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FATE OF PERCHLOROETHYLENE IN UNSATURATED SOIL ENVIRONMENTS

BY

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FATE OF PERCHLOROETHYLENE IN UNSATURATED SOIL ENVIRONMENTS

by

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ABSTRACT

Studies were undertaken to evaluate the behaviour of perchloroethylene, PCE, in unsaturated soil to provide remedial actions for minimizing the possible soil and groundwater contamination after a spill. Processes that were investigated included volatilization from water and soil, determination of degradation potential, evaluation of adsorption - desorption isotherms for various granular media and the simulation of a PCE spill on a soil column. Results were then used to calibrate a contaminant transport model.

Sandy loam soil, organic top soil, peat moss and granular activated carbon, GAC, were investigated for adsorption - desorption properties. It was determined that the adsorption - desorption processes were well represented by the Freundlich Isotherm. The governing factor in adsorption was the organic carbon content. The higher the organic carbon content, OC, the greater was the adsorption and retention of PCE by the medium. In dividing the K_f coefficient with the OC content, a K_{OC} of 330 L/mg was determined which indicates that PCE has medium mobility in soil. Results on residual saturation values for the four media indicated that peat moss could retain the highest quantity of pure PCE, 7.8 kg/kg, making it ideal for application at a spill site to retain the chemical. Desorption did not increase with a decrease in pH of the aqueous solution.

The experiments on volatilization of PCE from water indicated that this rate was rapid and that it was influenced by the area to volume ratio, A/V. The volatilization rate increased with an increase in A/V. The overall liquid film coefficient for the water-air interface was 0.009 m/h. Volatilization from soil was also a function of area to volume ratio. However, it was observed that the OC content of soil influenced the volatilization rate. The volatilization rate decreased with an increase in OC content. The mass flux experiment indicated that submerged PCE followed a first order mass transfer rate, with a flux rate of 0.028 kg/m^2/d. At the chemical-water interface the overall liquid film coefficient was found to be 0.006 m/h.

Equations for the prediction of breakthrough times in soil were determined. The soil properties greatly influenced the penetration distance and the front velocity. Under a 76 mm/d rainfall intensity, the PCE moved at 0.084 m/d and 0.026 m/d in the sandy loam soil and organic top soil respectively. The calibrated contaminant transport model for unsaturated soil predicts the breakthrough time and PCE concentrations. Furthermore, the model and column studies showed that the immiscible phase movement had a significant impact on the PCE concentrations observed in the soil profile.

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CHAPTER ONE

INTRODUCTION

1.1 Nature of the Problem

The number and quantity of synthetic chemicals being produced have been increasing steadily to meet the needs of society. During the past forty years more than 40,000 compounds have been manufactured and the number is increasing annually [Wilson et al., 1981]. These chemicals are being constantly released into the air, water and soil environments through manufacture, use and transport activities. Through these releases the exposure to humans is increased, which can cause detrimental health effects [Cohen, 1986]. Therefore, it is very important to understand how pollutants are released into the environment and how they react with various media, so that the health risks can be minimized.

Of all the synthetic compounds that currently exist in the environment, volatile organic compounds, VOCs, are at the forefront of concern because of their severe toxic effects [Sittig, 1985]. These effects include headaches, nausea, central nervous system disorders, blindness and even death when concentrations are sufficiently high [Keil, 1978 and Council on Environmental Quality, 1981]. Furthermore, many VOCs have shown evidence of animal or human carcinogenicity, mutagenicity and teratogenicity [National Cancer Institute, 1977]. Some VOCs can even be bioconcentrated [Block et al., 1984]. Unfortunately, this family of chemicals is experiencing large growth in production and usage because of the many industrial and domestic applications. The major applications include usage as refrigerants, fumigants, dry cleaning solvent, metal degreasing agent and air fresheners [La Poe, 1985].

Many VOCs are being released to the soil environment through improper waste disposal practices, including industrial impoundments, landfills and spreading of sludges on land [Roberts et al., 1982]. Additional sources of soil contamination include land treatment of wastewater, accidental spills during transport and handling, leaking storage tanks, applications of fertilizer and pesticides and septic tank cleaning [Asano, 1985 and Pye, 1983]. Once released to the soil, the VOCs migrate toward the groundwater. As such, the incidence of the contamination of the groundwater supplies is increasing [McCarty et al., 1981]. The severity of the problem has been recognized by Environment Canada [Mansfield, 1987] and the United States Environmental Protection Agency [1982]. What makes this type of contamination even more important is the fact that during the past two decades, the usage of groundwater in North America has been growing at an annual rate of 3.8 percent [Asano, 1985].

One of the most frequently found volatile organic compounds in groundwater supplies is perchloroethylene, PCE. In mutagenicity and teratogenicity [National Cancer Institute, 1977]. Some VOCs can even be bioconcentrated [Block et al., 1984]. Unfortunately, this family of chemicals is experiencing large growth in production and usage because of the many industrial and domestic applications. The major applications include usage as refrigerants, fumigants, dry cleaning solvent, metal degreasing agent and air fresheners [La Poe, 1985].

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One of the most frequently found volatile organic compounds in groundwater supplies is perchloroethylene, PCE. In the environmental conditions in water and soil. An experimental program was developed to determine these coefficients under different conditions. Two types of soil were chosen to gather information about PCE in soil. One was a sandy loam soil and the other a organic top soil, which had a higher organic carbon content. Two other media, peat moss and granular activated carbon, were also investigated during the adsorption/desorption phase, to characterize the effect of organic carbon on adsorption.

The tests were conducted with different initial PCE concentrations using the batch equilibrium method, a modified soil perfusion apparatus and soil column studies. This approach allowed the determination of both temporal and spatial variations in concentrations that occurred in the perfusion and column systems.

Analysis of the data provided rates of volatility of PCE for soil and water, the mass flux of submerged PCE into stagnant water, degradation/non-degradation in soil, adsorption /desorption on various media, leachability according to Regulation 309 [Government of Ontario, 1985] and the migration of PCE in soils. Then these rate coefficients were used in a contaminant transport model that was calibrated to account for all phases of PCE migration in unsaturated soil. This model, written for use on an IBM compatible microcomputer, is capable of predicting the breakthrough time and concentration of PCE at any depth below the soil surface for the types of soil tested.

CHAPTER TWO

LITERATURE REVIEW

2.1 Manufacture and Use of Perchloroethylene

Perchloroethylene, C_2Cl_4, was first prepared in 1821 by Faraday, through thermal decomposition of hexachloroethane [Keil, 1978], to satisfy research curiosity. Production, for commercial use as a dry cleaning agent, began before World War I in the United Kingdom and Germany, followed by the United States in 1925. Since 1960, there has been tremendous growth in production rates, roughly seven per cent per annum [Barbash and Roberts, 1986], to meet the industrial demand. The world production capacity and demand can be seen in Table 2-1 [Keil, 1978].

Table 2-1 PCE World Production Capacity and Demand in Thousands of Metric Tonnes

Area	Capacity	Demand
USA	474	331
Europe	517	431
Japan	83	57
Canada	26	15
Latin America	1	11
	1101	845

For many years perchloroethylene was produced almost exclusively from acetylene and chlorine via trichloroethylene [Keil, 1978]. However, because of the high cost of recovery of chlorine, other hydrocarbons are now employed as feedstocks. These include methane, ethane, propane or higher paraffins. The typical reactions that result are as follows:

$$CH_3 - CH_2 - CH_3 + 8Cl_2 \rightarrow CCl_2{=}CCl_2 + CCl_4 + 8HCl$$

$$2CCl_4 \rightarrow CCl_2{=}CCl_2 + 2Cl_2$$

In this process, Figure 2-1, chlorine, a light hydrocarbon and several recycle streams are mixed and fed to a chlorination furnace which is maintained at 550-700°C [Keil, 1978]. The products are carbon tetrachloride and perchloroethylene; the latter is probably formed largely by pyrolysis of the former. The effluent gases from the chlorinator are quenched, after which the chlorinated hydrocarbons are separated from the quenching medium in a blow-back column. The mixture of chlorohydrocarbons is then fractionated, and the more volatile carbon tetrachloride is recycled to the furnace. The crude perchloroethylene in the bottom fraction is purified by distillation, and the residues from this operation are also recycled to the chlorination furnace. The overall yield of perchloroethylene is more than 95%, based on chlorine consumption. Ethane is preferred for this process in the United States since it is the least expensive raw material.

PCE can also be manufactured through the use of ethylene dichloride [Keil, 1978]. Here perchloroethylene is a co-

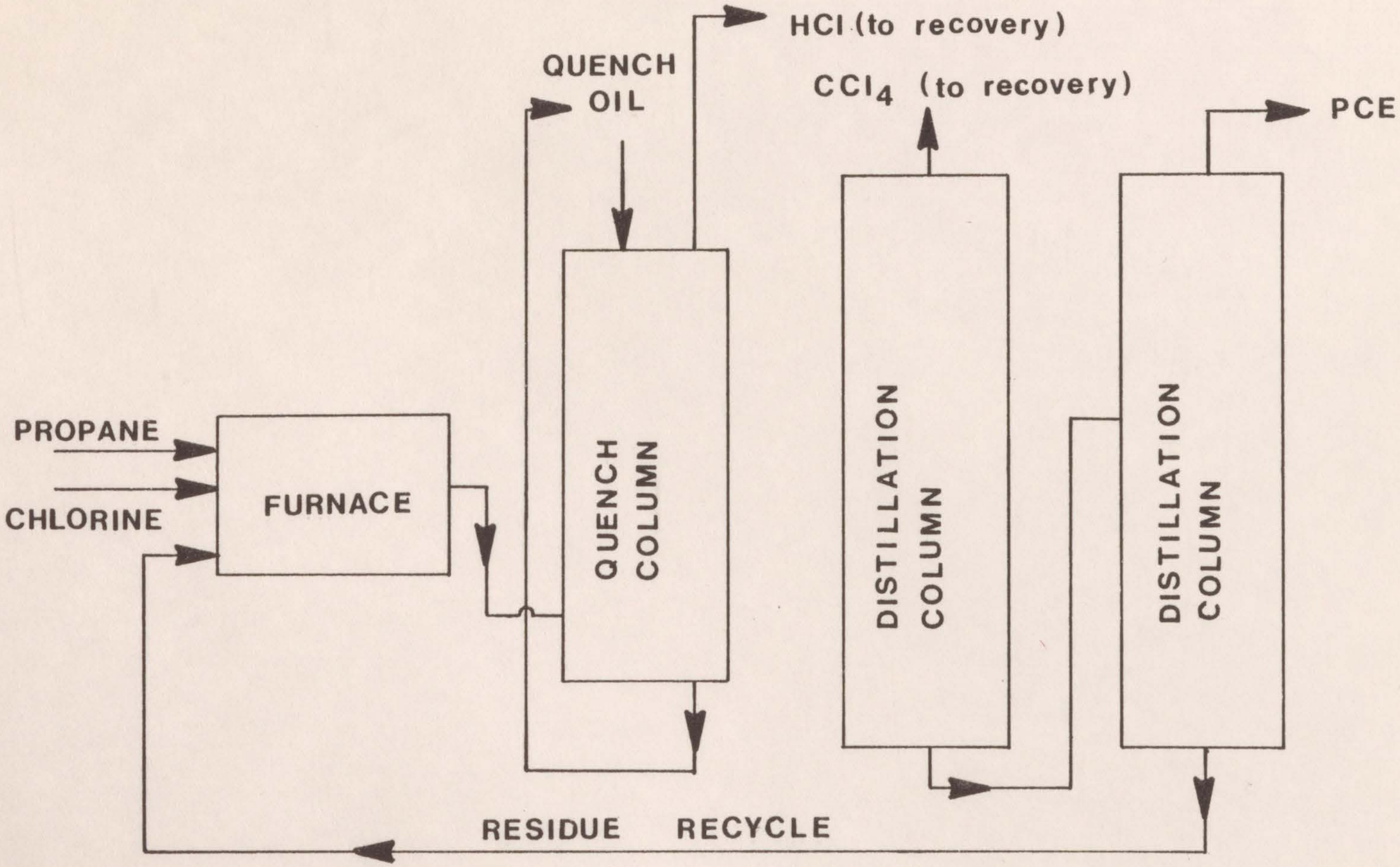


Figure 2-1 PCE PRODUCTION FROM PROPANE AND CHLORINE
[KEIL, 1978]

product with trichloroethylene in the single-stage oxychlorination of ethylene dichloride with chlorine. The ratio of trichloroethylene to perchloroethylene can be varied to some degree by adjusting mole feed ratios of ethylene dichloride, chlorine and oxygen. The reactions are as follows:

$$2ClH_2C - CH_2Cl + 5Cl_2 \rightarrow Cl_2HC - CHCl_2 + Cl_3C - CHCl_2 + 5HCl$$

$$Cl_2HC - CHCl_2 + Cl_3C - CHCl_2 \rightarrow Cl_2C{=}CHCl + 2HCl + Cl_2C{=}CCl_2$$

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2$$

overall:

$$8ClH_2C - CH_2Cl + 6Cl_2 + 7O_2 \rightarrow 4ClHC{=}CCl_2 + 4Cl_2C{=}CCl_2 + 14H_2O$$

As shown in Figure 2-2 [Keil, 1978], ethylene dichloride, chlorine, oxygen, steam and recycled chlorinated compounds are fed to a fluid-bed reactor employing an inexpensive oxychlorination catalyst such as potassium chloride and cupric chloride. The reactor is maintained at about 425° C and a pressure of 138-207 kPa. In the reactor, the feedstock can be either ethylene or chlorinated hydrocarbons, alone or in various combinations, to yield trichloroethylene, perchloroethylene or a mixture of the two.

After vent scrubbing, the condensed crude product and the weak hydrochloric acid by-product are separated and the crude product is dried by distillation. In the tetrachlor-trichlor column, the crude product is split into two streams,

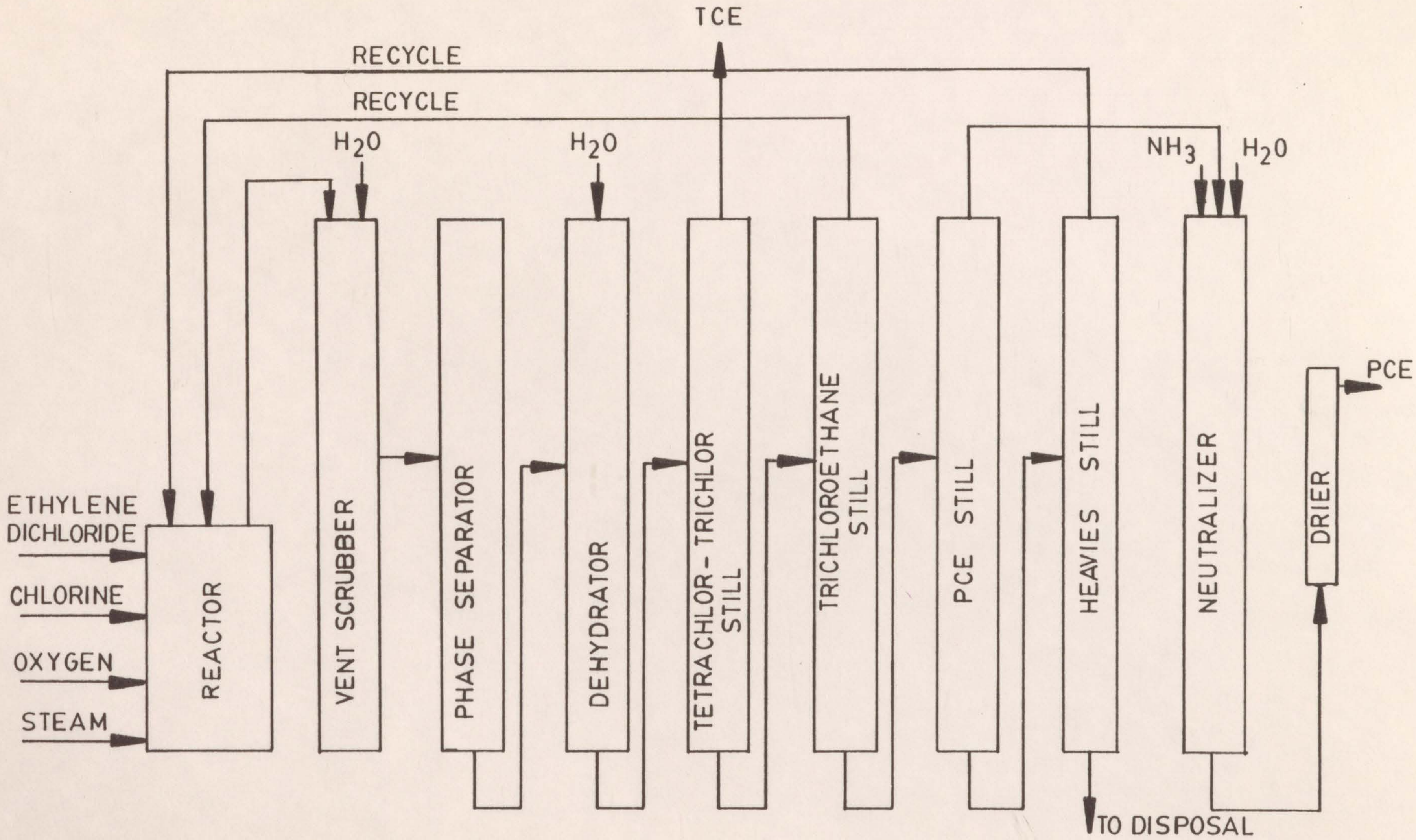


Figure 2-2 FLOW DIAGRAM OF THE SINGLE-STAGE OXYCHLORINATION PROCESS [KEIL, 1978]

one rich in trichloroethylene and the other in perchloroethylene. The latter, containing trichloroethane, perchloroethylene and components with boiling points higher than perchloroethylene is fed to the trichloroethane still. The overheads from this column are fed to the perchloroethylene column. The overhead from this column is over 99.9 % pure perchloroethylene; it is neutralized with ammonia, washed and dried. The bottoms from the perchloroethylene column are fed to a column that removes the heavier tars and carbon; the overheads are recycled to the reactor. About 35 percent of the PCE produced in the United States is made from ethylene dichloride [Keil, 1978].

The major use of PCE is in drycleaning. Other applications are vapour degreasing, cold cleaning of metals, textile processing and finishing and as a chemical intermediate in the manufacture of several fluorocarbons [Keil, 1978]. The various usage percentages are shown in Table 2-2. Previously perchloroethylene had also been used as a component in the manufacture of an anesthetic drug and other consumer products [Sittig, 1985]. However, with the toxicity data currently available, these uses have been eliminated.

2.2 Properties of Perchloroethylene

PCE is a non-flammable liquid with a pleasant ethereal odour and the most stable of the chlorinated ethanes and ethylenes, requiring only a small amount of stabilizers [Keil, 1978]. Perchloroethylene's important physical properties are listed in Table 2-3, while nomenclature and other information can be found in Table 2-4.

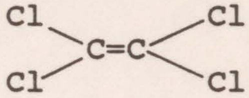
Table 2-2 Breakdown in PCE Usage
[Keil, 1978]

Activity	Percent Usage
drycleaning	66%
textile processing	13%
metal degreasing	13%
fluorocarbons manufacture	3%
miscellaneous	5%

Table 2-3 Physical Properties of Perchloroethylene

Property	Conditions	Value	Source
Boiling Point	@ 101kPa	121.2°	Keil, 1978
Melting Point		-22.7°C	Keil, 1978
Vapour Pressure	@ 15°C	0.932 mPa	Keil, 1978
	25°C	0.839 mPa	
	50°C	0.657 mPa	
Vapour Density	@ boiling point	5.8 kg/m^3	Keil, 1978
Specific Gravity	@ 10°C	1.63120	Keil, 1978
	20°C	1.62260	
	30°C	1.60640	
	120°C	1.44865	
Octanol/Water Partition Coefficient (K_{ow})		398	Chiou <u>et</u> <u>al</u>., 1977
log K_{ow}		2.6	
Solubility in 100g H_2O	@ 20°C	15 mg	Keil, 1978
Henrys' Law Constant	@ 20°C	0.535	Yurteri <u>et</u> <u>al</u>., 1987

Table 2-4 PCE Nomenclature

Parameter	Value
Common Names	tetrachloroethylene perchloroethylene carbon dichloride ethylene tetrachloride perclene tetrachloroethene
CAS Registry Number	CAS 127-18-4
Empirical Formula	C_2Cl_4
Structural Formula	
Molecular Mass	165.83

Sources
Sittig, 1985
Keil, 1978
Sax, 1984

2.3 Health Effects of Perchloroethylene

Through various health effect studies performed on PCE by government agencies, it has been observed that PCE has toxic affects on humans [Sittig, 1985 and Keil, 1978]. As a result, Transport Canada has labeled PCE a Poisonous Substance [1985]. Likewise, the Environmental Protection Agency, EPA, in the United States of America has included PCE on the list of priority pollutants [Callahan et al., 1979].

The toxicity of PCE is mainly a function of its anesthetic effect on the central nervous system [Keil, 1978, Sittig, 1985 and Sax, 1984]. As a central nervous system depressant, PCE causes headache, vertigo, tremors, nausea and vomiting, fatigue and unconsciousness. Anesthetic effects have been observed after two hours at concentrations of 280 ppm in air, while unconsciousness occurs in 30 minutes, when exposed to concentrations of 1500 ppm and greater. Over exposure can result in death.

Presently the 8-Hour Time Weighted Average, TWA, is 335 mg/m^3 (50 ppm), with a Short Term Exposure Limit, STEL, of 1340 mg/m^3 (200 ppm) [Cheminfo, 1987]. TWA is defined as the concentration for a normal 8-hour workday for a 40-hour work week. The STEL is defined as the 15-minute time weighted average exposure which should not be exceeded at any time of the workday. Exposure at STEL should not exceed 15 minutes and should not be repeated more than 4 times per day. The time between successive exposures should be at least 60 minutes. The STEL is recommended to prevent anesthetic effects, while both levels provide a wide margin of safety for prevention of liver injury. Rampy et al. [1978] observed no tumorigenic response on rats when exposed to vapours containing 300 or 600 ppm of PCE for 6 hours/day, 5 days/week for one year, over an entire lifetime.

For oral ingestion, Blair et al. [1979] observed tumors in mice due to metabolizing of PCE. Similarly, the PCE can cause cancer in mice but not rats [Wakeham et al., 1977]. Perchloroethylene has a LD_{50} of 8.85 mg/kg for rats, based on test animal body mass [Naylor and Loehr, 1982]. When using the scale proposed by Naylor and Loehr [1982], this level indicates a relative toxicity of two. A value of one is considered practically non-toxic while six is considered supertoxic. In the case of fish, a 96 h LD_{50} of 12.9 mg/L and 4.8 mg/L was determined for Bluegill Sunfish and Rainbow Trout respectively [Alexander et al., 1978]. An oral dose of 500 mg/kg did not produce death in humans [CCOHS, 1985]. Furthermore, when PCE is handled as a solvent or slightly diluted by water, it can cause dermatitis, especially when skin is exposed for an extended period [Sax, 1984].

These observations have resulted in a Recommended Maximum Contaminant Level, RMCL, being set for water [Federal Register, 1985]. For PCE occurrences in drinking water supplies, a zero RMCL has been set. However, once supplies like groundwater become contaminated, a zero concentration cannot be reached due to the adsorption of the compound on the aquifer material. Therefore, some risk must be accepted. Risk is set as either; (a) the probability that an individual exposed to a unit dose rate of a carcinogen throughout his or her lifetime will develop cancer, or (b) the additional incidence of cancer may be expected in an exposed population [Block et al., 1984]. The magnitude of risk is the same, but can be expressed from two different perspectives. For example a risk of 10^{-6} indicates that there will be one additional case of cancer for every one million people exposed. Using this risk level, the EPA has set the level for PCE in drinking water 0.8 μg/L. The EPA has also proposed a Suggested No Adverse Response Level, SNARL, of 40 μg/L over a lifetime of exposure, but this is currently under review. An important fact to remember is that for these suggested levels, no consideration was given to possible synergistic effects.

2.4 Occurrence of PCE in Groundwater

In a Groundwater Supply Survey carried out by the EPA Office of Drinking Water from December 1980 to December 1981, volatile organic compounds, VOCs, including PCE, were found to exist in drinking water wells [U.S. EPA., 1982]. These wells were located in 34 states across the country, and had in some instances concentrations of VOCs high enough to require their closure. Since then, eight more states have detected VOCs in various groundwater supplies [Pye et al., 1983].

This frequency of contamination of groundwater by VOCs is directly related to the rapid growth in production and general use of synthetic organic chemicals. For example, in the United States an estimated 19.5 million homes have septic tanks [Barbash and Roberts, 1986]. In order to clean these septic tanks, a gallon of cleaning fluid containing a variety of VOCs, including PCE, is flushed down the toilet every 1 to 2 years. This leads to considerable discharges of VOCs to the groundwater through the septic tiles. In 1979, 400,000 gallons of cleaning fluid were sold in Long Island alone, which is enough to contaminate more than 100 cubic miles of aquifer [Barbash and Roberts, 1986]. Besides this source, transportation, manufacturing and other human activities add

VOCs to the environment, that in some form or manner end up in the groundwater. Once in the groundwater, little can be done to reverse the damage, due to inaccessability and environmental conditions.

A more recent water supply survey [Westerick, 1984] indicates that 21 % of all water systems had one or more VOCs present. It was observed that PCE had the highest occurrence at 7.3 % in the wells determined to be contaminated, followed by trichloroethylene, TCE at 6.4 %. The ranges of concentrations for PCE and TCE were 0.1 to 69 μg/L and 0.2 to 160 μg/L, respectively.

2.5 The Soil Environment

The soil environment consists of solid, liquid and gaseous phases, which combine to form various physical, biological and chemical environments. In addition, different gas:liquid, liquid:solid and solid:gas interfaces exist, which increase the complexity of the soil environment [Walker, 1984].

The solid phase consists of minerals, amorphous precipitates and organic particles. These constituents vary in composition, particle size distribution and particle surface area, which also change with depth [Alexander, 1977 and Alrichs, 1972]. By noting the variation of soil with depth, one is able to classify a particular soil. There are essentially three horizons in the soil profile, A, B and C. The horizon A or the surface layer contains roots, small animals and the highest quantity of microorganisms as the organic matter concentration is the highest. The concentration of these components decreases in layers B and C as depth increases, with C being the parent material [Black, 1965 and Foth, 1978].

The organic matter contained in the soil is the remains of decomposed plants and animals. As the remains decompose, complex substances are formed. These complexes include aromatic and unsaturated ring structures, carboxyl, phenolic hydroxyl, alcoholic hydroxyl, carbonal, methoxyl and amino groups [Alrichs, 1972]. Felsot and Dahm, [1979] have observed that because of these functional groups, organic matter contributes 25-90 percent of the cation exchange capacity, CEC, in many types of soils. The CEC is defined as the sum of the exchangeable cations of a soil [Black, 1965]. The measurement is usually expressed as milli-equivalents of ions exchangeable per 100 grams of soil. This value indicates the cations held by the organic matter and clay of the soil, which can be replaced reversibly by cations of acid and salt solutions.

The physical parameters of the soil can be broken down into individual particles of silt, sand and clay according to size: clay, 0-2 μm; silt, 2-50 μm; sand, 0.05-2 mm [Bouwer, 1978]. These particles make up only 40-80 percent of the soil matrix. The remaining volume is comprised of pores filled with water, air and other gases.

The amount of pores in the soil matrix is dependent on the soil classification. Clays generally have high percentages of small pores, whereas sand has a low percentage. Organic matter also contributes small pores to the soil matrix. These small pores, or micropores as they are often called, can greatly enhance the soil capabilities to hold water [Hamaker and Thompson, 1972], as they are not free draining. Roberts et al., [1982], reports that the water held in the micropores is called the immobile domain, whereas the larger pores which are free draining are classified as the mobile domain.

The water phase in the soil matrix, consists of two components. One is the capillary water and the other is the gravitational water. The gravitational water is affected only by gravity, while capillary water depends on the polar nature of the water molecules and hydrogen bonding with the polar surface of the soil. Capillary water is held with a tension of roughly one-third atmosphere [Alrichs, 1972]. When the water content of the soil equals that of the capillary, the pores will contain large amounts of air and the soil will be considered unsaturated. However, if the pore space is completely filled with water and has only negligible amounts of air, the soil is considered saturated. Therefore, it can be seen that the gas and liquid phases of the soil are closely tied together.

As the gas phase moves through the soil, water is displaced, while the reverse is true when water enters the soil. However, it should be noted that the gas composition in the soil is different from the atmosphere. This difference is mainly due to the oxygen consumption and carbon dioxide production by plant roots and soil microorganisms. The oxygen level in the soil hovers around 21 percent, with decreases related directly to increases in carbon dioxide [Alrichs, 1972]. Studies have shown that the carbon dioxide in the soil air varies from 0.3 to 3.0 percent, whereas in the atmosphere it remains around 0.03 percent. Furthermore, as one travels deeper into the soil profile, the oxygen content decreases even further through restricted air exchange [Hamaker and Thompson, 1972].

The microorganisms that exist in the soil include all types from the five major groups; bacteria, actinomycetes, fungi, algae and protoza [Alexander, 1977], with bacteria being the most dominant. Their respective concentrations depend on soil type, moisture content and concentration of organic matter. Table 2-5 shows the changes in concentrations of microorganisms with depth, which are directly related to the organic matter present at each layer. Since organisms are attached to the soil particles either by electrostatic attractions or their extracellular secretions, the number of microorganisms that move with the water is severely restricted. This results in minimal biodegradation as one proceeds further down the soil profile.

Goring _et_ _al_., [1974] report that the optimum moisture level for microorganism growth is 50-75 percent of the moisture field capacity. Therefore as the moisture content

Table 2-5 Variation in Concentration of Microorganisms with Depth for a Typical Mineral Soil [Alexander, 1977]

Depth	Organisms/gram of soil (thousands)				
m	Aerobic	Anaerobic	Actinomycetes	Fungi	Algae
0.03-0.08	7,800	1,950	2,080	119	25
0.20-0.25	1,800	379	245	50	5
0.35-0.40	472	98	49	14	0.5
0.65-0.75	10	1	5	6	0.1
1.35-1.45	1	0.4	-	3	-

changes, so does the number of microorganisms. A neutral pH is also favourable for most microorganisms, but some have been found to exist at a pH of 3.0. Furthermore, the microorganisms often exist in a substrate limited growth pattern which takes off when a new source of organic matter is present. An increase in temperature also stimulates activity up to a point, whereas lower temperatures decrease their activity. One other important element is nutrients. If for example insufficient nitrogen exists in the soil, a nitrogen source will be needed to increase the microorganism biodegradation activity.

2.6 Chemical Movement in Soil

When an organic chemical is spilled on soil, the chemical's transport becomes a multi-phase phenomenon affected by many processes [Environment Canada, 1984] . These processes include volatilization from soil and water, adsorption and degradation, both chemical and biological [Pye et al., 1983]. Many studies have been completed with respect to pesticides and herbicides and various trace organics in aquifers [Walker, 1984]. Unfortunately, PCE has not been among those thoroughly studied and requires generalization with respect to the above processes.

2.6.1 Volatilization of PCE from Water

Volatilization can be defined as the loss of chemicals from any surface to the vapour phase, followed by movement in to the atmosphere [Spencer et al., 1982]. The potential to volatize depends on the chemicals vapour pressure as well as environmental conditions and factors that exist at the solid-air-water interface.

Henry's law is used to explain the mass transfer between the liquid and gas phases due to volatilization. It is a valid approximation for many environmental applications which take place at atmospheric pressure and temperature. The law states that at a constant temperature, the mass of gas dissolved in a given volume of a solvent is directly proportional to its partial pressure in the gas phase in equilibrium with the solution [Yurteri et al., 1987]:

$$p_i = K_{Hi} x C_{Li} \qquad (1\text{-}1)$$

At atmospheric pressures the gas phase approaches ideal behaviour, allowing one to express the law as:

$$H_i = K_{Hi}/RT_e = C_{Gi}/C_{Li} \qquad (1\text{-}2)$$

where, p_i = partial pressure of component i, atm,

K_{Hi} = Henry's law constant for i, m^3-atm/mole,

C_{Li} = equilibrium liquid phase concentration of i, mole/m^3,

C_{Gi} = equilibrium gas phase concentration of i, mole/m^3,

R = universal gas constant, atm-m^3/mole°K,

T_e = equilibrium temperature, °K,

H_i = dimensionless Henry's law constant for i.

Namkung and Rittmann [1987] studied two publicly owned treatment works and observed that the higher the Henry's law constant, the greater the rate of volatilization, Table 2-6. However, Yurteri _et_ _al_. [1987] have observed that Henry's law constant could be affected by the presence of salts, surfactants and humic material. Therefore, it is important to understand the nature of the impurities present and their effects on Henry's Law constant and the volatilization rate.

When PCE is spilled on an impervious surface or soil that does not drain quickly, volatilization can be expressed by Ficks first law of diffusion [Gowda and Lock, 1984]:

$$F = K_L(C_{SL}-C_L) = K_G(C_G-C_{SG}) \qquad (1-3)$$

where K_L and K_G are mass transfer coefficients (m/day), C_L and C_G are concentrations in the bulk liquid and gas phases respectively, and C_{SL} and C_{SG} are liquid phase and gas-phase concentrations at the interface.

Haque [1974] has reported that the molecular diffusion coefficients of organic compounds in air are inversely proportional to the square root of their molecular mass. The actual rate of mass transfer will be proportional to the diffusion coefficient and the vapour density. However, with the

Table 2-6 Henry's Law Constants and the Volatilization Losses of Various VOCs from a Wastewater Treatment Plant

Compound	Henry's Law Constant H, atm-m^3/mole	Volatilization percent
Benzene	4.6×10^{-3}	2.6
Chlorobenzene	4.0×10^{-3}	2.3
Chloroform	3.4×10^{-3}	43.6
1,2-dichloroethane	1.1×10^{-3}	20.0
Ethylbenzene	5.7×10^{-3}	3.2
Methylene chloride	2.5×10^{-3}	1.5
Perchloroethylene	23.0×10^{-3}	83.6
Toluene	5.7×10^{-3}	3.2
Trichloroethylene	10.0×10^{-3}	69.4

vapour density being proportional to the vapour pressure, P times molecular mass, X, the rate of loss under standard conditions from a pool will be proportional to $P(X)^{1/2}$.

Volatilization can occur from both the pure chemical and from an aqueous solution. Dilling et al. [1975] has reported that volatilization from water can be quite significant, Table 2-7. Using the calculated half-lives in Table 2-7, Dilling [1977] presented the following equation for flux from water:

$$\text{Flux from water} = 0.693VC/t_{1/2} \qquad (1\text{-}4)$$

where, $t_{1/2}$ = volatilization half life in Dillings system,

V = mL of water under 1.0 cm^2 in Dillings system,

C = μg of compound/mL of column effluent,

Flux from water = μg/cm^2/hr.

Using the above flux equation, Wilson et al. [1981] calculated the flux of various organic compounds from water shown in Table 2-8.

Table 2-7 Half-Lives of Various Chlorinated Compounds in Water [Dilling _et_ _al_., 1975]

Compound	Evaporation half-life (minutes) Calculated*	Measured
CH_2Cl_2	2.3	21
$CHCl_3$	1.4	21
CH_3CCl_3	0.34	20
$CHCl=CCl_2$	0.48	21
$CCl_2=CCl_2$	0.56	27

* Calculated from equation by Mackay and Wolkoff [1973]

Table 2-8 Flux of Various Volatile Organic Compounds from Soil and Water [Wilson _et_ _al_., 1981]

Compound	Concentration Applied	Measured from Water	Measured from Soil
	mg/L	-- $\mu g/cm^2/hour$ --	
Chloroform	0.9	3.9	0.38
1,2-Dichloroethane	0.81	4.8	0.38
Trichloroethane	0.90	3.0	0.34
Tetrachloroethane	0.15	1.8	0.103

2.6.2 Volatilization of PCE from Soil

Even though PCE is a relatively volatile chemical as indicated by Henry's law constant, little information can be found on its volatility in the soil environment. However, emerging data indicate that PCE may be significantly affected by vapour phase transport [Enfield, 1985]. Any information presently available is based on evaporation from aqueous solutions. Unfortunately, this is not predictive for PCE in an unsaturated soil environment [Kilzer _et al_., 1979]. However, it is felt that the shape of the surface, adsorption to soil, pH of soil, soil water content and air turbulence are important factors [Spencer _et al_., 1982 and Kilzer _et al_., 1979]. Volatilization from soil becomes even more complicated as these parameters also depend on the rate at which the chemical moves to and away from the soil surface [Farmer _et al_., 1973].

Volatilization from soil depends upon the diffusion to the surface and or convection or massflow in the evaporating water. Both methods can operate simultaneously and usually do [Spencer and Cliath, 1982]. The organic compounds diffuse through the soil matrix in both the vapour and non-vapour phases. The rates are controlled by the same factors controlling adsorption, i.e., temperature, chemical concentration, water content, organic matter and clay content. In addition, soil bulk density or soil compaction influences diffusion. Mayer _et al_., [1974] proposed four mathematical models for pesticide movement, where a diffusion coefficient for each compound in question is required.

As surface moisture evaporates, a suction gradient is produced in the soil as the soil water moves upward. While moving upward through convection, pollutants can move with it and this action is commonly referred to as the wick effect [Spencer and Cliath, 1974]. For pesticides it was observed that as air passed over the soil with varying humidity, there is a corresponding change in moisture loss. For this flux, Wilson et al. [1981] have used

$$\text{Flux from soil} = D_f A_f F_v / S_A \tag{1-5}$$

where, D_f = μg of compound/mL of feed solution,

A_f = mL of feed solution applied/hour,

F_v = fractional material applied that volatilized,

S_A = surface area of column, cm^2,

Flux from soil = $\mu g/cm^2/hr$.

Another flux equation proposed by Spencer et al. [1982] is

$$J = D_o P_a (10/3)(C_1 - C_{sb})/P_t 2L \tag{1-6}$$

where, J = vapour flux from soil surface, $\mu g/cm^2$ day,

D_o = vapour diffusion coefficient in air, cm^2/day,

P_a = soil air filled porosity, cm^3/cm^3,

C_1 = concentration of the volatilizing material in air at the surface of soil, μg/L,

C_{sb} = concentration of volatilizing material at bottom of soil layer, μg/L,

P_t = total soil porosity, fraction,

L = soil depth, cm.

However, while this equation has been experimentally verified for hexachlorobenzene (HCB), no results for PCE have been reported. Therefore, the various parameters for PCE must be evaluated under proper conditions to determine if this flux equation holds true for PCE [Paterson and Kodukla, 1981].

A more sophisticated approach has been reported by Allan et al., [1985]. It is a complex two dimensional mathematical model to study spilled or buried immiscible liquids. Unfortunately, there is a lack of field data to make any comparisons. A simulation run was made with benzene to see how the model worked. An artificial spill with kerosene was also analyzed and it was observed that a greater spill radius occurred than expected as a result of neglecting interfacial forces.

Generally, volatilization from soil is lower than from water. Kilzer et al. [1979] have reported that volatilization from soil is roughly a magnitude of one tenth less than from water. This has also been observed by Wilson et al. [1981], when volatilization from water was approximately 10 times that from soil as shown in Table 2-8.

2.6.3 Dispersion of Chemicals to Groundwater

Many studies have been conducted to model moisture movement through soil [Schwartzenruber, 1969, Reynolds and Walker, 1984, Bresler, 1973, Freeze and Cherry, 1979 and Bruch and Zywaloski, 1974]. These studies cover both the saturated and unsaturated conditions. However, when chemical transport is taken into consideration, less work has been completed. The problem lies with the lack of dispersion coefficients needed to model the flow. The flow through the soil matrix causes the chemicals in solution to disperse or spread as the result of changing permeablility, mixing in the pores and molecular diffusion [Walker, 1984].

