ADSORPTION OF CHLOROFORM BY SOILS IN A CONTINUOUS FLOW REACTOR

by

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ABSTRACT

Trihalomethanes are organic pollutants that may be formed during chlorination of wastewater. Some forms of trihalomethanes are known to cause cancer in laboratory animals and are suspected of posing human health risks.

The practice of applying wastewater to land both as a method of treatment and as a means of recharging groundwater has increased in recent years. The question has arisen as to whether harmful organic chemicals such as chloroform can be adequately removed in a land treatment system. Adsorption, or accumulation of a consituent at a solid-liquid interface, is one of the principal methods of removal of pollutants in land treatment systems. Sufficient removal is necessary to protect groundwater supplies from contamination.

In addition to a review of the environmental significance of trihalomethanes, land treatment and pollutant removal, and adsorption by soils, this paper discusses a laboratory investigation of the adsorption characterisitics of two soils. Each soil was placed in a sealed column and a solution of chloroform, a common trihalomethane, was applied at the upper end of the column with flow going downward. Water samples were removed at the column effluent and at various points along the column, and analyzed for chloroform with a gas chromatograph.

The purpose of the experiment was to quantify the adsorptive properties of each soil, and to determine an adsorption front velocity. The quantity adsorbed at a given concentration, q, is a measure of the amount of a constiuent adsorbed per unit weight of soil, while the adsorption front velocity describes the speed at which a constituent moves through a reactor.

The differences in adsorption characteristics of the two soils are discussed and compared to an earlier study using batch reactors. Consideration is given as to why these differences are found, and whether these soils would be suitable for a land application system in which chloroform is a contaminant.

CHAPTER 1

INTRODUCTION

Trihalomethanes (THMs) are formed when three of the four hydrogens of the methane molecule, CH_4, are substituted with chlorine, bromine, iodine, or a combination of these halogens. Some examples are chloroform, $CHCl_3$, bromoform, $CHBr_3$, and dichloroiodomethane, $CHCl_2I$.

THMs in general are volatile, more dense than water, and have limited solubility in water (National Research Council, 1978). The iodinated forms are chemically unstable and difficult to monitor, and for this reason they are less often discussed in the literature (Vogt, 1981). Chloroform is by far the most widely occurring THM; its properties are most often studied and quantified. It is a known carcinogen.

Trihalomethanes have stimulated a great deal of research interest in recent years. These potentially harmful chemicals have been found in low concentrations in water systems throughout the United States. The National Organics Reconnaissance Survey, concluded in 1975 by the U.S. Envirnomental Protection Agency (EPA), monitored total THM concentrations in water systems of many different localities, and found concentrations of up to .54 mg/L

(Vogt, 1981). Trihalomethanes in water supplies result mainly from the interaction between naturally occurring organics, such as humic and fulvic acids, and chlorine, added as a disinfecting agent (Banovic, 1981). The human health risks of THMS at actual exposure levels are difficult to assess. Chloroform induces liver and kidney tumors in laboratory animals at certain concentrations (National Research Council, 1978). Since humans share similar metabolic pathways, it is suspected to be a human carcinogen as well. Risks must be estimated from exposure data at much higher concentration levels. Health effects of other THMs are unknown, but are suspected of posing similar risks.

Various researchers have attempted to statistically predict cancer risk based on estimated exposures to THMs, but results are inconclusive. Other epidemiological studies have tried to correlate incidence of liver cancer with chlorinated water consumption. Results indicate a possible relationship, but are subject to interpretation (National Research Council, 1978).

There may be environmental as well as human health risks associated with THMs. Low concentrations of chloroform and other halomethanes have been shown to interfere with methyl transfer processes in certain bacteria, including E. coli B. The possibility exists that the increasing levels of these compounds in water might inhibit microbial fermentation processes, such as digestion

in a sewage treatment plant or natural degradation in a streambed (National Research Council, 1978).

Wastewater treatment plants commonly disinfect final effluent with chlorine. Because wastewater contains appreciable amounts of humic and fulvic substances, it is logical to assume that THMs will be formed upon chlorination. Different studies have found varying degrees of THM production following chlorination of wastewater. In one study, wastewater effluent was dosed in the laboratory with different concentrations of chlorine (Chambon, 1983). Up to 144 ug/L chloroform were produced following treatment with 2.5 mg/L Cl_2.

Another study showed that THMs were formed in relatively large concentrations following disinfection of effluents from nine wastewater treatment plants (Richard, 1980). When wastewaters were treated to produce a long-term free chlorine residual, as would occur in a wastewater reclamation system, THM levels were substantially higher than found in chlorinated drinking waters. Dominant THM species were also different in the chlorinated wastewaters. Bromine-substituted THMs accounted for 50 percent to 80 percent of the total THMs in the chlorinated effluents, while chloroform was the major compound in the chlorinated drinking waters. The researcher concluded that use of reclaimed wastewater as a source of potable water could increase human exposure to THMs.

THMs apparently are not found in high concentrations in all types of chlorinated wastewater. Oliver found that primary and secondary wastewater effluents produced very little chloroform when dosed with 10 mg/L chlorine, despite high total organic carbon concentrations (1979). The researchers postulated that ammonia in the wastewater reacted preferentially with chlorine to produce chloramines.

Because wastewater is ultimately incorporated into the water cycle, either by discharge into surface water or incorporation into groundwater through land application systems, it is a possible source of THM contamination. This paper focuses on the potential for groundwater contamination by THMs when wastewater is applied to soils.

THMs may also reach the groundwater through inadvertent contamination by industrial wastes, or through use of land disposal systems for industrial wastewater. Byer (1981) summarized instances of groundwater contamination from chlorinted hydrocarbons, including chloroform, of industrial origin. These chemicals are used in many manufacturing processes as solvents, cleaners, and extraction agents. Their physical properties make disposal difficult. They are more dense than water and only slightly soluble; in water treatment systems where settling ponds are used, they tend to sink to the bottom, where the potential for leaching into the soil and eventually into the groundwater is high.

A great deal of concern has been expressed both by the public and regulatory agencies that use of land treatment should not threaten groundwater quality. Aquifers are a main source of water for many uses. There is little or no volatilization, oxidation, or photolysis in these subsurface streams, and decontamination of an aquifer may take many years (Tomson, 1981).

