columns (Alben et al. 1995).

**Table 4.8**

Cumulative mass inputs (g) of volatile aromatic contaminants in successive chemical spills to pilot column I: values are also equivalent to the cumulative mass adsorbed since there was no breakthrough

	<b>Spill 1</b> <b>g</b>	<b>Spill 2</b> <b>g</b>	<b>Spill 3</b> <b>g</b>	<b>Spill 4</b> <b>g</b>
Days	48 - 55	92 - 100	137 - 142	180 - 184
benzene	0.38	1.33	2.41	2.75
toluene	0.15	0.97	2.14	2.42
o xylene	0.06	0.61	1.70	1.97
chlorobenzene	0.14	1.21	2.24	2.79

In principle, the cumulative mass adsorbed could be calculated for the volatile aromatic organics as shown by the following equation:

$$\text{Cumulative Mass Adsorbed from Water (t}_j\text{)} = \sum_i (\text{Influent (t}_j\text{)} - \text{Effluent (t}_j\text{)}) * \text{Volume (t}_j\text{)} \quad (4.6)$$

Since there was no significant breakthrough of the volatile aromatic contaminants, effluent concentrations are zero, and the cumulative mass adsorbed is equivalent to the mass input (Equation 4.5). The interpretation of water data for carbon tetrachloride, trichloroethylene, and tetrachloroethylene was similarly limited by the absence of breakthrough (Figure 3.24), but estimates of the mass adsorbed could still be cross-checked by a mass balance on the GAC data. In the case of the volatile aromatic contaminants, no GAC samples were analyzed. Therefore the values given in Table 4.8 are the only estimates of the cumulative mass adsorbed.



**APPENDIX A**

**MAXIMUM CONTAMINANT LEVELS AND PHYSICAL CONSTANTS FOR  
SYNTHETIC ORGANIC CHEMICALS REGULATED IN DRINKING WATER**

**Table A.1**

Synthetic organic chemicals, maximum contaminant levels (MCLs) and recommended (R) best available technology: packed tower aeration (PTA); granular activated carbon (GAC)\*

	CAS no.	MCL		Best available technology	
		Primary (mg/L)	Secondary (mg/L)	PTA	GAC
Acrylamide	79-06-1	-	-	-	-
Adipates [Di(ethylhexyl)adipate]	1330-86-5	0.5	-	R	R
Alachlor	15972-60-8	0.002	-	-	R
Aldicarb	116-06-3	0.01	-	-	R
Aldicarb sulfone	1646-88-4	0.04	-	-	R
Aldicarb sulfoxide	1646-87-3	0.01	-	-	R
Atrazine	1912-24-9	0.003	-	-	R
Benzene	71-43-2	0.005	-	R	R
Carbofuran	1563-66-2	0.04	-	-	R
Carbon tetrachloride	56-23-5	0.005	-	R	R
Chlordane	57-74-9	0.002	-	-	R
Chlorobenzene	108-90-7	0.1	-	R	R
Dalapon	75-99-0	0.2	-	-	R
Dibromochloropropane (DBCP)	96-12-8	0.0002	-	R	R
o-Dichlorobenzene	95-50-1	0.6	0.01	R	R
p-Dichlorobenzene	106-46-7	0.075	0.005	R	R
1,2-Dichloroethane	107-06-2	0.005	-	R	R
1,1-Dichloroethylene	75-35-4	0.007	-	R	R
cis-1,2-Dichloroethylene	156-59-2	0.07	-	R	R
trans-1,2-Dichloroethylene	156-60-5	0.1	-	R	R
Dichloromethane (Methylene chloride)	75-09-2	0.005	-	R	-
(2,4-Dichlorophenoxy)-acetic acid (2,4-D)	94-75-7	0.07	-	-	R
1,2-Dichloropropane	78-87-5	0.005	-	R	R
Dinoseb	88-85-7	0.007	-	-	R
Diquat	6385-62-2	0.02	-	-	R
Endothall	145-73-3	0.1	-	-	R
Endrin	72-20-8	0.002	-	-	R
Ethylene dibromide (EDB)	106-93-4	0.00005	-	R	R
Epichlorohydrin	106-89-8	-	-	-	-
Ethylbenzene	100-41-4	0.7	0.03	R	R
Glyphosate	1071-83-6	0.7	-	-	R
Heptachlor	76-44-8	0.0004	-	-	R
Heptachlor epoxide	1024-57-3	0.0002	-	-	R

(continues)