The general equation for this has been given as

$$\frac{\partial}{\partial t}(\theta C) = \theta D\frac{\partial}{\partial z}\left[\frac{\partial C}{\partial z}\right] - \frac{\partial}{\partial z}(qC) \qquad (1\text{-}7)$$

where, θ = moisture content, m^3/m^3,

C = pollutant concentration, g/m^3,

D = total of dispersion and diffusion through soil, m^2/d,

q = flow per unit area, $m^3/m^2/d$,

z = distance from soil surface, m,

t = time, days.

However, with the dispersion coefficient not available for a variety of chemicals, many studies have neglected dispersion [Schwarzenbach and Westall, 1981 and Enfield, 1985]. In fact, it is believed that dispersion is insignificant for certain chemicals like PCE, as they are denser than water, eliminating the need for the dispersion coefficient. More details are given in the theory section.

2.7 Adsorption of Chemicals by Soil

Braids [1981] reports that majority of all the chemicals entering the soil environment are removed through adsorption. This is also referred to as sorption, which is the combined affect of adsorption and absorption [Burns et al., 1982]. However, in most studies absorption is considered minimal in soil and the sorption process refers to adsorption. Adsorption can be stated as the condensation of gases on the soils free surfaces, or the fixation of solutes from a solution on the surface of a solid [Morrill et al., 1982]. These interactions involve the interface between two phases;

liquid:liquid, gas:liquid, gas:solid or liquid;solid [Weber and Morris, 1963]. Since soil is the environment being studied, the interface of most concern is liquid:solid. With liquid:solid adsorption, the two main driving forces are [Walker, 1984],

(i) the solvophobic (or hydrophobic in aqueous systems) nature of the solute within the solvent,

(ii) the degree of affinity of a solute (or adsorbate) for the solid surface (or adsorbent).

There are three different types of adsorption: exchange, physical and chemical. Rarely can soil adsorption be limited to only one type. Adsorption can be positive or negative [Morrill, et al., 1982]. Positive adsorption occurs when there is an attraction between the adsorbate and the adsorbent, resulting in a higher concentration of adsorbate at the surface-liquid interface than in the bulk solution. Negative adsorption, commonly referred to as desorption, is the opposite situation with repelling of the adsorbate.

The interaction of the various adsorption mechanisms depends on the chemical family and soil type [Darcel, 1984]. For example, hydrophobic chemicals will tend to accumulate in the soil organic phase [Weber et al., 1983], as the water molecules are repelled. Preference is then given to these non-polar chemicals, with high molecular mass, resulting in the weakly hydrophobic chemicals being rapidly transported to the groundwater [Gambrell et al., 1984]. This phenomenon has also been observed by Valocchi [1985]. The majority of chemicals found in the groundwater are weakly or moderately hydrophobic, including PCE [Roberts et al., 1982]. Solubility is also vital as reported by Voice et al. [1983]. The higher solubility makes it easier for the chemical to dissolve and percolate with water to the groundwater. In other words, the higher the insolubility the greater is the adsorption [Isaacson and Sawhney, 1983 and Kenaga, 1980]. Solubility has been shown to increase with temperature, resulting in a lower adsorption rate [Chiou et al., 1977].

With the soil matrix consisting of solid, liquid and gaseous phases, the heterogeneous nature greatly influences the physical and chemical properties of the soil [Travis and Etnier, 1981]. The organic fraction is very important, with the majority of adsorption occurring in it [Jury et al., 1984, Melcer, 1982, Kahn et al., 1975 and Rippen et al., 1984]. Organic matter is also important in desorption, as it is seen that the percentage of desorption decreases with increase in organic matter [Dekkers, 1977]. Dekkers [1977] reports that it would be desirable to know the composition of the soil organic matter to accurately predict adsorption for a particular chemical. However, at present little is known about humic substances which are the largest fraction of organic matter in soils. They are relatively high molecular mass (300 to 30000) complex materials that are generally regarded as polymers of aromatic compounds having large surface areas [Chiou et al., 1979]. Other organic substances are fulvic and humic acids which themselves can rapidly adsorb organic compounds [Wang et al., 1978]. However, in some instances, adsorption by the organic fraction may not apply and cation exchange capacity, CEC, pH or some other soil property may influence adsorption [Zamani et al., 1984].

The cation exchange capacity, usually given in terms of milligram equivalents per 100 grams of soil, is a measure of the readily exchangeable cations neutralizing negative charge in the soil. These charges may be viewed as being balanced by either (i) an excess of ions of opposite charge and a deficit (or negative adsorption) of ions of like charge, or (ii) the excess of ions of like charge, or (iii) the excess of ions of opposite charge over those of like charge [Page et al., 1982]. Total CEC in arable soils varies from 0.5 to 50, being higher in organic soils [Roberts et al., 1982]. Some of the CEC sites change in number with pH. The dominate exchange cations are Ca, Mg, K, N and Al [Cohen and Ryan, 1985]. Felsot and Dahm [1979] report that the higher the CEC, the greater the adsorption. It is also reported that the adsorption capability of a soil was more related to the organic content of the CEC than to CEC itself. Walker [1984] reports that the organic content contributes 25-90 percent of the CEC.

While change in pH affects the number of CEC sites, no correlation between changes in soil pH and adsorption of non-polar chemicals has been reported [Walker, 1984]. The only change in adsorption, related to pH variation, results when a change in soil components occurs. Many studies report pH values but do not discuss how any change would affect adsorption. Hamaker and Thompson [1972] and Walker [1984] report that the effects of pH, organic matter, CEC and other soil properties are so interrelated that it becomes extremely hard to separate their influences.

Organics can also be adsorbed by inorganics like sand and clay, when organic matter content is low [McCarty _et_ _al_., 1981]. This occurs through cation and anion exchange. In Canadian soils, anion exchange is considered negligible as soil particles are predominantly negatively charged [Gambrell _et_ _al_., 1984]. The size of these particles is also important because the smaller the particle size, the more surface area per unit volume is provided. This is especially evident with clay in which many binding sites are provided [Walker, 1984]. Schwarzenbach and Westall [1984] observed reduced adsorption when they washed the soil prior to use and observed reduced adsorption. The decrease in adsorption was attributed to the washing out of the fines, which decreased the total surface area available for adsorption. However, it should be noted that generally no agreement exists in the literature on particle size effect on adsorption [Walker, 1984]. Karickhoff [1981] and Karickhoff _et_ _al_. [1979] have stipulated that adsorption can also be increased with an increase in organic carbon content as it also provides for additional binding sites.

As mentioned earlier, there are three types of adsorption; exchange, chemical and physical. Exchange adsorption is the electrical attraction between the adsorbate and adsorbent, which allows ions in solution to bind with sites on the soil surface [Weber, 1972]. Exchange adsorption includes both cationic exchange and anion exchange [Morrill _et_ _al_., 1982]. In chemical adsorption, a chemical bond is formed between the adsorbate and adsorbent, preventing free movement of the molecule. In short term chemical adsorption, less than twelve hours, the amount of adsorption is minimal with importance increasing with time. Another term for chemical adsorption is chemisorption.

While chemisorption fixes a molecule, a physically adsorbed molecule can freely move around the surface. Usually the first layer is chemically fixed and all succeeding layers are held by physical means. Physical adsorption is attributed to van der Waals forces. These forces are weak and decrease rapidly with increase in distance from the surface. Never the less, physical adsorption is very important for large molecules whose shapes conform to adsorbing surfaces [Rao _et_ _al_., 1979].

Besides these three types of major forces, there exist other minor forces such as hydrogen bonding and hydrophobic interaction. Morrill _et_ _al_. [1982] report that hydrogen bonding is significant for binding polar organic molecules to clay surfaces. Even though various types of adsorption are known, no single mechanism fully explains the adsorption of an organic molecule on soil particles. Instead it is felt that a combination of different types of phenomenon affect the adsorption process and these can not be easily differentiated, especially with heterogeneous soil [Bohn et al., 1979, Hamaker and Thompson, 1972 and Hamaker, 1972].

2.7.1 Adsorption Isotherms

Equilibrium equations or isotherms have been developed to help explain the adsorption process and allow comparisons. These equations give a relationship between the solute in the liquid and solid phases when equilibrium is reached. The equation relates the mass of solute adsorbed per unit mass of adsorbent to the equilibrium concentration in the liquid phase. These equilibria are established by adding a known amount of adsorbate to a known amount of adsorbent and determining the amount of adsorbate removed from the liquid phase. The observed data are then used to generate appropriate correlation equations such as the Langmuir Isotherm and the Freundlich Isotherm [Banerji et al., 1985, Briggs, 1981, Walker, 1984, La Poe, 1985 and Elliot and Stevenson, 1977].

The Langmuir Isotherm was initially developed by Langmuir in 1916 for the adsorption of gases on solids [Harter and Baker, 1977]. The development was based on three assumptions [Morrill et al., 1982]; (i) energy of adsorption remains constant and independent of surface coverage, (ii) adsorption is on localized sites with no interaction between adsorbate molecules and (iii) the maximum adsorption possible is a complete monolayer. The original equation has been modified to explain adsorption from solution, and is in the form:

$$\frac{X}{M} = \frac{Q^{*}bC}{1+bC} \tag{1-8}$$

where, X/M = mass of solute adsorbed per unit mass of adsorbent,

Q^{*} = mass of adsorbed solute per unit mass of adsorbent required to form a complete monolayer on the surface,

b = constant indicative of the energy of adsorption,

C = equilibrium concentration of solute in solvent.

However, limited use for this equation is found in the literature when discussing organic adsorption on soil and none for PCE. La Poe [1985] reasoned that the Langmuir Isotherm was basically limited to monolayer adsorption, and not multilayer, which occurred with organic chemicals.

The Freundlich Isotherm has been frequently used for the adsorption of organics on soil. It has the form;

$$X/M = K_{f}C^{1/n_{f}} \tag{1-9}$$

where, X = mass of adsorbate adsorbed on adsorbent,

M = mass of adsorbent,

K_f = equilibrium constant indicative of adsorptive capacity,

C = solution concentration at equilibrium after adsorption,

n_f = constant indicative of adsorption intensity.

Theoretically, this equation predicts that the adsorption will increase indefinitely. As a result, Eq. 1-9 should not be extrapolated past the range of solute concentrations for which it was developed [Bohn et al., 1979, Weber, 1972 and Belfort, 1980]. Furthermore, it does not reduce to a linear equation at low concentrations as does the Langmuir Isotherm. Still, it has be used extensively in soil adsorption studies for a variety of organic chemicals, including PCE. Table 2-9 shows some of the constants found for various chemicals in different soils [Friesel et al., 1984]. The reported correlation coefficients are quite good indicating that the Freundlich Isotherm can be used successfully in soil adsorption for PCE and other organics.

Table 2-9 Freundlich Constants for Various Soils

Soil	Chemical	K_f	$1/n_f$	r
Acid Peat	TCE	6.6	1.08	0.98
	PCE	12.9	1.04	0.96
	1,1,1-TCE	5.1	1.03	1.00
Acid Humic Topsoil	TCE	3.0	1.16	0.99
	PCE	10.4	1.12	0.94
	1,1,1-TCE	5.1	1.01	0.99
Calcareous Humic Topsoil	TCE	2.0	0.93	1.00
	PCE	5.8	0.91	1.00
	1,1,1-TCE	1.3	1.00	0.98
Subsoil rich in iron oxides	TCE	1.3	0.88	0.87
	PCE	2.3	0.98	0.95
	1,1,1-TCE	2.7	0.81	0.80
Clay subsoil	TCE	1.9	0.70	0.81
	PCE	0.5	0.95	0.70
Sand subsoil	TCE	1.5	0.71	0.91
	PCE	0.9	0.60	0.90

Many studies that used the Freundlich Isotherm, have reported n_f values close to unity. In fact, the smaller the value of $1/n_f$ the higher the affinity between the adsorbate and adsorbent. However, when n_f equals one, the isotherm equation describes the distribution or partitioning between the two phases in terms of the linear relationship:

$$X/M = K_pC \qquad (1\text{-}10)$$

X/M = mass of solute adsorbed per unit mass of adsorbent,

C = equilibrium concentration of solute,

K_p = linear partition coefficient.

The linear partition equation has found wide use in describing organics in soil, especially in low concentrations [Schwartzenbach and Westall, 1981, Kenaga, 1982 and Melcer, 1982] including PCE [La Poe, 1985 and Roy and Griffen, 1985]. Karickhoff _et_ _al_. [1979] report that K_p is relatively independent of soil mass present but is directly related to the organic carbon content. However, Weber _et_ _al_. [1983] and Karickhoff _et_ _al_. [1979] report that solids concentrations affect K_p, while Bredehoft and Pinder [1973] indicate that as adsorbates differ, so do correlation factors. Furthermore, Bredehoft and Pinder [1973] also believe that that K_p is inversely related to the solubility. These conflicting opinions reveal that each organic chemical behaves differently in changing soil conditions, requiring appropriate studies for each situation.

Due to differing opinions on the effect of soil type on K_p, several researchers attempted and were successful in correlating adsorption with soil organic carbon content, OC, [Darcel, 1984b]. This was done by normalizing K_p with OC, resulting in a soil-water partition coefficient, K_{oc}. K_{oc} is a measure of the partitioning of a compound between an aqueous phase and a stationary phase, consisting mainly of humus [Gambrell *et al.*, 1984]. This is called a hydrophobic tendency in which the more hydrophobic a molecule is, the greater it partitions from aqueous to organic media [McCall *et al.*, 1981]. Non-polar molecules like PCE primarily adsorb on soil through this mechanism [DeWalle *et al.*, 1982].

The soil-water partition coefficient becomes an important factor in adsorption studies as adsorption is now related to a single factor, organic carbon content, which is independent of soil type. Studies have shown that compounds with a K_{oc} value of about 1000 are quite tightly bound to the organic matter in the soil and are considered to be immobile [Kenaga, 1980]. Those chemicals with a K_{oc} below 100 for a certain soil are considered moderately to highly mobile. Therefore, K_{oc} is valuable in determining the potential leachability of compounds through soil or their potential to bind to the soil.

Roy and Griffen [1985] determined a K_{oc} of 303 for PCE in a saturated soil-water infiltration system. They reported this as medium mobility, considering that the value was between the two bench marks. La Poe [1985] observed an average

K_{oc} of 451 for PCE in mineral soil, peat, muck, humic acid and lignin sorbent, indicating medium mobility.

Schwarzenbach and Westall [1981] and others have indicated that another parameter can also be used to estimate K_p [Chiou et al., 1977 and Kahn et al., 1975]. This coefficient is called octanol water partition coefficient, K_{ow}. Karickhoff [1981] states that organic carbon in soil acts similarly to a solvent in a water: immiscible solvent extraction. Therefore, a correlation was developed between K_p and K_{oc}. This was completed for a series of polycyclic aromatic compounds and chlorinated hydrocarbons that had water solubilities ranging from 1 mg/L to 1000 mg/L. On correlation it was determined that;

$$K_{oc} = 0.63 \times K_{ow} \qquad (1\text{-}11)$$

where, K_{oc} = organic carbon partition coefficient,

K_{ow} = octanol water partition coefficient.

Then by applying organic carbon content, this equation can be written as;

$$K_p = 0.63 \times K_{oc} \times f_{oc} \qquad (1\text{-}12)$$

where, K_p = linear partition coefficient,

f_{oc} = fraction of organic carbon present.

Similarly, Schwarzenbach and Westall [1981] obtained the following relationship for natural aquifer material;

$$\log(K_p) = 0.72\log(K_{ow}) + \log(f_{oc}) + 0.49. \qquad (1\text{-}13)$$

All these equations predict K_p within a factor of two for non-polar organics in soil or sediment. However, they are only truly valid for the type of compounds and their concentrations that were studied. Any extrapolation beyond the upper limit can greatly increase the magnitude of error [Walker, 1984].

Another advantage of using K_{ow} is that it may be calculated directly from water solubility by using the simple relationship developed by Chiou et al. [1977]. The regression equation arrived at is,

$$\log(K_{ow}) = 5.00 - 0.670 \times \log(S) \qquad (1\text{-}14)$$

where, K_{ow} = octanol-water partition coefficient,

S = aqueous solubility of chemical in μmol/L.

For PCE, Chiou et al. [1977] determined a $\log(K_{ow})$ of 2.60 with a solubility of 3820 μmol/L at 25°C. The World Health Organization, WHO, reported a $\log(K_{ow})$ of 2.88 at a temperature of 20°C [WHO, 1984]. While the majority of organics are within one order of magnitude, Mingelgrin and Gerstl [1983] have shown that the less polar an organic, the more applicable is K_{ow} for indication of soil uptake, since chemicals with higher $\log(K_{ow})$ values are more readily adsorbed by soil [Kahn et al., 1975]. Jaffe and Ferrara [1983] also report that the higher the K_{ow} coefficient, the more accurate is the equilibrium model for adsorption. Furthermore, if it is greater than 100, i.e. $\log(K_{ow})$ is between 2 to 3, the chemical can be considered moderately hydrophobic [Roberts et al., 1982].

2.8 Desorption of Chemicals from Soils

Very few desorption studies have been performed on synthetic organics because considerable time is required to conduct such studies [La Poe, 1985]. Desorption is determined by first allowing a solute to attain equilibrium with a known mass of soil by adsorption. After equilibrium, the solution is removed and replaced with a fresh solvent containing no solute. This new system is re-equilibriated and new X/M values determined. The data are plotted to produce a desorption isotherm.

The desorption is believed to be a slower process than adsorption and losses due to volatilization and degradation can occur [La Poe, 1985]. This can lead to an over estimation of the quantity of solute still remaining adsorbed [Rao et al., 1979 and Rogers et al., 1980]. As a result of these difficulties, Schwarzenbach and Westfall [1981] did not perform any desorption studies for the volatile organics they studied, which included PCE. They felt the more one handled the adsorbent, the more errors could arise, affecting the reliability of the results. Therefore, for desorption tests the methodology used is vital as has significant impact on the results.

When the desorption studies are properly carried out, the isotherms do not necessarily overlap the adsorption isotherm. This noncoincidence is referred to as hysteresis. The usual effect of hysteresis is that desorption isotherms show higher desorptive capacity than adsorption capacity at lower equilibrium concentrations [Felsot and Dahm, 1979, Hamaker, 1972, Koskinen, 1979 and Schwarzenbach and Westall, 1981]. Other than unknown experimental losses, hysteresis can be attributed to non-attainment of equilibrium or to changes in strength of adsorption during desorption over time. These two causes can be interrelated and are hard to separate due to the soil's heterogeneity [Hamaker and Thompson, 1972]. Occasionally studies have been done to evaluate the breakthrough and elution curves. When they exhibit tail curves, or asymemetrical curves, nonequilibrium is believed to exist [Rao et al., 1980]. This nonequilibrium is also attributed to soil hysteresis. Schwarzenbach and Westall [1981] determined the extent of hysteresis from the tailing effect without performing desorption tests.

Felsot and Dahm [1979] report that organic carbon content is important in desorption. They observed for insecticides that the quantity of desorption decreased as organic carbon increased. More evidence for this pattern was obtained by oxidizing organic matter and observing an increase in desorption. Others [Hamaker et al., 1969, Hilton and Yuen, 1963 and Saha et al., 1969] have reported that if soil is dried and then rewetted after the sorption phase, the sorbed chemical may be hard to extract. La Poe [1985] has reported desorption isotherms above the sorption isotherm for PCE. This was not caused by slow desorption kinetics but rather by slow adsorption kinetics. La Poe [1985] showed that the longer the sorption study, the closer was the agreement between the adsorption and desorption isotherms, indicating reversible action at concentrations between 0 and

150 $\mu g/L$. La Poe [1985] also suggests that the negative adsorption of PCE can be attributed to the very hydrophobic nature of the soil being studied. This causes the water molecules to be strongly attracted to the soil surfaces, producing significant portions of the soil zones containing solute free water.

2.9 Degradation of PCE in the Unsaturated Soil Environment

Once a synthetic organic enters the environment, it may be altered or degraded by three main processes [Howard et al., 1978] depending on the existing environmental conditions. These three categories are: chemical degradation where degradation is affected by chemical agents; photochemical degradation which is nonmetabolic degradation requiring light energy; and biodegradation where degradation is affected by the living organisms.

When a chemical is present in the soil matrix, the above three mechanisms are not considered to be important. With the sun's energy being adsorbed by the soil, energy available for the photolytic reactions at the surface is diminished [Hamaker and Thompson, 1972, Zepp et al., 1984 and Roberts et al., 1982]. Since there is minimum photodegradation at the soil surface, there will be considerably less just below the soil surface. Therefore, photodegradation of organics in soil, for many chemicals including PCE, can be neglected [Friesel et al., 1984].

Chemical degradation is also minor as reported for TCE in water [Walker, 1984]. This type of degradation occurs through hydrolysis where pH and temperature are the primary factors. Suffet et al. [1980] report that the longer it takes for a chemical to hydrolyze, the more significantly will volatilization and biodegradation affect the chemical. Wolfe et al. [1980] have indicated that if a compound hydrolyzes in less than one hour at a pH of 7, it will not persist in the environment. Chodola [1988] reports that when PCE is mixed with water, it does not hydrolyze. Unfortunately, very little work has been done for PCE in water or in the more complex soil environment.

Of the three mechanisms of degradation of synthetic organics in soil, biodegradation is the most significant [Howard et al., 1978]. Two types of biodegradation that can occur in the environment involve homogeneous and heterogenous processes [Tomson et al., 1981]. In the homo- geneous process, the compound is highly soluble in water and its corresponding concentration in the aqueous phase is appropriate for microbial growth. The heterogeneous process concerns insoluble organics. Insolubility is the limiting factor since the chemicals become unavailable for microbial degradation. The majority of persistent toxic organics fall in the latter category.

Generally, the ability of microorganisms to degrade numerous organic compounds is well documented in the literature for both natural and synthetic compounds [Sparling et al., 1981]. However, while laboratory conditions indicate some possible biodegradation for various chemicals, they still persist in the environment. The reason for this phenomenon is the resulting acclimatization of the microorganisms to the organic chemicals. Unfortunately, the field conditions are quite different as compared to those in the laboratory. Therefore, it is important to properly simulate the natural environment for accurate biodegradation results to be obtained in the laboratory [Means and Anderson, 1981].

The natural environment contains a complex mixture of natural and man-made chemicals that may synergistically increase or decrease the biodegradation rate [Means and Anderson, 1981]. The biodegradation rate is affected by temperature, pH, salinity, dissolved oxygen, substrate concentration, concentration and type of trace organic chemicals, nutrients present and time. Elliot and Stevenson, [1977] report that all types of microorganisms exist in the soil environment, indicating that some type of microorganism are always available for biodegradation. The number of organisms present depends on the variables listed above. It has been estimated that the live weight of organisms varies from 0.5 to 4 tonnes in the top 0.15 m of soil covering 1 hectare.

Bacteria are the most predominant microorganisms present in soil and they can be both autotrophic and heterotrophic, with the majority being in the latter category. Heterotrophic bacteria need organic compounds for their energy and carbon needs. However, it is important to note that a diverse population is required for any biodegradation to occur.

Some subsurface environments naturally provide adequate nutrients for colonization and the introduction of contaminants may provide additional nutrients for increased growth [Kretschek and Krupka, 1983]. However, generally the microorganisms in the subsurface exist under low-nutrient stress. This dormant phase [Sparling et al., 1981], can change quickly to an active phase if readily assimilated carbon substrate becomes available in the soil [Behera and Wagner, 1974]. However, the organisms will react differently to various chemicals [Means and Anderson, 1981]. With some chemicals, the dormant microorganisms may not withstand the shock of the chemical being introduced into their environment and the toxic effects will result in the decline of their population [Kretschek and Krupka, 1981]. When this occurs, the chemicals will pass through the unsaturated soil zone to the groundwater, where it is unlikely or very difficult for any natural reduction in concentration to occur.

Wilson and McNabb [1983] report that, in water table aquifers, there are no prospects for degradation under aerobic conditions, while the possibility does exist for anaerobic degradation. Vogel and McCarty [1985] have reported that some reduction in PCE had occurred in small anaerobic continuous flow reactors. About 74 percent of the PCE was reduced to TCE, which in turn can be reduced to dichloroethylene, DCE, or vinyl chloride, VC. This reductive dehalogenation can in turn also be a problem as the resulting products are themselves designated substances [Parsons et al., 1984 and Bouwer, 1984]. Darcel [1984] observed a PCE decrease of 76±10% in a methanogenic biofilm reactor. However, when the biofilm was aerobic, there was an increase in PCE concentrations due to a release of PCE from the adsorbed state. Wilson and Wilson [1985] observed that PCE was resistant to biodegradation in the aerobic subsurface. Hutchins and Ward [1984] found a 81±16 % removal of PCE in a saturated column. They determined that the majority of PCE was lost through volatilization. Namkung and Rittmann [1987] have reported that, in conventional activated sludge plants, biodegradation of PCE is negligible. This happens in an environment which is conducive to biodegradation with plenty of living matter and oxygen present.

This confirms the current opinion among the researchers that PCE is non-biodegradable in water and soil. However, current research may in the future provide a solution to enhance on-site biodegradation through modified biochemical processes [Research Needs, 1988].

CHAPTER THREE

MATERIALS AND METHODS

The materials and methods used in conducting this study are described below.

3.1 Soils

Two types of soil were selected to evaluate the behaviour of PCE in unsaturated soil. One was a sandy loam soil and the other was a prepared organic top soil. The sandy loam soil was collected from Mersea Township, located in the southeast of Essex County in southwestern Ontario. The organic top soil was purchased from a local nursery where Essex County top soil is mixed with schredded peat moss to ensure high organic matter content. These two soils were chosen for their differences in soil characteristics which affect PCE behaviour in soil.

3.1.1 Collection of Soil

The soil samples were collected in the field and placed in bulk containers for transport to the laboratory. Care was taken to ensure that only surface soil (top 200 mm) was collected, to minimize variations. However, it should be pointed out that the sandy loam deposits exist for several meters in depth, as southeast Essex County has many such deposits [Soil Survey, 1939]. In the laboratory, the soils were air dried and sieved to pass a 2.00 mm sieve [Peter, 1982 and Black, 1965]. This ensured homogeneity of the sub samples needed for the various studies. After air drying and sieving, the soil was placed in wooden and steel containers for storage until required.

3.1.2 Analysis of Soil

The soil samples were analyzed for the various properties listed in Table 3-1. The procedures outlined by Black [1965] in the Methods of Soil Analysis were used.

3.2 Analysis of PCE Concentrations in Water and Soil

With the research undertaken to study the behaviour of PCE in both water and soil, an analytical method capable of analyzing PCE concentrations in the two media was required. Therefore, an extensive literature search was carried out to determined the most reliable and accurate method for each medium.

3.2.1 PCE Concentrations in Water

In choosing a procedure for the determination of PCE in water, three criteria had to be met:

(i) the method would have to be quick and accurate

Table 3-1 Properties of Soils Studied

Property	Sandy Loam	Organic Top Soil
pH	7.2	7.7
Sand %	95	79
Silt %	3	21
Clay %	2	-
Cation Exchange Capacity, meq/100g	14.2	23.3
Organic Matter Content, %	R_{50}=0.63 R_{100}=0.42 R_{pan}=1.79 comp=2.35	R_{50}=31.7 R_{100}=19.0 R_{pan}=24.0 comp=27.5
Organic Carbon Content, %	R_{50}=0.27 R_{100}=0.18 R_{pan}=0.76 comp=1.0	R_{50}=13.5 R_{100}= 8.1 R_{pan}=10.2 comp=11.74
surface area, m^2/g	22.0	N.A.
field capacity, %	18.0	31.0

R_{50} - passing 2.00 mm sieve and retained on sieve size 50, 0.297 mm
R_{100} - passing sieve size 50, 0.297 mm, and retained on sieve size 100, 0.147 mm
R_{pan} - passing sieve size 100, mm
N.A. - not available

since a large number of samples would have to be analyzed;

(ii) the procedure should easily adapt to the analytical equipment available;

(iii) the method must ensure an accuracy in the 5 to 150 mg/L range, as these concentrations were expected in spill simulations.

The Civil Engineering Department had a HP-5890A gas chromatograph, with a FID detector and a methyl-silicon capillary column. Various procedures available with this instrument included, liquid:liquid extraction, LLE, purge and trap and headspace gas chromatography. The liquid extraction procedure is accepted as an accurate method for PCE determination in water at concentrations in the μg/L range [Glasser et al., 1981, Henderson et al., 1976, Richard and Junk, 1977 and U.S.EPA, 1979]. Unfortunately, it is very time consuming and has limitations when the concentrations are high [U.S.EPA, 1979]. Purge and trap has also been used successfully for PCE analysis in water [Brass, 1982, Keith, 1981, Renberg, 1978 and Trussel and Umphres, 1978]. However, for this technique, additional laboratory equipment was required which was not available. Considering these limitations, the headspace method was chosen for PCE analysis in this research.

The headspace technique, or static headspace as it is commonly called, is based on the distribution of the volatile organics between the liquid and gaseous phases. When this distribution reaches equilibrium in a sealed container, the concentration in the headspace is proportional to the concentration in the water [Castello et al., 1982, Dietz and Singley, 1981, Kepner, 1964, Trussel and Umphres, 1978, Miedre, 1981 and Walker, 1984]. The distribution between the two phases is a function of vapour pressure, temperature and ratio of headspace to liquid volume. Accuracy of this method is ensured if the temperature is held constant and volume of headspace is properly measured and kept consistent. Therefore, if one keeps all the factors constant, the concentration in the vapour phase is dependent only on the concentration in the aqueous phase. Any deviation from the set values can greatly affect the results.

There are various advantages in using the static headpace technique for analysis [Castello et al., 1982, Dietz and Singley, 1979, Walker, 1984, Morris et al., 1983 and Hachenberg and Schmidt, 1977]. These include:

(i) only volatile organics can be analyzed using this approach, thereby providing a form of sample cleanup. The less volatile organics will not partition into the gaseous phase, thereby not affecting the analysis;

(ii) this procedure can be effectively used for a large range in concentrations, including μg/L concentrations;

(iii) the method is very quick and time efficient, and still provides the desired accuracy;

(iv) with a form of cleanup being provided, substances that could contaminate the column and detector are not injected. As a result many hours of trouble free analysis can be performed, which is not available with the other methods investigated.

3.2.1.1 Gas Chromatograph Operating Conditions

The literature was reviewed to determine the GC operating conditions. For a HP-5890A equipped with a FID Detector, the following conditions were used:

- Initial Column Temperature: 40°C
- Final Column Temperature: 150°C
- Injector Temperature: 225°C
- Detector Temperature: 250°C
- Temperature Program Rate: 50°C/min
- Carrier gas flowrate (Nitrogen): 25 mL/min
- Detector gas flowrate
    Hydrogen: 50 mL/min
    Air: 25 mL/min
- Column: HP-1 methyl silicon gum
    5 m x 0.53 mm x 2.65 μm film thickness
- Integrator: HP 3393A

With the above preprogrammed conditions, one sample run required about 6.5 minutes. Since the samples were injected manually, considerable time was needed. A Hewlett-Packard Company representative [Moy, 1986] suggested that the temperature program rate could be eliminated if detector fouling was not a problem. Since sharp distinct peaks were being obtained with the integrator, the program was changed to hold the oven (column) temperature constant at 40°C for the entire analysis. Consequently, a sample run could be completed in 1.0 min because the retention time for PCE was 0.85 min under the above conditions. This provided a good sample turn around time and no detector fouling was observed under this isothermal programme. However, it should be pointed out that after analyzing a complete set of samples, the column and detector were conditioned at 200°C and 300°C respectively, to remove any residual traces of PCE on the column. It is important to note, that for the mg/L analysis conducted in this research no difference in accuracy was observed between these two programs.

3.2.1.2 Standard Preparation

In order to accurately measure unknown samples, reliable standards must be made. The first step involved the proper cleaning of glassware. All glassware was washed with laboratory soap and rinsed with tap water, followed by methanol, tap water and distilled deionized water, DDI. The glassware was then placed in an oven to be dried at 150°C over night [Dietz and Singley, 1979]. This high temperature drying procedure ensured that no organic traces remained on the glassware.

The standards were prepared to allow accurate determination of PCE in water at the expected concentration. The maximum concentration expected was that at saturation, which for PCE is 150 mg/L in pure water. In preparing their standards other researchers have used methanol to aid in dissolving of PCE in water [Dietz and Singley, 1979 and Castello et al., 1982]. However, in doing so the partitioning properties between the gaseous and liquid phases are altered, affecting the headspace analysis. Furthermore, when PCE is spilled in the environment, is unlikely that methanol would be present. Therefore, the standards were prepared without methanol.

Consequently, the maximum standard concentration prepared was 112.5 mg/L to ensure that the PCE was completely dissolved in water. All subsequent standard concentrations were prepared by sequential dilutions of this concentration.

The standard was prepared in a 2.3 L brown bottle. This provided a large volume container with a minimum headspace to aid in dissolving the pure PCE and also making it possible to accurately measure the quantity of pure PCE. Being relatively dense, only a minute portion of PCE was required to attain a concentration of 112.5 mg/L. The pure PCE was purchased from BDH Chemicals Canada Ltd., using their Omnisolv Grade. For preparation of the standard, 160 μL of PCE was measured, using a micro-pipette, and added to 2.3 L of DDI water. A magnetic stirrer was placed in the bottle and the solution was stirred overnight. In the morning, the standard solution was placed in the refrigerator for storage. Subsequent analyses of the standard solution indicated that the aqueous standard could be stored for one month without any detectable losses as the calibration curves would overlap each other.

3.2.1.3 Sample Containers

For analysis, the unknown samples and standards were placed in screw cap vials. Vials of two sizes, 15 mL and 5 mL were used. The size chosen depended on the volume of sample available for analysis. The vials were made of glass with teflon-rubber septums. The teflon side faced inwards as it did not adsorb PCE [Chromatographic Specialities, 1986]. With a large number of samples to be analyzed, it was investigated if the septums could be reused. It was observed that the septum leaked after one injection and therefore did not provide the proper seal. Further investigation revealed that an aluminum foil disc could be placed between the teflon disc and the vial. This seal was excellent and the disc could be reused approximately ten times. The aluminum foil disc was stamped from new foil and heat treated at 150°C to ensure that no chemical traces existed. Repeated tests had indicated that no difference in results existed between new and reused discs. Therefore, new and used discs were used interchangeably, without due care as to which disc was used for a particular sample.

With vial volumes of 5 mL and 15 mL the headspace volumes of 2 mL and 5 mL respectively were chosen. These volumes provided air:liquid ratios consistent with those reported in the literature [Kolb et al., 1983 and Walker, 1984]. The headspace volumes were created by withdrawing the required volume from a full vial with constant volume pipettes. Constant volume precision pipettes ensured consistency of the headspace volumes created.

3.2.1.4 Equilibriation of Samples

After creating the headspace and properly sealing the vials, they were shaken for 1 minute [Dietz and Singley, 1979] and then placed in constant temperature bath, with the temperature set at 30°C. It should be pointed out that the temperature value itself was not critical, but rather it was important to hold the temperature constant for all the vials in order to maintain the accuracy of the results. The vials were left in the water bath for at least one-half hour, such that equilibrium could be reached. It is assumed that at equilibrium the concentrations reach their maximum level and stay there. Some researchers have used a shorter equilibrium time, while others have used a longer time [Dietz and Singley, 1979, Richter, 1981 and Walker, 1984]. An investigation was carried out on both the large and small vials. These vials were taken from the refrigerator set at 4°C, and placed in a 30°C water bath. It was observed that the maximum concentration level was attained within 5 minutes. Therefore, the 30 minutes used for equilibrium was not only convenient but also quite satisfactory.

3.2.1.5 Injection of Samples

After the samples were properly equilibriated, the vials were reshaken for 15 seconds [Dietz and Singley, 1979]. They were then allowed to stand for 30 seconds before a volume of gas was withdrawn and injected into the GC. The gas was withdrawn with the aid of a gas tight syringe supplied by the Hamilton Syringe Company. Two models were used, one with 250 μL volume and the other with 500 μL volume. Generally 100 μL of gas was sufficient for analysis. Larger volumes were used only when the GC had been standardized for a certain concentration range and the sample was at the low end of the range. This meant that a larger gas volume could be injected to increase the sensitivity of the scan. The use of 100 μL volumes was also beneficial in the case where a sample was lost. Since this volume was small when compared to the headspace volume, no major change in the concentration was expected. However, since the pierced disc did not provide a true seal, the results obtained from a repeated sample were used only for comparison with the second vial of the same sample.

The concentration of PCE was determined by comparing samples to the standards and using the following equation:

$$\text{Concentration of PCE} = F \times \frac{\text{peak area of sample}}{\text{peak area of standard}} \qquad (3\text{-}1)$$

where,

$$F = \frac{\text{injection volume of standard}}{\text{injection volume of sample}}$$

With a large number of samples being injected daily, it was imperative that the needles and syringes themselves were kept clean. For this, the syringe and needle were purged with prepurified Nitrogen gas between samples. After purging, regular injection of the needles containing room air indicated no contamination of the syringe assembly.

3.2.1.6 Sample and Standard Storage

Since PCE is a highly volatile chemical, it was important that care was taken in storing the samples or standards. When the samples were put in vials that were completely full and properly sealed and subsequently placed in a refrigerator at 4°C, results had shown negligible losses. Standards kept in vials over a month were checked and found to be consistent with freshly made standards.

Generally, the samples were analyzed the same day they were taken. If this was not possible, they were placed in the refrigerator until the next day. The only samples that could not be analyzed within two days were those obtained during the perfusion studies. Since each run had a duration of eight days, all the samples were collected and stored until the last perfusion apparatus was shut down, and then all samples were analyzed together.

3.2.2 Analysis of PCE in Soil

When PCE exists in soil, the matrix is more complex. Even then the headspace technique can be used with minor modifications. The soil sample was placed in a vial and sealed to allow the headspace pressure to form [Kiang and Grob, 1986, Kiang and Grob, 1986b Runyon and Thompson, 1987 and Mills and Bobra, 1987]. The gas was withdrawn the same way as for water and injected into the GC. It was important that the soil mass was held constant along with temperature. Another parameter that was held constant was the moisture content. First the moisture contents of the soil samples were calculated. Then the standards were prepared with the same moisture content to ensure consistency in the matrix.

All steps followed in the GC analysis were similar to those performed for water, except for shaking the vials. The vials were not shaken as the soil mass was quite small, easily allowing the PCE to diffuse away from the soil.

3.3 Volatilization of PCE from Soil and Water

Batch experiments were run to determine the rate of volatilization of PCE from water and soil. Various amounts of soil and water were placed in vials, graduated cylinders and beakers to give different ratios of area:volume. These containers were then placed in a fume hood. The fume hood had two functions, one to remove the PCE vapours from the laboratory and the other to induce a constant air flow across the soil and water surfaces. The air velocity across the vials was held constant at 10 km/h, by keeping the fume hood door at a constant height. The room temperature was held constant at 22°C with the help of a room air conditioner.

3.3.1 Volatilization of PCE from Water

To determine the rate of loss from water, ten identical containers were placed in the fume hood. This permitted sampling every 30 minutes, with two samples per time step. The type and size of container was changed in each experiment to obtain the desired area to volume ratios. PCE solutions at different concentrations, 18.5, 37.5, 75.0 and 112.5 mg/L, were made daily and stored in the refrigerator in a closed flask until required. The solutions were then carefully poured into the containers to minimize volatilization due to agitation. At appropriate time intervals, two samples were drawn and placed in the 15 mL vials. The headspace was created immediately and the vials were sealed. The analysis was completed on the same day to ensure minimum volatilization losses through handling.

3.3.2 Mass Flux of Submerged PCE into Stagnant Water

The flux movement of PCE from a pool of pure PCE through a stagnant column of water was completed with the aid of a 2-litre graduated cylinder. The cylinder was completely filled with two litre DDI and placed in a fume hood. One hundred mL of pure PCE was placed at the bottom of the cylinder with a pump whose discharge tube was submerged to the bottom of the cylinder. Care was taken, while withdrawing the tubing, to ensure that minimum turbulence was created. Samples were withdrawn at the 800, 1200 and 1600 mL markings for the first seven days. Subsequent samples were drawn at the 1200 mL level, as analysis indicated no difference in concentration between the various levels.