CHAPTER 2

LAND TREATMENT AND POLLUTANT REMOVAL

Use of land treatment as a method of disposing and stabilizing domestic and agricultural wastes has increased in recent years. There were 360 land treatment sites in the United States in 1981, and many more were in the planning stages (Tomson, 1981). Land treatment is generally less expensive than other treatment methods, in terms of initial capital, operational costs, and energy consumption (Morrison, 1983). Legislation such as Public Law 92-500 has encouraged water reuse through land application methods.

In addition to chlorinated wastewater effluents, the potential also exists for groundwater pollution from THMs in hazardous waste disposed of by land application. These topics are discussed more fully below.

General Description

In land treatment systems, wastewater is applied to the soil in a variety of ways, and treatment takes place as water moves through the soil matrix. Adsorption, volatilization, and biodegradation are the principal methods for reducing chemical contaminants in this type of system (Tomson, 1981).

Design parameters for land application systems vary with the type of waste. Most domestic wastewaters are disposed of by the rapid infiltration method, where water is applied to shallow cells or basins and allowed to percolate through the soil and into the underlying groundwater (Tomson, 1981). Alternatively, wastewater effluent is dispersed through sprinkler irrigation (Tchobanoglous, 1979). More sophisticated systems, such as the one studied by Tomson, have holding ponds and a system for recovering renovated water for agricultural use.

Injection wells are another proposed method of land treatment for wastewater. In a pilot study in California, reclaimed water was injected directly into an aquifer by a series of injection wells (Roberts, 1978). Extraction wells were located approximately 1000 feet from the injection wells. In this system, pollutants were assumed to be attenuated through adsorption and possibly biodegradation as they passed through the aquifer.

Land Treatment and Hazardous Wastes

Currently, there is considerable interest in land treatment of hazardous wastes. An estimated 1 percent to 3 percent of hazardous wastes in this country are land treated at this time, and some experts propose that up to 25 percent of these wastes could eventually be treated in this way (Morrison, 1983).

The EPA has stringent standards on design of land application systems for hazardous wastes. Final regulations were issued on July 26, 1982, and went into effect in January 1983. Guidelines include depth of treatment zone, spreading and mixing requirements of wastes with soil, run-on and run-off control systems, testing for suitability of wastes, and extensive monitoring of surrounding groundwater and soil zones. The EPA requires that these facilities "degrade, transform, or immobilize" harmful constituents (Morrison, 1983).

Pollutant Removal Studies

In a field study of a rapid infiltration site, 67 different organics were detected in a wastewater before application (Tomson, 1981). The overall removal for these organics was 92 percent. Removal efficiency was a function of chemical type, and varied from 70 percent to 100 percent. Removal efficiency of the chloroalkanes, to which chloroform is associated, was the lowest, at 70 percent.

In evaluating an injection well treatment system, it was found that chloroform concentrations within the saturated aquifer dropped from an initial level of 20 ug/L to about 5 ug/L within 150 days (Roberts, 1980). In the well pair that responded most rapidly, the half-time response for the injection water was eleven hours. The trihalomethanes, chloroform included, were the first trace organics to appear in the extraction water. These compounds

moved through the aquifer at a slower rate than the injection water itself, with a half-time response of about five times as great as the injection front (Roberts, 1978). The less volatile, more highly chlorinated organics, such as chlorobenzene and dichlorobenzene isomers, moved even more slowly through the aquifer. These compounds may have been preferentially adsorbed by the aquifer material.

Wilson conducted a laboratory study of the transport and fate of selected pollutants in soil (Wilson, 1981). The soil was very sandy (92 percent) and low in organic matter. A column of soil 140 cm in depth was used. Soil was not dried or sieved, in an effort to maintain the biota, and the original soil profile was retained as much as possible. Chloroform was applied at an initial concentration of 0.90 mg/L. Fifty-four percent of this concentration was volatilized, 41 percent appeared in the column effluent, and 5 percent was degraded or otherwise removed from solution. Wilson concluded that chloroform, among other organic pollutants, is readily transported through soil. Groundwaters in the vicinity of soils of this sort used for land treatment would be susceptible to pollution.

Volatilization was a significant mode of chloroform loss in Wilson's study. In any land application project, especially a spray irrigation system, volatilization of chloroform and other THMs should be considered. Laboratory studies confirm the volatility of chloroform. Dilling

(1975) reported that in a 1 ppm stirred solution, 50 percent of the chloroform evaporated in 18 minutes, and 90 percent in 62 minutes.

Tare and Bokil (1982) studied the role of particle size distribution as a factor in wastewater treatment by soils. Although trace organics were not used as a parameter in this study, the conclusions in general may apply to the fate of such chemicals in land application systems. The finer soil fractions, i.e. clays and silts, with an average diameter of less than 0.75 um, greatly increased the removal efficiency of many parameters. However, the soil was deemed no longer feasible for wastewater application if the finer fraction exceeded 40 percent because percolation rate was greatly decreased.

CHAPTER 3

ADSORPTION BY SOILS

Adsorption is generally described as the concentration of a material at the interface between two phases. Land application of wastewater involves a liquid-solid system in which THMs are the adsorbate, water is the solvent, and soil in the adsorbent. The concentration of chloroform occurs at the interface between the water and the soil.

Two forces are important in adsorption. One is the degree of affinity between the adsorbate and the adsorbent, and the other is the lack of affinity of the absorbate for the solvent (Weber, 1972). Usually these two forces act together to produce adsorption. The role of the adsorbent is primary in land application systems.

Types of Adsorption by Soils

Two different types of adsorption occur between an organic adsorbate and a soil adsorbent. These are termed specific and non-specific adsorption (Morrill, 1982). Specific adsorption involves the reaction between charged sites on the adsorbent and molecules or reactive units of a certain configuration on the adsorbate. This is an important mechanism for many organic adsorbates. All other types of adsorption on soil are termed non-specific, and

include physical adsorption, hydrogen bonding, ion exchange, chemisorption, and coordination or non-ionic adsorption (Morrill, 1982).

Physical adsorption is present to some degree in all adsorption reactions, and is due to van der Waals forces between the adsorbate and adsorbent. Hydrogen bonding, which is a partial charge interaction, is a major mechanism for binding polar organic molecules to clay surfaces. Bonding occurs between the surface oxygen on clay surfaces, and water, carbonyl, NH, and other groups on the adsorbate.