Table A.1 (continued)

	CAS no.	MCL		Best available technology	
		Primary (mg/L)	Secondary (mg/L)	PTA	GAC
Hexachlorobenzene	118-74-1	0.001	-	-	R
Hexachlorocyclopentadiene (HEX)	77-47-4	0.05	-	R	R
Lindane	58-89-9	0.0002	-	-	R
Methoxychlor	72-43-5	0.4	-	-	R
Oxamyl (Vydate)	2315-22-0	0.2	-	-	R
PAHs [Benzo(a)pyrene]		0.0002	-	-	R
PCBs (as C <sub>12</sub> Cl <sub>10</sub> )	1336-36-3	0.0005	-	-	R
Pentachlorophenol	87-86-5	0.2	0.03	-	R
Phthalates [Di(ethylhexyl)phthalate]	117-81-7	0.004	-	-	R
Picloram	1918-02-1	0.5	-	-	R
Simazine	122-34-9	0.001	-	-	R
Styrene	100-42-5	0.005 / 0.1	0.01	R	R
2,3,7,8-TCDD (Dioxin)	1746-01-6	0.000005	-	-	R
Tetrachloroethylene	127-18-4	0.005	-	R	R
Toluene	108-88-3	2.	0.04	R	R
1,2,4-Trichlorobenzene	120-82-1	0.009	-	R	R
1,1,1-Trichloroethane	71-55-6	0.2	-	R	R
1,1,2-Trichloroethane	79-00-5	0.005	-	R	R
Trichloroethylene	79-01-6	0.005	-	R	R
2-(2,4,5-Trichlorophenoxy)-propionic acid (2,4,5-TP; Silvex)	93-72-1	0.05	-	-	R
Toxaphene	8001-35-2	0.005	-	-	R
Vinyl chloride	75-01-4	0.002	-	R	-
Xylenes (o-, m-, p-)	1330-20-7	10.	0.02	R	R

\* USEPA 1989a, 1990.



Table A.2

Physical constants for volatile synthetic organic compounds and trihalomethanes

Formula	Mol wt (g/mole)	Solubility in water* (mg/L)	Henry's law coeff.† (atm-L/mole)	log K <sub>ow</sub> ‡	Freundlich coefficients§ KF (mg/g)(L/μg) <sup>1/n</sup> 1/n
Benzene	78.1	1780	5.5	2.13	1.26 0.533
Bromodichloromethane	163.8	4500	2.4	1.88	0.241 0.655
Bromoform	252.7	3010	0.56	2.30	0.929 0.665
Carbon tetrachloride	153.8	800	30.2	2.83	0.387 0.594
Chlorobenzene	112.6	500	3.9	2.84	9.17 0.348
Chlorodibromomethane	208.3	4000	1.0	2.08	0.585 0.636
Chloroform	119.4	8000	2.9	1.97	0.092 0.669
Dibromochloropropane (DBCP)	236.4	1000	0.3	-	6.91 0.501
o-Dichlorobenzene	147.0	145	1.9	3.38	19.3 0.378
p-Dichlorobenzene	147.0	79	3.1	3.39	4.97 0.691
1,2-Dichloroethane	99.0	8690	0.91	1.48	0.129 0.533
1,1-Dichloroethylene	96.9	400	21.	2.13	0.470 0.515
cis-1,2-Dichloroethylene	96.9	600	3.4	1.86	0.202 0.587
trans-1,2-Dichloroethylene	96.9	800	7.2	2.09	0.618 0.452
Dichloromethane (Methylene chloride)	84.9	2000	2.2	1.30	0.0062 0.801
1,2-Dichloropropane	113.0	2700	2.3	2.28	0.313 0.597
Ethylene dibromide (EDB)	187.8	4300	0.7	-	0.888 0.471
Ethylbenzene	106.1	152	6.6	3.13	9.27 0.415
Hexachlorocyclopentadiene (HEX)	272.8	0.80	16.	4.00	43.0 0.504
Styrene	104.2	300	2.6	2.95	12.2 0.479
Tetrachloroethylene	165.8	150	15.3	2.60	4.05 0.516

(continues)

Table A.2 (continued)