3.3.3 Volatilization of PCE from Soil

Two different approaches were used to determine the rate of loss from soil. In one PCE dissolved in water was spilled on soil at field capacity, whereas in the other case pure PCE was spilled. Basically the same procedures as used for determining volatilization from water were carried out. Different containers were used to obtain different area to volume ratios. However, the containers chosen were vials that could be tightly closed with a septum and a cap. This was necessary because it was difficult to transfer soil from a beaker to a vial without affecting the volatilization rate. The amounts of soil used were 5.55 g of sandy loam soil and 3.30 g of organic top soil.

For the aqueous PCE solution, the soils were wetted at concentrations similar to those used in the study with water. The amount of solution applied depended on the field capacity of the soil being tested. For the sandy loam soil, 1 mL was applied whereas for the organic top soil, 1.6 mL was used. Field capacity was used as the major criteria as it was desired to obtain volatilization rates at this moisture content. However, it should be noted that the amount of water used for the organic soil was greater than the measured field capacity. Laboratory experiments indicated that 31% water was insufficient to uniformly wet the sample. Therefore the water content for the organic soil was increased to 48%. Different area to volume ratios were tested at different concentrations.

For the volatilization of pure PCE from soil, the soils were prepared as before with one modification. First the soils were wetted to the same moisture contents as for the aqueous PCE study by applying DDI water. One half hour later one hundred μL of PCE was spilled on the surface. The vials were closed at 30 min hour intervals for a total duration of six hours, and the concentrations were analyzed.

3.4 Adsorption - Desorption Isotherms

Adsorption and desorption isotherms were evaluated for sandy loam, organic top soil, peat moss and granular activated carbon, GAC. The commercial peat moss was purchased at a local nursery and its properties are given in Table 3-2. The activated carbon was 4 x 10 mesh Nuchar, purchased from Westvaco and its properties are shown in Table 3-2. The isotherms were evaluated with batch equilibrium experiments, using fixed amounts of granular media and aqueous PCE solution ranging in concentration from 22.5 to 150 mg/L. The basic procedure reported in the literature was followed [Richard and Junk, 1979, Walker, 1984, Koskinen and Cheng, 1983, Peter, 1982 and La Poe, 1985].

The 15 mL GC vials were used to determine the sorption characteristics of the sandy loam soil, organic top soil and peat moss. For the GAC, 50 ml heavy duty centrifuge tubes were used. The mass of media used in each test was 5000 mg for the sand loam soil, 5000 mg for the organic top soil, 400 mg for the peat moss and 50 mg for the GAC.

Table 3-2 Properties of Peat Moss and Granular Activated Carbon

Property	Peat Moss	Granular Activated Carbon
pH	3.49	7.02
Organic Carbon Content, %	49.4	74.1
Cation Exchange Capacity, meq/100g	Approx. 150	N.A.
Surface Area, m^2/g	0.399*	1300**

* La Poe, 1985
** Broughton, 1981
N.A. - not available

3.4.1 Adsorption

The adsorption isotherms for the sandy loam, organic top soil and peat moss were determined after the media had been air dried and sieved to pass a 2.00 mm sieve. Isotherms were also determined for sandy loam and organic top soil retained on sieves sizes of 0.297 mm, 0.147 mm and the bottom pan. The GAC was used as received from the manufacturer.

The following steps were followed in conducting these experiments:

1. Containers were cleaned using laboratory soap and rinsed with tap water followed by methanol. After the methanol rinse, the containers were rinsed again with tap water and DDI water. After rinsing, the containers were placed in an oven at 150°C for a minimum of 2 h to drive off any residual organics.

2. Clean containers were filled with granular media and weighed on an electronic balance with a tolerance of ± 10 mg, except for the GAC in which case the actual mass was recorded.

3. Aqueous PCE solutions were mixed at concentrations of 22.5, 45.0, 67.5, 90.0 and 112.5 mg/L. Solutions were chilled to 4°C to minimize volatilization losses during transfer to adsorption containers. It was observed that, with the containers being of relatively small volume, the temperature of a container with soil-PCE solution returned to the room temperature within 5 minutes, after being removed from the refrigerator.

4. PCE solutions were measured with a graduated cylinder and transferred to the adsorption containers. Since each granular media had a different bulk density, the volume of solution added varied with the medium. The volumes added were 14.0 mL for sandy loam, 13.0 mL for organic top soil, 15.5 mL for peat moss and 56.0 mL for activated carbon. These volumes were choosen so to minimize the headspace in the containers while providing sufficient space for complete mixing.

5. After filling, the containers were capped immediately to minimize volatilization losses. Containers containing no granular medium were filled also and were used as blanks. These blanks were used to determine volatilization losses during the experiment and were handled in the same manner as the containers containing soil. It should be noted

that two separate containers were used for each PCE concentration for comparison. After all the containers were filled, they were placed on the shaker. The duration of shaking was based on the respective equilibrium times of each granular media.

6. After shaking, the containers were placed in the refrigerator to cool down to a temperature of 4°C. After cooling the containers were spun in a refrigerated centrifuge for a fixed time and RPM [Walker, 1984].

7. When separation of granular media and PCE solution was complete, a constant volume pipette was used to withdraw a sample from each container. The sample was placed in a 5 mL vial for analysis on the same day. The results obtained combined both adsorption and absorption by the various mediums, as no attempt was made to quantify the absorption portion.

3.4.2 Desorption

Three types of desorption isotherms were evaluated: one with unaltered DDI water, another according to Regulation 309 with pH above 5.00 and the third according to Regulation 309 with pH 5.00±0.2 [Government of Ontario, 1985]. Two different tests according to Regulation 309 were performed since the sandy loam soil and the organic top soil had natural buffering capacity and the pH rose after initial lowering to 5.0 with acetic acid. Since the granular activated carbon had no buffering capacity only one test was performed according to

Regulation 309. Peat moss was not tested according to Regulation 309, as peat moss had a pH of 3.49, already below Regulation 309's limit of 5.00±0.2.

3.4.2.1 Desorption with Distilled-Deionized Water

The desorption study with DDI water was carried out on the samples used for the adsorption test. After centrifuging the adsorption samples, an appropriate sample volume was withdrawn and the remaining supernatant liquid was discarded into a waste bottle. Immediately thereafter, DDI water was placed in the container without disturbing the soil at the bottom and the container resealed tightly. The volume of the DDI water added to the soil was slightly less than that used for the adsorption study, as the soil had retained some moisture. The volumes added were 12.5 mL, 10.5 mL, 13.0 mL and 56 mL for sandy loam, organic top soil, peat moss and activated carbon respectively. After recapping, the containers were shaken vigorously to resuspend the granular media in the solution to allow uniform mixing. Then the containers were handled in the same manner as described in the adsorption experiment.

3.4.2.2 Desorption According to Regulation 309 with pH above 5.0

Regulation 309 is a leaching test recommended by the Ontario Government [1985]. It is suggested for use in determining the leachability of various substances in wastes and soils under adverse pH conditions. The pH is lowered by adding 0.5N acetic acid. The soil solution is maintained at pH 5.0±0.2 for 24 hours. Then the supernatant liquid is analyzed to determine the quantity of substances released by lowering the pH.

With PCE being a highly volatile organic, it was impossible to continuously monitor the pH as suggested by Regulation 309. Therefore, the pH was initially lowered and then measured again after the desorption time had expired. The amounts of acid added to the DDI were 0.1 mL, and 2.0 mL for the sandy loam soil and organic top soil respectively. Following equilibrium, the pH had risen to 6.26 and 6.15 respectively for the sandy loam and organic top soil due to their buffering capacity.

3.4.2.3 Desorption According to Regulation 309 with pH Approximately 5.0

Additional amounts of acid were required to counteract the buffering capacity of the soil. Therefore, a total of 0.3 mL and 5.0 mL of acetic acid were added for the sandy loam soil and organic top soil respectively. Since the GAC had no buffering capacity, no additional acid was required and a total amount of 0.04 mL was used.

3.5 Perfusion Apparatus

The perfusion apparatus has been used extensively in determining the rate of degradation for pesticides [Longden and Claridge, 1976, Kaufman, 1966, Temple, 1951, Wildung, Biggar and Chesters, 1969 and Wright and Clark, 1969]. In these studies no attention has been given to the chemical loss through volatilization and most of the systems were open to the atmosphere. However, since PCE is a very volatile chemical, modifications were made to the perfusion apparatus to make it a closed system, so that the volatilization could be accounted for.

The perfusion apparatus used in this study is shown in Figure 3-1. The soil sample was placed in the a Buchner Type 42.5 mm filtering funnel (Pyrex No. 6060) with a gravel filter. Then the filter was plugged with a rubber stopper covered with aluminum foil to prevent adsorption of PCE by the rubber. The rubber stopper had three openings; one for perfusate, the second for incoming atmosphere and the third for exiting atmosphere. The incoming atmosphere was dry compressed air. The exiting air was passed through a water scrubber to remove the PCE gas from the air and dissolve it in the water. Subsequently this solution was analyzed for PCE. Another modification was made after initial testing of the system. The inlet and outlet atmosphere openings were short circuited. This modification ensured that no volatilized PCE existing above the soil sample would be carried away with the exiting air.

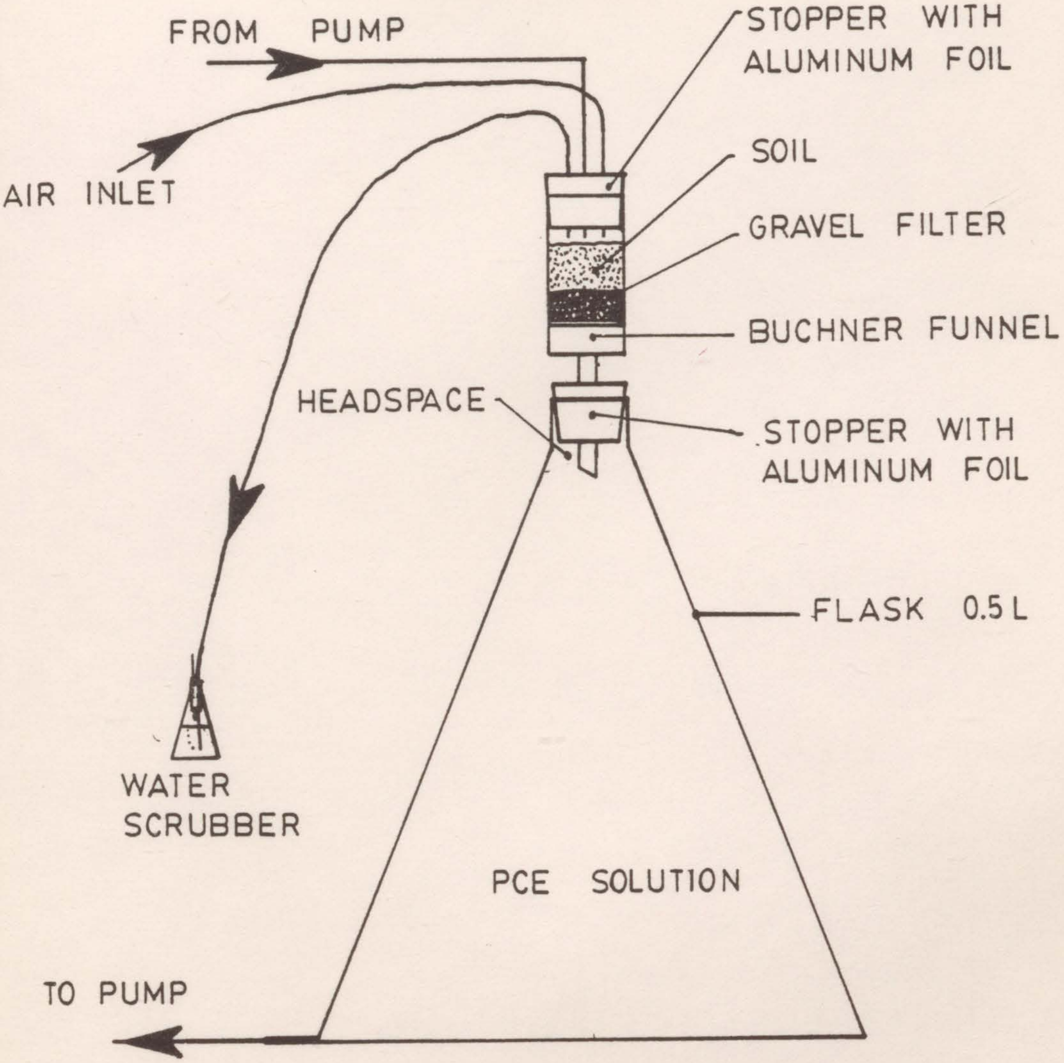


Figure 3-1 PERFUSION APPARATUS

The 500 mL flask in the apparatus was completely filled with perfusate, 570 mL. The flask was completely filled to ensure that no headspace was available for the PCE to volatilize. Headspace was allowed only above the soil sample and in the filter funnel. The headspace in the filter funnel was required to maintain unsaturated flow in the soil. The perfusate was recycled through the use of a multi-channel Autoclude pump. The 1.5 mm diameter tubing provided a flow rate of 1130 mL/d and maintained the unsaturated flow condition. A multi-channel pump was used as several units were in operation at the same time. In all, eight units were used with soil and one without soil. All units were started at the same time, and one at a time was taken out of operation to obtain samples. This procedure enabled the experiment for a particular run to be completed in eight days if samples were drawn on consecutive days.

3.5.1 Natural Soil Conditions

For the natural soil conditions, the air-dried sieved soil was placed in the filter funnel, at bulk densities similar to those used in the column studies. The quantity of soil used was 50 mg for sandy loam soil and 40 mg for organic top soil. Then DDI water was pumped over the soil to wet it. After sufficient wetting had occurred, usually a day, the pump was turned off and the water in the flask was replaced with perfusate.

The perfusate solution was prepared on the day the units were started. Concentrations of 120.0 and 11.25 mg/L were used to simulate the high and the low levels of PCE expected at a spill site. The solutions were carefully poured into the flasks and the funnel filters were replaced immediately on the flask. Once all the flasks were full, the pump was started.

Samples were drawn once every 24 hours after starting the experiment, until all the perfusion units were shutdown. Two separate samples were withdrawn from the flask using a pipette and were placed in a 15 mL vial without leaving any headspace. The vials were stored in a refrigerator until all samples were ready for analysis. Samples were stored no longer than eight days as all were analyzed on the day the last perfusion apparatus was taken out of operation. Analyses were carried out using the basic headspace procedure for PCE in water.

3.5.2 Sterilized Soil Conditions

In order to determine whether the microbiological activity present in the unsaturated soil degraded PCE, parallel runs were made under sterilized and natural conditions.

The soil was autoclaved to kill the existing microorganisms. This method was considered to be the most effective with minimum side effects and was adopted after consulting the literature [Sparling and Cheshire, 1979, Rogers et al., 1980 and Dao et al., 1982]. The air-dried sieved soil was placed in a beaker and covered with paper and placed in the autoclave. Autoclaving was done at 121°C and 103.5 kPa pressure for a duration of two hours. Each sample was autoclaved three separate times, to ensure complete sterilization.

The glassware used in the perfusion apparatus could not be sterilized as described above because of the fear of breakage. Therefore, it was carefully washed and rinsed with sterile DDI water and placed in the incubator at 60°C for two days. After the soil and glassware were prepared, the sterilized soil and sterilized filter gravel were measured and placed as before. Sterile DDI water was added to the flask and was pumped as the perfusate to wet the soil. Then the experiment followed the procedures set forth for the natural soil conditions.

3.6 Diffusion of Gaseous PCE Through Soil

A simple batch experiment was carried out to determine how PCE moved through a soil core. The apparatus shown in Figure 3-2 was used. A soil core was placed between the two vertical cylinders. This soil core was prepared by packing the hollow core with soil at the same density as used in the column studies, i.e., 1500 kg/m^3 for sandy loam soil and 1000 kg/m^3 for organic top soil. After packing, the soil cores were moistened to their respective field capacities.

For evaluating the diffusion rates, different concentrations of PCE in gaseous form were placed in one of the vertical cylinders. Then the other cylinder was monitored, at regular intervals, by withdrawing headspace samples and

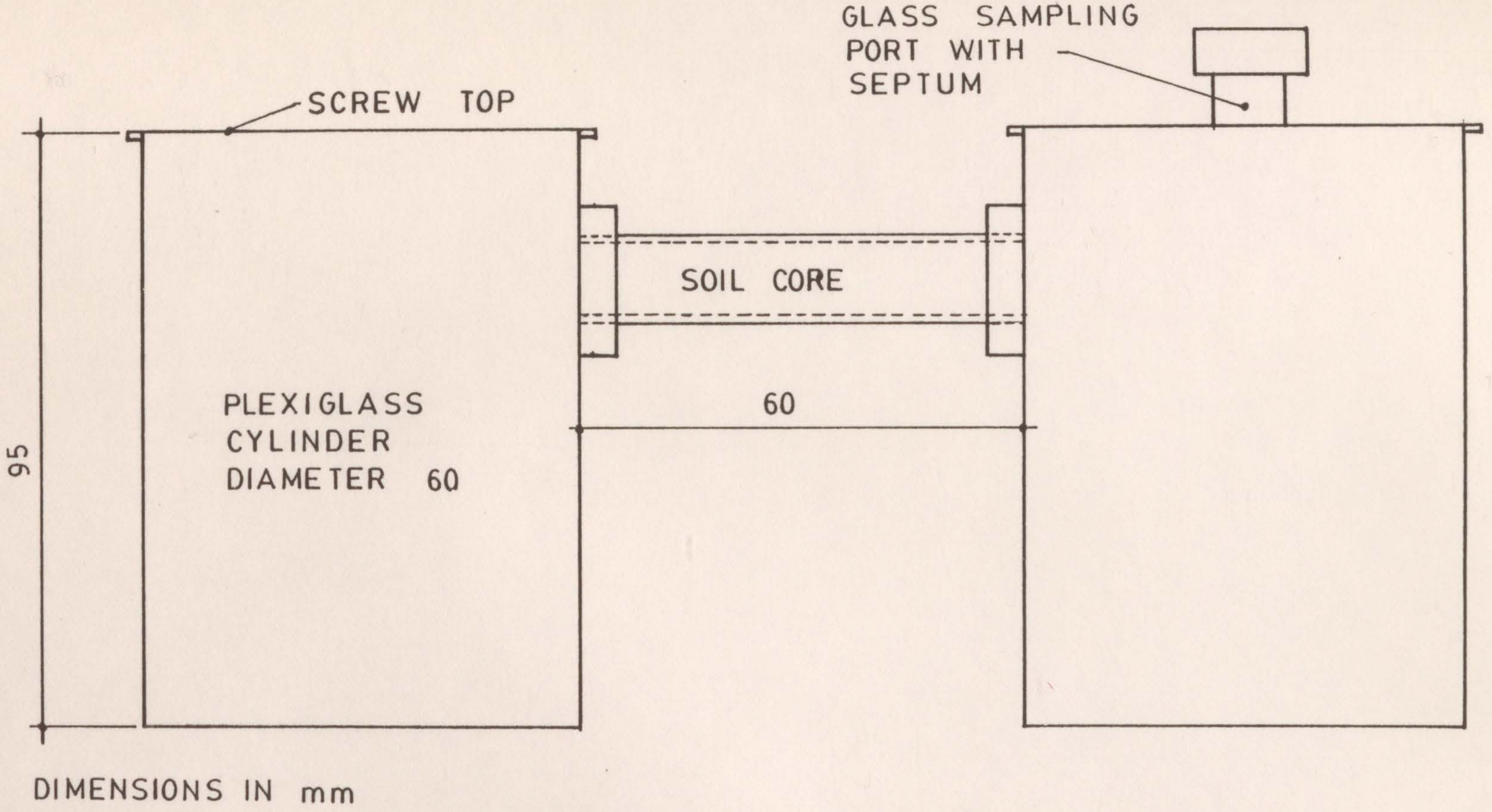


Figure 3-2 DIFFUSION APPARATUS

analyzing for the concentrations.

3.7 Column Studies

The soil columns used in this study are shown in Figure 3-3. The columns were constructed out of plexiglass tubes, a material which has been used successfully by others to study organic chemical behaviour in granular media [Salenieks and Henry, 1986 and Hoag and Marley, 1986]. The tubes had a inside diameter of 100 mm, a thickness of 5 mm and were 1 m in length. The ends of the tubes were threaded, providing leak proof seals when capped. The bottom cap was beveled on the inside toward the middle, to funnel the collected fluid to the center. A compression fitting was installed at the center. This compression fitting allowed the samples to be withdrawn through a piece of tygon tubing. More details are provided later in the section on sampling procedure. The top cap, made from solid plexiglass, was used to completely seal the column when required.

All the columns were placed in a wooden rack to permit easy access. The racks, each holding three columns, were placed in the laboratory were the ambient temperature was maintained at 22°C, Figure 3-4.

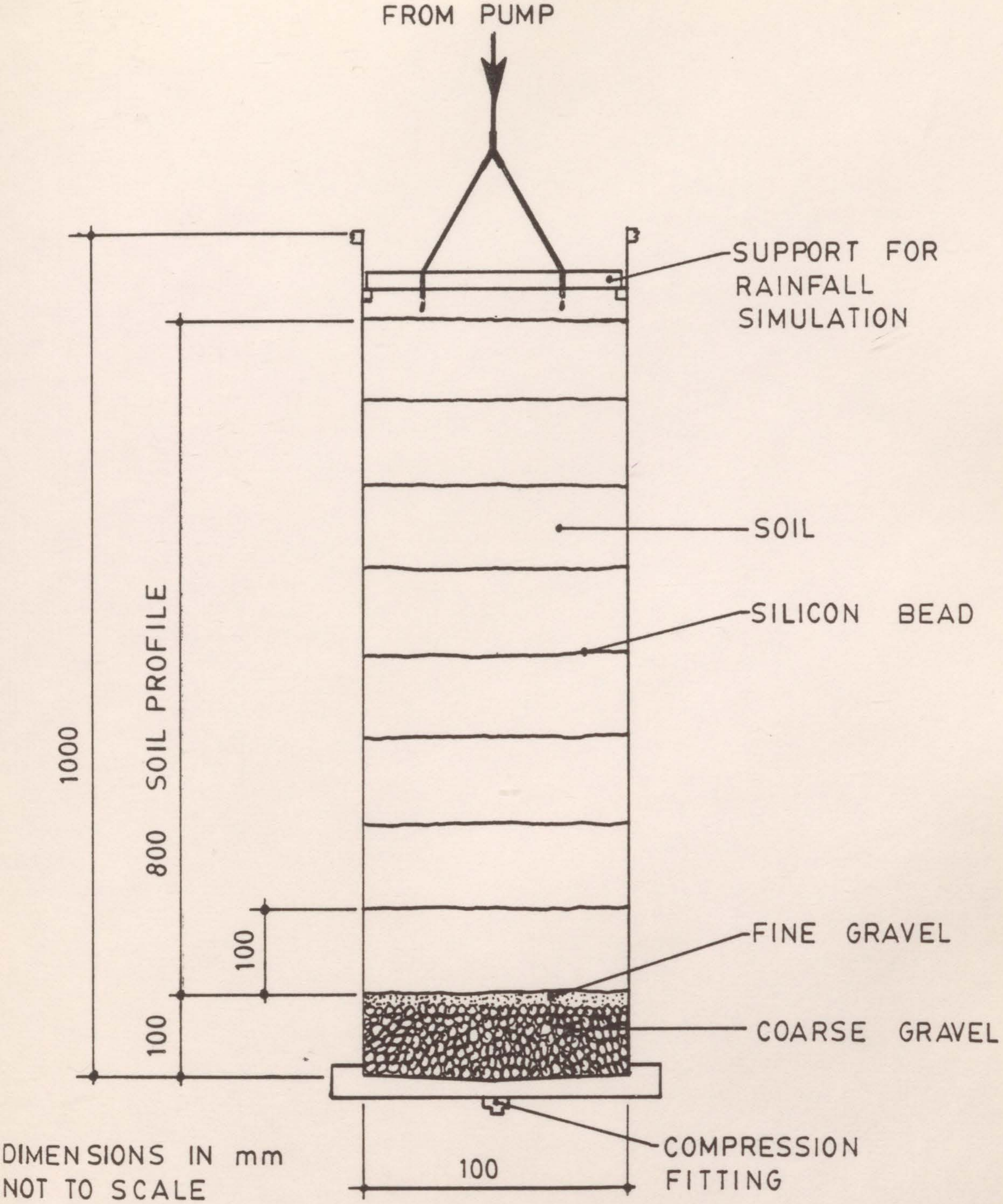


Figure 3-3 SOIL COLUMN

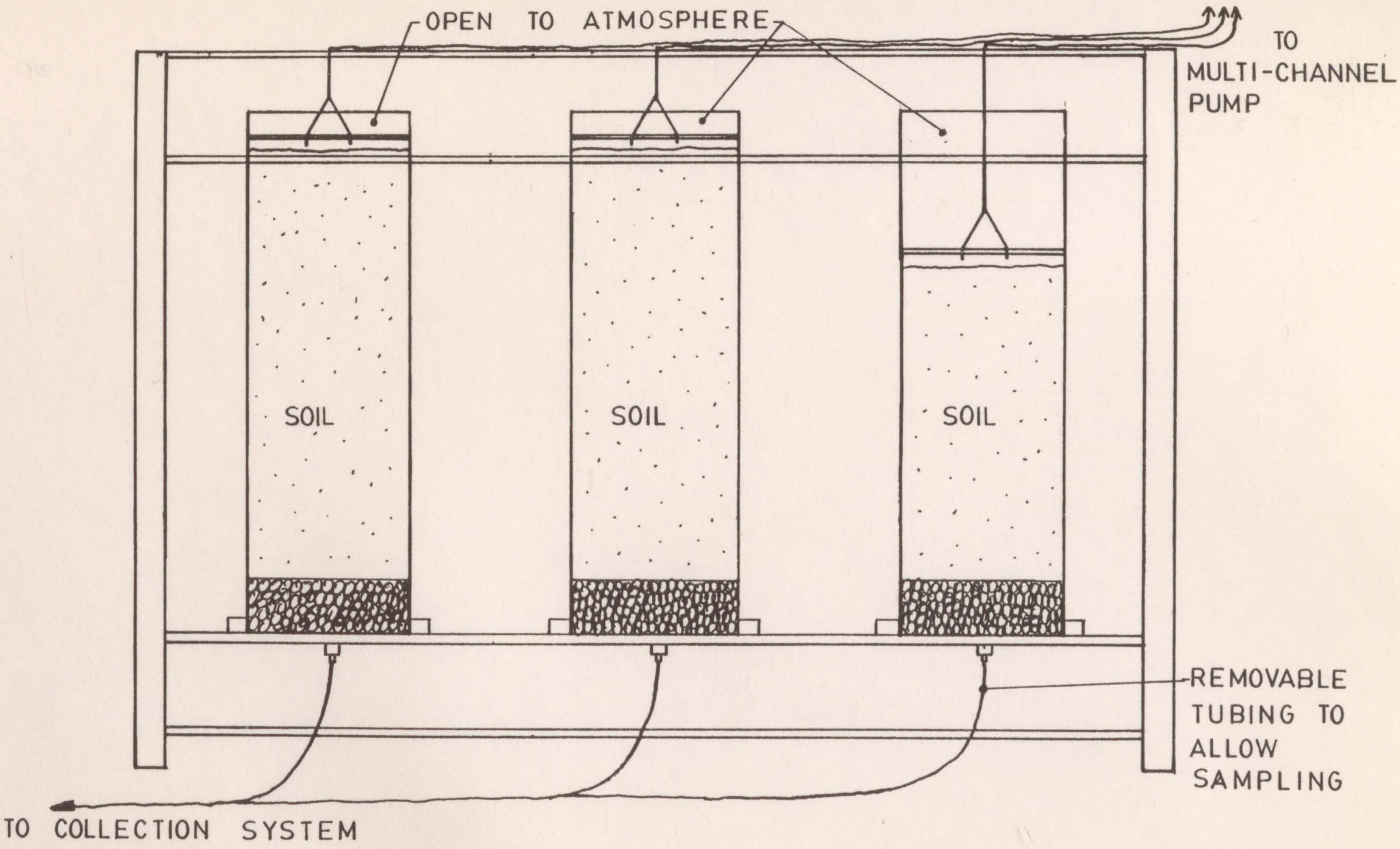


Figure 3-4 RACK TO HOLD COLUMNS

3.7.1 Preparation of Columns

The columns were washed with soap and water, rinsed with tap water and followed by a methanol rinse. Finally the columns were rinsed with tap water followed by DDI water. The columns were then permitted to air dry in the room as they could not withstand the normal 150°C temperature used in other areas of the experiment. Once dry, a silicon bead was applied to the inside of the columns at every 100 mm. This silicon bead prevented channeling between the soil and column wall.

After curing the silicon beads for 24 hours, the bottom cap was screwed on and the bottom filter was put in place. A filter bed consisting of gravel ranging in size from 2.00 mm to 12.7 mm was placed at the bottom, Figure 3-3. This filter supported the soil and also provided the necessary drainage so that the bottom part of the soil column remained in an unsaturated condition. The gradation in gravel size was necessary to prevent the washing out of the fines. Subsequent experiments with the columns proved this to be correct as the effluent was clear.

The soil volume required to fill 0.8 m length of the column was calculated. Using this volume and the corresponding density of the soil, the required dry mass of soil was calculated. The density of the sandy loam was kept at 1500 kg/m^3 which is considered to be an average for this type of soil [Wilson et al., 1981 and Ritter et al., 1981]. To maintain a uniform density in the column, the soil was packed in quarter sections of the column with the corresponding mass of soil. After filling one column, it was determined how much compaction was required to arrive at the desired density. The shorter soil profiles of 0.6 m, 0.4 m and 0.2 m were prepared in the same manner as the 0.8 m profile. The organic top soil was packed following the same procedure as the sandy loam soil, except that the density was kept at 1000 kg/m^3.

3.7.2 Moisture Content

In order to attain the desired field capacity of each soil, first the columns were flooded with DDI water. The bottom drain was left open and the DDI water was applied at the top at the rate of 76 mm per day. Since the soils were dry, it took two days before any fluid reached the drain. Once fluid was observed, the drain was plugged to allow the columns to flood. After flooding, the application of water was ceased and the columns were drained for approximately 48 hours until there was no flow. The spill experiments were started immediately after the moisture in the columns had reached their field capacities.

3.7.3 Application of PCE Spill

For a proper PCE spill, it was necessary that the mass of PCE applied was in excess of the adsorptive capacity of the soil column. Therefore, the Freundlich Isotherms determined previously were used to calculate that 1.31 g (0.809

mL) of pure PCE would be required for equilibrium adsorption on the sandy loam soil when the PCE was dissolved in water, Appendix A. In order to ensure an excess of PCE, 10 mL (16.22 g) of pure PCE was used for both soils. This amount was applied to each column using a constant volume pipette. Care was taken to ensure that the chemical had no impact at the column surface, by placing the pipette mouth as close to the surface as possible. After applying the spill, rainfall was initiated immediately.

3.7.4 Rainfall Simulation

Rain was applied through the use of a multi-channel autoclude pump as seen in Figure 3-4. The pump had 1.5 mm diameter tubes which could consistently deliver 650 mL/d (approx. 3 in/day). The discharge side of the pump was attached to tygon tubing which branched into a Y just above the soil surface, permitting two points of applications. This Y branch was supported with a plexiglass disc. The disc was rotated every second day to ensure that no flow channels in the soil column would develop.

The effluents from the columns were collected and measured on days according to a predetermined schedule. The effluent volume was measured to calculate the total mass of PCE passing through the column. It was also monitored to ensure that the application rate was uniform. The tubing used with the pump was replaced whenever the effluent exceeded 800 mL in one day.

The simulated rainfall consisted of DDI water. Since it had a low pH, 5.8 - 5.9 , it simulated acid rainfall. The use of DDI water had another advantage as it was the same water used in mixing the standards. By having the same matrix in both the samples and the standards, analysis of the results were more consistent.

3.7.5 Sampling of Column Effluent

Effluent samples were collected daily except for Sunday, for the first 45 days of operation. After 45 days, samples were collected every other day. Grab samples were taken to minimize losses through volatilization. In continuous sampling, the sample container would have to be open to the atmosphere through which PCE could volatilize.

Grab samples were taken with a 125 mL flask under vacuum. The flask was fitted with a proper size stopper, through which a 7 mm glass tube was intoduced. On the top end of the glass tube, an 80 mm length of 6 mm diameter tygon tubing was attached to match the size of the compression fitting at the bottom of the column. The stopper face exposed to the flask contents was covered with aluminum foil to prevent adsorption of PCE by the stopper. Before sampling, the flasks were evacuated with a vacuum pump. The vacuum was maintained by clamping the tygon tubing with a hose clamp. Once all the flasks were ready, they were attached to the columns through the compression fittings, and the vacuum was released. The fluid in the column was drawn slowly into the flask which minimized losses through volatilization. Since 5 mL vials were used for the headspace analysis, only 20 mL of effluent was required for duplicate analyses. After collecting the samples, the flasks were disconnected quickly and the contents were transferred to the vials.

Analysis was carried out every second sampling day due to the large number being analyzed. All samples were stored in the refrigerator for no longer than two days before analysis.

3.7.6 Application of Chlorides

The tracer study designed to determine aqueous fluid velocity in the unsaturated soils was conducted on fresh soil columns prepared in a similar manner to that used in the PCE study. After attaining field capacity moisture, 15 mL of DDI water containing 300 mg of Cl^- was spilled on the soil surface. Rainfall was then started immediately. Concentrations of Cl^- were measured using an Orion Cl^- Electrode.

CHAPTER FOUR

THEORY

4.1 Volatilization Rate of PCE

The volatilization of an organic chemical from a water body to the atmosphere depends on the physical and chemical properties of the compound, the physical and chemical properties of the water body and the properties of the atmosphere above the water surface [Gowda and Lock, 1984]. The physical and chemical properties of the organic compound which affect volatilization include molecular diameter, molecular mass, Henry's Law Constant and the diffusion coefficient. The chemical properties of the liquid are influenced by certain modifying materials such as adsorbents, electrolytes, emulsions and organic films. The physical properties of the water body include area, volume and temperature. Important atmospheric properties are wind speed and temperature.

The two-film theory presented by Lewis and Whitman [1924] is used to theoretically describe the volatilization of organic compounds. The two-film model assumes that the bulk air and water phases are uniformly mixed, and both phases are separated by thin gas and liquid films as indicated in Figure 4-1.

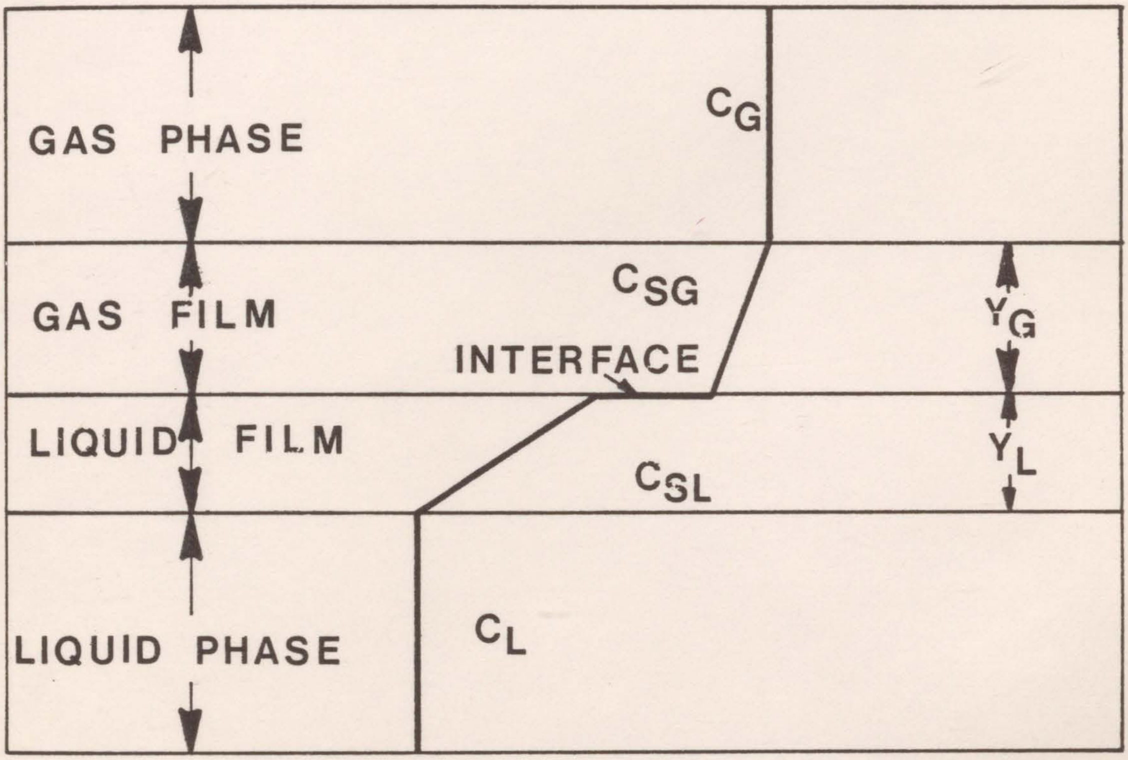


Figure 4-1 Representation of Two-Film Theory [Gowda and Lock, 1984]

The main resistance to mass transfer of a substance is encountered in the interfacial layers. As such, the two-film concept in differential form can be expressed by Fick's first law of diffusion according to [AWWA, 1971]:

$$\text{Total Flux} = Aj = -D_L A[\partial C/\partial y_L]_1 = -D_G A[\partial C/\partial y_G]_2 \quad (4\text{-}1)$$

where

$[\partial C/\partial y_L]_1$ = concentration gradient through liquid film, $kg/m^3/m$,

$[\partial C/\partial y_G]_2$ = concentration gradient through gas film, $kg/m^3/m$,

D_L = diffusion coefficient through liquid, m^2/h,

D_G = diffusion coefficient through gas, m^2/h,

A = cross-sectional area, m^2,

j = mass flux, $kg/m^2/h$,

t = time, h.

Assuming that the concentrations immediately on either side of the interface are in equilibrium and that convection is negligible, the transport across the two-layer system in Figure 4-2 can be represented by:

$$\partial X/\partial t = -Aj = D_{OL}A(\partial C/\partial y) \qquad (4\text{-}2)$$

where

$\partial X/\partial t$ = mass flow rate, kg/h,

D_{OL} = overall diffusion coefficient, m^2/h,

$\partial C/\partial y$ = overall concentration gradient, $kg/m^3/m$.