Ion exchange, especially cation exchange, is the mode of adsorption that has been most extensively studied in soil science (Morrill, 1982; Fetter, 1980). It is important in adsorption reactions for both organic and inorganic molecules, and is often expressed as the cation exchange capacity, or CEC, in milliequivalents exchangeable cations per 100 grams soil. In this process, one type of ion in solution is exchanged for another type that is contained or adsorbed upon the adsorbent. Organic molecules may be ionized under certain pH conditions and adsorbed this way.

Coordination adsorption is seen in certain nonionic polar compounds. The coordination number refers to the number of atoms, ions, or groups that are directly attached to a central metallic ion or molecule. The type of metal ion contained within the clay molecule is a factor in this type of adsorption.

A specific adsorption mechanism for chloroform on soil is not described in the literature. Little work has been done on the adsorption by soils of straight-chain hydrocarbons, to which chloroform is structurally related (Morrill, 1982). Straight-chain hydrocarbons are nonpolar molecules, and do not compete well with water for sites on the exchange complex. Adsorption of this type of molecule is generally due to van der Waals forces, and takes place on the external surfaces of clay minerals. One may postulate that chloroform is adsorbed in a similar fashion.

Role of Adsorbent

Clay particles and organic material are the most important adsorption sites in clay systems. Metal oxides or hydroxides, mainly aluminum or iron, may also be sites of specific or non-specific adsorption (Morrill, 1982).

Clays are important in adsorption because they have a high surface area per unit mass, and significant surface electrical charge (Fetter, 1980). The surface charge arises from either isomorphous replacement within the clay lattice or broken bonds.

Both surface charge and specific surface area vary with the type of clay mineral. For example, montmorillonite clay has a specific surface area of 700-800 m^2/g, whereas kaolinite clay has a specific surface area of 25-50 m^2/g (Morrill, 1982). There is isomorphic substitution by various ions in montmorillonite, but none in kaolinite,

therefore montmorillonite clay has a higher surface charge. For these reasons montmorillonite is a more efficient adsorbent per unit weight than kaolinite. Thus the type of clay mineral, as well as the proportion of clay to other soil constituents, is a factor in adsorption.

Degree of adsorption is proportional to the fraction of adsorbent surface area available for adsorption. Decreased particle size and increased porosity of a solid both increase adsorption per unit mass of a given adsorbent (Weber, 1972).

Solvent-Solute Interactions

The lack of affinity between a solvent and an adsorbate, in this case between water and chloroform, helps to determine the degree of adsorption in any given system. This is mainly determined by the solubility of the adsorbate in the solvent (Weber, 1972). The less soluble, or more hydrophobic an adsorbate is in aqueous solution, the more it tends to be adsorbed. Chloroform has a moderately low solubility in water, 7950 ppm at 25° C (Kirk-Othmer, 1964), therefore it should be adsorbed.

Surface tension of an adsorbate compared to that of a solvent is also a factor in adsorption. Surface tension results from the attractive forces between molecules in a liquid. If an adsorbate is added to a solvent with a relatively larger surface tension, that adsorbate will decrease the surface tension of the sytem and will tend to

migrate to a surface or a boundary; that is, it will be adsorbed. This is because the solvent molecules have a larger attractive force for each other than for the molecules of the adsorbate (Weber, 1972). The surface tension of water is relatively high, 73.05 dynes/cm in air at 20° C, whereas the surface tension of chloroform in air is significantly lower, 27.14 dynes/cm at 20° C (CRC Handbook of Chemistry and Physics, 1972). Thus chloroform will tend to decrease the surface tension of water and be adsorbed at an interface.

Mode of Application of Adsorbate to Adsorbent

In a system of positive adsorption, the rate of adsorption depends on the concentration of adsorbate in solution. Adsorptive capacity of soils is usually determined by batch reaction, i.e. by shaking a known mass of soil in solutions of varying concentrations of adsorbate (Fetter, 1980). As adsorption proceeds, the concentration of adsorbate in contact with the soil decreases, and adsorption efficiency decreases. In a flow-through system like the one used in this study, fresh solution is fed continuously, and the concentration of adsorbate applied to a given increment of soil is relatively constant (Weber, 1972). Therefore one would predict that a column-type continuous flow reactor would be more efficient in adsorption.

Breakthrough Curve Analysis

In a fixed-bed, continuous flow system such as the one used in this study, adsorption efficiency is evaluated through analysis of a breakthrough curve. Concentration of adsorbate in solution is plotted against effluent volume or time. A generalized breakthrough curve is illustrated in Figure 1, along with a schematic drawing of the passage of an adsorption wave through a column. A concentration gradient develops in a column in the direction of flow (Perry, 1963). As adsorption sites in the upper layers of the column become occupied with adsorbate, the adsorption wave moves downward through the column (Figure 1, a). The movement of this adsorption wave or front is generally slower than the linear velocity of the fluid through the column. Even when the upper sections of the column are saturated, that is, have the same concentration of absorbate as the influent, the effluent concentration is substantially zero (Figure 1, b). As the adsorption front approaches the end of the column, concentration of adsorbate in the effluent begins to increase (Figure 1, c), and the column has reached breakpoint. Beyond breakpoint, concentration of adsorbate in the effluent continues to increase until it approaches concentration in the influent (Figure 1, d). At this point, adsorption capacity of the column is exhausted. The shape of the breakthrough curve varies with different