Formula	Mol wt (g/mole)	Solubility in water* (mg/L)	Henry's law coeff. † (atm-L/mole)	log K <sub>ow</sub> ‡	Freundlich coefficients § K <sub>F</sub> (mg/g)(L/μg) <sup>1/n</sup>	1/n
Toluene	92.1	515	6.7	2.65	5.01	0.429
1,2,4-Trichlorobenzene	181.4	31	2.3	4.02	(63.8)	(0.324)
1,1,1-Trichloroethane	133.4	4400	18.	2.18	0.335	0.531
1,1,2-Trichloroethane	133.4	4500	0.9	2.18	0.365	0.652
Trichloroethylene	131.4	1100	9.1	2.53	2.00	0.482
Vinyl chloride	62.5	1100	2780.	0.60	-	-
o-Xylene	106.1	175	5.3	2.95	9.76	0.474
p-Xylene	106.1	198	7.1	3.18	12.6	0.418

\* An effort is made to give representative values for solubilities at 20 to 25 °C, although there is considerable variation among the references used: Hayes (1982); Howard et al. (1990); Kenaga and Goring (1980); Mackay et al. (1980); Miller et al. (1985); Montgomery and Welkom (1990); Shiu and Mackay (1986); Verscheuren (1983); Worthing and Walker (1987)

† Conversion factors used for Henry's Law coefficients: 1 atm = 1.013 \* 10<sup>5</sup> Pa; 1 m<sup>3</sup> = 1000 L.  
Howard et al. (1990); Kenaga and Goring (1980); Mackay et al. (1980); Miller et al. (1985); Montgomery and Welkom (1990); Shiu and Mackay (1986); USEPA (1989a, 1990).

‡ Briggs (1981); Kenaga and Goring (1980); Montgomery and Welkom (1990); Howard et al. (1990).

§ Freundlich coefficients determined for adsorption to Calgon F400. Speth and Miltner (1990).

Table A.3

Physical constants for semivolatile synthetic organic compounds

Formula	Mol wt (g/mole)	Solubility in water* (mg/L)	Henry's law coeff.† (atm-L/mole)	log Kow‡	Freundlich coefficients§ Kf (mg/g)(L/μg) <sup>1/n</sup>	1/n
Acrylamide	71.1	2050000	0.0000003	-0.67	-	-
Adipates [Di(ethylhexyl)adipate]						
C <sub>22</sub> H <sub>42</sub> O <sub>4</sub>						
Alachlor	269.8	242	-	2.92	81.7	0.257
Aldicarb	190.3	6000	-	1.57	8.27	0.402
Aldicarb sulfone	222.3	>330000	-	-0.57	-	-
Aldicarb sulfoxide	206.3		-			
Atrazine	215.7	70	-	2.68	38.7	0.291
Carbofuran	221.3	700	-	1.6	16.4	0.408
Chlordane	409.8	0.056	0.048	6.00	-	-
Dalapon	143.0	502000	-	0.8	4.92	0.224
(2,4-Dichlorophenoxy) acetic acid (2,4-D)	221.0	890	-	1.57	-	-
Dinoseb	240.2	52	-	-	30.4	0.279
Diquat	362.1					
C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>5</sub>						
C <sub>12</sub> H <sub>12</sub> Br <sub>2</sub> N <sub>2</sub> ·H <sub>2</sub> O						
Endothall	204.2	100000	-	-	-	-
C <sub>8</sub> H <sub>10</sub> O <sub>5</sub> ·H <sub>2</sub> O						
Endrin	380.9	0.200	0.00050	4.56	-	-
C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O						
Epichlorohydrin	92.5	60000	-	0.30	-	-
C <sub>3</sub> H <sub>5</sub> ClO						
Glyphosate	169.1	12000	-	-	87.6	0.119
C <sub>3</sub> H <sub>8</sub> NO <sub>5</sub> P						
Heptachlor	373.3	0.056	2.3	5.44	-	-
C <sub>10</sub> H <sub>5</sub> Cl <sub>7</sub>						
Heptachlor epoxide	389.3	0.35	0.032	5.40	-	-
C <sub>10</sub> H <sub>5</sub> Cl <sub>7</sub> O						
Hexachlorobenzene	284.8	0.11	1.7	5.45	-	-
C <sub>6</sub> Cl <sub>6</sub>						

(continues)

Table A.3 (continued)