If the overall liquid mass transfer coefficient, K_{OL}, (m/h), is defined as the overall diffusion coefficient, D_{OL}, divided by overall two-layer thickness, y, Equation 4-2 can be written as:

$$\partial X/\partial t = (D_{OL}/y)A(C_L-C_G) \qquad (4\text{-}3a)$$

or

$$\partial X/\partial t = K_{OL}A(C_L-C_G) \qquad (4\text{-}3b)$$

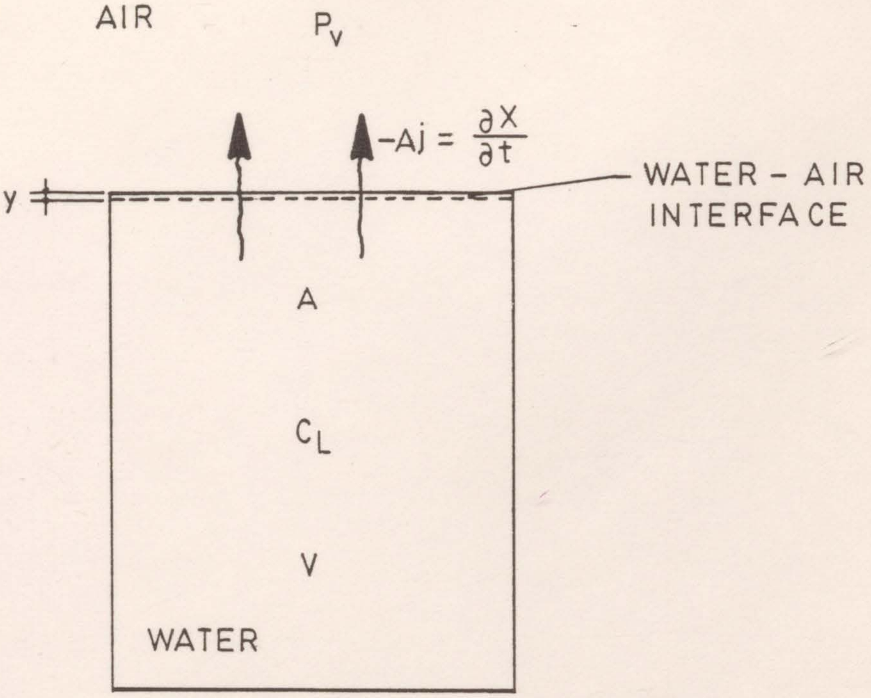


Figure 4-2 Representation of Volatilization Transport

If C_G is written in terms of Henry's law constant, then:

$$C_G = P_V/H \tag{4-4}$$

where

P_V = atmospheric partial pressure, atm,

H = Henry's Law Constant, m^3-atm/kg.

However, as the existing air currents in the atmosphere carry away any volatilized solute, almost no build up of chemical will occur. It can, therefore, be assumed that C_G approaches 0. Consequently, Eq.4-3 can be simplified to:

$$\partial X/\partial t = K_{OL}AC_L \tag{4-5}$$

Given that

$$\partial X = -\partial C_L V \qquad (4\text{-}6)$$

where

V = bulk liquid volume, m^3.

Subsituting Equation 4-6 into Equation 4-5 gives:

$$\frac{\partial C_L}{\partial t} = -\frac{K_{OL} A C_L}{V} \qquad (4\text{-}7)$$

Letting $K_{OL}\,\frac{A}{V} = k'$, give (4-7b)

$$\frac{\partial C_L}{\partial t} = -k' C_L \qquad (4\text{-}8)$$

In order to solve Eq. 4-8, the following boundary conditions are used:

$C_L = C_o$ at t=0 and $C_L = C$ at t=t.

Thus,

$$\frac{\partial C_L}{C_L} = -k' \partial t \qquad (4\text{-}9a)$$

and

$$\int_{C_o}^{C} \frac{dC_L}{C_L} = -\int_{0}^{t} k' dt \qquad (4\text{-}9b)$$

$$\ln(C_L) \Big|_{C_o}^{C} = -k't \Big|_{0}^{t} \qquad (4\text{-}9c)$$

$$\ln(C/C_o) = -k't \qquad (4\text{-}9d)$$

$$C/C_o = e^{-k't} \quad (4\text{-}9e)$$

with $k' = 2.303k,$ (4-10)

$$C/C_o = e^{-2.303kt} \quad (4\text{-}11)$$

or

$$C/C_o = 10^{-kt} \quad (4\text{-}12)$$

where

C = final concentration in liquid, kg/m^3,

C_o = initial concentration in liquid, kg/m^3,

k = volatilization rate, 1/h,

t = time, h.

4.2 Mass Flux from a PCE Pool Submerged in a Body of Water

In this case, two diffusion layers consist of a pure chemical film and a liquid film. Using the two-film layer theory presented in Section 4.1, and Figure 4-3, Equation 4-13 can be written to describe the mass flow of a substance into the water.

$$\partial X_1/\partial t = K_{OL1}A(C_{is}-C_L) \quad (4\text{-}13)$$

where

C_L = concentration of chemical in water, kg/m^3,

$\partial X_1/\partial t$ = mass flow rate at chemical - water interface, kg/h

A = cross-sectional area of vessel, m^2.

K_{OL1} = overall liquid film coefficient at chemical - water interface, m/h,

C_{is} = saturation concentration of the chemical liquid at the interface, kg/m^3.

Since

$$\partial X_1 = V\partial C_L \quad (4\text{-}14)$$

$$V\partial C_L/\partial t = K_{OL1}A(C_{is} - C_L) \quad (4\text{-}15)$$

In order to solve Eq. 4-15, the following boundary conditions are used:

$C_L=0$ at $t=0$ and $C_L=C_F$ at $t=t$.

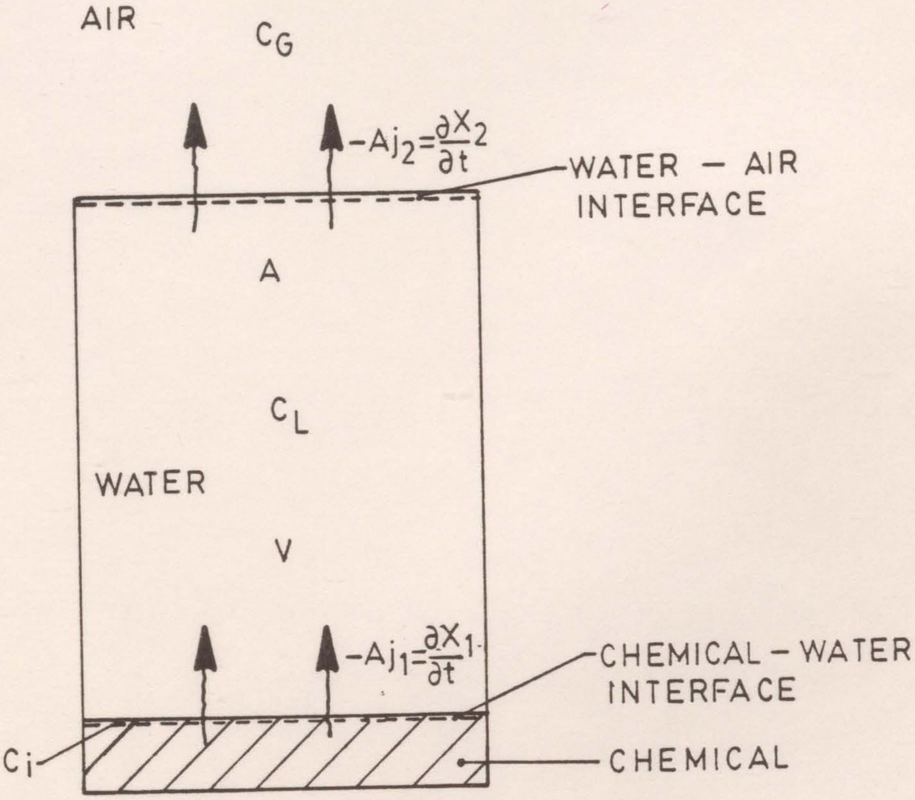


Figure 4-3 Representation of Mass Flux into Water and Volatilization into the Atmosphere

Therefore, rearranging and solving Equation 4-15 gives:

$$\int_{0}^{C_F} \frac{dC_L}{K_{OL1}(C_{is} - C_L)} = \int_{0}^{t} \frac{A}{V}\,dt \tag{4-16a}$$

$$-\frac{1}{K_{OL1}} \ln\left[K_{OL1}(C_{is} - C_L)\right]\Bigg|_{0}^{C_F} = \frac{A}{V}\,t\Bigg|_{0}^{t} \tag{4-16b}$$

$$\ln\left[\frac{K_{OL1}C_{is} - K_{OL1}C_F}{K_{OL1}C_{is}}\right] = -\,K_{OL1}\frac{A}{V}\,t \tag{4-16c}$$

$$1-(C_F/C_{is}) = e^{-K_{OL1}(A/V)t} \tag{4-16d}$$

$$C_F/C_{is} = 1-e^{-K_{OL1}(A/V)t} \tag{4-16e}$$

4.3 Combining Volatilization and Mass Flux of PCE

Using the two-film theory presented in Section 4.1, Equations 4-17 and 4-18 can be written to represent the combined effects of mass transfer from the pure substance into water and subsequent volatilization of the chemical into the atmosphere as shown in Figure 4-3.

$$\partial X_1/\partial t = K_{OL1}A(C_{is}-C_L) \tag{4-17}$$

$$\partial X_2/\partial t = K_{OL2}A(C_L-C_G) \tag{4-18}$$

where

$\partial X_1/\partial t$ = mass flow rate at chemical-water interface, kg/h,

$\partial X_2/\partial t$ = mass flow rate at water-air interface, kg/h,

K_{OL1} = overall liquid film coefficient at chemical -water interface, m/h,

K_{OL2} = overall liquid film coefficient at water - air interface, m/h,

C_{is} = saturation concentration of the chemical in liquid at the interface, kg/m^3,

C_L = concentration of the chemical in water, kg/m^3.

Again assuming that $C_G = 0$, Eq. 4-18 gives

$$\partial X_2/\partial t = K_{OL2} A C_L \tag{4-19}$$

From a material balance on Fig. 4-3 it follows that:

$$V \frac{\partial C_L}{\partial t} = \frac{\partial X_1}{\partial t} - \frac{\partial X_2}{\partial t} \tag{4-20}$$

and combining Eqs. 4-17 and 4-19 with Eq. 4-20 results in

$$V \frac{\partial C_L}{\partial t} = A\left[K_{OL1}C_{is} - K_{OL1}C_L - K_{OL2}C_L\right] \tag{4-21}$$

Equation 4-21 can be solved analytically with the following initial conditions:

$C_L=0$ at $t=0$ and $C_L=C_L$ at $t=t$.

Therefore,

$$\int_0^{C_L} \frac{dC_L}{K_{OL1}C_{is} - (K_{OL1} + K_{OL2})C_L} = \frac{A}{V}\int_0^t dt \tag{4-22a}$$

$$\frac{-1}{K_{OL1} + K_{OL2}} \ln\left[K_{OL1}C_{is} - (K_{OL1} + K_{OL2})C_L\right]\Bigg|_0^{C_L} = \frac{A}{V}\,t\Bigg|_0^t \qquad (4\text{-}22b)$$

$$\ln\left[K_{OL1}C_{is} - (K_{OL1} + K_{OL2})C_L\right] - \ln(K_{OL1}C_{is}) = - (K_{OL1} + K_{OL2})\frac{A}{V}t \qquad (4\text{-}22c)$$

$$\ln\left[\frac{K_{OL1}C_{is} - (K_{OL1} + K_{OL2})C_L}{K_{OL1}C_{is}}\right] = - (K_{OL1} + K_{OL2})\frac{A}{V}t \qquad (4\text{-}22d)$$

$$\ln\left[\frac{1 - (K_{OL1} + K_{OL2})C_L}{K_{OL1}C_{is}}\right] = - (K_{OL1} + K_{OL2})\frac{A}{V}t \qquad (4\text{-}22e)$$

$$\frac{(K_{OL1} + K_{OL2})}{K_{OL1}}\left[\frac{C_L}{C_{is}}\right] = - e^{-(K_{OL1} + K_{OL2})(A/V)t} \qquad (4\text{-}22f)$$

$$\frac{C_L}{C_{is}} = \frac{K_{OL1}}{(K_{OL1} + K_{OL2})}\left[1 - e^{-(K_{OL1} + K_{OL2})(A/V)t}\right] \qquad (4\text{-}22g)$$

4.4 Perfusion Apparatus

When the perfusion apparatus is in operation, the solute continuously passes through the soil mass. Even though the contact time that the solution has with the soil is minimal, there will be a change in concentration as a result of adsorption. A mass balance can be written for the process, using the terms shown in Figure 4-4 and defined as below:

Q = Recirculation rate, m^3/h,

V_ℓ = Bulk liquid volume in flask, m^3,

C = Solute concentration in bulk liquid, kg/m^3,

C_e = Solute concentration in liquid leaving soil, kg/m^3.

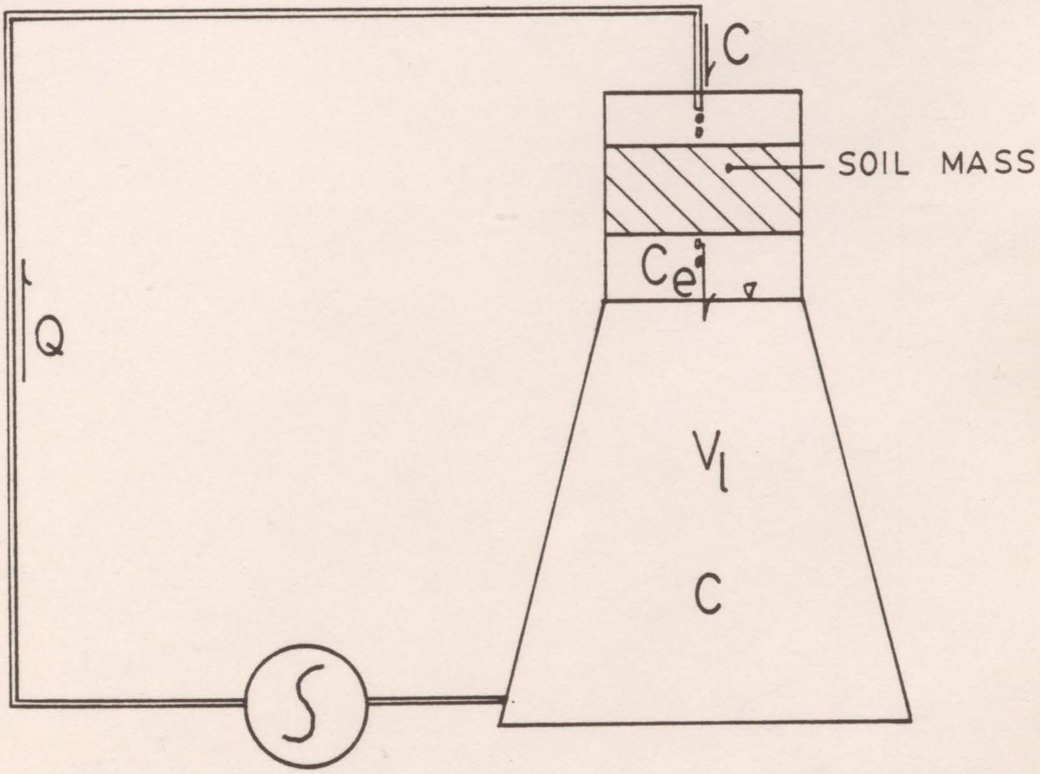


Figure 4-4 Perfusion Apparatus

Considering a time interval, ∂t, at time t, when a volume, $Q\partial t$, is pumped through the soil mass, resulting in a change in concentration, ∂C, in the bulk liquid, the mass balance is:

$$\text{(Initial Mass - Final Mass)} = \text{Adsorbed Mass} \tag{4-23}$$

or

$$V_\ell \partial C = (QC - QC_e)\partial t \tag{4-24a}$$

$$-\partial C = \frac{QC - QC_e}{V_\ell}\partial t \tag{4-24b}$$

$$-\frac{\partial C}{\partial t} = \frac{Q(C - C_e)}{V_\ell} \tag{4-24c}$$

Assuming that the soil mass completely adsorbs the chemical mass applied on it, i.e., $C_e=0$,

and

$$-\frac{\partial C}{\partial t} = \frac{QC}{V_\ell} \tag{4-25a}$$

$$\int_{C_o}^{C} \frac{dC}{C} = -\frac{Q}{V_\ell}\int_0^t dt \tag{4-25b}$$

$$\ln\frac{C}{C_o} = -\frac{Q}{V_\ell}t \tag{4-25c}$$

$$C = C_o e^{-(Q/V_\ell)t} \tag{4-25d}$$

where Q/V_ℓ is defined as the theoretical adsorption rate.

Equation 4-25d gives the concentration of chemical remaining in the flask at any time t.

4.5 Soil Column Breakthrough

When a solute is applied to a fixed-bed column, the concentration in the effluent will increase as the sorption zone moves toward the bottom of the column. A typical solute breakthrough curve is given in Figure 4-5. From the breakthrough curve two important points can be determined, breakthrough and exhaustion. Breakthrough is defined as the throughput volume at which the effluent concentration attains a finite value. This concentration is commonly taken as $0.05C_o$ [Reynolds, 1982]. Exhaustion is defined as the throughput at which the effluent concentration approached the influent concentration. This concentration is commonly taken as $0.95\ C_o$.

The total mass of solute adsorbed can be determined from the breakthrough curve. The total adsorbed mass is the area above the breakthrough curve, and can be represented by:

$$\int_0^X dX = (C_o - C)\int_0^{V_t} dV_t \qquad (4\text{-}26)$$

where

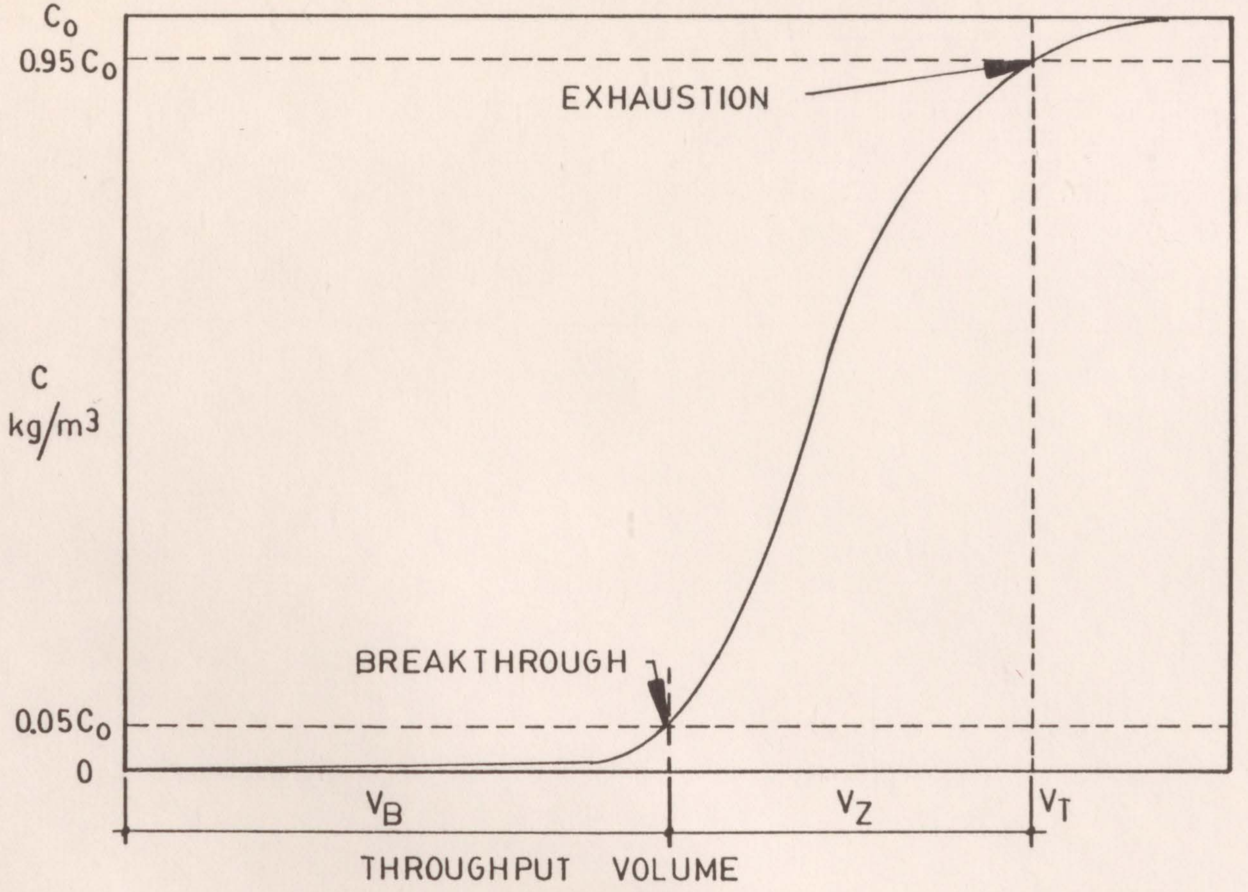


Figure 4-5 TYPICAL BREAKTHROUGH CURVE

X = mass of solute, kg,

C_o = initial concentration of solute, kg/m^3,

C = final concentration of solute, kg/m^3,

V_t = throughput volume, m^3.

Solving Equation 4-26 gives:

$$X = (C_o - C)V_t \qquad (4\text{-}27)$$

Adsorption of compounds on soil is commonly reported as X/M, the mass of solute adsorbed per unit mass of soil. Therefore, solute adsorption on soil in a column can be expressed as

$$\frac{X}{M} = \frac{V_t(C_o - C)}{LA\gamma} \qquad (4\text{-}28a)$$

where

L = length of soil column, m,

A = cross-sectional area, m^2,

X/M = mass of solute/mass of soil, mg/kg,

γ = density of soil, kg/m^3.

and

$$\frac{X}{M} = \frac{V_t}{L} \times \frac{(Co - C)}{A\gamma} \qquad (4\text{-}28b)$$

The ratio V_t/L, can be determined by running column studies and plotting the various breakthrough and exhaustion throughput volumes versus their respective depths. By plotting the throughput volume on the ordinate versus column length on the abscissa, V_t/L is defined as the slope of the line passing through the origin.

4.6 Moisture Transport in Unsaturated Soil

A mathematical model depicting the breakthrough of a chemical spilled on an unsaturated soil column is derived in this section. Since the chemical transport in the unsaturated zone depends on the moisture movement, the differential equation for an unsaturated flow in a soil column is derived first.

When the interconnecting pores of a soil mantle are not filled completely with water, the soil is considered to be unsaturated. It is assumed that Darcy's Law is applicable, where the coefficient of proportionality becomes a function of moisture content. This assumption has been proven experimentally by Childs and Collis-George [1950]. It should be noted that since Richards [1931] derived these equations initially the last version is usually referred to as Richards Equation [Freeze, 1969, Kirkham and Powers, 1972 and Swartzendruber, 1969].

Consider the flow element, $\Delta x \cdot \Delta y \cdot \Delta z$, shown in Figure 4-6. where v_x, v_y and v_z are the fluid velocities approaching the element. The changes in fluid velocities through the element are given by $\frac{\partial (v_x)}{\partial x} \cdot \Delta x$, $\frac{\partial (v_y)}{\partial y} \cdot \Delta y$ and $\frac{\partial (v_z)}{\partial z} \cdot \Delta z$.

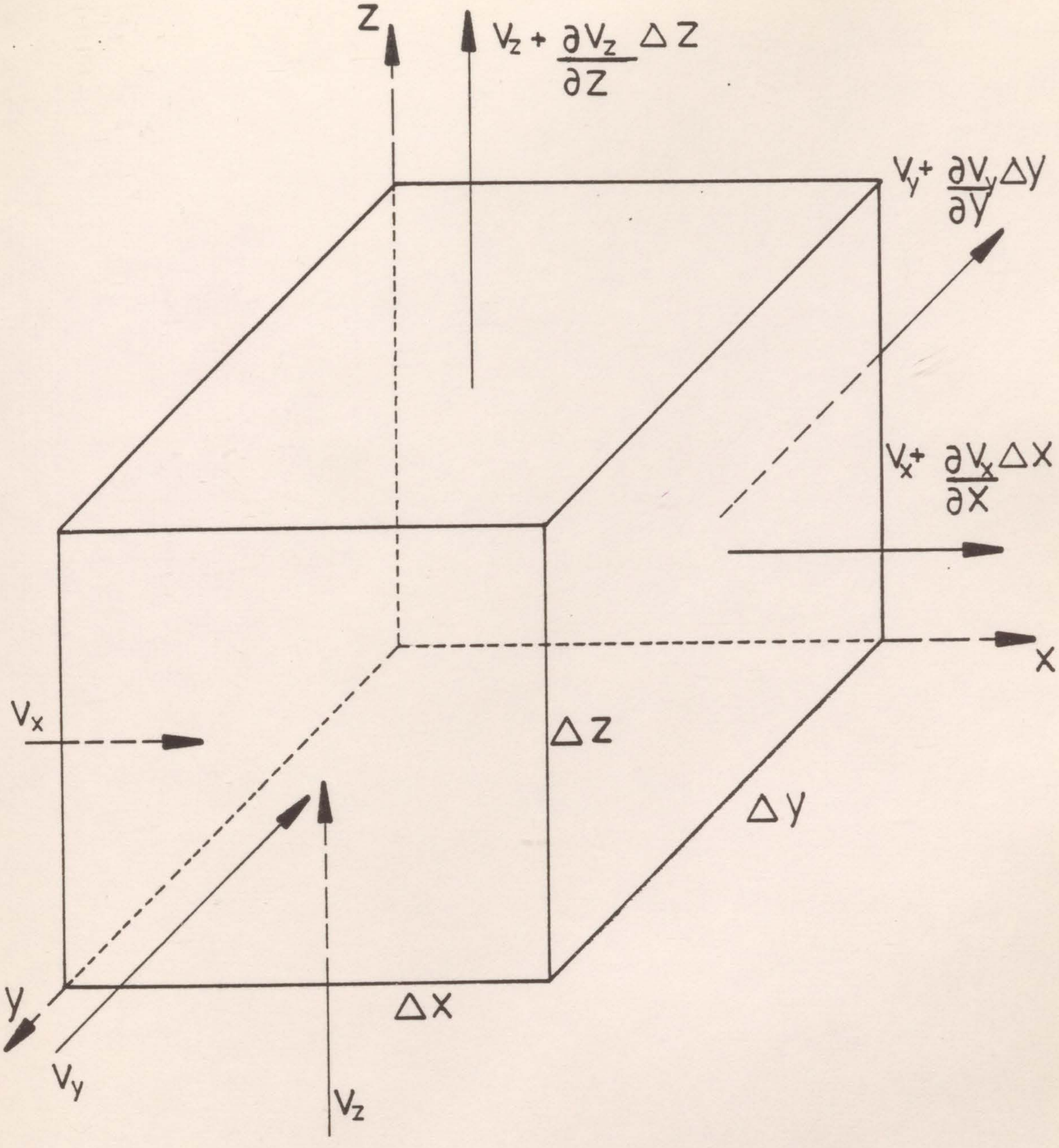


Figure 4-6 FLOW ELEMENT

By using the principle of conservation of mass it can be shown that:

rate of moisture accumulation = mass inflow rate - mass outflow rate (4-29)

or

$$\text{rate of moisture accumulation} = \Delta x \Delta y \Delta z \frac{\partial}{\partial t}(\rho \theta) \tag{4-30}$$

where, ρ is the moisture density and θ is the moisture content on a volume basis, i.e., volume of moisture per unit volume of matrix, m^3/m^3. The matrix is defined as the granular skeleton plus the enclosed pores. Therefore,

$$\begin{aligned} \Delta x \Delta y \Delta z \frac{\partial}{\partial t}(\rho \theta) = {} & \rho v_x \Delta y \Delta z - [\rho v_x + \frac{\partial}{\partial x}(\rho v_x) \Delta x] \Delta y \Delta z + \\ & \rho v_y \Delta x \Delta z - [\rho v_y + \frac{\partial}{\partial y}(\rho v_y) \Delta y] \Delta x \Delta z + \\ & \rho v_z \Delta x \Delta y - [\rho v_z + \frac{\partial}{\partial z}(\rho v_z) \Delta z] \Delta x \Delta y \end{aligned} \tag{4-31}$$

or

$$\begin{aligned} \Delta x \Delta y \Delta z \frac{\partial}{\partial t}(\rho \theta) = {} & - \frac{\partial}{\partial x}(\rho v_x) \Delta x \Delta y \Delta z \\ & - \frac{\partial}{\partial y}(\rho v_y) \Delta x \Delta y \Delta z - \frac{\partial}{\partial z}(\rho v_z) \Delta x \Delta y \Delta z. \end{aligned} \tag{4-32}$$

or

$$\frac{\partial}{\partial t}(\rho \theta) = - \frac{\partial}{\partial x}(\rho v_x) - \frac{\partial}{\partial y}(\rho v_y) - \frac{\partial}{\partial z}(\rho v_z) \tag{4-33}$$

Assuming that water is incompressible and remains constant, it follows that:

$$\frac{\partial \theta}{\partial t} = - \frac{\partial}{\partial x}(v_x) - \frac{\partial}{\partial y}(v_y) - \frac{\partial}{\partial z}(v_z) \tag{4-34}$$

According to Darcy's Law for unsaturated flow;

$$v_x = -K_x \frac{\partial h}{\partial x}, \; v_y = -K_y \frac{\partial h}{\partial y} \quad \text{and} \quad v_z = -K_z \frac{\partial h}{\partial z}, \tag{4-35}$$

where K is the capillary conductivity rather that the hydraulic conductivity. Since capillary conductivity increases with moisture content, it can be written as a function of θ, i.e., $K(\theta)$. When soil becomes saturated, θ is considered as a constant and $K(\theta)$ approaches the hydraulic conductivity, K. In this analysis h is the total head measured positively upward from an arbitrary reference level.

Therefore,

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left(K_x(\theta)\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y(\theta)\frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z(\theta)\frac{\partial h}{\partial z}\right) \tag{4-36}$$

Since soil is assumed to be isotropic, $K_x=K_y=K_z=K$. However, since K is still a variable depending on moisture content, the above equation can be written as

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left(K(\theta)\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K(\theta)\frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K(\theta)\frac{\partial h}{\partial z}\right) \tag{4-37}$$

The total h consists of pressure or tension head, h_t, plus gravitational head, z. Therefore, for the unsaturated soil $h=h_t+z$. Substituting this value for h into Equation 4-37 gives,

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left(K(\theta)\frac{\partial h_t}{\partial x}\right) + \frac{\partial}{\partial y}\left(K(\theta)\frac{\partial h_t}{\partial y}\right) + \frac{\partial}{\partial z}\left(K(\theta)\frac{\partial h_t}{\partial z}\right) + \frac{\partial}{\partial z}K(\theta) \tag{4-38}$$

Since h_t is a function of θ, and θ is a function of x,y,z and t, therefore, $h_t=f[\theta(x,y,z,t)]$. Assuming that θ and h_t are continuous and using the chain rule

$$K(\theta)\frac{\partial h_t}{\partial x} = K(\theta)\frac{dh_t}{d\theta}\frac{\partial\theta}{\partial x}\ ;\ K(\theta)\frac{\partial h_t}{\partial y} = K(\theta)\frac{dh_t}{d\theta}\frac{\partial\theta}{\partial y}\ ;$$

$$K(\theta)\frac{\partial h_t}{\partial z} = K(\theta)\frac{dh_t}{d\theta}\frac{\partial\theta}{\partial z}.$$

Since it is known that moisture in unsaturated soil does not move continuously but moves by jumps as pores empty, the assumption of continuous θ and h_t may be questionable. However, reported experimental results have shown continuity to be valid [Freeze, 1969, Kirkham and Powers, 1972 and Swartzendruber, 1969]. Therefore,

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial x}\left(K(\theta)\frac{dh_t}{d\theta}\frac{\partial\theta}{\partial x}\right) + \frac{\partial}{\partial y}\left(K(\theta)\frac{dh_t}{d\theta}\frac{\partial\theta}{\partial y}\right) + \frac{\partial}{\partial z}\left(K(\theta)\frac{dh_t}{d\theta}\frac{\partial\theta}{\partial z}\right) + \frac{\partial}{\partial z}K(\theta) \qquad (4\text{-}39)$$

The diffusion coefficient D for moisture in unsaturated soil is defined as the ratio of the capillary conductivity, K, to the specific moisture content $\frac{d\theta}{dh_t}$, where the specific moisture content is defined as the change in moisture in the porous medium for a unit change in tension or suction head. Therefore, substituting $D=K\cdot\frac{dh_t}{d\theta}$ into Eq. 4-39 gives:

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial x}\left(D(\theta)\frac{\partial\theta}{\partial x}\right) + \frac{\partial}{\partial y}\left(D(\theta)\frac{\partial\theta}{\partial y}\right) + \frac{\partial}{\partial z}\left(D(\theta)\frac{\partial\theta}{\partial z}\right) + \frac{\partial}{\partial z}K(\theta) \qquad (4\text{-}40)$$

Considering flow only in the z direction gives

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}\left(D(\theta)\frac{\partial\theta}{\partial z}\right) + \frac{\partial}{\partial z}K(\theta) \qquad (4\text{-}41)$$

Since the datum is taken at the soil surface, Equation 4-41 is modified to make z positive in the downward direction.

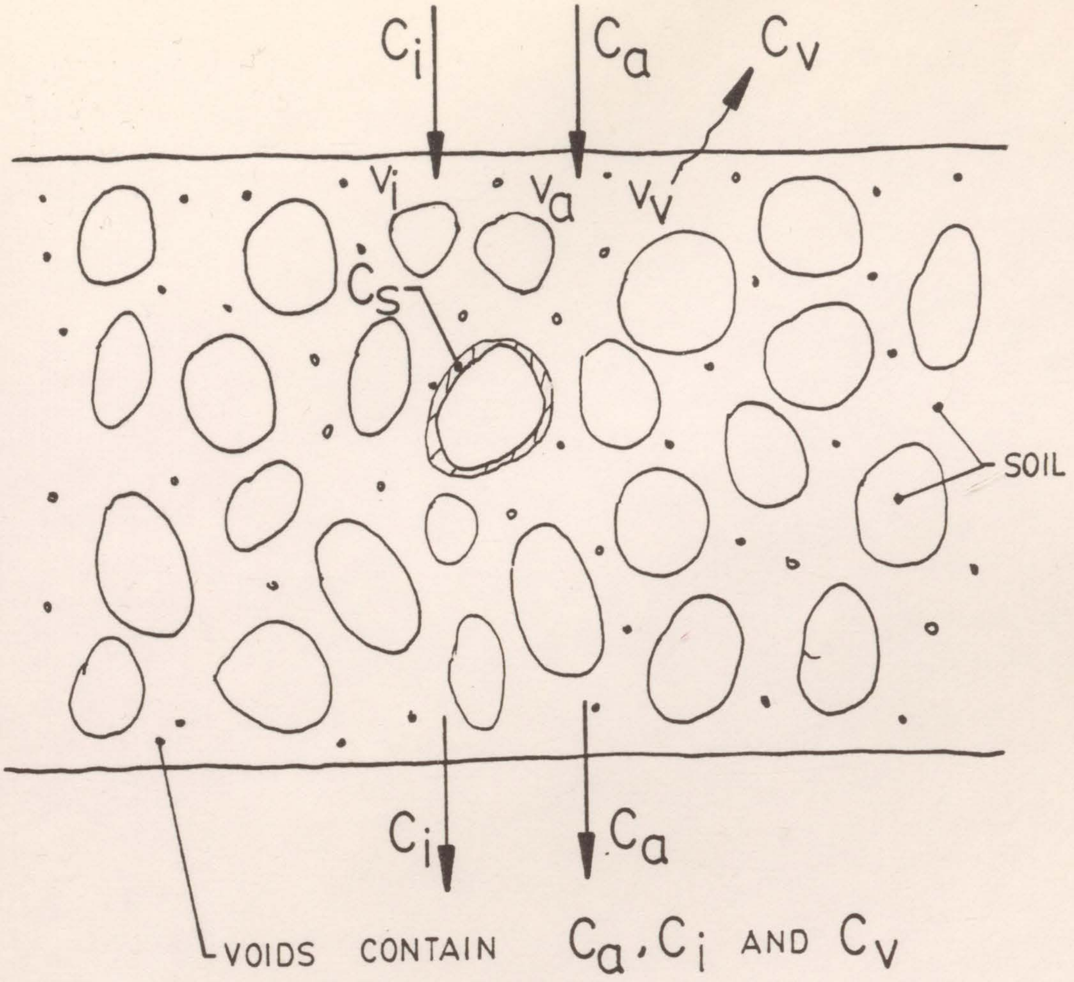
$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}\left(D(\theta)\frac{\partial\Theta}{\partial z}\right) - \frac{\partial}{\partial z}K(\theta) \qquad (4\text{-}42)$$

It should be noted that Equation 4-42 is non-linear since all terms are dependent on θ, and as such it has no known analytical solution.

4.6.1 Pollutant Transport in Unsaturated Soil

After certain modifications, Eq. 4-42 can be used to model the transport of a contaminant as it moves toward the groundwater. It becomes necessary to replace the moisture content, Θ, with the desired concentration in the aqueous or vapour phases, and to assume a constant D and K. In addition, a source/sink term must be introduced to account for the adsorption, degradation, and volatilization, as the contaminant migrates down the soil profile [Short, 1985].

As illustrated in Figure 4-7, four different phases of the chemical can coexist: vapour phase, adsorbed phase, aqueous (dissolved phase) and the pure or immiscible phase.



C_s	ADSORBED CHEMICAL, mg/kg
C_a	DISSOLVED CHEMICAL, kg/m^3
C_i	PURE CHEMICAL, kg/m^3
C_v	VOLATILIZED CHEMICAL, kg/m^3
v_a	DISSOLVED VELOCITY, m/d
v_i	IMMISCIBLE VELOCITY, m/d
v_v	VAPOUR VELOCITY, m/d

Figure 4-7 TRANSPORT OF A POLLUTANT IN SOIL

For a total mass balance for all four phases, each phase is first derived separately and then combined into one mass transport equation [Short, 1985 and Palmer, 1987]

4.6.1.1 Aqueous Phase

The dissolved chemical will move toward the groundwater through dispersion and advection. Some decay is possible, with the rate depending on the nature of the chemical and environmental conditions. In differential form this process can be expressed as [Short, 1985]:

$$\frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial z^2} - v_a \frac{\partial C_a}{\partial z} - \mu_a C_a \qquad (4\text{-}43)$$

where

C_a = concentration of chemical in dissolved phase, kg/m^3,

D_a = dispersion coefficient of chemical through soil, m^2/h,

v_a = advection of chemical through soil, m/h,

μ_a = decay rate of chemical in aqueous phase, 1/h,

t = time, h,

z = vertical distance in soil profile, m.

With the moisture content, θ, m^3/m^3, known, the mass of chemical present per unit volume of soil at any time t can be determined by multiplying Eq. 4-43 by θ.

$$\theta \frac{\partial C_a}{\partial t} = \theta D_a \frac{\partial^2 C_a}{\partial z^2} - \theta v_a \frac{\partial C_a}{\partial z} - \theta \mu_a C_a \tag{4-44}$$

4.6.1.2 Adsorbed Phase

The following equation accounts for the mass of chemical adsorbed per unit volume at any time t

$$\gamma \frac{\partial C_s}{\partial t} = -\mu_s \gamma C_s \tag{4-45}$$

Since the linear partition coefficient, K_p, can be used to relate adsorption to dissolved concentration by using $C_s = K_p C_a$, Equation 4-45 can be modified to give

$$\gamma K_p \frac{\partial C_a}{\partial t} = -\mu_s \gamma K_p C_a \tag{4-46}$$

where

C_s = concentration of adsorbed chemical on soil, mg/kg,

K_p = linear partition coefficient for the chemical between water and soil, m^3/kg,

μ_s = decay rate of chemical in adsorbed phase, 1/h,

γ = density of soil, kg/m^3.

4.6.1.3 Vapour Phase

Similar to the aqueous phase transport, the vapour phase transport can be expressed by the following differential equation for dispersion and advection [Short, 1985]:

$$\frac{\partial C_V}{\partial t} = D_V \frac{\partial^2 C_V}{\partial z^2} - v_V \frac{\partial C_V}{\partial z} - \mu_V C_V \qquad (4\text{-}47)$$

where

C_V = concentration of chemical in vapour phase, kg/m^3,

D_V = diffusion coefficient of chemical through soil, m^2/h,

v_V = advection of vapour, m/h,

μ_V = decay rate of chemical in vapour phase, 1/h.