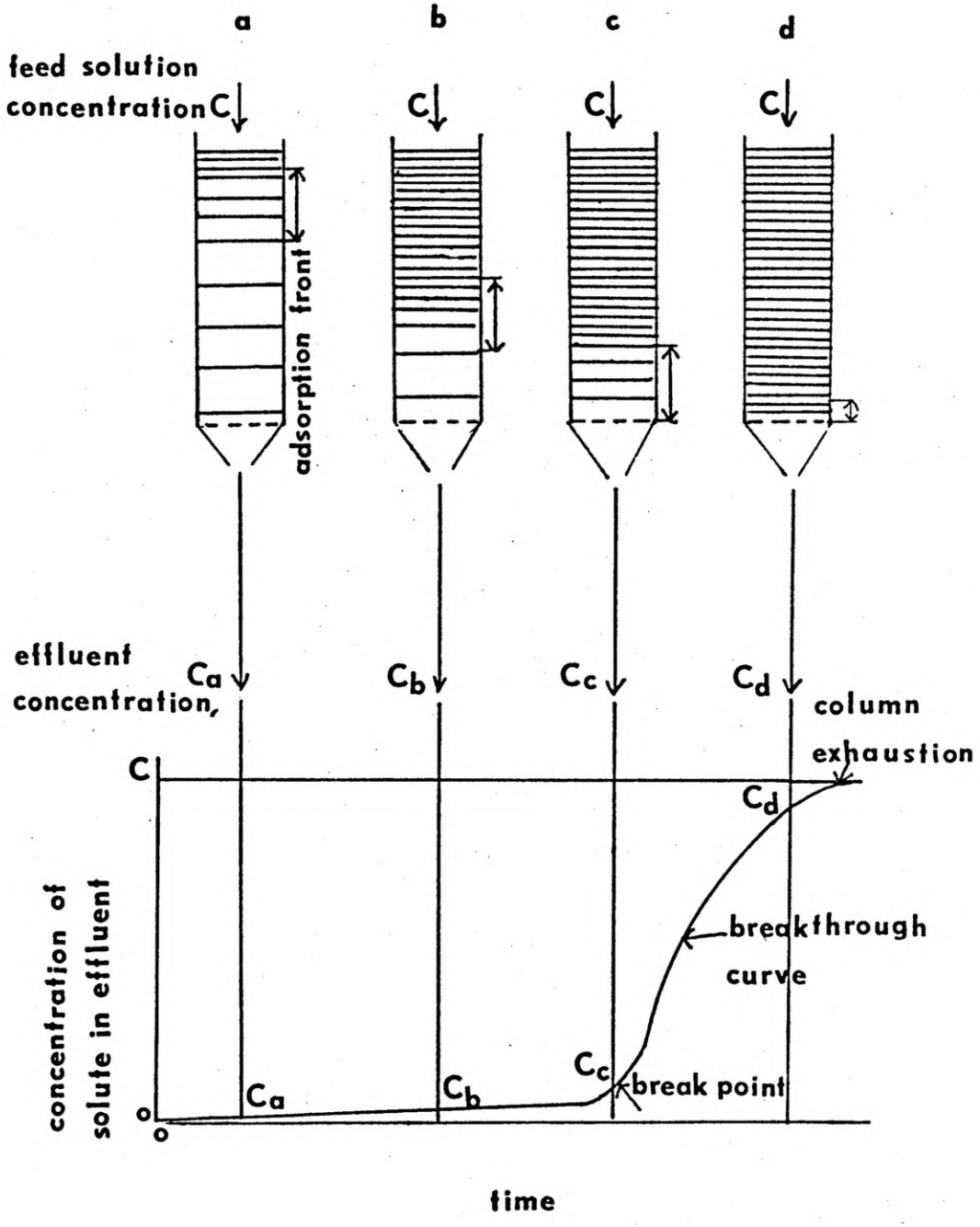

FIGURE 1: PASSAGE OF ADSORPTION FRONT THROUGH FIXED BED (PERRY, 1963)

systems, and is a function of fluid velocity, concentration of adsorbate in influent solution, and the rate and mechanism of the adsorption process.

CHAPTER 4

EXPERIMENTAL EQUIPMENT AND PROCEDURES

Apparatus

The experimental apparatus was modeled on a rapid infiltration system. It consisted of an acrylic tube, 61 cm in length and 7.3 cm inside diameter, which was filled with soil (Figure 2). Soil was held in place in the column by a nylon mesh placed between rubber gaskets. Chloroform solution was pumped through the soil at approximately the rate that water flowed through the column under gravity flow, 10.95 ml/minute for the first run and 11.50 ml/minute for the second run. A Sigmamotor 1/8 horsepower finger pump was used. The column was completely enclosed to prevent loss of chloroform due to volatiliztion. Sample withdrawal ports were located at four points along the column, at 11.4, 24.1, 36.8, and 49.5 cm from the top of the column. Each withdrawal port consisted of a large bore hypodermic needle, glued into a threaded plastic fitting and screwed into the side of the column. The tip of the needle extended into the center of the column, and was wrapped with fine gauge brass screen that was held in place with epoxy. The other end of the needle extended to the outside of the column, and was capped with a clamped piece of plastic tubing. Sample