Formula	Mol wt (g/mole)	Solubility in water* (mg/L)	Henry's law coeff. † (atm-L/mole)	log Kow ‡	KF (mg/g)(L/(µg)1/n)	Ereundlich coefficients § 1/n
Lindane	290.8	7.5	0.00048	3.70	15.0	0.433
Methoxychlor	345.7	0.04	-	4.30	-	-
Oxamyl (Vydate)	219.2	28	-	-	1.74	0.793
PAHs						
Benzo(a)anthracene	228.3	0.010	0.00066	5.91	-	-
Benzo(b)fluoranthene	252.3	0.014	0.012	6.57	-	-
Benzo(k)fluoranthene	252.3	0.00055	1.04	6.85	-	-
Benzo(a)pyrene	252.3	0.003	<0.0024	5.98	-	-
Chrysene	228.3	0.006	7.3 * 10 <sup>-17</sup>	5.60	-	-
Dibenzo(a,h)anthracene	278.4	0.0005	7.3 * 10 <sup>-6</sup>	6.36	-	-
Indenopyrene	276.3	0.062	3.0 * 10 <sup>-17</sup>	7.70	-	-
PCBs						
4-chlorobiphenyl	188.7	1.2	0.426	4.5	-	-
2,2'-dichlorobiphenyl	223.1	1.0	0.592	4.9	-	-
2,4'-dichlorobiphenyl	223.1	1.0	0.967	5.1	-	-
2,2',5-trichlorobiphenyl	257.5	0.40	0.922	5.6	-	-
2,2',4',5'-tetrachlorobiphenyl	292.0	0.016	0.203	6.1	-	-
2,2',5,5'-tetrachlorobiphenyl	292.0	0.030	0.476	6.1	-	-
2,2',3,4,5'-pentachlorobiphenyl	326.4	0.004	0.248	6.5	-	-
2,2',4,5,5'-pentachlorobiphenyl	326.4	0.010	0.358	6.4	-	-
Pentachlorophenol	266.3	0.03	0.0034	5.01	42.6	0.339

(continues)

Table A.3 (continued)

Formula	Mol wt (g/mole)	Solubility in water* (mg/L)	Henry's law coeff. † (atm-L/mole)	log Kow ‡	Freundlich coefficients § KF (mg/g)(L/μg) <sup>1/n</sup>	1/n
Phthalates [Di(ethylhexyl)phthalate]	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	0.4	0.011	4.20	-	-
Picloram	C <sub>6</sub> H <sub>3</sub> O <sub>2</sub> N <sub>2</sub> Cl <sub>3</sub>	430.	-	0.3	23.4	0.180
Simazine	C <sub>7</sub> H <sub>12</sub> N <sub>5</sub> Cl	5.	-	1.51	31.3	0.227
2,3,7,8-TCDD (Dioxin)	C <sub>12</sub> H <sub>4</sub> O <sub>2</sub> Cl <sub>2</sub>	0.000019	5.4 * 10 <sup>-20</sup>	8.93	-	-
2-(2,4,5-Trichlorophenoxy)- propionic acid (2,4,5-TP; Silvex)	C <sub>9</sub> H <sub>7</sub> Cl <sub>3</sub> O <sub>3</sub>	140	-	2.44	-	-
Toxaphene	C <sub>10</sub> H <sub>10</sub> Cl <sub>8</sub>	3	63.8	3.30	-	-

\* An effort is made to give representative values for solubilities at 20 to 25 °C, although there is considerable variation among the references used: Hayes (1982); Howard et al. (1990); Kenaga and Goring (1980); Mackay et al. (1980); Miller et al. (1985); Montgomery and Welkom (1990); Shiu and Mackay (1986); Verscheuren (1983); Worthing and Walker (1987)

† Conversion factors used for Henry's Law coefficients: 1 atm = 1.013 \* 10<sup>5</sup> Pa; 1 m<sup>3</sup> = 1000 L.

‡ Howard et al. (1990); Kenaga and Goring (1980); Mackay et al. (1980); Miller et al. (1985); Montgomery and Welkom (1990); Shiu and Mackay (1986); USEPA (1989a, 1990).

§ Briggs (1981); Kenaga and Goring (1980); Montgomery and Welkom (1990); Howard et al. (1990).  
Freundlich coefficients determined for adsorption to Calgon F400. Speth and Miltner (1990).