Multiplying Eq. 4-47 by the volumetric air content, n, m^3/m^3, to obtain the mass present and using Henry's Law for partitioning, C_V=$K_H C_a$, gives

$$nK_H \frac{\partial C_a}{\partial t} = nD_V K_H \frac{\partial^2 C_a}{\partial z^2} - nv_V K_H \frac{\partial C_a}{\partial z} - n\mu_V K_H C_a \qquad (4\text{-}48)$$

4.6.1.4 Immiscible Phase

When a chemical applied on the soil surface is only slightly soluble in water, part of the chemical mass will migrate toward the groundwater in the undissolved form. This phase tranport can be represented by the following differential equation [Short, 1985]:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial z^2} - v_i \frac{\partial C_i}{\partial z} - \mu_v C_i \qquad (4\text{-}49)$$

where

C_i = density of chemical, kg/m^3,

D_i = dispersion coefficient of immiscible chemical through soil, m^2/h,

v_i = advection of undissolved chemical through soil, m/h,

μ_i = decay rate of pure chemical, 1/h.

As with the other phases, the mass of undissolved chemical can be determined by multiplying Eq. 4-49 by the volumetric immiscible phase content, Φ, m^3/m^3, present in the soil. In order to relate the solubility of the chemical to C_i, the relationship C_i=$K_i C_a$ was used, K_i is the partition coefficient between the chemical and water based on solubility [Briggs, 1981].

Accordingly

$$\Phi K_i \frac{\partial C_a}{\partial t} = \Phi D_i K_i \frac{\partial^2 C_a}{\partial z^2} - \Phi v_i K_i \frac{\partial C_a}{\partial z} - \Phi \mu_i K_i C_a \qquad (4\text{-}50)$$

4.6.1.5 Total Mass Transport Equation

The total mass of chemical per unit volume of soil can be written as:

$$\begin{array}{c} \text{Total} \\ \text{Mass} \end{array} = \begin{array}{c} \text{Mass in} \\ \text{dissolved} \\ \text{Phase} \end{array} + \begin{array}{c} \text{Mass in} \\ \text{vapour} \\ \text{Phase} \end{array} + \begin{array}{c} \text{Mass in} \\ \text{adsorbed} \\ \text{Phase} \end{array} + \begin{array}{c} \text{Mass in} \\ \text{pure} \\ \text{Phase} \end{array}$$

Changes in each of the phases can be expressed as:

$$\partial \begin{array}{c} \text{Total} \\ \text{Mass} \end{array} = \theta \partial C_a + n \partial C_v + \gamma \partial C_s + \Phi \partial C_i \qquad (4\text{-}51)$$

Finally, the rate at which the total chemical mass changes per unit volume of soil at any time t can be expressed as:

$$\frac{\partial \text{(Total Mass)}}{\partial t} = \theta \frac{\partial}{\partial t} C_a + n \frac{\partial}{\partial t} C_v + \gamma \frac{\partial}{\partial t} C_s + \Phi \frac{\partial}{\partial t} C_i \qquad (4\text{-}52)$$

or

$$\begin{aligned} (\theta + nK_H + \gamma K_p + \Phi K_i) \frac{\partial}{\partial t} C_a = {} & (\theta D_a + nK_H D_v + \Phi K_i D_i) \frac{\partial^2}{\partial z^2} C_a + \\ & (-\theta v_a - n v_v K_H - \Phi v_i K_i) \frac{\partial}{\partial z} C_a + \qquad (4\text{-}53) \\ & (-\theta \mu_a - n \mu_v K_H - \mu_s \gamma K_p - \Phi \mu_i K_i) C_a \end{aligned}$$

Eq. 4-53 expresses the transport of a pollutant through the aqueous, adsorbed, vapour and immiscible phases. This was done by writing a material balance for each phase and assuming local equilibrium [Short, 1985]. In assuming local equilibrium, the net interphase transport is zero. For example, this means that the rate of mass transfer of the pollutant from the aqueous phase to the solid phase is exactly equal to the rate of mass transfer from the solid phase to the aqueous phase. One other assumption made was that the relative amounts of each phase, aqueous, adsorbed, vapour and immiscible remain constant through the soil profile [Short, 1985].

In order to simplify Eq. 4-53, the various coefficients have been combined, to give

$$B\frac{\partial}{\partial t}C_a = D\frac{\partial^2}{\partial z^2} C_a + v_c\frac{\partial}{\partial z}C_a + UC_a \qquad (4\text{-}54)$$

where

$$B = (\theta + \gamma K_p + nK_H + \Phi K_i), \qquad (4\text{-}55)$$

$$D = (\theta D_a + nK_H D_v + \Phi K_i D_i), \qquad (4\text{-}56)$$

$$v_c = (-\theta v_a - nv_v K_H - \Phi v_i K_i), \qquad (4\text{-}57)$$

$$U = (-\theta\mu_a - n\mu_v K_H - \mu_s \gamma K_p - \Phi\mu_i K_i). \qquad (4\text{-}58)$$

4.7 Solutions of the Transport Equations

Since Eqs. 4-42 and 4-54 are non-linear differential equations, a numerical technique is required to solve them. The approach choosen is presented in the following section.

4.7.1 Moisture Transport Equation

Of the available numerical methods, two were selected for solving Eq. 4-42. They were the Crank-Nicolson implicit central differencing scheme and the 5th Order Runge-Kutta Scheme [Ahuja and Swartzendruber, 1973, Aschroft et al., 1962, Crank and Nicolson, 1947, Hanks and Bowers, 1962 Hayhoe, 1978, Smith 1985 and James et al., 1985]. However, after completing a few initial simulation runs, it was determined that the available Runge-Kutta scheme had stability problems as the time steps could not be as large as those used in Crank-Nicolson. Furthermore, the Runge-Kutta Routine available in the university mainframe did not provide sufficient flexibility, as one was limited to the number of distance steps allowed. This prevented the use of small distance steps. Therefore, the Crank-Nicolson scheme was chosen as flexibility was available which allowed small distance steps and relatively large time steps. The large time steps were important in minimizing computer time usage to provide a faster simulation, while maintaining accuracy. Finally, many researchers believe that the implicit finite difference technique of Crank-Nicolson is one of the better approaches to model the complex unsteady unsaturated flow, as it provides the required stability and flexibility [Freeze, 1969 and Bresler, 1973].

Using traditional Crank-Nicolson procedure, Eq. 4-42 can be written as:

$$\frac{\theta_{i,j+1}-\theta_{i,j}}{DT} = \frac{1}{2DZ^2}\Big[D(\theta_{i+1/2,j+1/2})\left[\theta_{i+1,j+1} + \theta_{i+1,j} - 2\theta_{i,j+1}\right]$$

$$+ D(\theta_{i-1/2,j+1/2})\left[\theta_{i-1,j+1} + \theta_{i-1,j} - 2\theta_{i,j}\right]\Big]$$

$$- \frac{1}{2DZ}\left[K(\theta_{i+1,j}) - K(\theta_{i-1,j})\right] \qquad (4\text{-}59)$$

Since D(θ) varies from i-1/2 to i+1/2, Equation 4-59 must be modified to equally weigh the diffusion coefficient on both sides of point i,j. A physical representation can be seen in Figure 4-8.

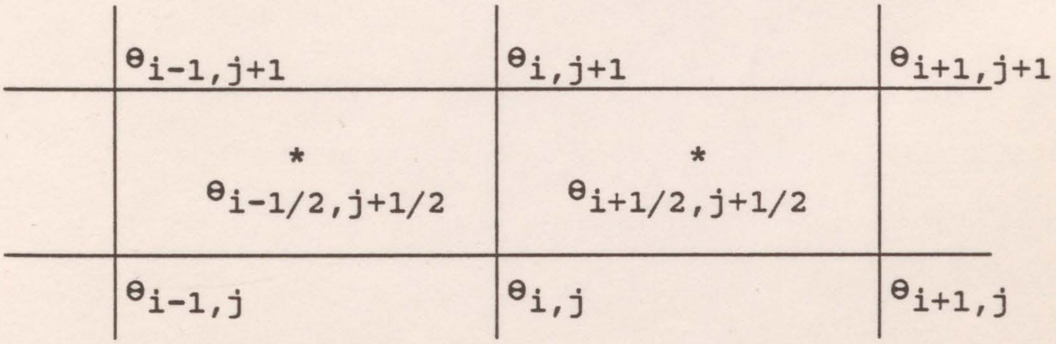


Figure 4-8 Representation of Nodes

Therefore,

$$\frac{\theta_{i,j+1} - \theta_{i,j}}{DT} = \frac{1}{2(DZ)^2}\Big[D(\theta_{i+1/2,j+1/2})[\theta_{i+1,j+1} + \theta_{i+1,j} - \theta_{i,j+1} - \theta_{i,j}] + D(\theta_{i-1/2,j+1/2})[\theta_{i-1,j+1} + \theta_{i-1,j} - \theta_{i,j+1} - \theta_{i,j}]\Big] - \frac{1}{2DZ}[K(\theta_{i+1,j}) - K(\theta_{i-1,j})] \tag{4-60}$$

Since both D and K are functions of θ in Eq. 4-60, difficulty arises in the solution because both are required for each j+1 level. However, by assuming θ at j+1 to be equal to θ at j, an estimate of D and K can be made, which in turn will provide an estimate of θ. This procedure is repeated until $\theta_{i,j+1}$ for all i's are within a tolerance limit.

The program developed and used to solve the moisture flow equation from sandy loam is given in Appendix F.

4.7.2 Pollutant Transport Equation

On the basis of the success obtained from the Crank-Nicolson approach for the more complex unsaturated moisture movement model, the same approach was used to solve Eq. 4-54. In replacing C_a with C, Eq. 4-54 can be written as:

$$\frac{C_{i,j+1} - C_{i,j}}{DT} = \frac{D}{B2}\frac{1}{(DZ)^2}\left[C_{i-1,j} + C_{i+1,j} - 2C_{i,j} + C_{i-1,j+1} + C_{i+1,j+1} - 2C_{i,j+1}\right] + \frac{v_c}{B2}\frac{1}{DZ}\left[C_{i+1,j} - C_{i-1,j}\right] + \frac{U}{B}\left[C_{i,j}\right] \quad (4\text{-}61)$$

However, it should be noted that certain assumptions were made to arrive at Equation 4-61. The column experiments were set up to provide constant rainfall for the entire duration of the spill simulation, i.e., D and V were held constant. In other words, the moisture content did not change during the experiment. The program written to solve Equation 4-61 is provided in Appendix F.

CHAPTER FIVE

PRELIMINARY INVESTIGATIONS

Prior to the start of the regular protocol for various tests, certain operating procedures and parameters had to be established. These were determined by conducting a series of preliminary tests under unknown conditions as described in the following sections.

5.1 Analysis of PCE in Water and Soil

The following operating parameters were established for analyzing PCE in water and soil.

5.1.1 Injection Equilibrium Time

It was important that consistency was maintained in the volume and temperature of the headspace in order to ensure accuracy in the measurement of the PCE concentrations. Constant headspace volume was attained by using a pipette that delivered a set volume, while constant temperature was maintained through the use of a water bath. In addition, it was ensured that an equilibrium had been reached between the liquid and headspace concentrations in the vial. This equilibrium was necessary to accurately compare the samples and the standards.

As stated in Chapter Three, the vials containing samples were allowed to sit for one-half hour in the water bath before injecting the sample into the GC column. Some studies in the literature indicate this time to be sufficient, while others suggest that a longer time is required. Therefore, preliminary tests were conducted to establish this equilibrium time. Large and small vials were completely filled with an aqueous standard of 112.5 mg/L, capped and placed in the refrigerator at 4°C. After the samples had attained 4°C, the vials were removed and a headspace was created in them. The gas samples from the headspace in the vials were analyzed at five minute intervals for a total of 40 minutes.

Figure 5-1 indicates that the samples reached their maximum concentration within five minutes. This indicates that the half-hour equilibrium time used in the subsequent analyses was more than sufficient to ensure that all samples had reached their equilibrium before analysis. In fact, the results indicated that the samples could have been analyzed within five minutes of placing vials in the water bath.

5.1.2 Calibration Curves for PCE Analysis

For analysis of PCE with a GC, it was necessary to determine if a linear calibration relationship existed over the entire range of concentrations being analyzed, as the samples were compared to the relationship established with standards.

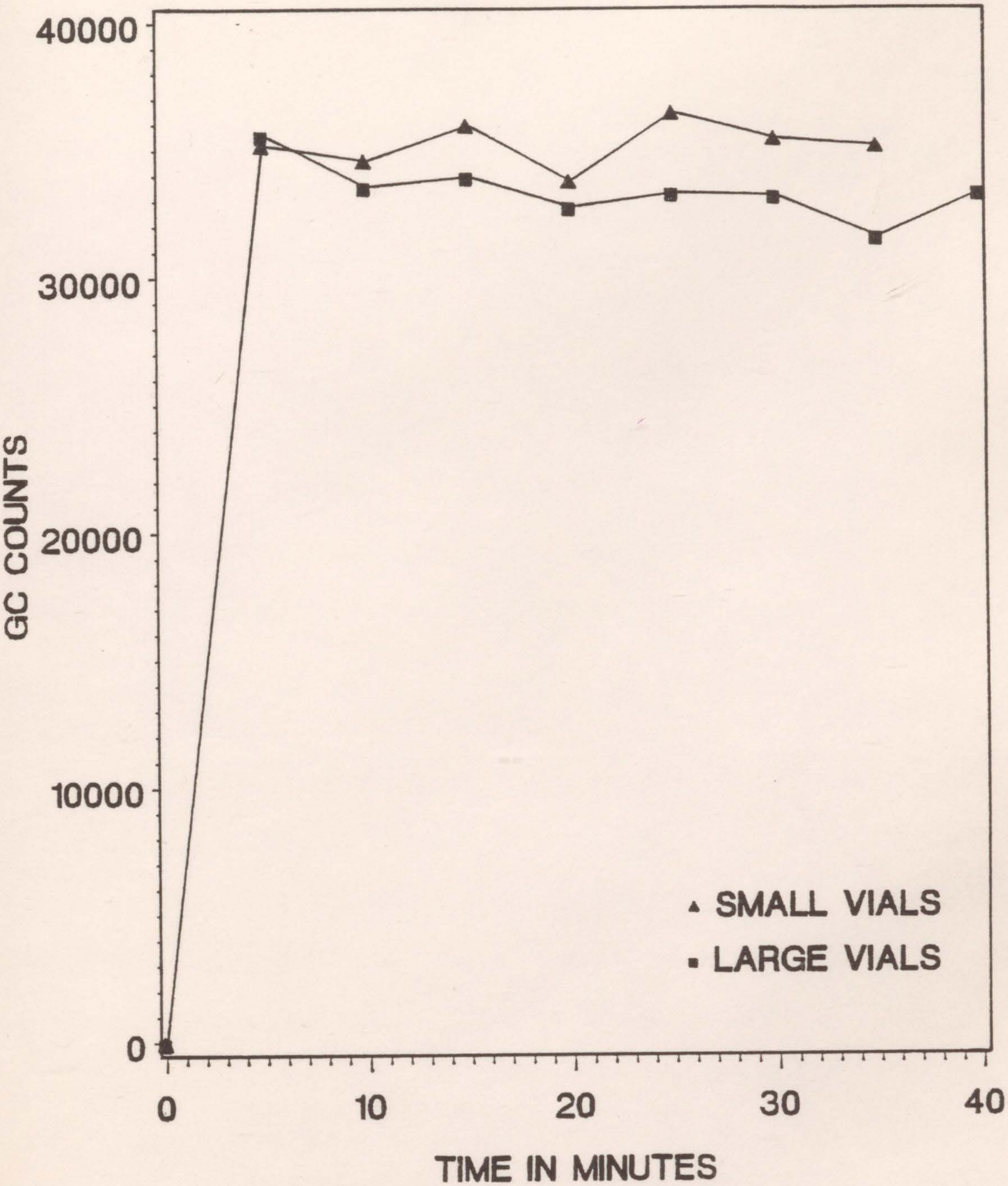


Figure 5-1 EQUILIBRIUM OF PCE HEADSPACE IN LARGE AND SMALL VIALS

5.1.2.1 Calibration Curve for PCE in Water

As Figures 5-2 and 5-3 indicate, both the large and small vials gave a linear relationship when analyzing PCE at concentrations from 0 to 112.5 mg/L. The correlation coefficients, r^2 are very high, providing confidence in the results obtained. Figure 5-4 shows that when the concentration range was lowered, 0 to 6 mg/L, a similar relationship was obtained with excellent correlation coefficients for both vial sizes. Therefore, for the concentrations studied in this research work, the GC conditions chosen for analysis were ideal. In addition, a new calibration curve was prepared on each day of analysis, to account for any possible loss in GC sensitivity.

5.1.2.2 Calibration Curve for PCE in Soil

Calibration curves were also prepared to determine the amount of PCE present in soil. The only difference in procedure was that the standards were prepared using clean soil which was the sample matrix. As Figure 5-5 indicates, a linear relationship was found for a concentration range of 0 to 30 mg/kg, with good correlation. It must be noted that these tests were done when all the vials had the identical moisture content. When the moisture content approached saturation, the results obtained were erratic because there existed an excess fluid and the PCE volatilized not only from the soil surface, but also from the fluid pool. Therefore, when analyzing soil in an unsaturated state via the headspace technique, the standards must have the same moisture content

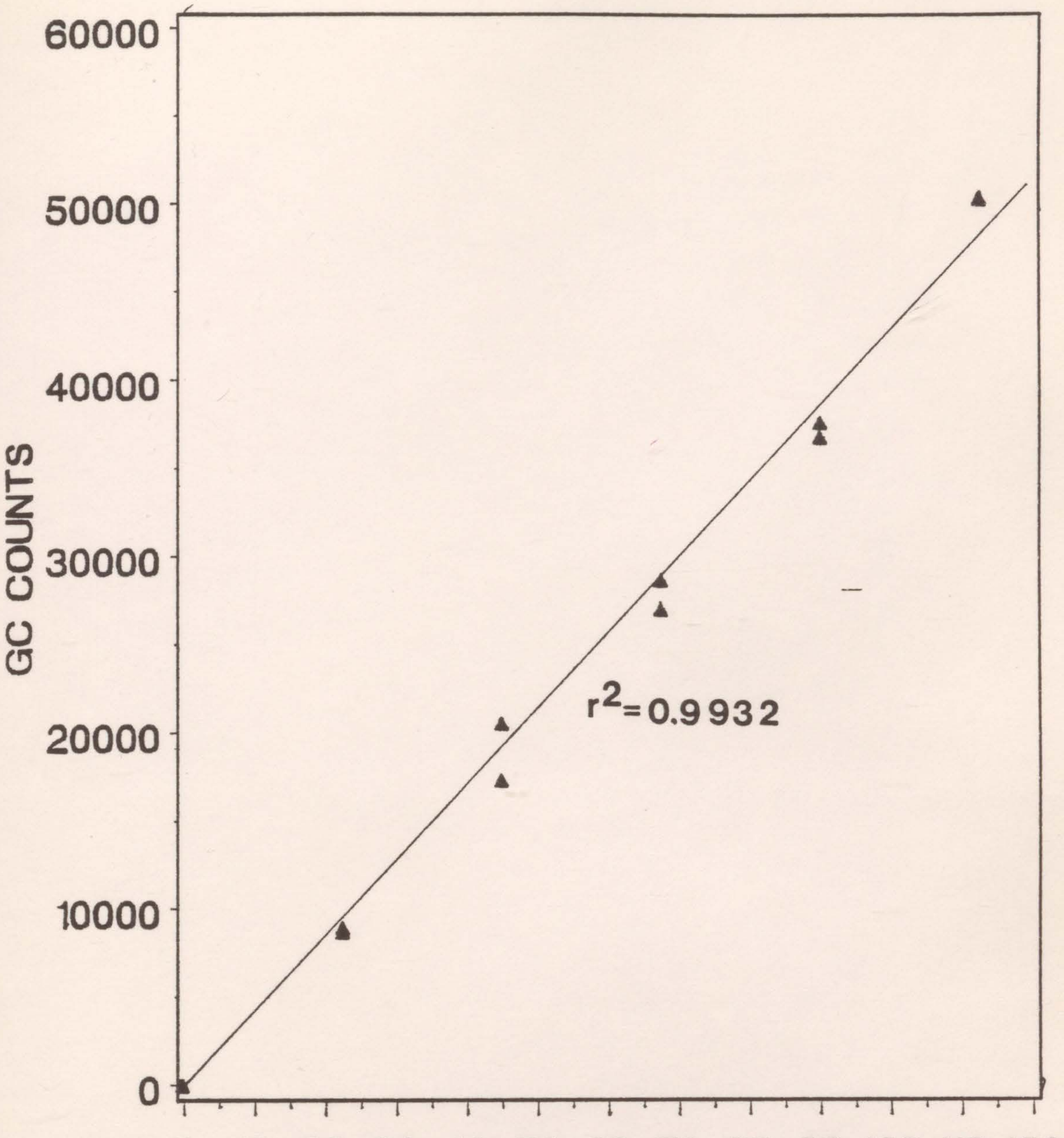


Figure 5-2 CALIBRATION CURVE FOR PCE IN AQUEOUS SOLUTION---LARGE VIALS

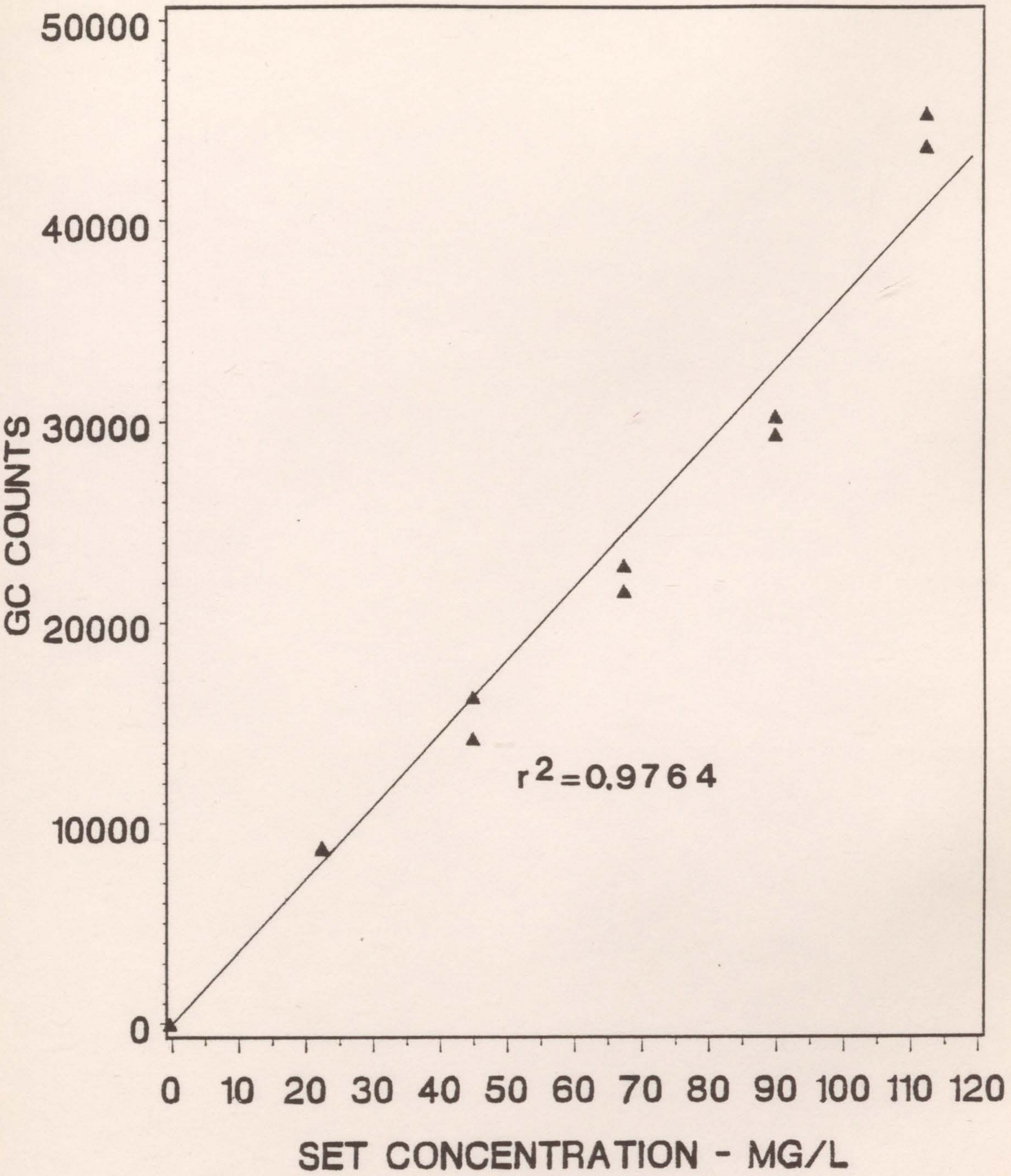


Figure 5-3 CALIBRATION CURVE FOR PCE IN AQUEOUS SOLUTION---SMALL VIALS

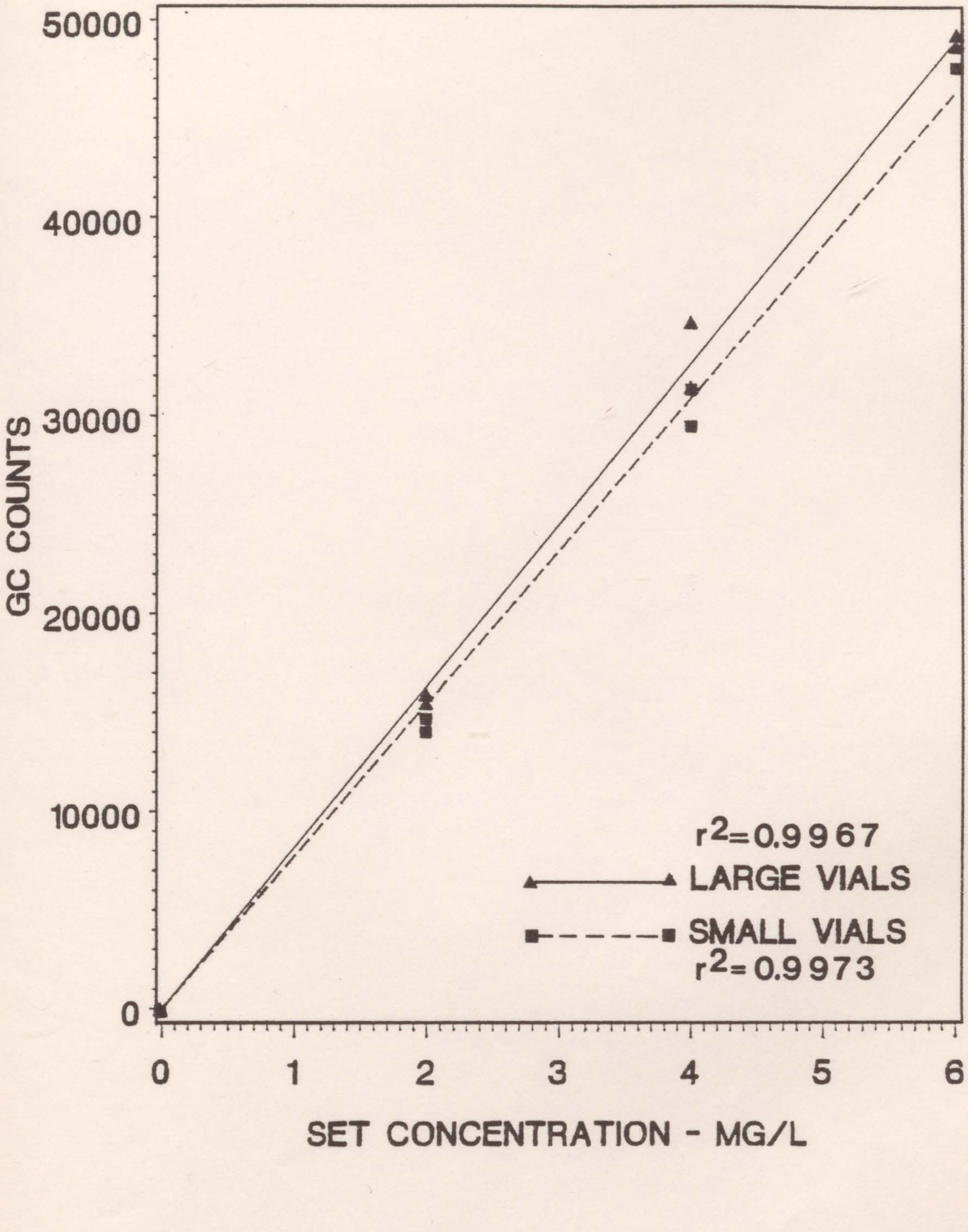


Figure 5-4 CALIBRATION CURVE FOR PCE IN AQUEOUS SOLUTION---LOW CONCENTRATIONS

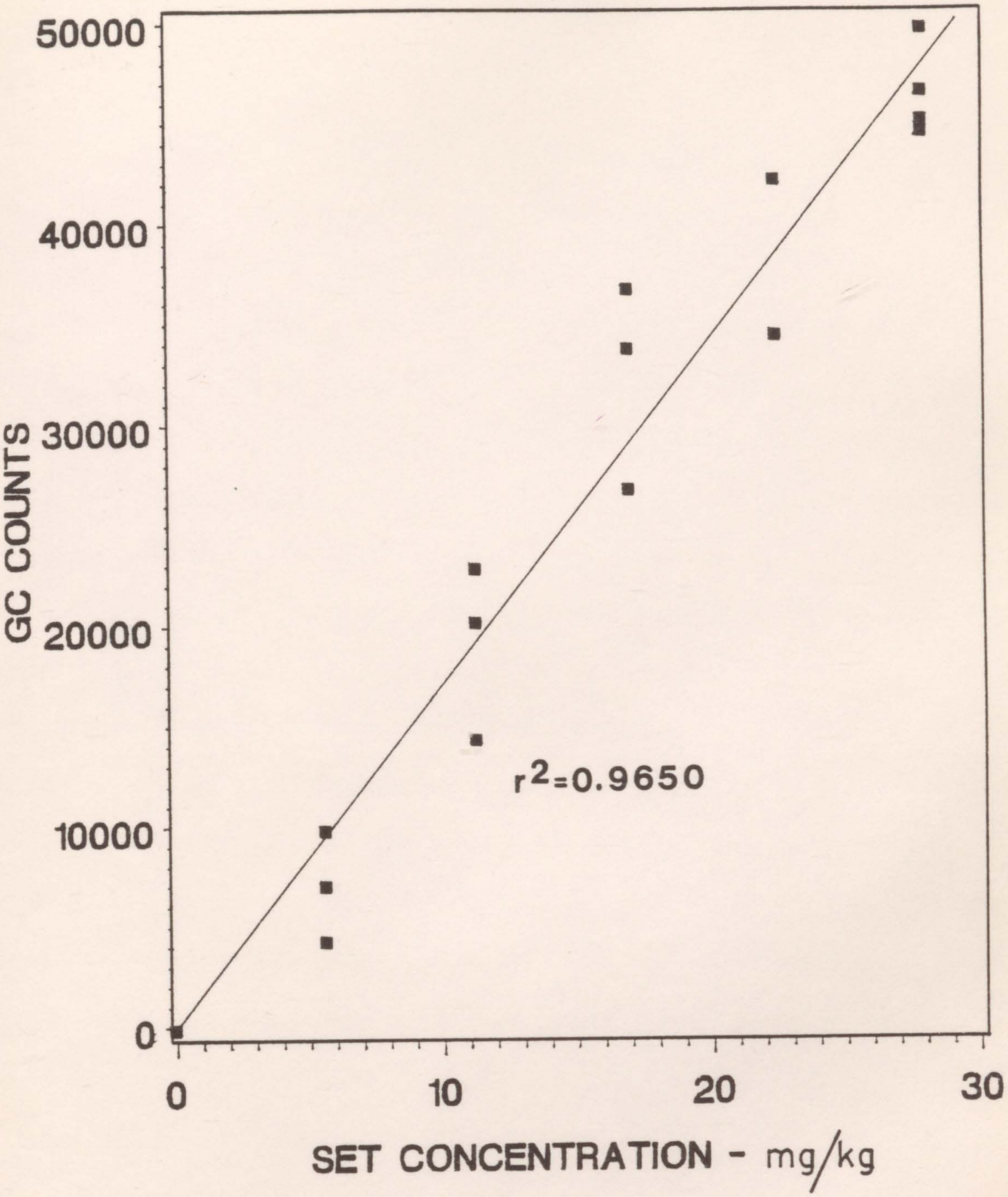


Figure 5-5 CALIBRATION OF PCE IN SANDY LOAM SOIL

as the samples.

5.1.3 Detection Limits of the Gas Chromatograph

The Hewlett-Packard GC used in the analysis of PCE has a detection limit of 100 pg/L for organics [Moy, 1987]. This limit is attainable under ideal operating conditions, i.e., clean column, prepurified carrier gas, automatic sampler, etc. Since PCE is highly volatile, two separate studies were carried out to determine the repeatability of results for the operating conditions used in this research. One study involved the mixing of five sets of standards from different stock solutions. Analysis showed that the calibration curves overlapped and the standard deviations for all the standards averaged 3.0 mg/L. In the second study, 30 data sets were analyzed, where the concentration in each data set was identical. The average of the standard deviations for each data set was 2.0 mg/L. Therefore, considering that the chosen analytical procedure was conducted through the manual injection of samples, the procedure shows a high degree of repeatability and is considered to be acceptable for this study.

5.2 Storage of PCE Standards and Samples

Aqueous standards used in this research were quite difficult to make, as the PCE did not dissolve easily in the DDI water. Therefore, it was necessary to store standards in the refrigerator and use whenever needed. In order to determine how long the standards could be stored, both old and fresh standards were continuously compared. It was observed that the 112.5 mg/L standard could be stored in the refrigerator at 4°C, for approximately one month without measurable change in concentration. This was a direct result of the low storage temperature and small headspaces allowed in the storage container.

For samples, it was determined that if the vials were completely full and tightly sealed, they could be stored up to one month without any measurable losses in PCE concentrations. This information was beneficial for studies involving perfusion experiments, where each run required a minimum of eight days of sample collection. In another storage experiment, a headspace was created in the vials before storing them in the refrigerator. Results indicated that when the vials were removed after three days, shaken and placed in the water bath, a 5% loss in PCE had occurred. This information was useful because if samples were prepared for analysis and something unforeseen had developed, the samples could be stored in the refrigerator until the next day. However, subsequent studies also indicated that if the vials were left in the refrigerator for periods exceeding seven days, the losses had exceeded 50%.

5.3 Sorption Experiments

The following operating conditions were established for adsorption/desorption experiments.

5.3.1 Containers

For studies on the sorption properties of various granular media, the first priority was to select proper containers. Initially two types of containers were available: 50 mL centrifuge tubes made from glass and from teflon. The teflon tubes seemed ideal as they were inert to the PCE and could withstand the large centrifugal forces required to separate the solids from the liquid. However, initial isotherm runs indicated a problem as the losses due to volatilization approached 40% which were deemed unacceptable. Likewise, initial results with glass tubes indicated a loss of over 80% as the tubes had caps lined with rubber. This problem was rectified by placing a piece of aluminum foil below the caps, so that the rubber would not make contact with the solution. Consequently the losses were reduced to an acceptable 20%. However, the glass containers broke when filled with soil and spun at the necessary high speeds. Peat moss and GAC caused no problem as their specific gravity was low. It was felt that the tubes were of insufficient strength and, therefore, heavy duty Kimax tubes from Fisher Scientific were purchased. These tubes also failed the centrifugal test. Finally, it was decided to use only 15 mL GC vials which performed satisfactorily. These containers showed an additional advantage since the losses through volatilization were quite small. The observed losses were 5% for 112.5 mg/l, 4% for 90 mg/L, 3% for 67.5 mg/L and 2% for both 45 and 22.5 mg/L concentrations.

5.3.2 Mass of Adsorbent

A sufficient quantity of material must be used in the experiments to accurately determine the sorption properties of various adsorbents. The appropriate mass of adsorbent was determined by running preliminary adsorption runs, once the containers had been selected. These runs indicated that 5000.0 mg of material was sufficient for the experiments with sandy loam and organic top soils. For peat moss, 400.0 mg was used as it has a lower density and a higher adsorption capacity. These quantities are within the ranges reported by other researchers [Walker, 1984, Rogers _et_ _al_., 1980, Koskinen and Cheng, 1983 and Peter, 1982]. For the GAC, it was determined that no centrifugal force was required because the grains were quite large. Therefore, 50 mg of GAC in heavy duty centrifuge tubes, lined with aluminum foil were used for the sorption experiments. Although this quantity is low when compared to the other media, it worked well because GAC has a high adsorption capacity.

5.3.3 Centrifuge Settings

In order to minimize volatilization losses, it was deemed necessary to place the centrifuge in a walk-in refrigerator maintained at 4°C. Initial experiments conducted at room temperature had indicated that the containers were getting warm while being spun, as the centrifuge motor increased the temperature in the compartment where the vials were held. Once the centrifuge was placed in the refrigerator, there was no longer a problem a with change in temperature.

A high centrifugal force was required to separate the media from the solution after shaking. This force is created by the centrifuge through spinning at high RPM. The time required to separate particles 0.05 μm and greater in size at 4000 RPM was calculated using Stokes equation [Black, 1965 and McCall et al., 1981]. The sandy loam soil required a spin time of 15.2 minutes whereas the organic top soil required 30.0 minutes, Appendix B. Peat moss was buoyant in the aqueous solution and as such even an infinite spin time did not separate it completely. However, it was determined that after spinning for 15 minutes at 2400 RPM the larger particles had settled out. This provided a zone of clear solution which could be sampled with the use of a pipette. As stated earlier, GAC containers were not centrifuged but were placed in the refrigerator to cool the solution to 4°C before samples were withdrawn.

5.3.4 Sorption Equilibrium Times

For accurate determination of the adsorption and desorption characteristics of PCE on the media tested, it was necessary to establish their respective equilibrium times for shaking. It was assumed that after the equilibrium time no further adsorption or desorption occurred.

5.3.4.1 Adsorption Equilibrium Times

In order to determine the equilibrium times, batch experiments were performed. A large number of samples were prepared identically and the adsorption process was initiated at the same time. At various time intervals, samples were taken and the concentrations of PCE adsorbed were calculated. All the values were plotted as shown in Figures 5-6 to 5-9. These plots were used to determine the maximum concentration and equilibrium time. Figures 5-6 to 5-9 indicate that the equilibrium times for sandy loam soil, organic top soil, peat moss, and GAC were 36, 30, 6 and 20 hours respectively.

5.3.4.2 Desorption Equilibrium Times

The same basic procedure used for the adsorption was followed to determine the desorption equilibrium times. After various media had been charged with PCE through adsorption, the media were tested for desorption at various time intervals. These values are plotted in Figures 5-10 and 5-11 with the respective equilibrium times. It should be noted that the above tests were performed only for organic top soil and peat moss.

For the sandy loam top soil it was determined that both the adsorption and desorption isotherms overlapped and this indicates that the sandy loam soil has no retention capacity for PCE and will desorb whatever was adsorbed. As such the desorption equilibrium time was equal to the adsorption time.