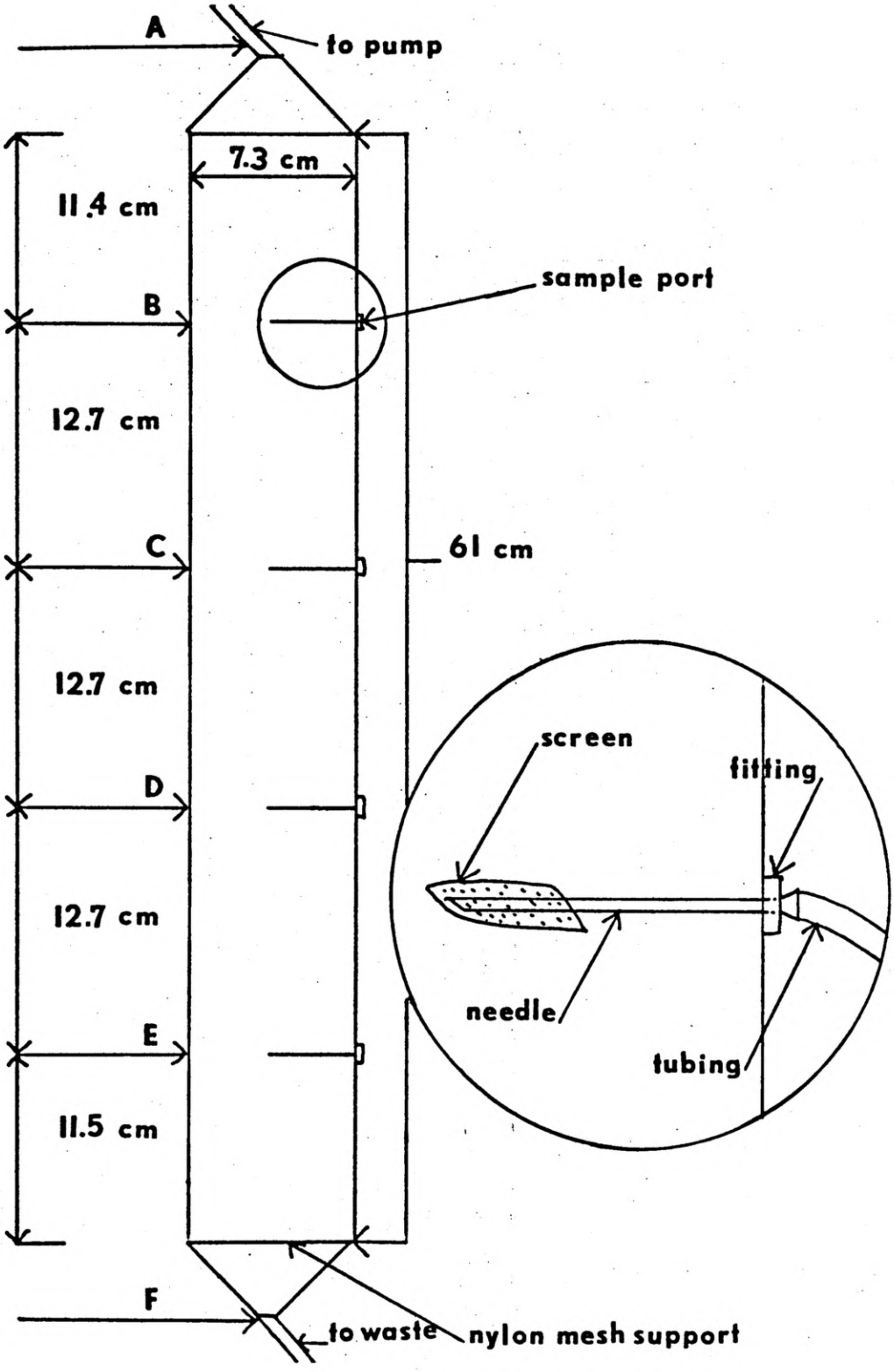

FIGURE 2: EXPERIMENTAL APPARATUS

collection points were also located at the column influent and effluent.

Soil Preparation

Soil used in both runs was prepared by first sieving through a #10 (2.00 mm) sieve to break up clods and remove debris, then igniting in a muffle furnace at 550° C for one hour to remove any remaining organic components. A standard hydrometer analysis was performed on the soils for particle size determination.

Preparation of Standards and Solutions

Glassware preparation, preparation of chloroform solutions and standards, extraction, and analysis were all performed according to procedures outlined in the EPA regulations on THM analysis (USEPA, 1979).

Chloroform-free water was produced by running distilled water through a Barnstead multipurpose column. Reagent grade chloroform was used for the standards and solutions; 2,2,4-trimethylpentane was the extraction agent (both chemicals from Burdick and Jackson, Muskegon, Michigan). The calibration standards and the chloroform solution applied to the column were prepared from a stock solution of chloroform dissolved in methyl alcohol (J.T. Baker, Phillipsburg, New Jersey), according to EPA specifications. Appropriate solutions were then made from the stock solution with the organic-free water. Both the water and the

extraction agent were analyzed prior to sample analysis to check for chloroform contamination.

Experimental Procedures

For the first run, a blank and duplicates of five calibration standards were run. The researcher attempted to withdraw samples from the column by removing the piece of plastic tubing from the end of the needle, attaching a 10 ml glass syringe, and withdrawing a sample. This plan had to be abandoned early in the run due to clogging and jamming of the syringe. However, column influent and effluent samples were collected at regular intervals. Transfer of samples to extraction vessels was also hampered by clogging of the syringe.

A blank and seven serial dilutions were used in the second run. In processing these standards and the samples from the column, the researcher had to deviate from standard procedures (USEPA, 1979; 4.8.i,f; 7.1-7.5). To avoid clogging problems experienced in sample collection in the first run, approximately 15 mls of sample were collected directly from the sample port into a beaker, and 10 mls were quickly pipeted from the beaker into an extraction vessel. Standards were handled in a similar manner to maintain a consistent procedure, using 10 ml volumetric pipets rather than syringes for the transfer step. EPA methods recommend using a syringe rather than a pipet for transfer in order to minimize contact between the sample and the atmosphere.

Chloroform and other THMs are volatile, and contact with the air may lead to sample loss. Interestingly, precision appeared to be improved, rather than degraded, by the use of pipets. Correlation coefficient (r) for the second curve was .998, compared to .82 for the first calibration curve.

Analysis

All samples and standards were analyzed on a Varian model 6000 gas chromatograph, using a ^{63}Ni electron capture detector. the capillary column was 0.255 mm internal diameter by 25 m length, packed with fused silica. An automatic integrator analyzed peak areas of samples and standards. Concentrations of samples were determined by comparison to a calibration curve developed from the standards. The electron capture detector responded linearly for the range of standards used, from 0 ug/L to about 200 ug/L.

CHAPTER 5

RESULTS

Table 1 summarizes properties of the soils used in two separate column analyses.

Table 1. Properties of Soils Used in Column Analyses

Property	Soil I	Soil II
Descriptive term	Loamy sand	Sandy loam
Size distribution:		
Sand: 2000-50 um	84%	77%
Silt: 50-2 um	14%	14%
Clay: Less than 2 um	2%	9%
Bulk density in column	1.75 g/cm^3	1.44 g/cm^3
Estimated porosity*	34%	46%
pH (15 g soil in 40 mls $CHCl_3$ sol'n)	7.1	7.4
Soil in column, g	4480.5	3666.0
Ave. applied $CHCl_3$ concentration	132 ug/L	118 ug/L
Estimated adsorption	35.7 ng/g soil	106.9 ng/g soil

*Estimated by dividing bulk density by average density of soil particle (2.65 g/cm), and subtracting from 1.