## APPENDIX B

### WATER TREATMENT AND WATER QUALITY AT LATHAM WATER DISTRICT

While studies at Waterford were being conducted, a limited number of water samples were also collected from Latham Water Works. A schematic of the Latham Water Works is given in Figure B.1. The main water supply is from the Mohawk River which flows into the Hudson River at Cohoes, just south of Waterford. At the time of this project in 1987, treatment at Latham was based on a combination of unit processes similar to those used at Waterford for surface water treatment:

1. aeration to convert dissolved iron to insoluble oxides
2. coagulation with alum to remove suspended particulates
3. addition of powdered activated carbon to adsorb substances causing taste and odor
4. addition of a polymer N100P to improve filtration
5. prechlorination for disinfection and further oxidation of dissolved iron, manganese, and natural organics
6. sedimentation for removal of floc
7. filtration for removal of fine particulates and microorganisms
8. addition of caustic soda to control the pH and minimize corrosion in the distribution system
10. postchlorination to maintain a chlorine residual for disinfection of the distribution system

Typical operating conditions, chemical feed concentrations, and water quality for the Latham Water Works in 1987 are given in Table B.1. After this project, the treatment process at Latham Water Works was modified, to make use of additional water from four wells near the river-bank intake, and from the Stony Creek Reservoir, across the river in Clifton Park. Other changes included the use of permanganate to remove dissolved manganese, and use of chlorine dioxide to reduce the formation of chlorination byproducts (Yang 1995).

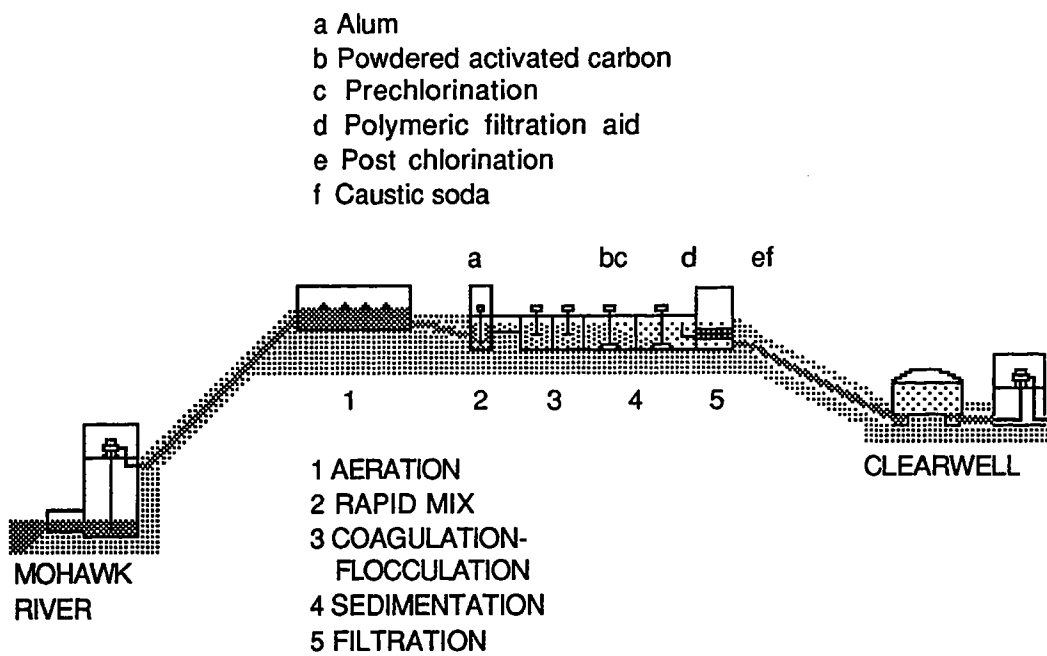


Figure B.1 Schematic of the Latham Water Works



**Table B.1**

Typical operating conditions, chemical feed concentrations, and water quality for the Latham Water Works (Maswick and Mostert 1987; Wagner 1987; Wang 1994; Yang 1995)

Operation		Average	±	Standard Deviation	Relative Standard Deviation (%)
Mohawk River flow	ft <sup>3</sup> /sec	5325	±	6836	128
	MGD	3440	±	4416	128
Latham Water Works production	MGD	10.73	±	3.22	30
Alum	mg/L	525	±	94	18
Powdered activated carbon	mg/L	115	±	18	16
Pre-chlorine dose	mg/L	45.8	±	12.3	27
Filter aid (Clarifloc N 100P)	mg/L	1.76	±	0.90	51
Caustic soda	mg/L	301	±	79	26
Post chlorination	mg/L	42.6	±	6.4	15
<b><u>Water quality</u></b>					
Raw water turbidity	NTU	9.75	±	8.03	82
Raw water pH	-	7.84	±	0.38	5
Raw water TOC	mg/L	4.13	±	0.73	18
Finished water pH	-	7.68	±	0.19	2
Finished water TOC	mg/L	2.05	±	0.54	26