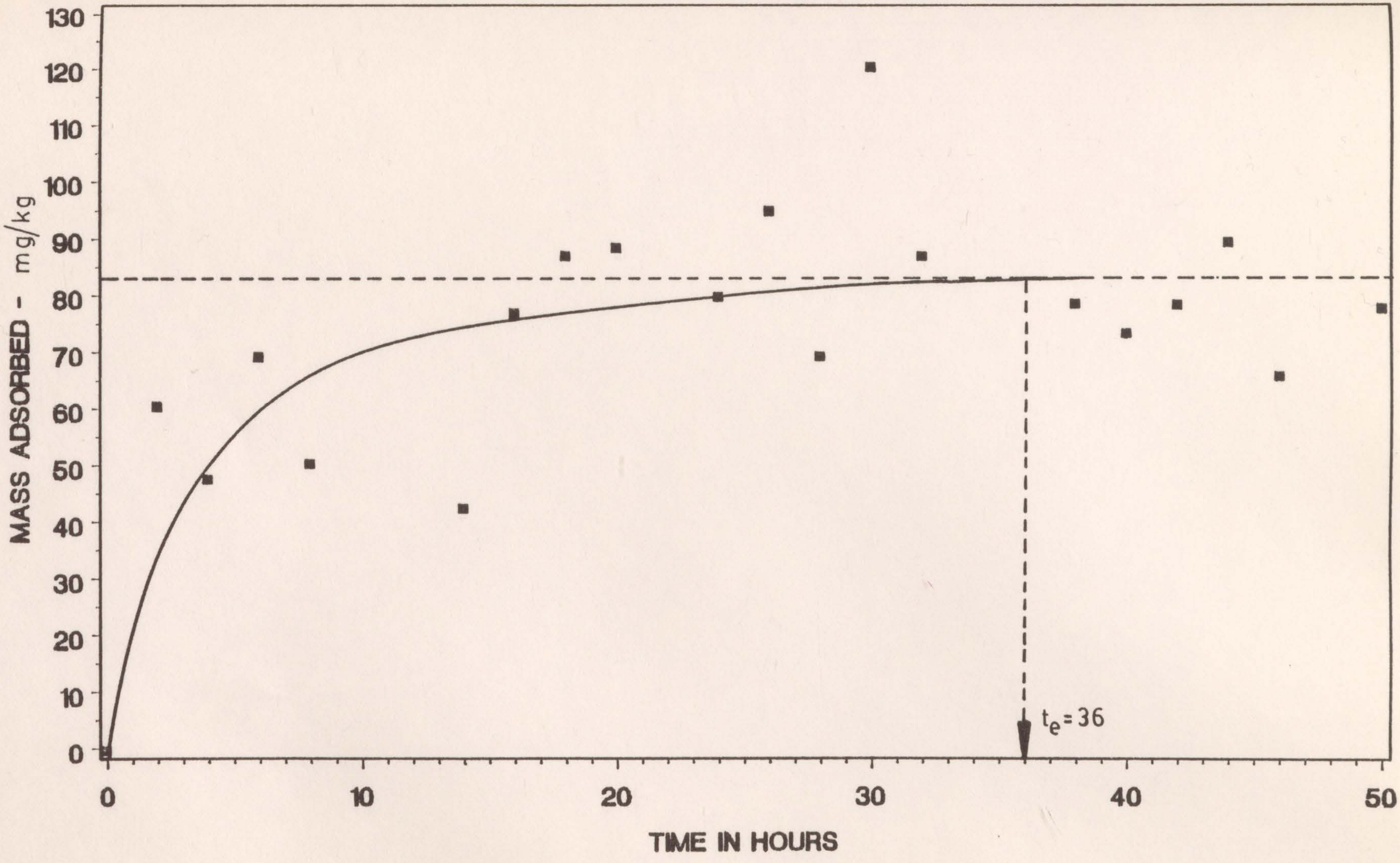


Figure 5-6 EQUILIBRIUM TIME FOR ADSORPTION - SANDY LOAM SOIL

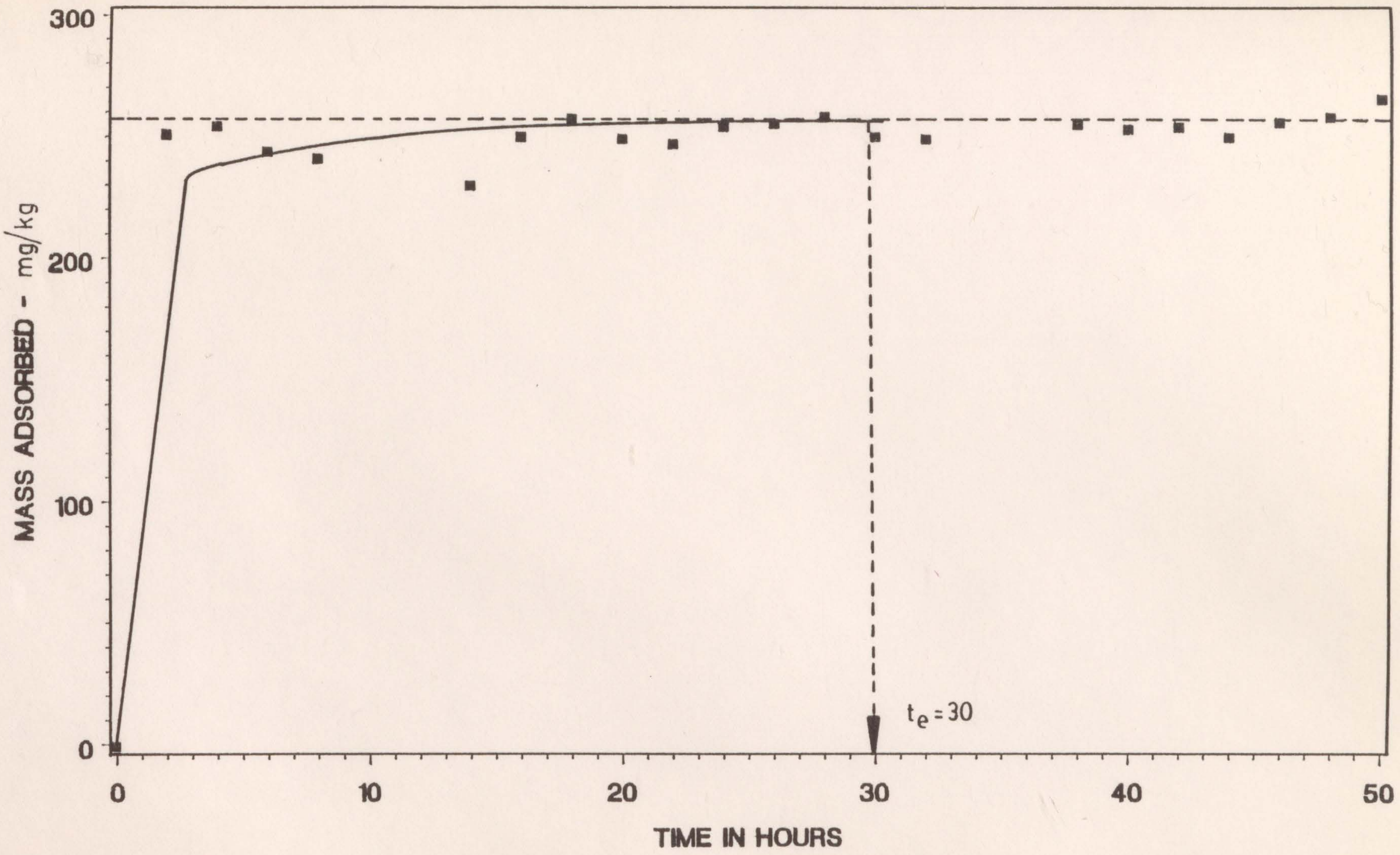


Figure 5-7 EQUILIBRIUM TIME FOR ADSORPTION - ORGANIC TOP SOIL

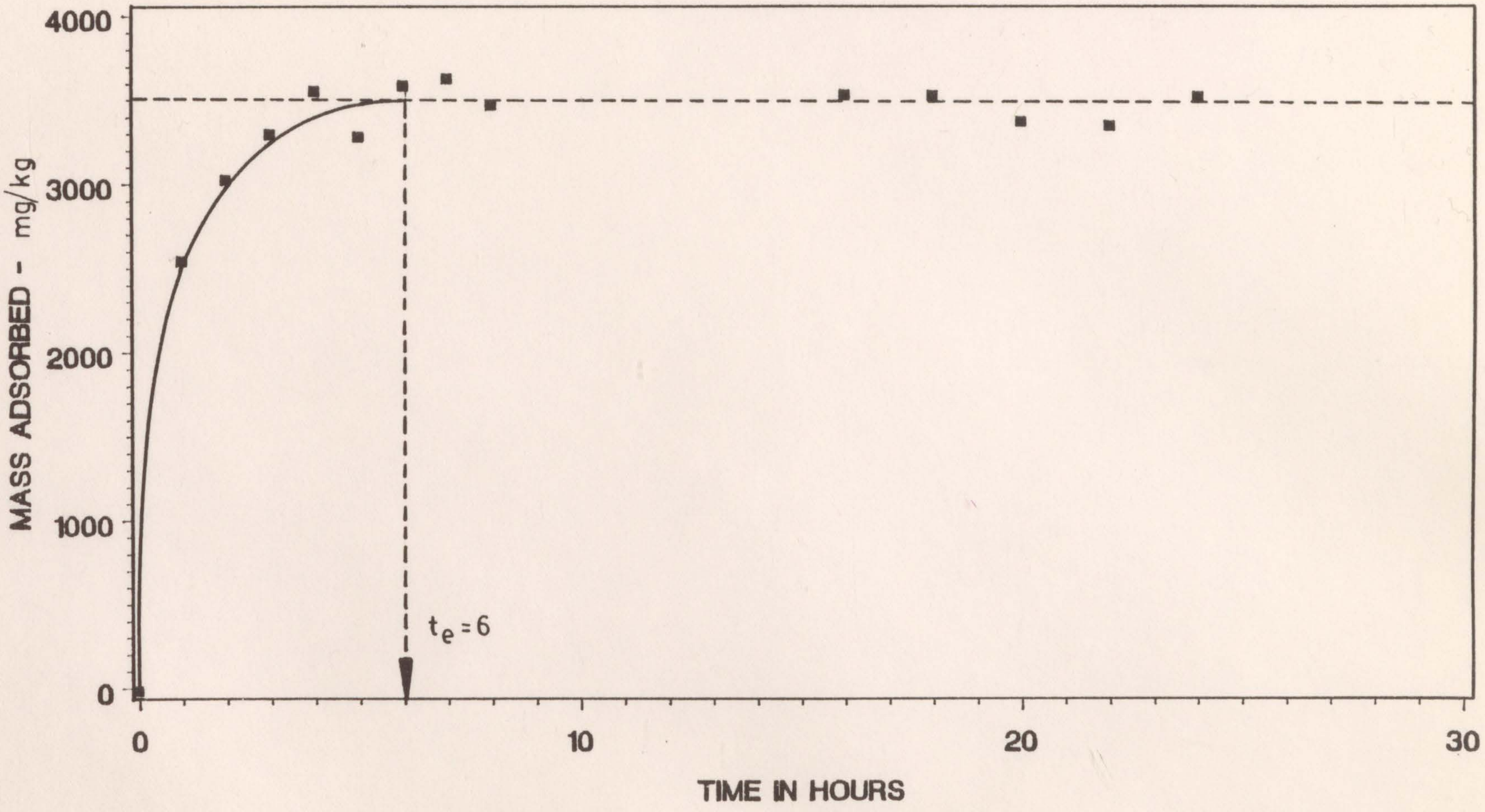


Figure 5-8 EQUILIBRIUM TIME FOR ADSORPTION - PEAT MOSS

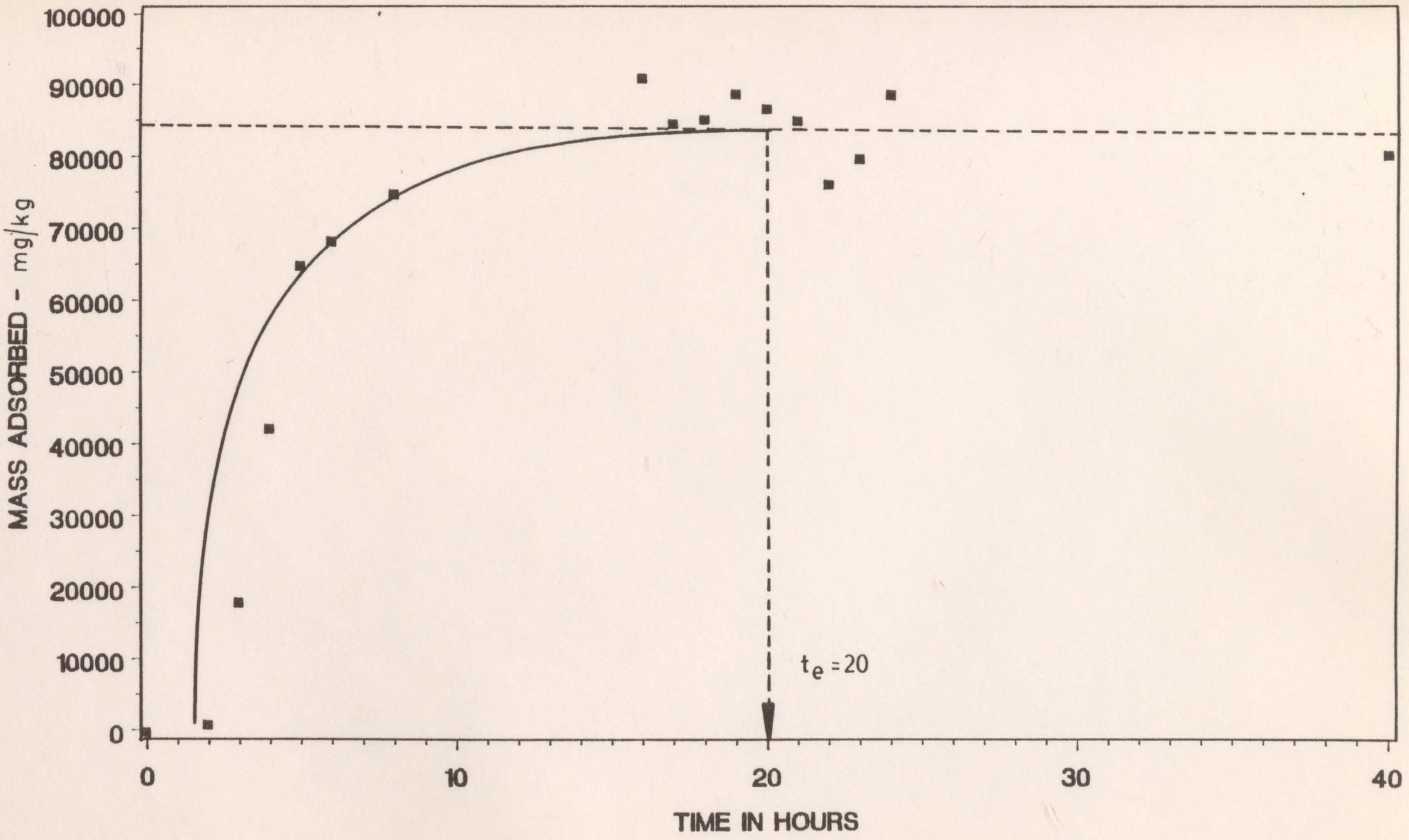


Figure 5-9 EQUILIBRIUM TIME FOR ADSORPTION - GAC

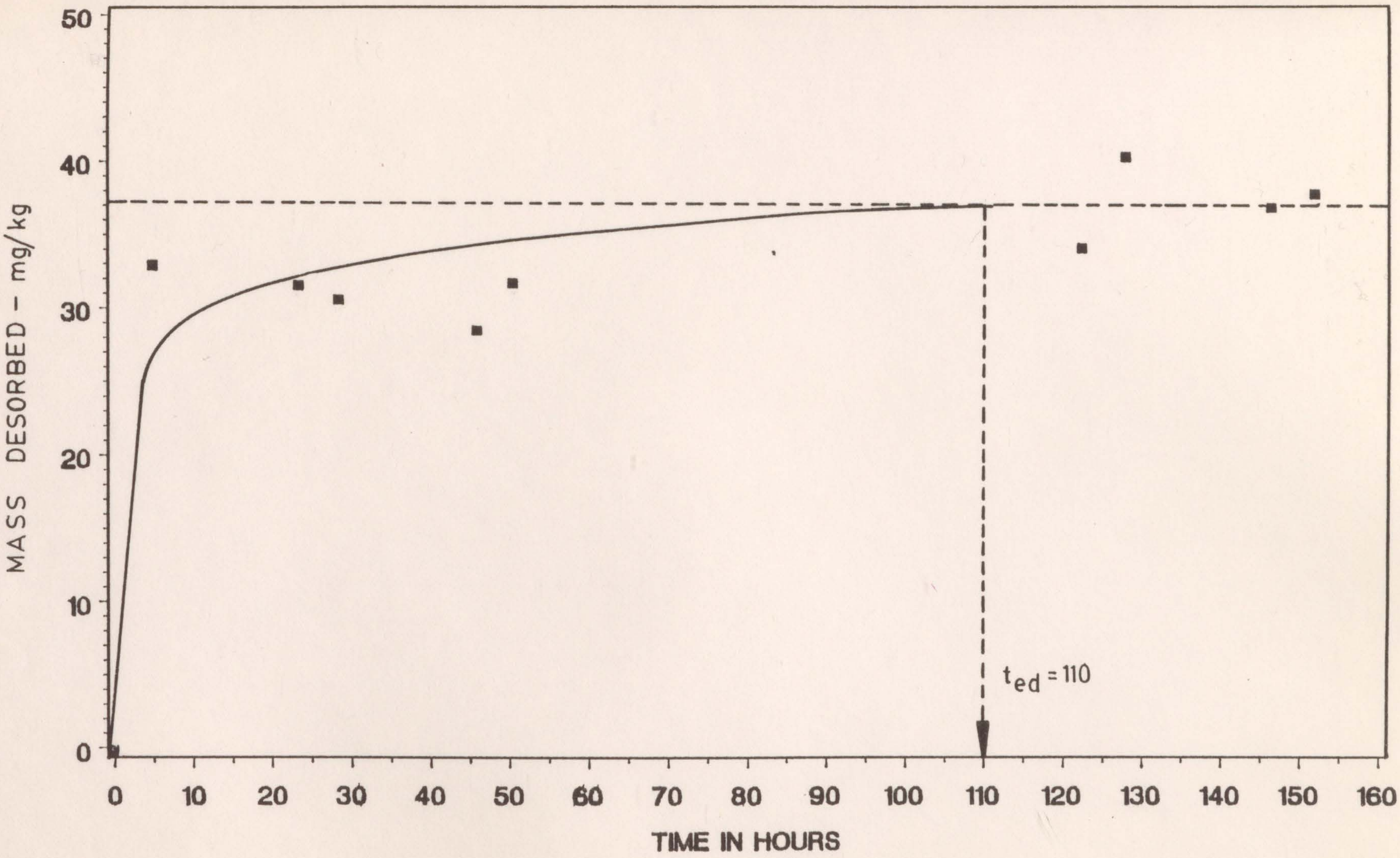


Figure 5-10 EQUILIBRIUM TIME FOR DESORPTION - ORGANIC TOP SOIL

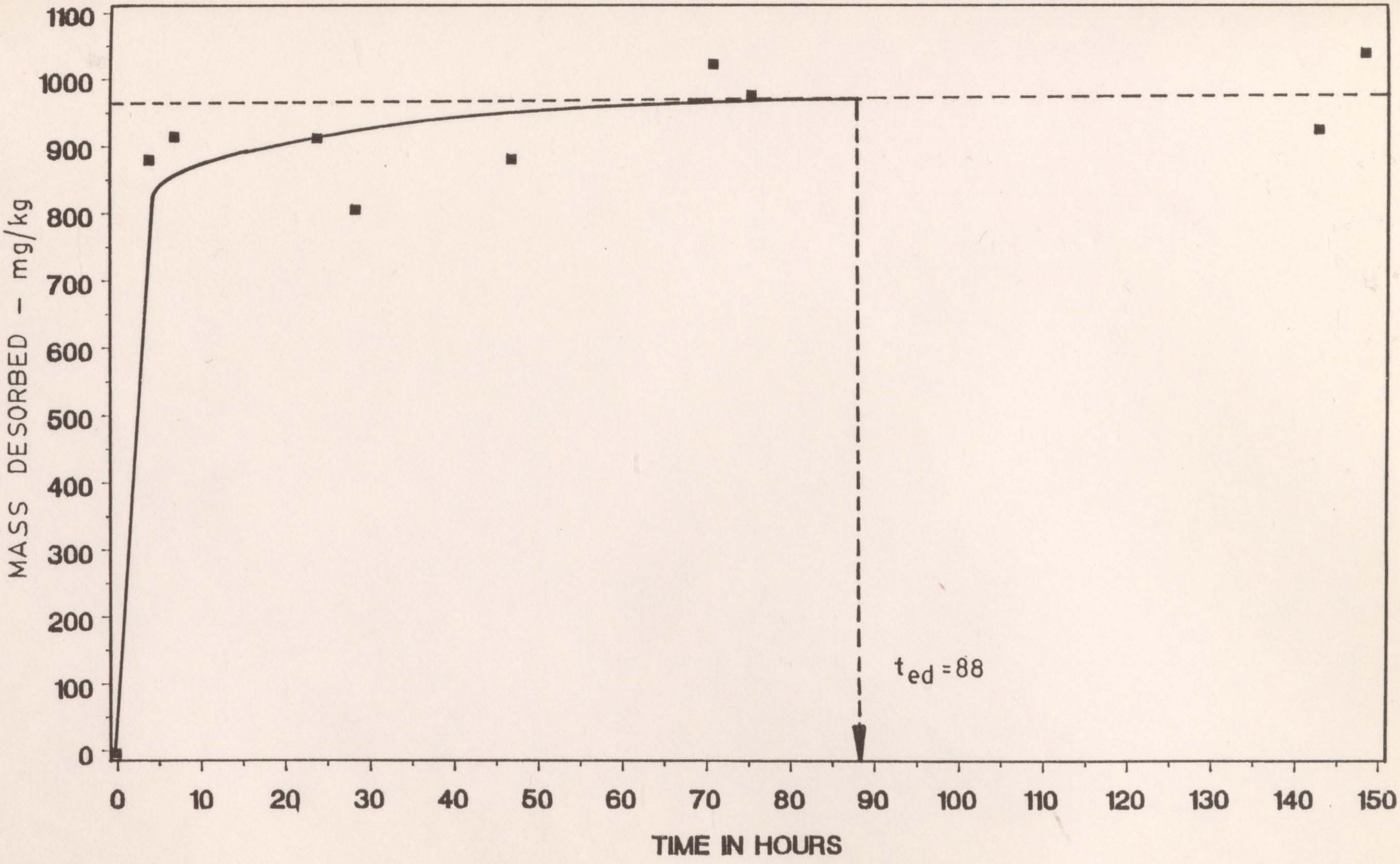


Figure 5-11 EQUILIBRIUM TIME FOR DESORPTION - PEAT MOSS

For GAC, the same equilibrium time as determined for adsorption was used since the mass of adsorbent use in the study was quite small.

5.3.5 Adsorption of PCE by Glass

Additional adsorption experiments were carried out with glass beads to ensure that the glass containers used to determine the various sorption isotherms did not adsorb any PCE. The results indicated that the glass used did not adsorb PCE.

Blanks were consistently tested to ensure that the glassware was properly cleaned and gave no desorption of PCE.

5.3.6 Adsorption of PCE by Gravel

Since both the column and perfusion apparatus experiments required gravel filters for drainage, the adsorptive capacity of that material was investigated. The adsorption experiments indicated that the washed gravel did not adsorb any PCE.

5.4 Perfusion Apparatus

The following parameters were investigated.

5.4.1 Airflow

The initial runs with the perfusion apparatus indicated that no volatilization of chemical was occurring. The analysis of both the water scrubber and the gas carried in the outlet air tube showed no PCE. However, it was still felt that some PCE may be volatilizing at concentrations below the detectable levels. Therefore, a modification was made to the perfusion apparatus, whereby the inlet and outlet air lines were removed. This procedure created a stagnant atmosphere above the soil surface.

Subsequent runs with the perfusion apparatus indicated no difference in the results with or without air, as the rates of reduction were identical. Consequently, all future runs were conducted without airflow.

5.4.2 Microbiological Activity of Soil

Tests were conducted to enumerate the number of total bacteria, yeast and fungi present in the soil to ensure that the soil was biologically active. The analysis methods suggested by Wollum [1982] were used. The soils were tested both when they were received and after storage for six months in their air-dried state. The soils stored for six months were rewetted for one day before testing.

The results shown in Table 5-1 indicate that both soils were biologically active. It is important to recognize that organisms in soils are never static in numbers, and that an enumeration of a population represents a point in time [Wollum, 1982]. This point is in dynamic equilibrium with the physical, chemical and biological environment.

Table 5-1 Microorganism Population in Sandy Loam Soil and Organic Top Soil per g of Soil*

Organism	Sandy Loam		Organic Top Soil	
	A	B	A	B
Total Bacteria	10^6	10^6	10^6	10^6
Yeast	10^3	10^3	10^3	10^3
Fungus	10^6	10^6	10^6	10^6

A Soil as received
B Soil after storage for 6 months (air dried and rewetted)
* Dry weight basis

5.5 Column Studies

The following operating conditions were established for conducting column studies.

5.5.1 Sampling Under Unsaturated Flow Conditions

When the columns were being constructed, sample collections at various points in the soil profile were considered. Different approaches were taken for this purpose. The options tried were a small drain tube surrounded by gravel, a trough filled with gravel and a drain tube attached to a vacuum while collecting. All were unsuccessful because either insufficient sample was withdrawn or the soil column was disturbed. Along with the sampling difficulties was the fact that PCE is a very volatile chemical, and if exposed to the atmosphere, losses would occur. Therefore, it was decided that grab samples should be taken at the bottom of the column. In order to gather information on PCE behaviour with a change in soil profile, columns with varying lengths of soil profiles were setup.

5.5.2 Absorption of PCE by Plexiglass Columns

As mentioned earlier, other researchers have used Plexiglas columns to study the behaviour of organic chemicals in soil. However, there was some concern on the possibility of PCE losses through absorption of PCE by the Plexiglas. In order to quantify these losses, an aqueous solution containing 112.5 mg/L of PCE was placed in a short column. The column was sealed and left for seven days. After seven days the solution concentration was measured and a decrease of 20% was observed. This decrease was considered acceptable since PCE in a similar aqueous solution was observed to completely volatilize in a day when left open to the atmosphere. Furthermore, since both soil types were to be analyzed in the same type of column, absorption effects for all the columns would be identical. This consistency would allow comparisons on PCE behaviour in different unsaturated soils.

5.5.3 Simulation of Rainfall

The first method tried to apply DDI water on soil columns involved the use of a constant head tank. A tube from the constant head tank was used to feed water via gravity to a Plexiglas disc on top of the soil column. The disc had holes through which the tube was placed, after branching it in four directions. A set screw was installed to each branch to vary the pressure on the tube in order to adjust the flow rate. In each disc, the set screws were calibrated to ensure the proper drip rate of DDI water. Unfortunately, this calibration kept changing every day. In some cases the rates had increased, while in other cases rates had decreased. It was thought that the flow was too small for four branches and the branches were reduced to two, with no improvement in duration of calibration. Another consideration was that the tubing was possibly too small, causing large capillary forces and that the headlosses in the system were too large. As such, any movement or jarring of the tubes would disrupt equilibrium and the flow rate would change.

In order to overcome this problem, the eight feed tubes were connected to a multichannel pump. Proper care was taken that the pump tubing was constantly checked for wear by monitoring the flow rate daily. Whenever the flowrate exceeded 800 mL/day, the tubing was replaced. Some tubes lasted for a week, while others lasted for a month.

5.6 Diffusion of PCE Through Soil

The initial experiments conducted with the diffusion apparatus proved to be unsuccessful. The results indicated that the construction method and/or material chosen for the apparatus were incorrect, as the gaseous PCE would attack the Plexiglas and disappear within one day.

CHAPTER SIX

RESULTS AND ANALYSIS

6.1 Adsorption of PCE by Granular Media

The results obtained on adsorption of PCE by different granular media are described in the following sections.

6.1.1 Isotherms for Composite Granular Media

The data collected for the adsorption and desorption of PCE on sandy loam soil, organic top soil, peat moss and GAC, are plotted in Figs. 6-1 to 6-4 to fit the Freundlich Isotherm Equation. For better comparison, all the adsorption isotherms are placed together in Fig. 6-5. Tables 6-1 and 6-2 show Freundlich coefficients of adsorption and desorption for different media and the corresponding correlation coefficient for each isotherm. Table 6-3 gives the Freundlich coefficients for Regulation 309. Appendix C provides an example on how the experimental data were analyzed.

6.1.2 Isotherms for Different Sizes of Soil Particles

The sandy loam soil and organic top soil were sieved into three different size fractions after passing the a 2.0 mm sieve: retained on a #50 sieve, retained on a #100 sieve