Breakthrough Curve, Soil I

Figure 3 illustrates the breakthrough curve for soil I. Chloroform concentration in the effluent increased with time

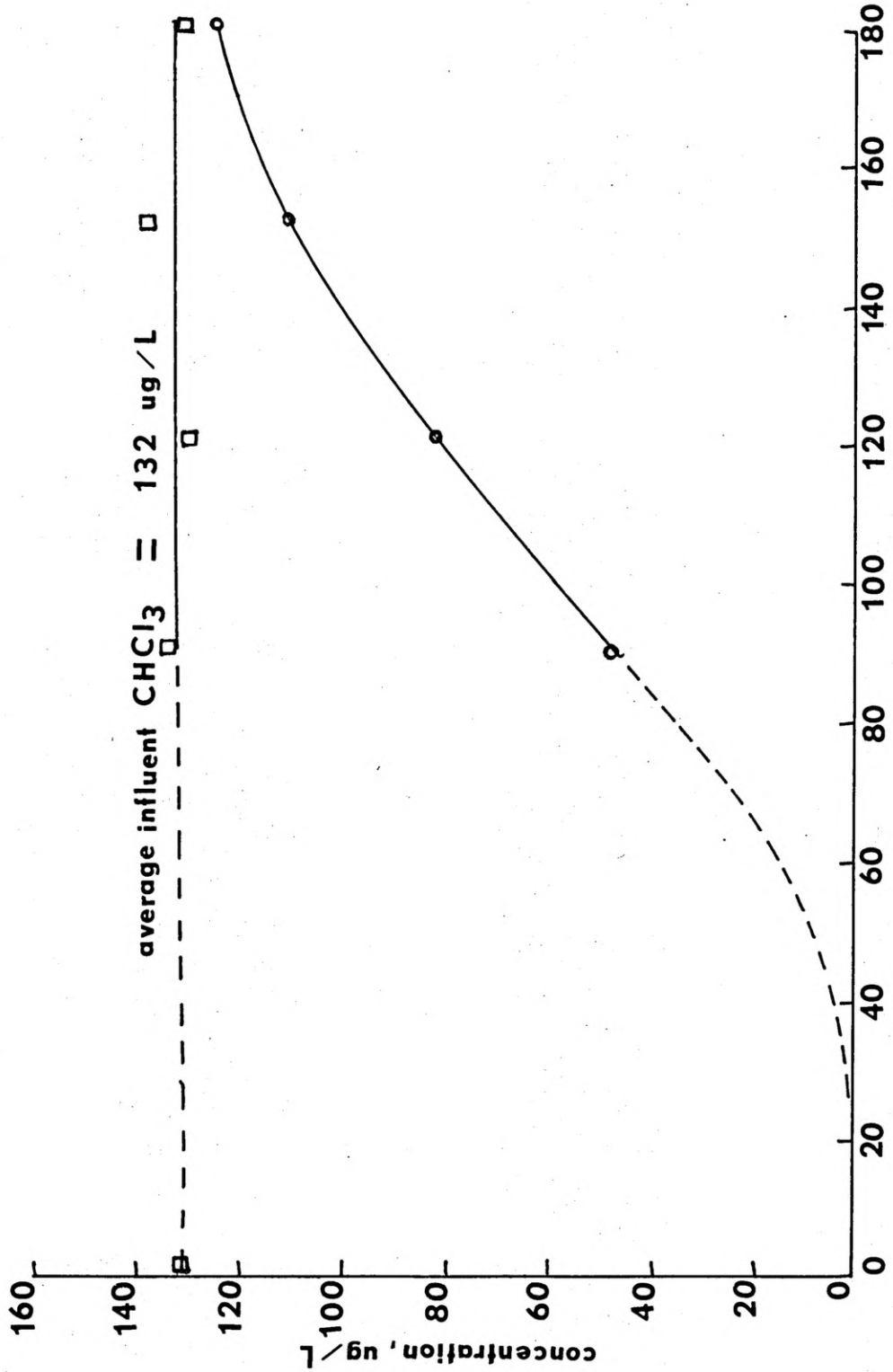

FIGURE 3: BREAKTHROUGH CURVE, SOIL I

until it approached the average influent concentration of 132 ug/L. Data points for 30 minutes and 60 minutes were lost in the gas chromatograph analysis step, therefore the approximate curves between 0 and 90 minutes are indicated by a broken line. Data in Table 2 were used in drawing the breakthrough curve.

Table 2. Changes in $CHCl_3$ Concentration, ug/L, with Time, Soil I.

Time, minutes	Point A	Point F
0	132	0
30	-	-
60	-	-
90	136	50
120	127	80
150	140	115
180	126	125

Determining q

In order to assess the average adsorption per gram of soil during the run, the area under the breakthrough curve is numerically integrated:

$$\int C(t)\,dt = \text{concentration that passed through column over a given period of time (not adsorbed).}$$

$$\begin{pmatrix}\text{total concentration applied over time}\end{pmatrix} - \begin{pmatrix}\text{concentration that passed through column column over time}\end{pmatrix} = \begin{pmatrix}\text{concentration that was adsorbedover time, in ug·min/L}\end{pmatrix}$$

concentration adsorbed over time	X	average flow rate	=	
ug·min/L	X	L/minute	=	ug $CHCl_3$ adsorbed

Dividing this value by the mass of soil in the column yields a value for q, in ug/g; multiply by 1000 for q in ng/g.

Therefore:

$$\int C(t)dt = 9162.5 \text{ ug·min/L}$$

Total chloroform applied in 180 minutes:

132 ug/L X 180 minutes = 23,760 ug·min/L

23,760 ug·min/L - 9162.5 ug·min/L = 14,597.5 ug·min/L

14,597.5 ug·min/L X .01095 L/min = 159.8 ug $CHCl_3$

159.8 ug ÷ 4480.5 g soil =

.0357 ug/g, or 37.7 ng/g = q

Determining Front Velocity

Fluid velocity through the saturated soil can be estimated through data on porosity and flow rate:

total cross-sectional area	X	porosity	=	cross-sectional area of voids

velocity through the voids = flow rate
- cross-sectional area of voids

Therefore:

$$41.85\ cm^2 \times .34 = 13.23\ cm^2$$

$$10.95\ mls/min = 10.95\ cm^3/min$$

$$\text{and } 10.95\ cm^3/min \div 13.23\ cm^2 = .77\ cm/min$$

The time required for chloroform to move through the column is estimated by dividing the column length by the time for $CHCl_3$ to appear in significant amounts in the effluent:

$$61\ cm/90\ minutes = .68\ cm/minute = \text{front velocity}$$

The water moved through the column about 1.13 times faster than the chloroform.