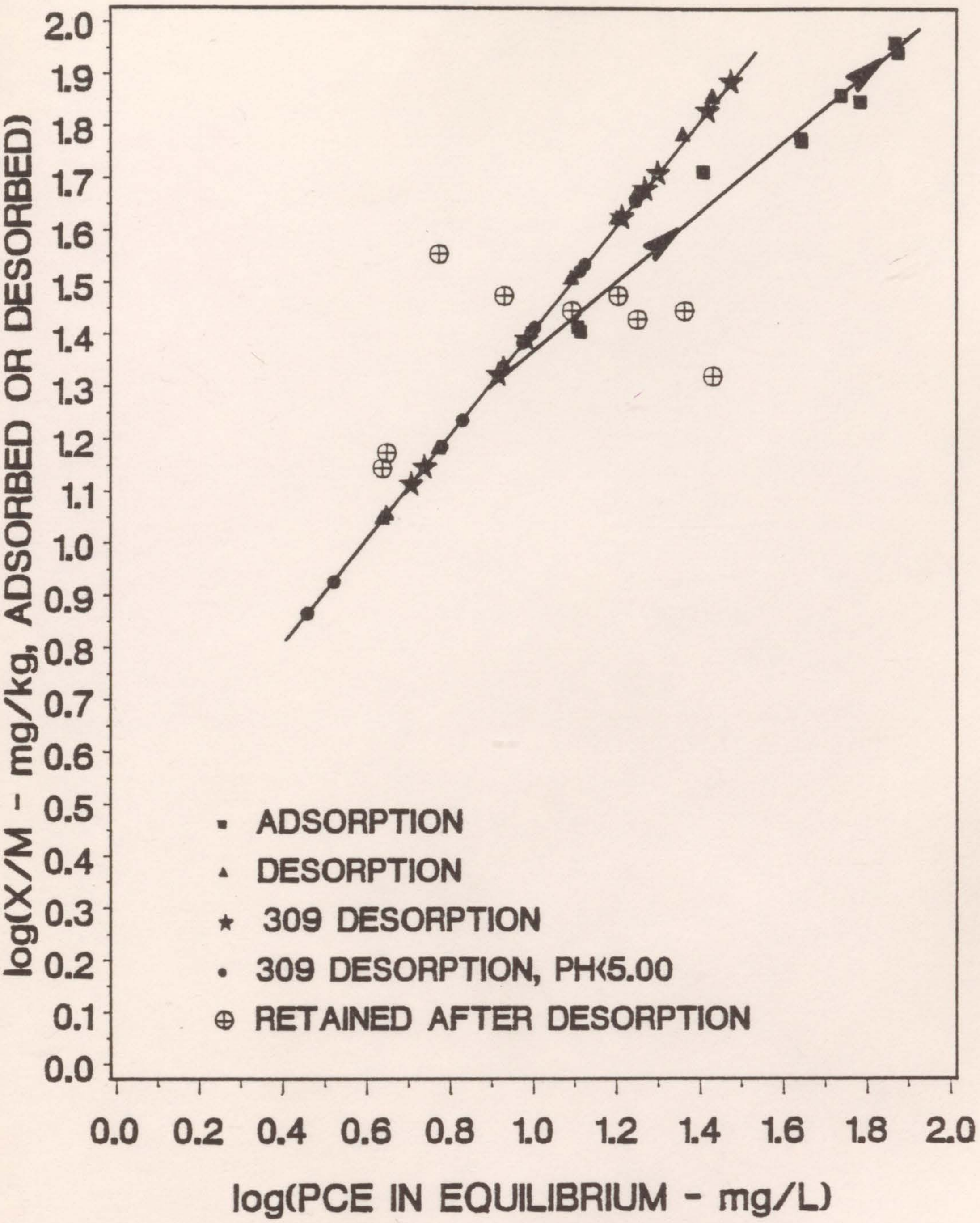


Figure 6-1 ADSORPTION AND DESORPTION ISOTHERMS FOR SANDY LOAM SOIL

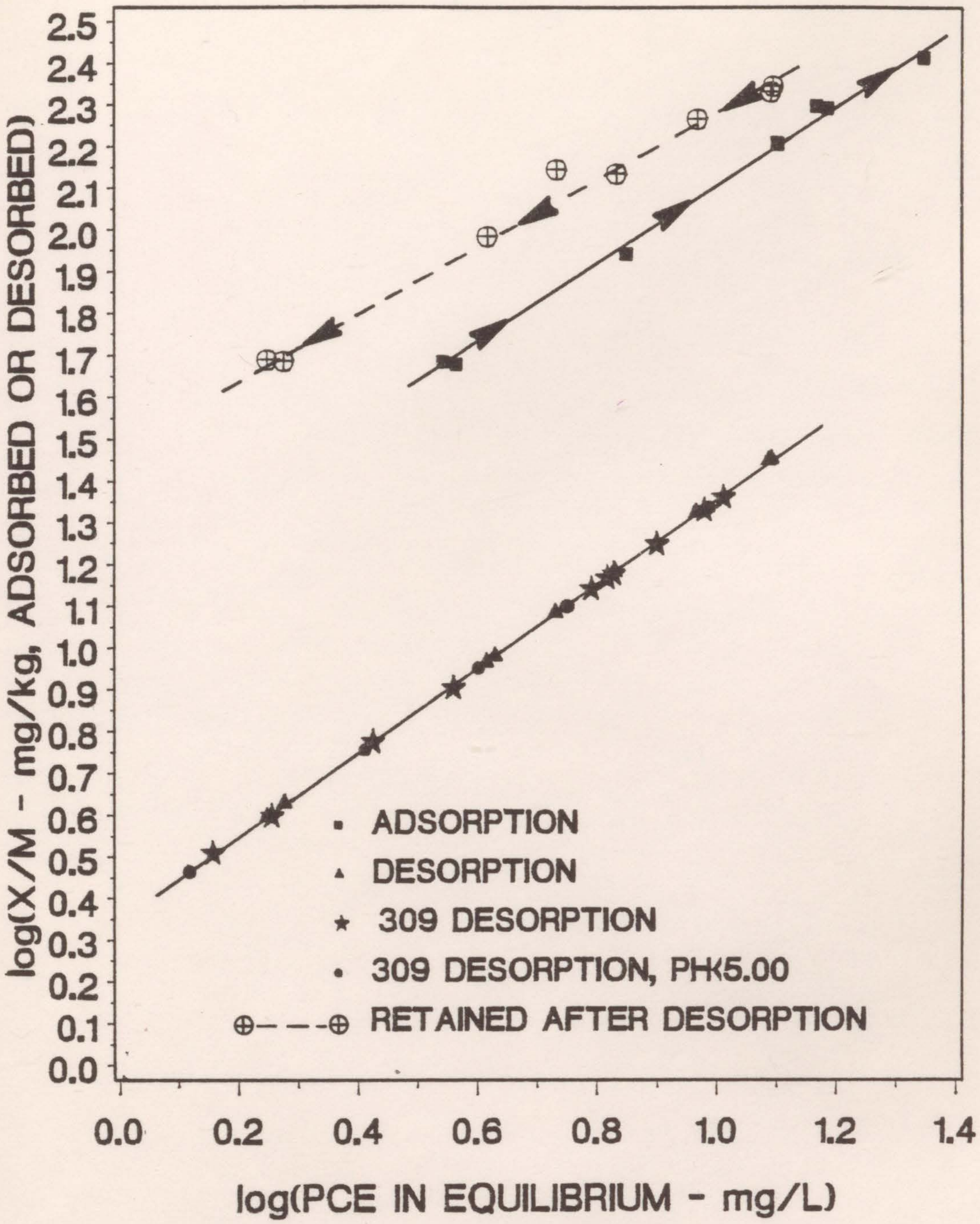


Figure 6-2 ADSORPTION AND DESORPTION ISOTHERMS FOR ORGANIC TOP SOIL

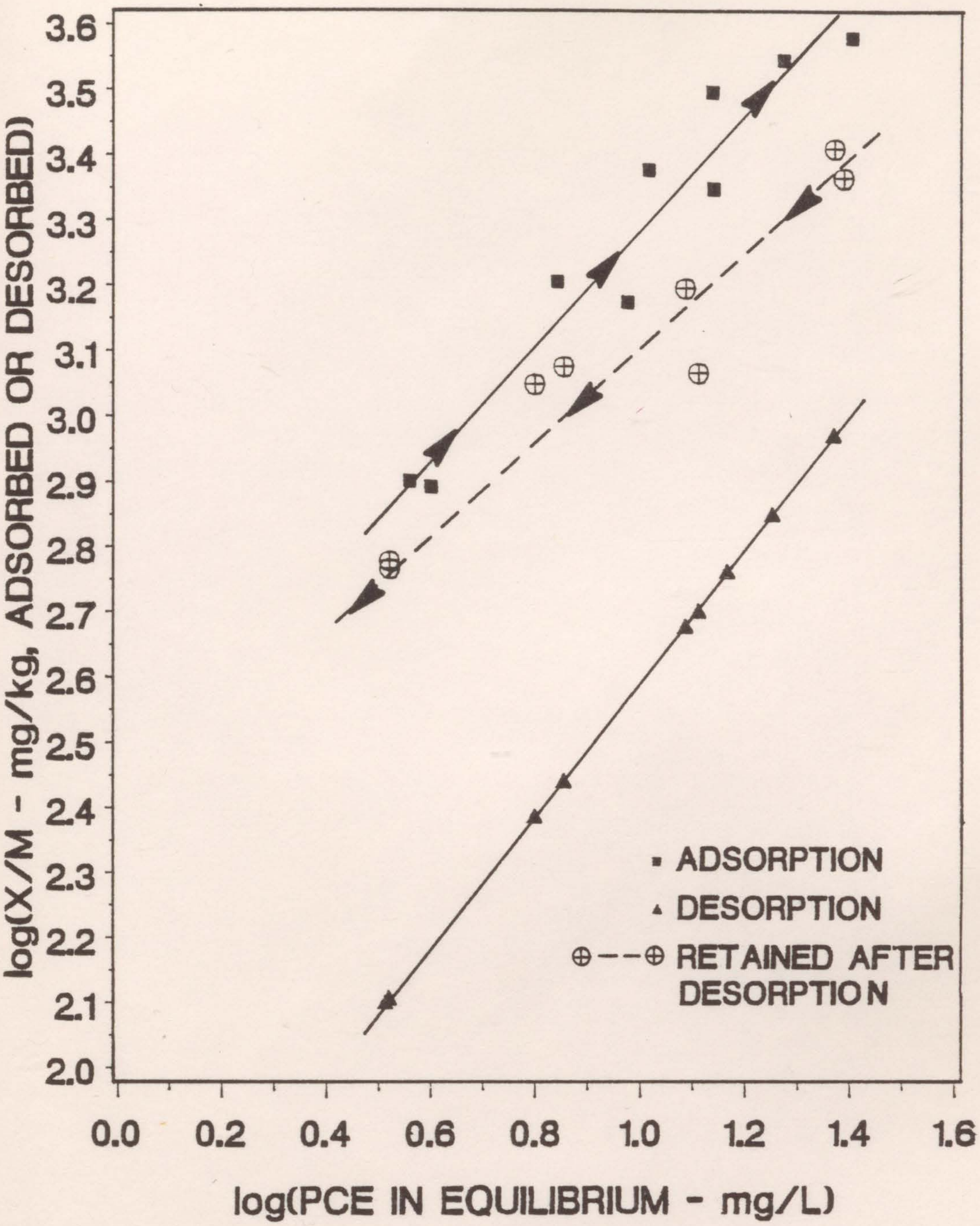


Figure 6-3 ADSORPTION AND DESORPTION ISOTHERMS FOR PEAT MOSS

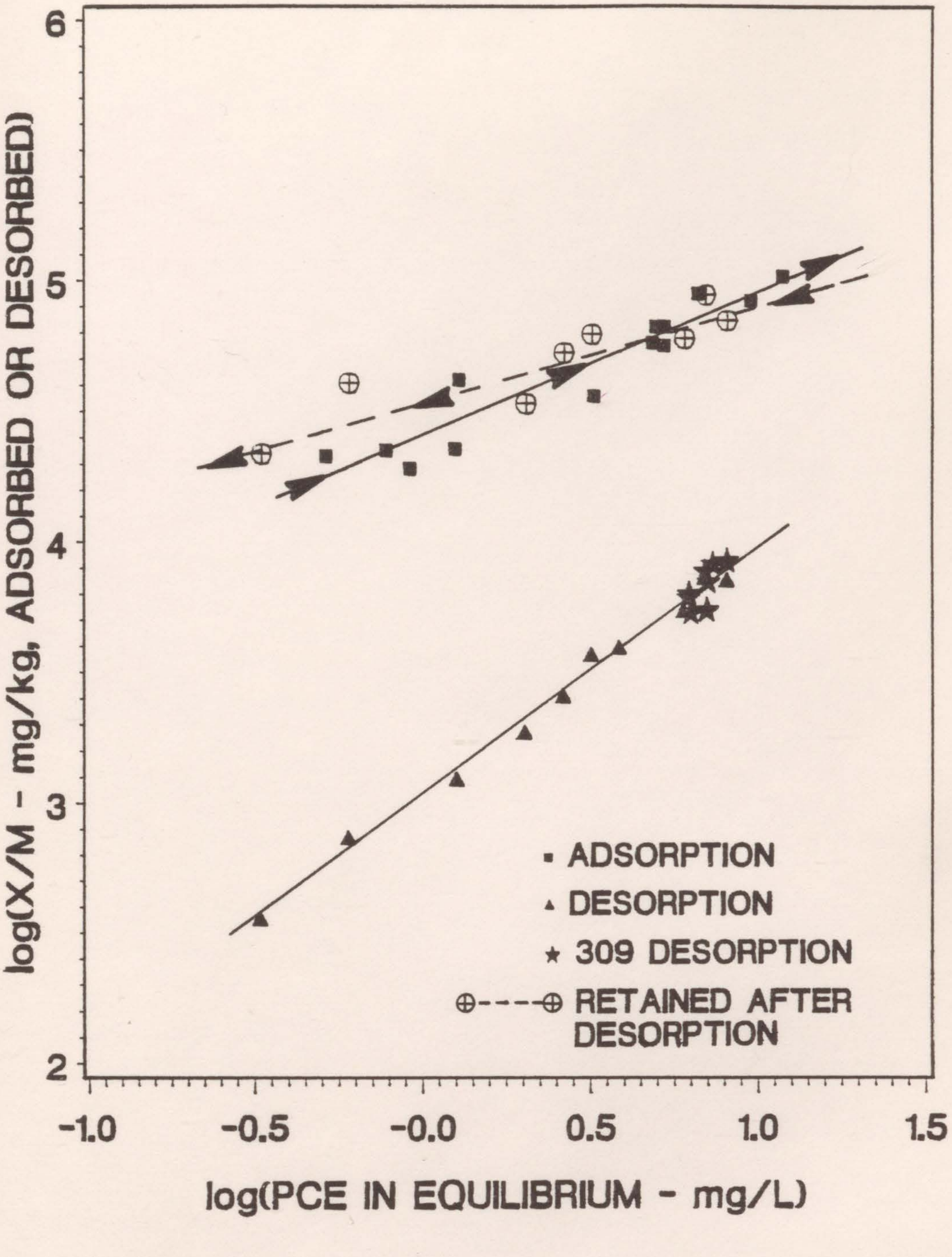


Figure 6-4 ADSORPTION AND DESORPTION ISOTHERMS FOR ACTIVATED CARBON

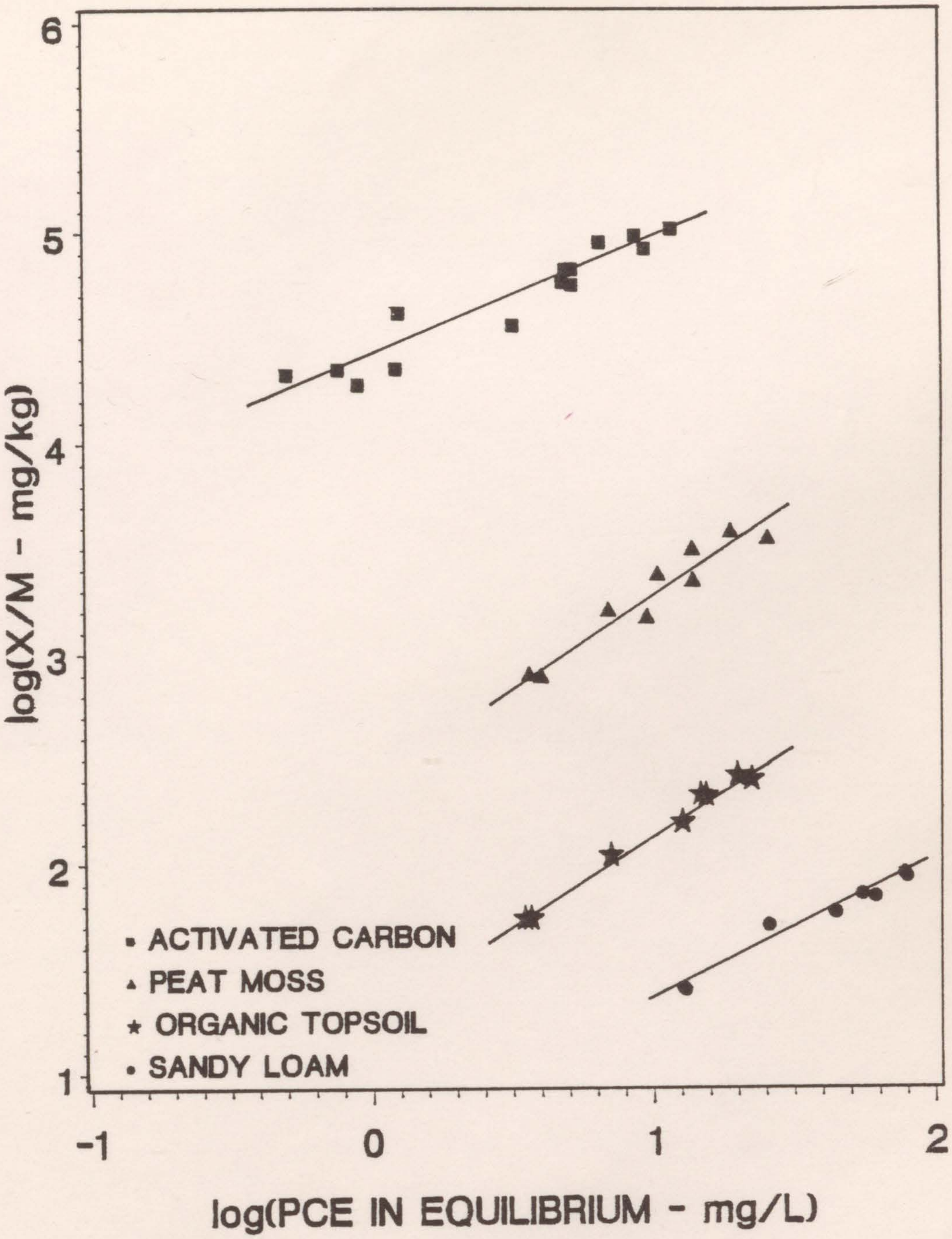


Figure 6-5 ADSORPTION ISOTHERMS FOR ALL SOILS

Table 6-1 Freundlich Coefficients for Adsorption on Different Media

MEDIUM	K_f $\left\|\frac{mg}{kg}\right\| \left\|\frac{L}{mg}\right\|^{1/n_f}$	$1/n_f$	r^2
Sandy Loam Soil	5.19	0.66	0.9465
Organic Soil	14.46	0.95	0.9979
Peat Moss	264	0.87	0.9386
GAC	25280	0.57	0.9481

Table 6-2 Freundlich Coefficients* for Desorption from Different Media using Distilled Deionized Water

MEDIUM	K_{fd} $\left\|\frac{mg}{kg}\right\| \left\|\frac{L}{mg}\right\|^{1/n_{fd}}$	$1/n_{fd}$	r^2
Sandy Loam Soil	2.51	1.02	1.0000
Organic Soil	2.61	1.01	1.0000
Peat Moss	40.2	1.01	1.0000
GAC	1077	0.94	0.9916

* X/M based on mass of PCE desorbed (released)

Table 6-3 Freundlich Coefficients* for Desorption from Different Media using Regulation 309

MEDIUM	K_{fd} $\left\|\frac{mg}{kg}\right\| \left\|\frac{L}{mg}\right\|^{1/n_{fd}}$		$1/n_{fd}$		r^2	
	A	B	A	B	A	B
Sandy Loam	2.54	2.54	1.01	1.01	1.0000	1.0000
Organic	2.60	2.60	1.00	1.00	0.9997	1.0000

A Desorption with pH higher than Regulation 309

B Desorption with pH equal to Regulation 309 limits

* X/M based on mass of PCE desorbed (released)

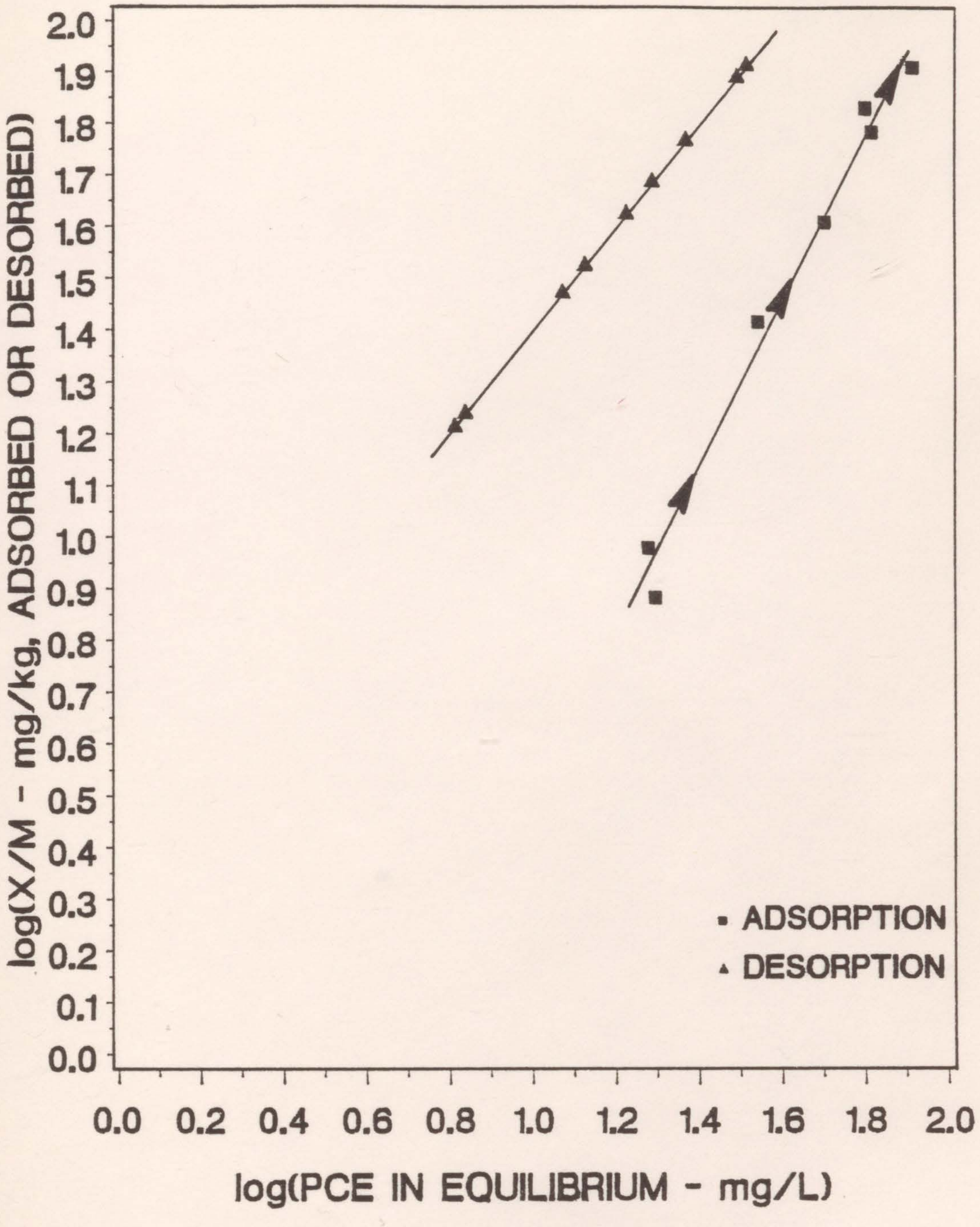


Figure 6-6 SORPTION ISOTHERMS FOR SANDY LOAM SOIL RETAINED ON No. 50 SIEVE

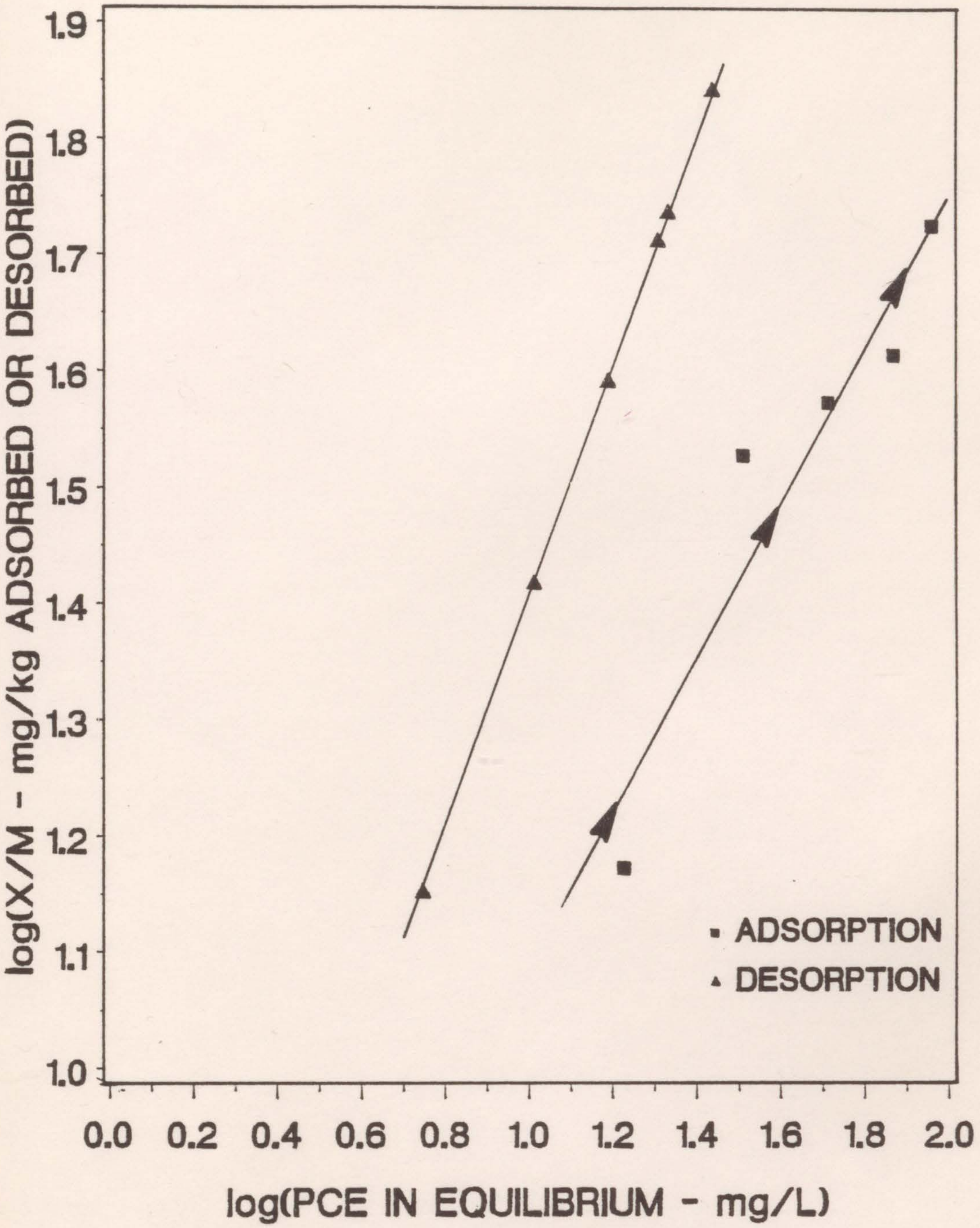


Figure 6-7 SORPTION ISOTHERMS FOR SANDY LOAM SOIL RETAINED ON No. 100 SIEVE

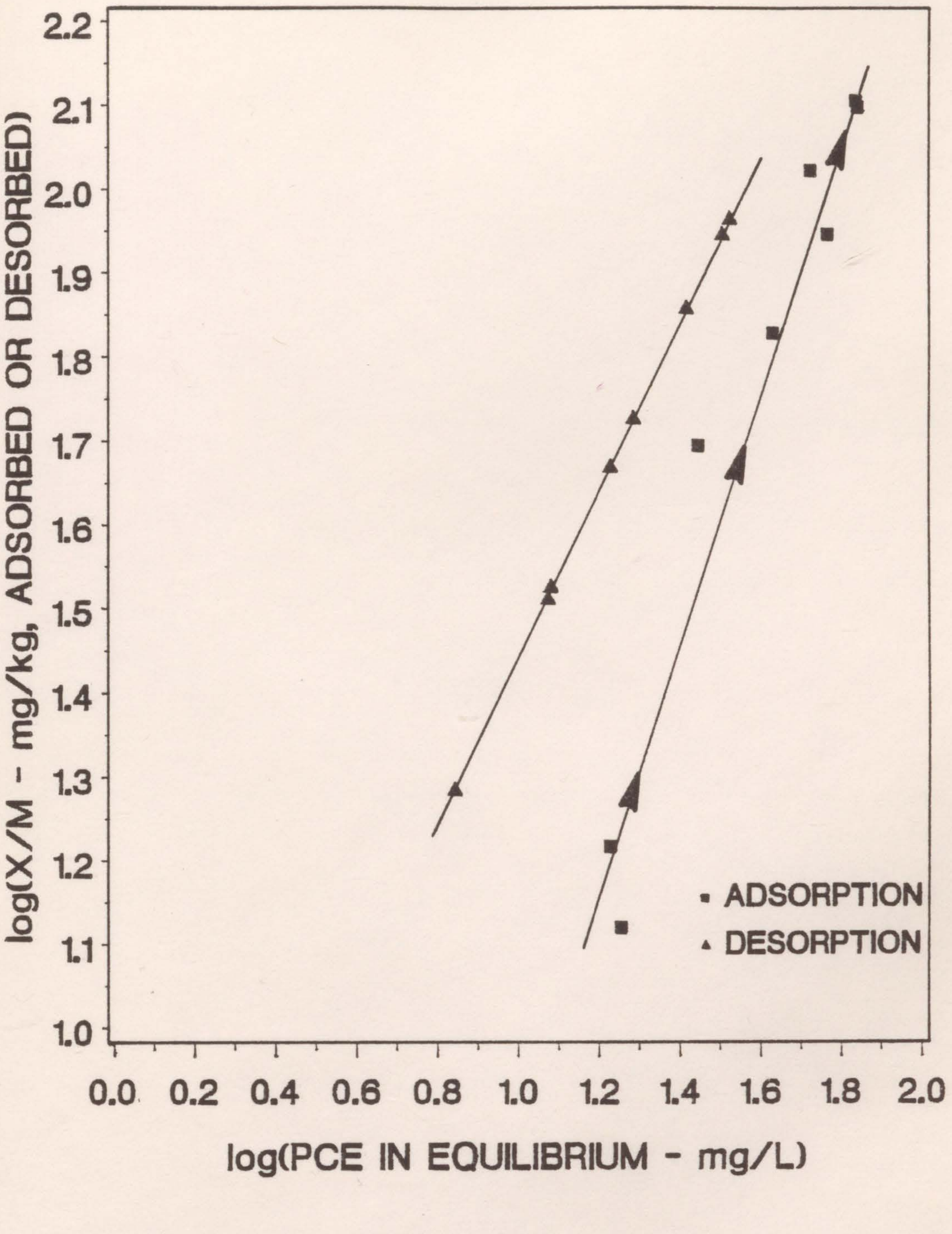


Figure 6-8 SORPTION ISOTHERMS FOR SANDY LOAM SOIL PASSING No. 100 SIEVE

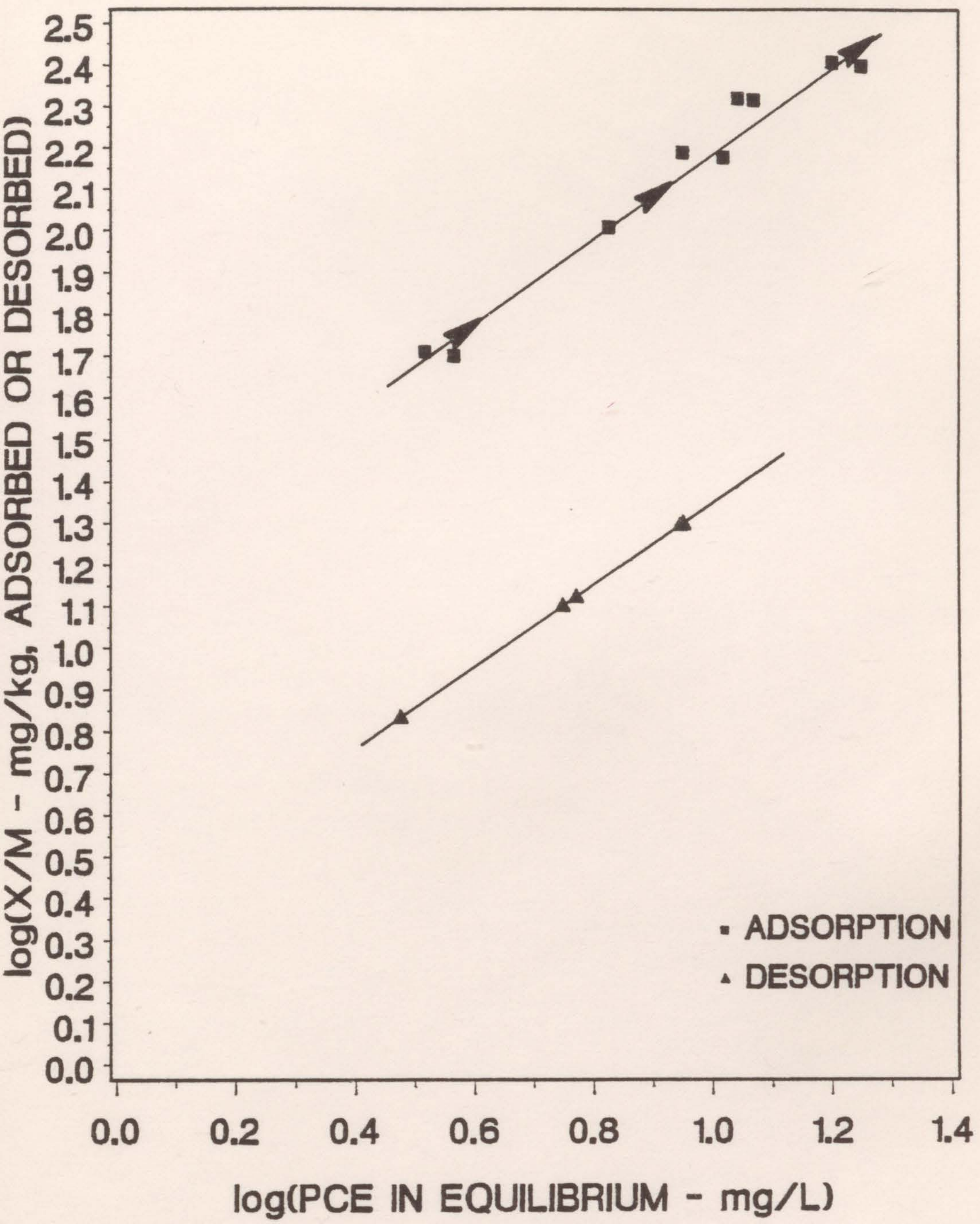


Figure 6-9 SORPTION ISOTHERMS FOR ORGANIC TOP SOIL RETAINED ON No. 50 SIEVE

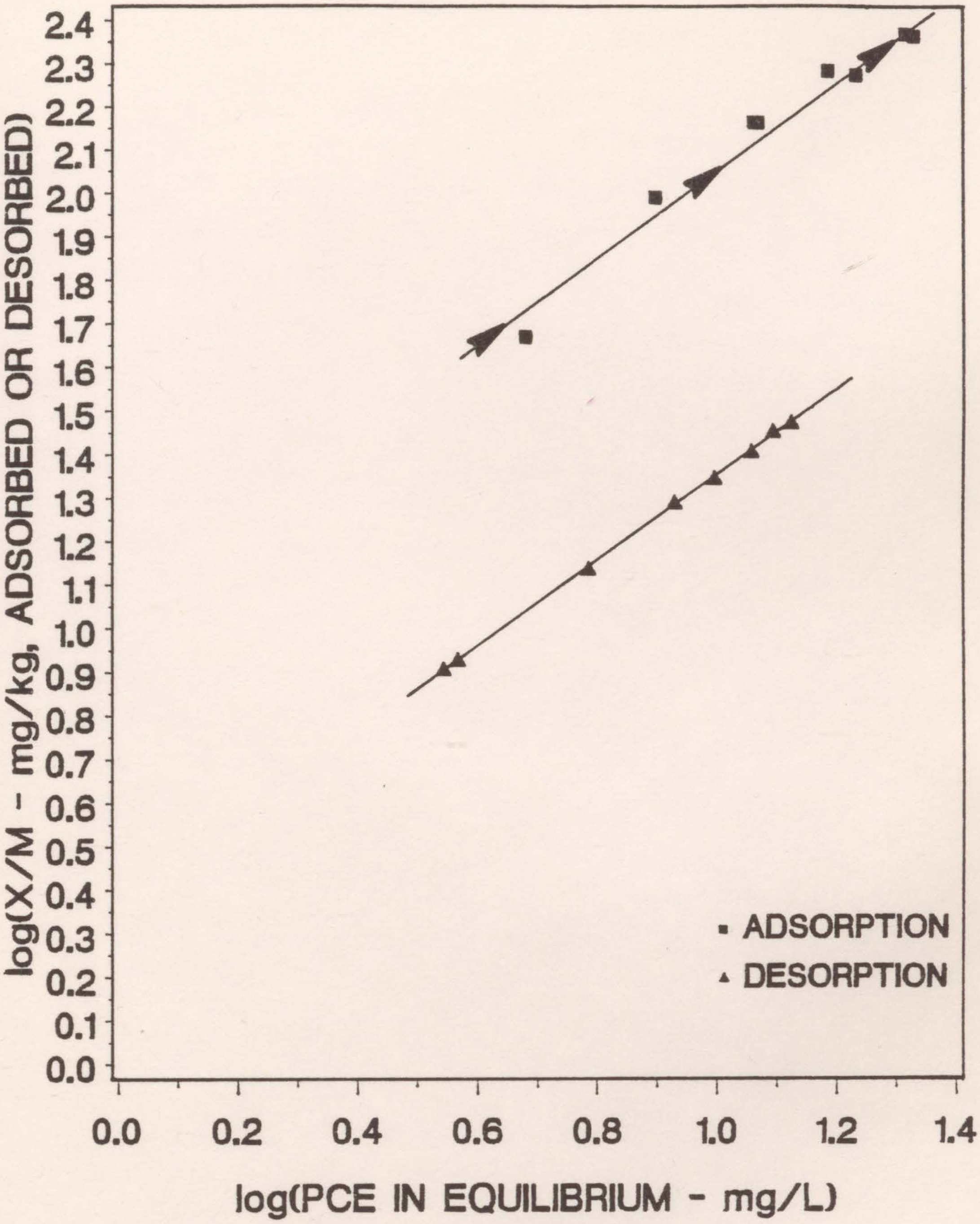


Figure 6-10 SORPTION ISOTHERMS FOR ORGANIC TOP SOIL RETAINED ON No. 100 SIEVE

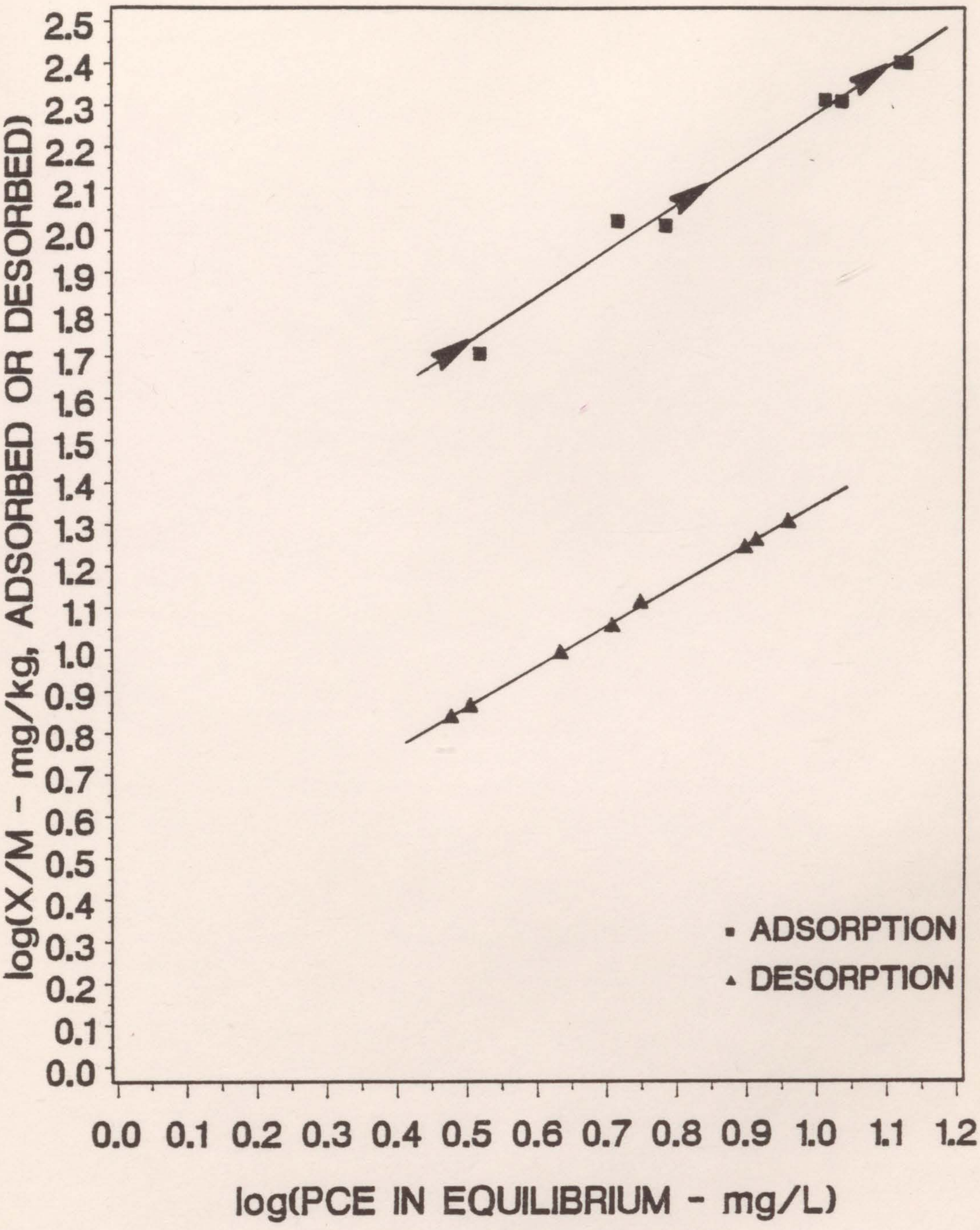


Figure 6-11 SORPTION ISOTHERMS FOR ORGANIC TOP SOIL PASSING No. 100 SIEVE

further be normalized with the organic carbon content of the media being studied, to give K_{oc}. Table 6-6 gives the Koc values obtained for the various granular media studied. The K_{oc} values for the organic top soil, sieved to various sizes, are given in Table 6-7.

Table 6-6 K_{oc} Values for Various Granular Media

MEDIUM	K_p $\left\lvert\frac{mg}{kg}\right\rvert \left\lvert\frac{L}{mg}\right\rvert^{1/n_f}$	ORGANIC CARBON (%)	K_{oc}
Sandy Loam	5.19	1.0	- *
Organic	14.46	11.74	123
Peat	264	49.42	534
GAC	25280	74.10	- *

* Note: Slope of regression equation not equal to 1

Table 6-7 K_{oc} Values for Organic Top Soil Sieved to Various Sizes

SOIL	PARTICLE SIZE	K_p $\left\lvert\frac{mg}{kg}\right\rvert \left\lvert\frac{L}{mg}\right\rvert^{1/n_f}$	ORGANIC CARBON (%)	K_{oc}
Organic	Ret. #50	14.32	13.5	106
	Ret. #100	10.62	8.1	131
	Pass. #100	14.70	10.8	136

6.1.4 Adsorption of Pure PCE by Granular Media

When a spill of PCE occurs in the environment, generally it is in the pure form. A a result, the soil gets saturated with pure PCE and the front migrates from the spill site. If no moisture is added to the spill area, the soil will eventually approach its field capacity, residual saturation, with the pores containing pure PCE. Table 6-8 gives the residual saturation of PCE in the various granular media tested.

Table 6-8 Residual Saturation of Pure PCE in Various Granular Media

MEDIUM	RESIDUAL SATURATION kg/kg
Sandy Loam Soil	0.427
Organic Soil	0.771
Peat Moss	7.763
GAC	0.587

6.2 Volatilization of PCE from Water and Soil

The experiments conducted to study the volatilization of PCE from water and soil surfaces are described in the following sections.

6.2.1 Volatilization of PCE from Stagnant Water

The experiments conducted to determine the volatilization rate of PCE from water involved four different concentrations and four different area to volume ratios. The data are presented in Figures 6-12 to 6-15 with semi-log plots. Table 6-9 gives the various coefficients obtained by mean-square regression for curve fitting (SAS, 1985).