Breakthrough Curves, Soil II

Figure 4 illustrates three partial breakthrough curves for soil II, representing appearance of chloroform in solution over time for collection points B, C, and D (See Figure 2). Adsorption in this soil was much greater than had been predicted, and column exhaustion was not observed at any sample collection point, even after three hours. Table 3 contains data used in drawing the curves.

Adsorption values from the partial breakthrough curves were calculated through numerical integration, as

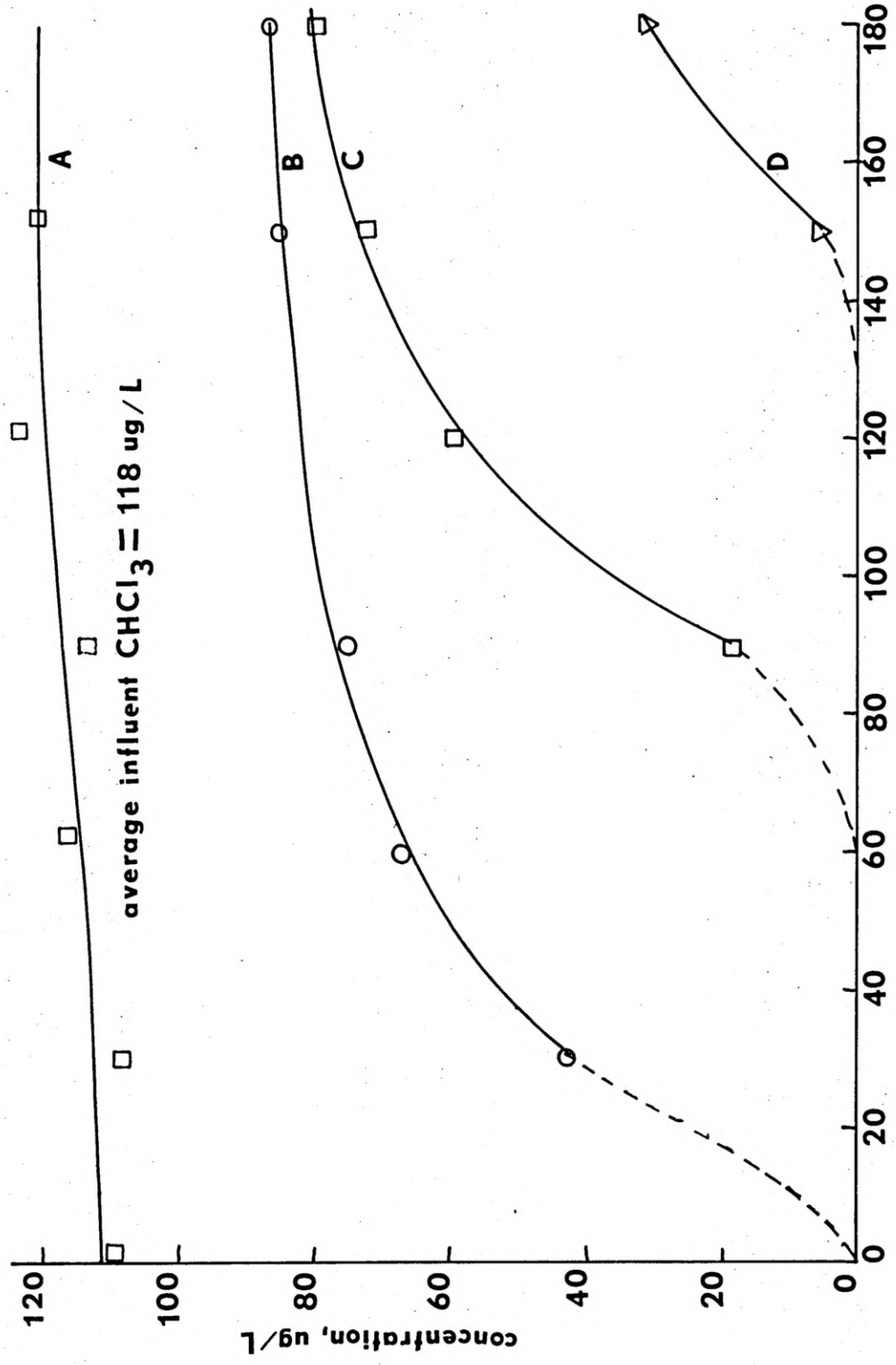

FIGURE 4: BREAKTHROUGH CURVES, SOIL II

demonstrated for soil I (See Table 4). From these calculations, a value of q for a section of soil between sampling points can be estimated. For example:

(ug adsorbed between A & C)	-	(ug adsorbed between A & B)	=	(ug adsorbed in B - C)
177.4 ug	-	108.8 ug	=	68.8 ug

$$68.6 \text{ ug} \div 766 \text{ g soil} \times 1000 = 89.6 \text{ ng/g (q for section B-C)}$$

These results are presented in Table 5.

Table 3. Changes in $CHCl_3$ Concentration, ug/L, with Time, Soil II.

Time Minutes	Point A	B	C	D	E	F
0	115.09	0	0	0	0	0
30	108.63	43.29	0	0	0	0
60	118.37	67.47	0	0	0	0
90	114.71	75.49	20.44	0	0	0
120	124.18	-	59.19	0	0	0
150	115.08	86.19	71.87	5.93	0	0
180	129.76	86.35	78.18	30.76	0	0

Discussion of Results

Soil I was included in an earlier batch reactor adsorption study (Liltved, 1983). Results from that investigation will be used for comparison and interpretation of column test results. Soil II was not in the original study, and only general comparisons can be made.

Table 4. Calculated Values from Breakthrough Curves, Soil II.

Soil Section	Area of Curve, ug·min/L	Avg $CHCl_3$ applied (118 ug/l X 180 min)	ug/L Adsorbed (for 180 min. at .0115 L/ min.)
A - B	11,782.5	21,240	108.8
A - C	5,812.5	21,240	177.4
A - D	622.5	21,240	237.1

Table 5. Adsorption Efficiency for Soil Section Soil II

Soil Section	Adsorption, ug	Soil mass, g	q, ng/g soil
A - B	108.8	687	158.4
B - C	68.6	766	89.6
C - D	59.7	765	78.0

Soil I. According to Liltved's results, this soil adsorbed 31.5 ng/g following application of 129 ug/L $CHCl_3$ (Liltved, 1983, Table 5). This value compares very well to q = 35.7 ng/g at an initial concentration of 132 ug/L chloroform for the column reactor. Both the batch reactor and the fixed bed flow-through reactor yielded similar results in this case. In the general discussion on adsorption, it was stated that a flow through reactor is theoretically more efficient, because adsorption efficiency is a function of concentration and a flow-through reactor provides a continuous supply of fluid with a high adsorbate

concentration. However, other factors may come into play to decrease the efficiency of a flow-through reactor. Development of an extended adsorption front or concentration gradient may decrease efficiency. Swelling of clay particles in a column reactor may decrease porosity and thus decrease surface area available for adsorption. Swelling would not have the same effect in a batch reactor.

Breakpoint was reached rapidly with this soil, some time before 90 minutes. Within 180 minutes, the column was approaching exhaustion. Chloroform moved rapidly though the soil column, with an estimated retardation factor of 1.13. That is, water moved through the soil 1.13 times faster than chloroform. This compares well to results obtained by Wilson (1981) on a column study of a similar soil. In a soil that was 92 percent sand, 6 percent silt, and 2 percent clay, he established a retardation factor on the movement of chloroform through soil to be less than 1.5. In the injection well study discussed under land treatment systems, researchers reported that water moved through the aquifer at about five times the speed of chloroform (Roberts, 1978). In comparison, chloroform indeed moved rapidly through this soil.

Soil II. There were no batch reactor results for comparison to soil II. However, a comparison was made on the basis of clay content alone with the loam soil used in the batch test (Liltved, 1983). This soil contained 14

percent clay by weight, while soil II contained 9 percent clay by weight. If clay content were the only factor in adsorbance, the loam soil from Liltved's study should have adsorbed more than soil II. At an initial concentration of 118 ug/L, adsorption was approximately 35 ng/g for the loam, a q value not much greater than that for soil I. On the basis of these predictions, three hours should have been adequate time for the coumn to reach exhaustion, at least in the upper sampling points.

When results were analyzed, it was apparent that the adsorptive capacity of soil II was much greater than anticipated. In 150 minutes, chloroform was just beginning to appear at sample point D, 36.8 cm from the top of the column (See Figure 4). Average adsorption for the portion of the column between points A and D was 106.9 ng/g over three hours' time.

Soils in this study were only analyzed for sand, silt, and clay fractions. Clay types were not determined. It is this researcher's opinion that different clay types probably accounted for the great differences in adsorption between soil II used in the column test and the loam soil used in the batch test. Presence of metal oxides and hydroxides, which also serve as adsorption sites, could also have accounted for some of the differences.

In addition, pH of the soil-chloroform solution in the batch study was 9.5 (Liltved, 1983), while the pH of the

soil-choloroform solution used in the column study was 7.4. Adsorption may be influenced by pH for a variety of reasons; adsorption of organics from water is generally increased with decreased pH (Weber, 1972). The lower pH in the soil II adsorption system possibly improved adsorption in this case.

The difference in adsorption between soils I and II can be explained as a function of clay content (2 percent as opposed to 9 percent) and also as a function of porosity (34 percent and 46 percent respectively). Porosity is the ratio between the volume of void space to a total volume of earth material. Certain clay-rich soils have a high porosity due to electrostatic charges on clay surfaces that cause the particles to be repelled by each other (Fetter, 1980). Particle shape and orientation also influence porosity. Increased porosity leads to an increase in available surface area for adsorption.

The difference in adsorption between soils I and II was probably not due to pH. Soils I and II in chloroform solution had similar pH values, 7.1 and 7.4 respectively, and were both in the neutral range.

When adsorption was analyzed for separate sections of the column (see Table 5), each section being that portion between two sampling points, it was evident that adsorption per gram soil decreased with depth. The top section A-B had a q value of 158.4 ng/g, q was 89.6 ng/g for section B-C,

and 78.0 ng/g for section C-D. This indicated that there was a concentration gradient within the adsorption front and as concentration decreased with depth, adsorption efficiency also decreased. None of the sections became saturated with chloroform; that is, effluent chloroform concentration did not approach influent concentration for any of the sampling points.

CHAPTER 6

CONCLUSIONS

In conclusion, soil I showed limited adsorption and rapid adsorption front velocity. Soil II showed approximately three times the adsorptive efficiency of soil I, for that portion of the column penetrated by the adsorption front. Because none of the sampling points for soil II approached the initial chloroform concentration, front velocity could not be estimated. Higher percent clay by weight and greater porosity probably accounted for enhanced adsorption by soil II.

Soil II had a much higher q value than a loam soil with a greater clay content, which was used in an earlier batch study. This was probably due to differences in clay minerals and pH of reaction solution. Decrease in q values with increased column depth for soil II indicated a concentration gradient within the adsorption zone.

These conclusions are very general, and if one were to evaluate the applicability of a specific soil for land treatment of chloroform, many other factors besides texture, porosity, and pH would have to be evaluated. To quote Morrill:

> "Many researchers have attempted to correlate adsorption with soil properties (percent clay, clay type, organic material, cation exchange capacity, pH, surface area, and others) and have come to a variety of conclusions...In evaluating the influence of soil characteristics on the fate of organic compounds in soil, it should be recognized that soil components do not exist as discrete entities, but as intricate complexes or mixtures, responding as one hetergeneous reactive surface."

In evaluating a soil or a site for land application of chloroform in a laboratory study, other considerations might be:

1. Application of chloroform in a solution that is chemically similar to the wastewater in question. If there are significant amounts of other solutes in solution, adsorption of chloroform will be decreased (Weber, 1972).
2. Evaluation of the effects of other solutes on the aggregation properties of that soil. For example, application of Na^+, which is commonly found in wastewater, to soil may cause a well aggregated soil to become more dispersed over time, which would cause a decrease in porosity and a decrease in surface area available for adsorption (Hillel, 1982).
3. Evaluation of the significance of other removal mechanisms, such as volatilization and biodegradation, over a period of time.

This researcher recommends that wastewater containing chloroform should be land treated only in a system such as described by Tomson (1981), where renovated water is recovered and held before discharge, and evaluated for the presence of harmful constituents. Although it is possible that a land treatment system may effectively "degrade, transform, or immobilize" chloroform, evidence to date is not conclusive and one would not want to risk groundwater contamination.

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