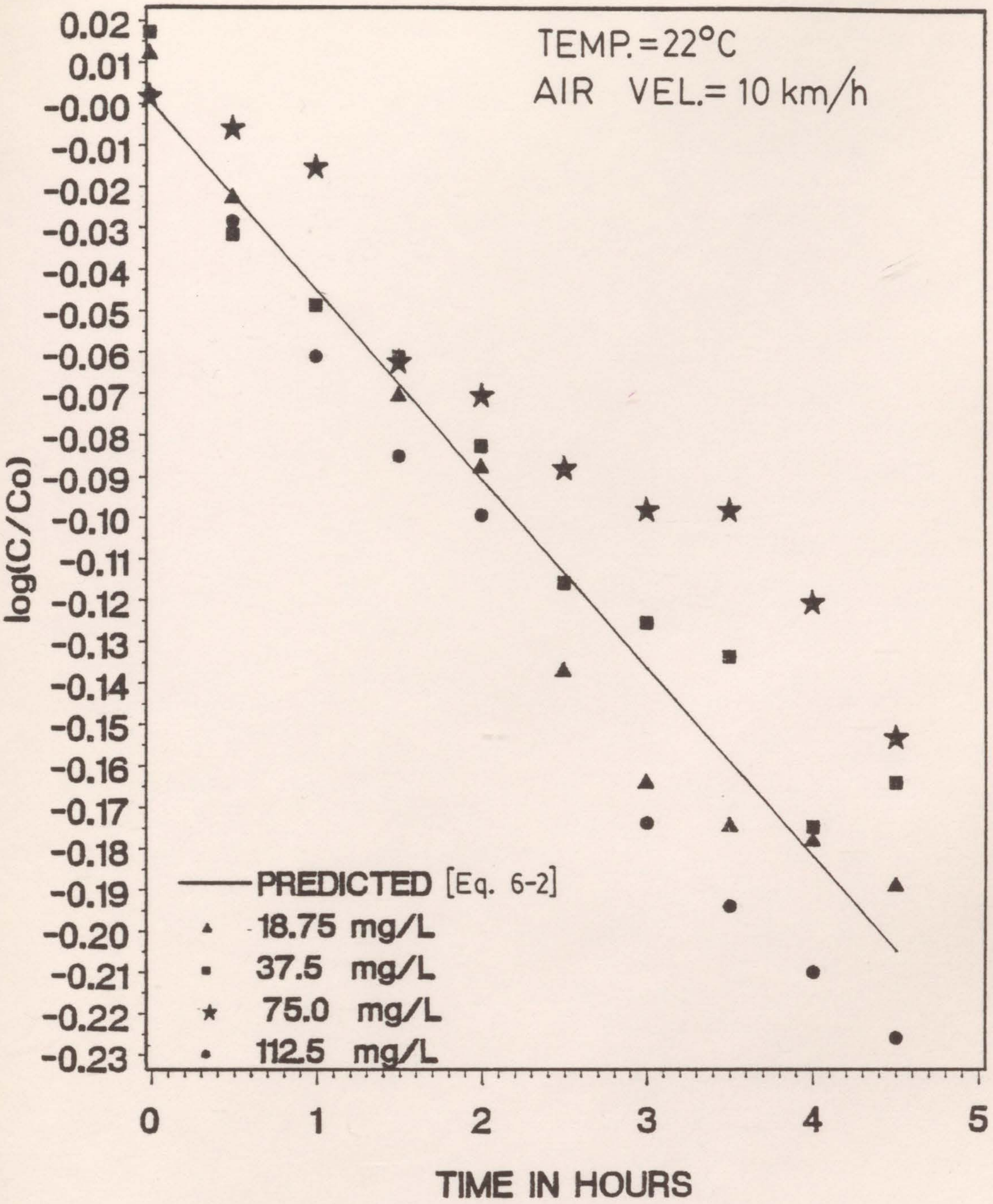


Figure 6-12 VOLATILIZATION FROM STAGNANT WATER WITH AN AREA/VOLUME OF 2.08(1/m)

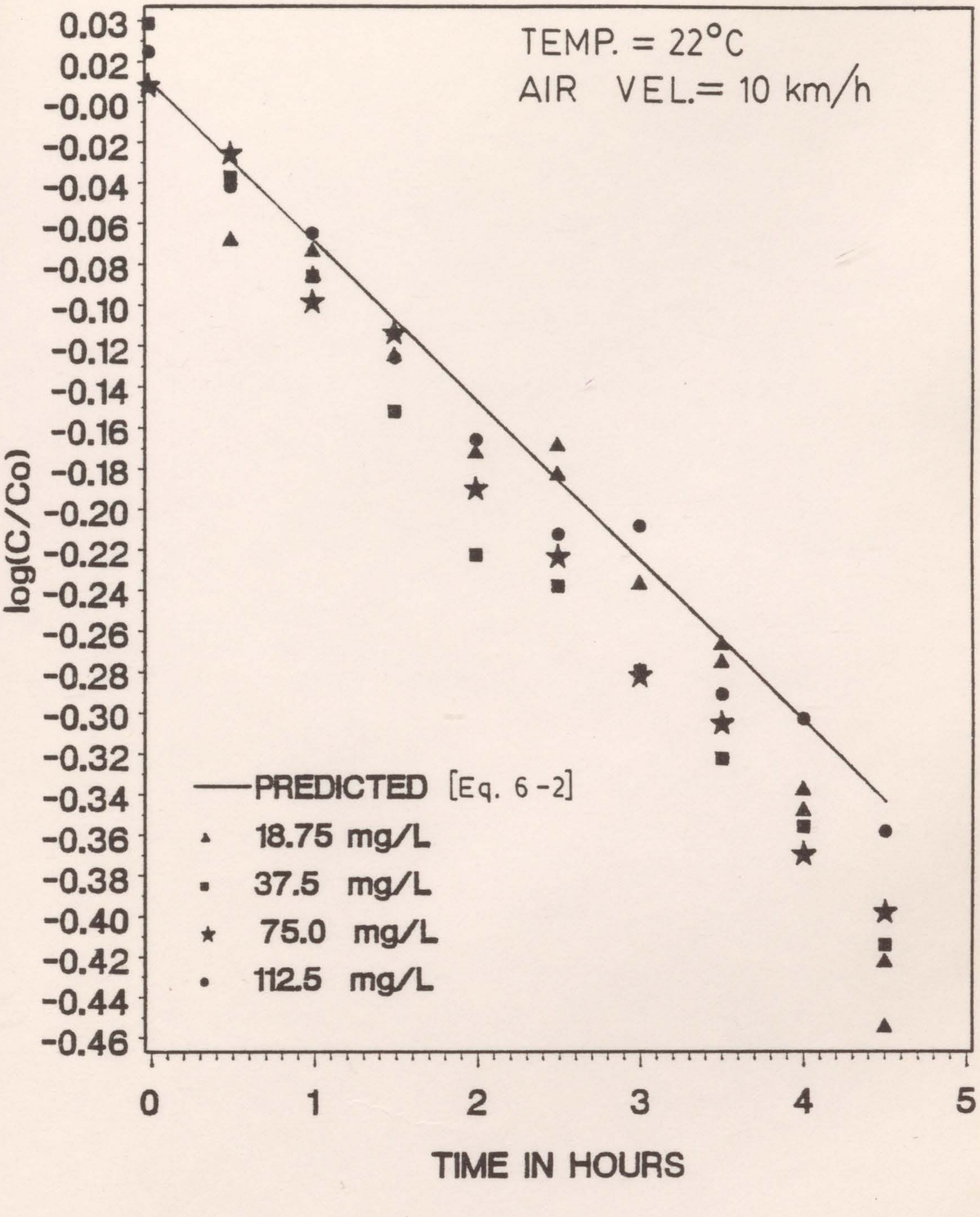


Figure 6-13 VOLATILIZATION FROM STAGNANT WATER WITH AN AREA/VOLUME OF 22.4 (1/m)

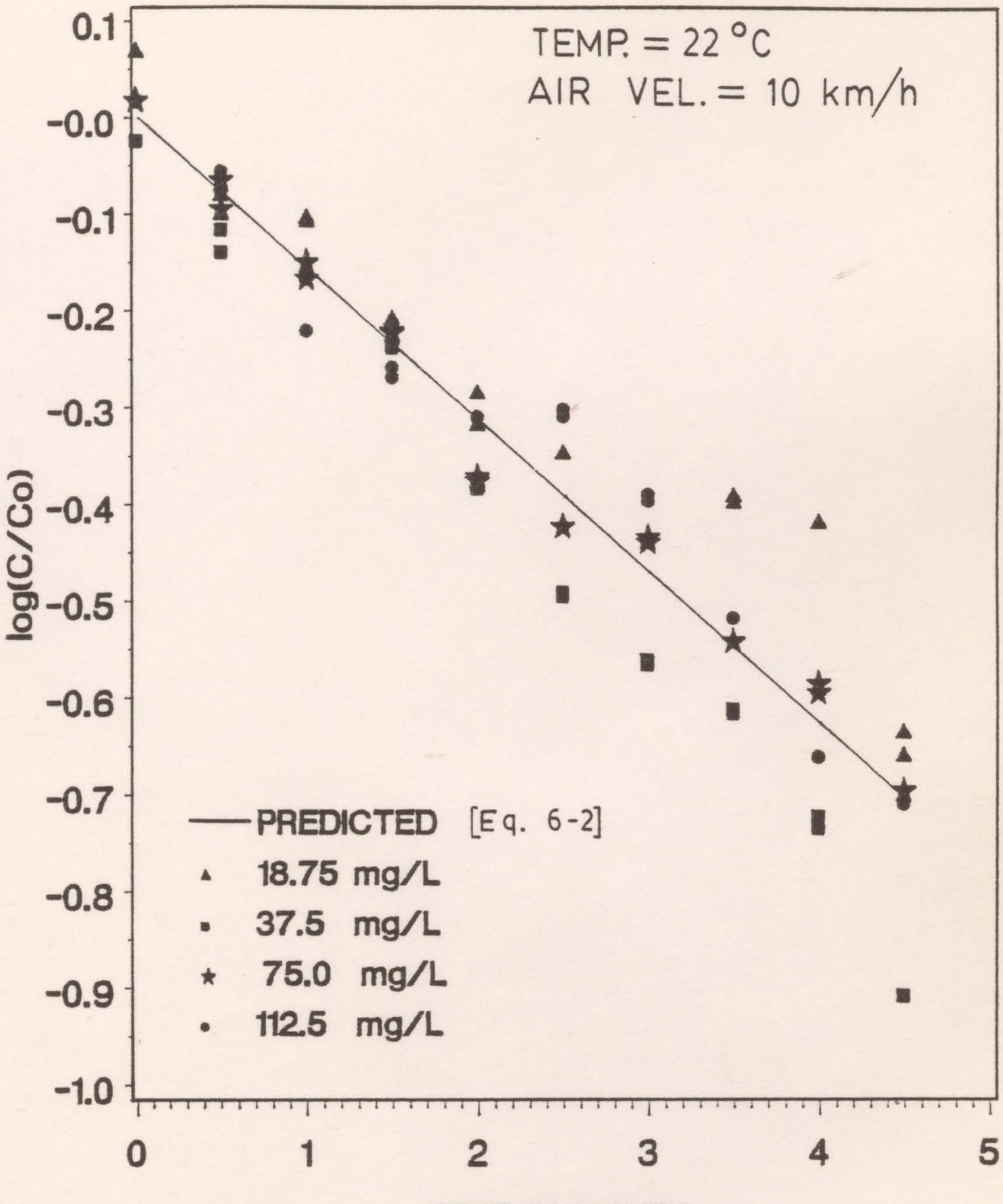


Figure 6-14 VOLATILIZATION FROM STAGNANT WATER WITH AN AREA/VOLUME OF 50.0 (1/m)

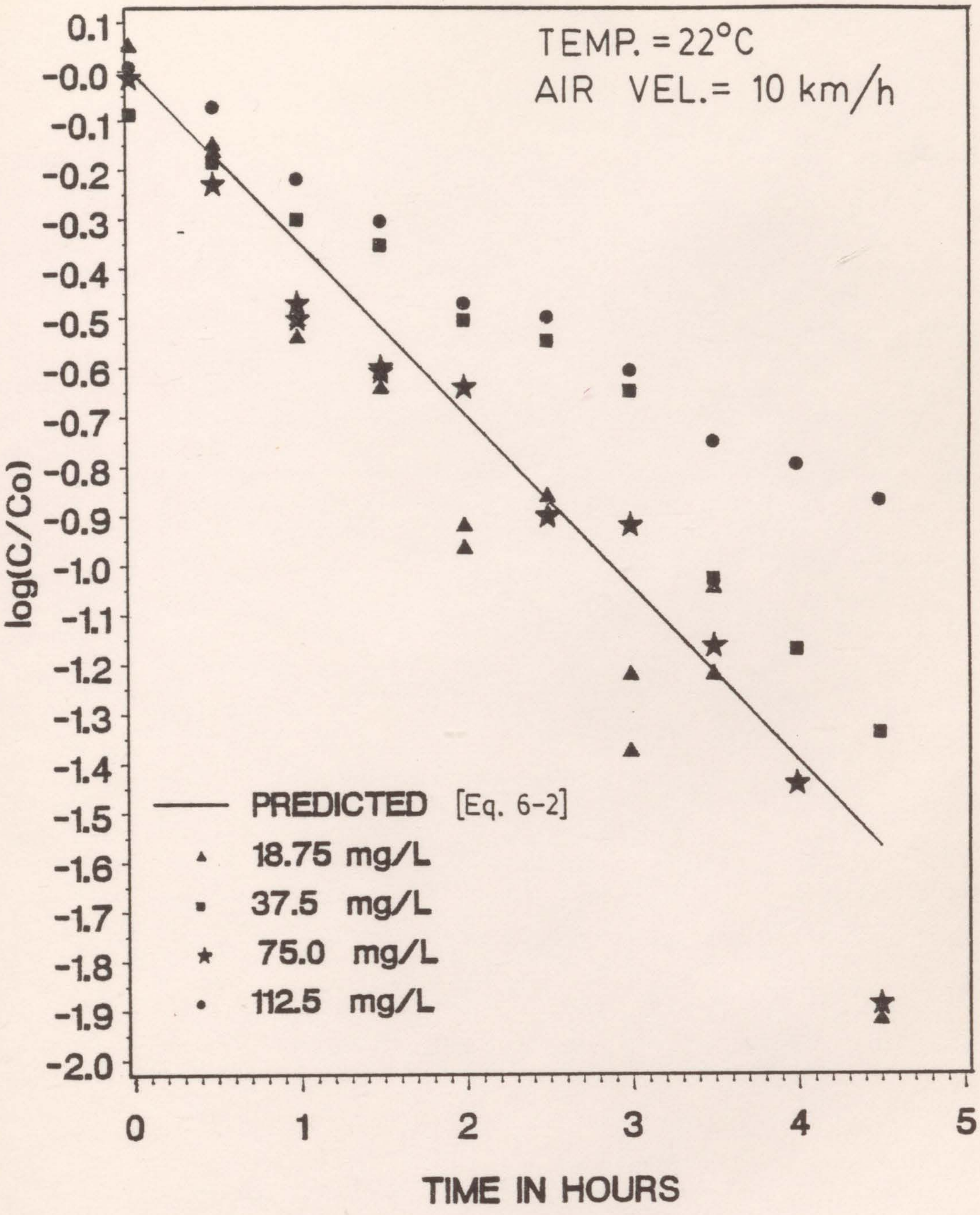


Figure 6-15 VOLATILIZATION FROM STAGNANT WATER WITH AN AREA/VOLUME OF 81.0 (1/m)

The data presented in Table 6-9 were regressed statistically to determine a relationship between the area/volume and the corresponding volatilization rate constants. The data were regressed using semi-log curve fitting, Fig. 6-16, and the coefficients determined are presented in Table 6-10.

Table 6-9 Regression Coefficients for Volatilization of PCE from Stagnant Water

CONCENTRATION mg/L	AREA/VOLUME (1/m)	SLOPE	INTERCEPT x 10^{-7}	r^2
18.75	2.08	-0.0468	-3.35	.9583
	22.4	-0.0842	-2.16	.9650
	50.0	-0.1257	-5.45	.9343
	81.0	-0.3874	8.16	.9328
37.5	2.08	-0.0403	-5.66	.9617
	22.4	-0.0937	2.59	.9831
	50.0	-0.1861	0.31	.9814
	81.0	-0.2753	4.23	.9393
75.0	2.08	-0.0321	0.99	.9627
	22.4	-0.0907	-2.66	.9931
	50.0	-0.1545	1.87	.9869
	81.0	-0.3666	-28.3	.9475
112.5	2.08	-0.0522	-1.31	.9489
	22.4	-0.0796	-1.59	.9844
	50.0	-0.1551	292.	.9702
	81.0	-0.2016	0.58	.9873

As indicated in Table 6-10, the data were regressed separately for each concentration, resulting in equations dependent on concentration. However, closer evaluation of Fig. 6-16 indicates that all the volatilization rate constants and area to volume values can be correlated with one regression equation.

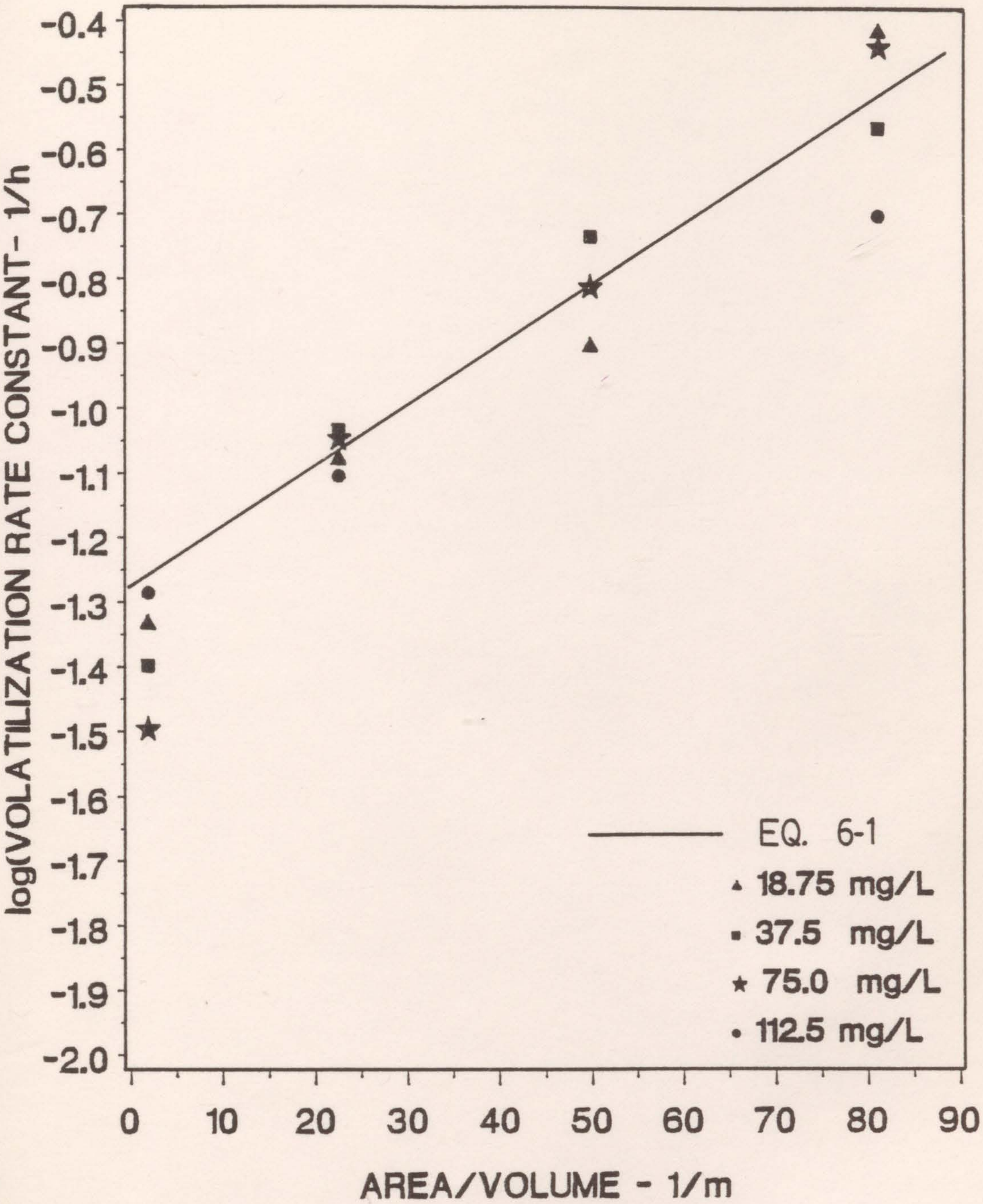


Figure 6-16 VOLATILIZATION RATE CONSTANT VS AREA/VOLUME RATIO FOR PCE IN WATER

Table 6-10 Regression Coefficients for Volatilization Rate Constant Versus Area/Volume Plots

CONCENTRATION mg/L	SLOPE	INTERCEPT	r^2
18.75	0.011	-1.3628	0.9727
37.5	0.010	-1.3309	0.9405
75.0	0.013	-1.4392	0.9672
112.5	0.007	-1.2685	0.9566

When all the data were regressed together, the following equation was obtained with an r^2 of 0.9537.

$$k_W = 10^{(0.011(A/V)-1.365)} \qquad (6-1)$$

where

k_W = volatilization rate constant from water, 1/h,

A = cross-sectional surface area, m^2,

V = volume of fluid, m^3.

Therefore, Eq. 6-1 can be used to calculate the volatilization rate constant for any area to volume ratio, independent of concentration. However, it should be noted that Eq. 6-1 was developed for a wind velocity of 10 km/h, and an ambient temperature of 22°C.

By substituting Eq. 6-1 into Eq. 4-12, Eq. 6-2 is obtained to calculate the concentration of PCE remaining in the water after time t.

$$\log(C/C_o) = -k_W t \qquad (6-2)$$

Similarly, Eq. 6-3 can be used to determine the mass of PCE remaining after time t.

$$\log(X/X_o) = -k_W t \qquad (6\text{-}3)$$

where

C/C_o = final and initial concentration ratio,
X/X_o = final and initial mass ratio,
t = time, h.

As mentioned in Section 4.1, k_W divided by A/V gives K_{OLW}. Therefore, if the compiled values for k_W and the corresponding A/V values are plotted linearly and the curve is forced through the origin, then its slope when combined with Eqs. 4-7b and 4-10 gives:

$$K_{OLW}(A/V) = 2.303(k_W) \qquad (6\text{-}4a)$$

$$= 2.303(0.0038(A/V)) \qquad (6\text{-}4b)$$

$$= 0.00875(A/V) \qquad (6\text{-}4c)$$

Thus, the overall liquid film coefficient at liquid-gas interface, K_{OLW}, was calculated to be 0.009 m/h.

6.2.2 Flux of PCE into Stagnant Water

When pure PCE is spilled in a body of water, large or small, it will sink to the bottom because of its higher density. Once at the bottom, the PCE will begin to diffuse into the water and dissolve. Figure 6-17 indicates the change in PCE concentration in water with time, as was measured in the flux experiment. The following empirical equation was deter-

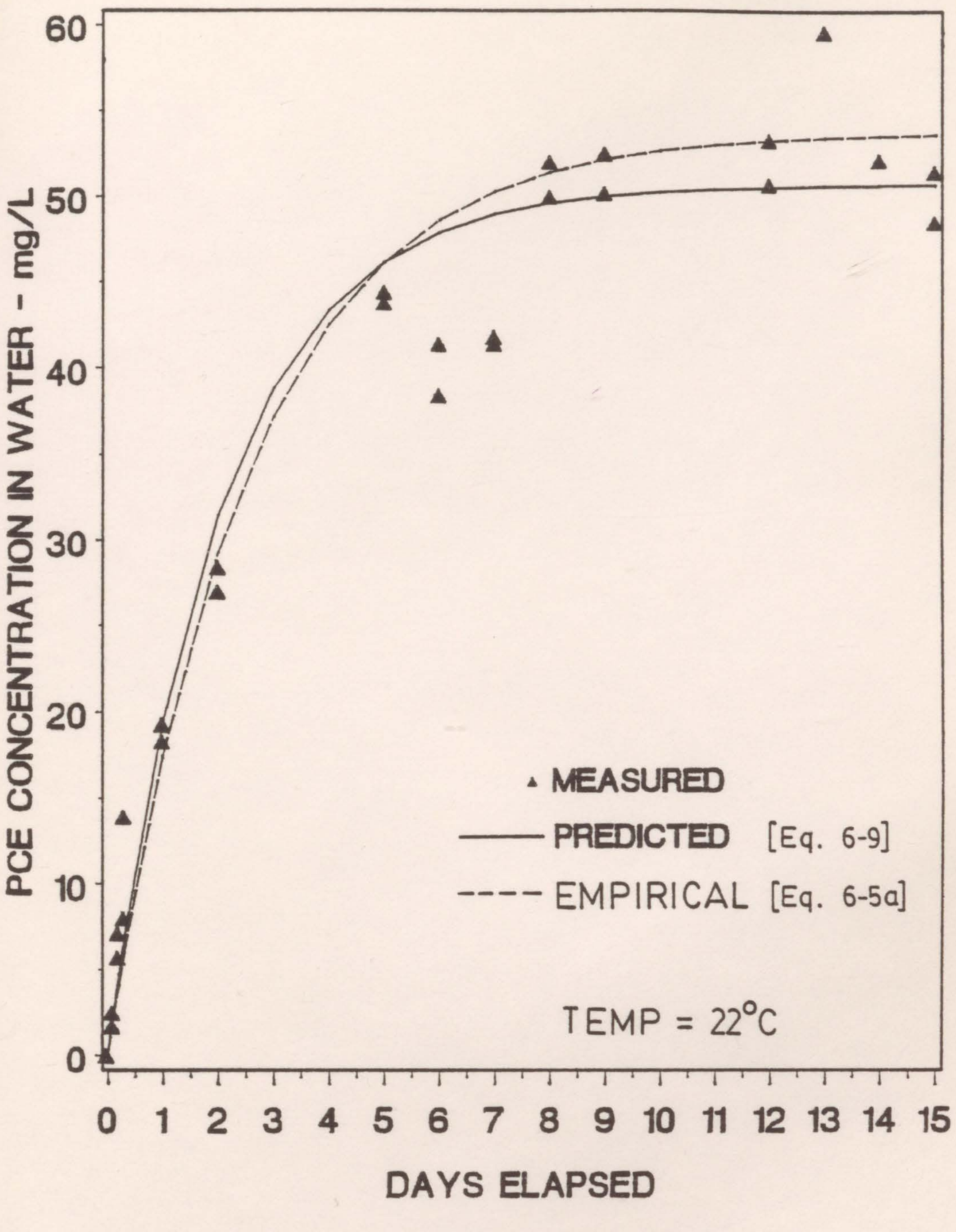


FIGURE 6-17 CONCENTRATION OF PCE MEASURED IN FLUX EXPERIMENT

mined to express the concentrations as a function of time. Appendix D contains the procedure used to calculate the necessary coefficients.

$$C_L = 54(1.0-e^{-0.39t}), \qquad (6\text{-}5a)$$

Since mass transport of PCE into the water may be a more desirable expression, Eq. 6-5a was modified to Eq. 6-5b.

$$X_L = 108(1.0-e^{-0.39t}) \qquad (6\text{-}5b)$$

where

C_L = concentration of PCE in water, mg/L,

X_L = mass of PCE in water, mg,

t = time, d.

6.2.2.1 Combining Flux and Volatilization

Once the PCE begins to diffuse into the water body, volatilization into the atmosphere will occur simultaneously. Therefore, flux into the water and volatilization of PCE must be combined to predict the overall situation and to compute the total flux. Total flux, X_F, is the total mass of PCE lost to the environment from the pure PCE pool and is equal to the mass of PCE in the liquid, X_L and mass of PCE volatilized at the surface, X_V. Therefore,

$$X_F = X_L + X_V \qquad (6\text{-}6)$$

Since X_V depends on X_L, a computer program was developed to calculate the X_V, X_L and X_F values in small time steps. Appendix D shows the computer program and the generated data.

Figure 6-18 gives a plot of the generated X_F values versus time. By using the technique mentioned earlier, Eqs. 6-7 and 6-8 were developed from the data presented in Figure 6-18.

$$X_F = 178(1-e^{-0.28t}) \tag{6-7}$$

$$C_F = 89(1-e^{-0.28t}) \tag{6-8}$$

where

X_F = total flux mass, mg,

C_F = concentration fluxing into water, mg/L,

t = time, d.

By comparing Eqs. 6-8 and 4-16e, values for the saturating concentration at the interface between chemical and water, C_i, and the overall liquid film coefficient at the chemical-water interface, K_{OLPCE}, are determined as 89 mg/L and 0.006 m/h respectively. Using these coefficients in Eq. 4-22g, the overall liquid film coefficient for the water-atmosphere interface from the flux data, K_{OLWF}, is calculated as 0.004 m/h. Therefore, the overall equation for predicting PCE concentration in water becomes.

$$C_{LT} = 51[1-e^{-0.48(A/V)t}] \tag{6-9}$$

where

C_{LT} = theoretical prediction of chemical concentration in water, mg/L,

A = cross-sectional area, m^2,

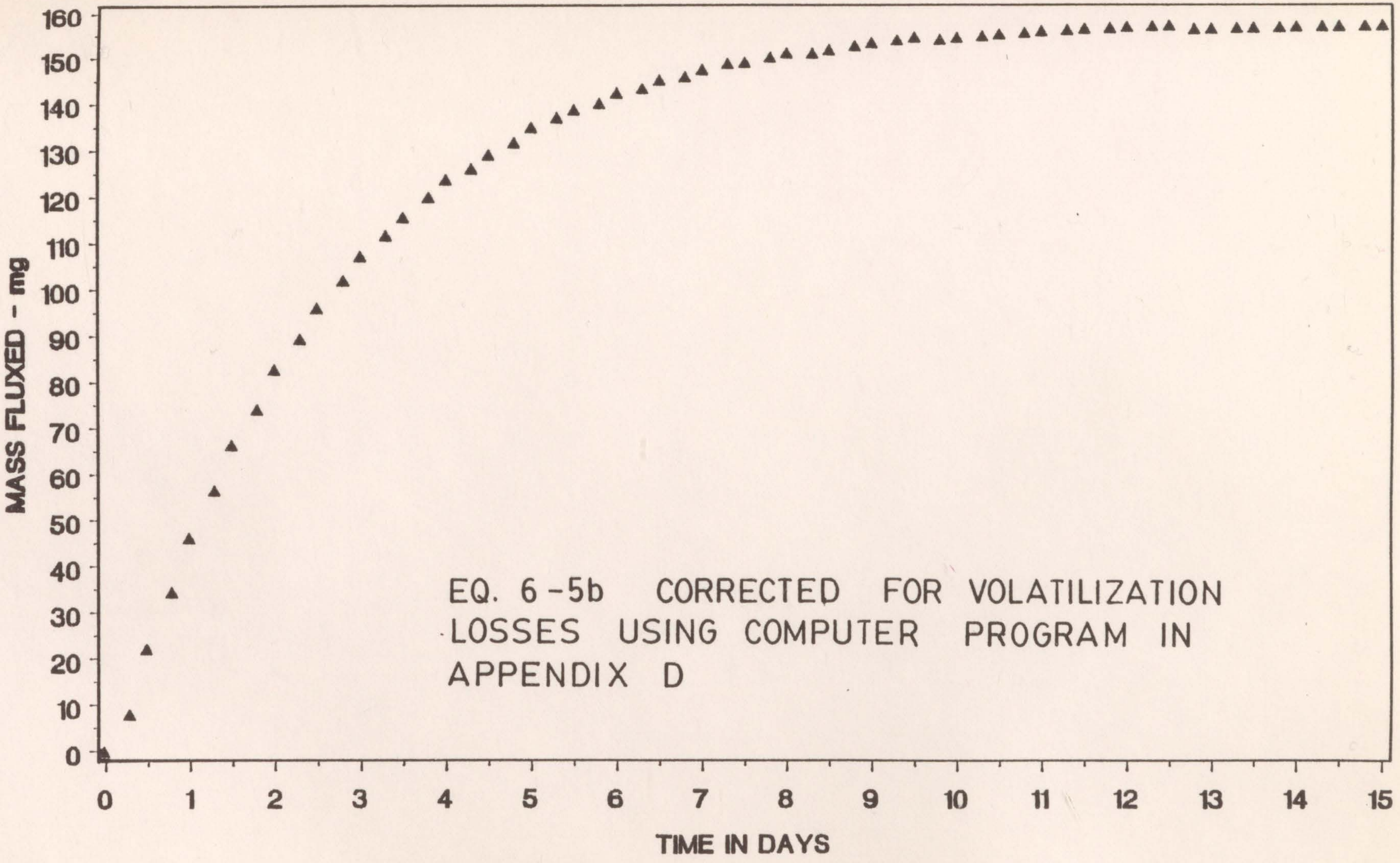


Figure 6-18 TOTAL MASS FLUX FOR PCE IN STAGNANT WATER

V = volume, m^3,

t = time, d.

Figure 6-17 shows a comparison of the empirical and theoretical prediction curves to the measured data.

6.2.3 Volatilization of Aqueous PCE from Soil

The study on volatilization losses of aqueous PCE from soil was carried out using batch experiments. Runs were completed with three concentrations and three area to volume ratios.

6.2.3.1 Sandy Loam Soil

Figures 6-19 to 6-21 show semi-log plots of the data collected from these experiments. Table 6-11 lists the regression coefficients obtained from the curve fitting procedure.

Table 6-11 Regression Coefficients for Aqueous PCE Volatilization from Sandy Loam Soil

CONCENTRATION mg/kg	AREA/VOLUME 1/m	SLOPE	r^2
6.75	0.377	-0.1292	0.8422
	0.77	-0.1893	0.8899
	1.429	-0.4498	0.9246
13.51	0.377	-0.2907	0.9854
	0.77	-0.2295	0.8648
	1.429	-0.4637	0.8860
20.27	0.377	-0.2579	0.8817
	0.77	-0.2950	0.9045
	1.429	-0.5523	0.9565

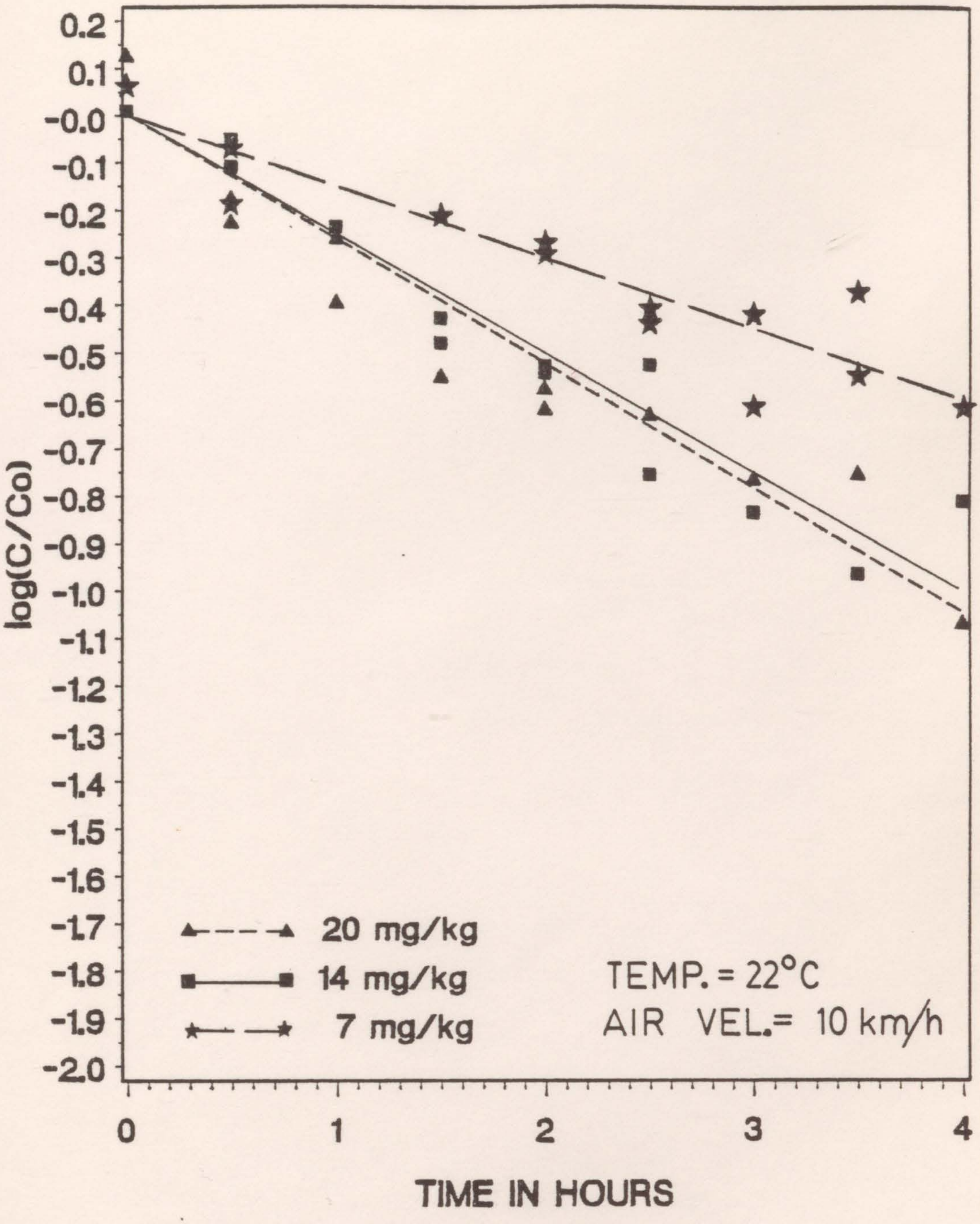


Figure 6-19 VOLATILIZATION OF AQUEOUS PCE FROM SANDY LOAM SOIL--AREA/VOLUME=0.377 (1/m)

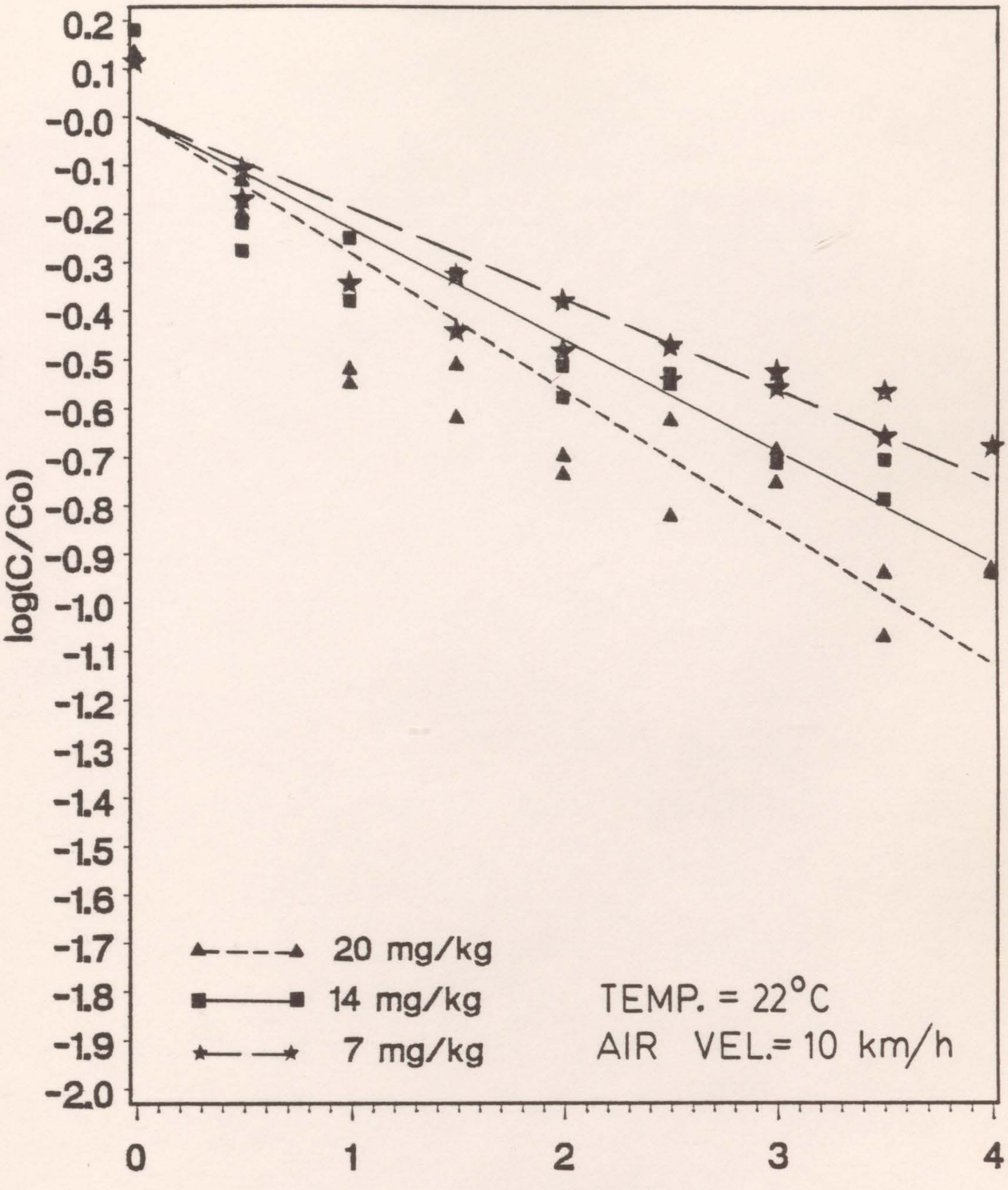


Figure 6-20 VOLATILIZATION OF AQUEOUS PCE FROM SANDY LOAM SOIL--AREA/VOLUME=0.77 (1/m)

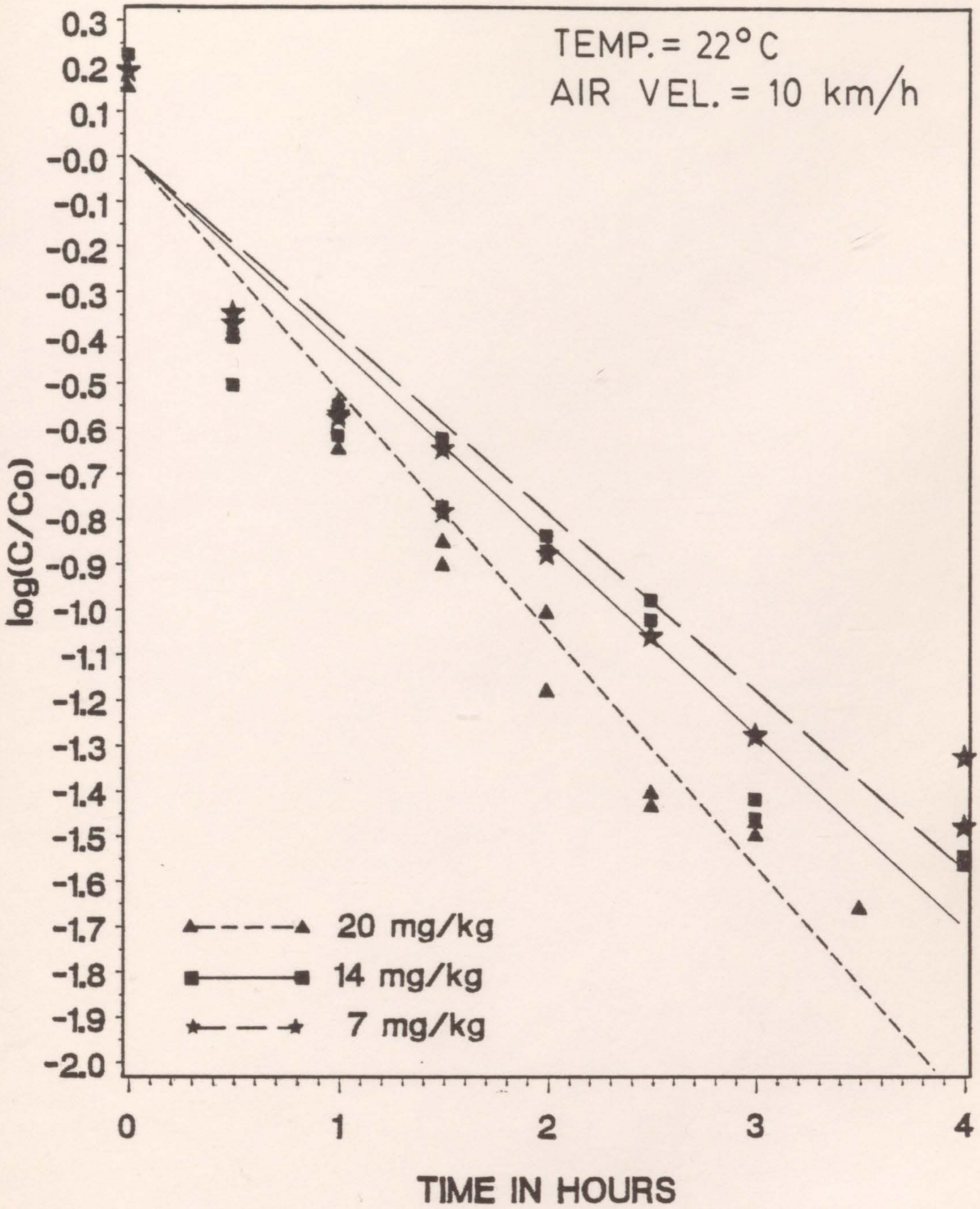


Figure 6-21 VOLATILIZATION OF AQUEOUS PCE FROM SANDY LOAM SOIL--AREA/VOLUME=1.429 (1/m)

The data in Table 6-11 were plotted in Fig. 6-22 on semi-log graph paper to determine the relationship between the volatilization rate constants and area/volume. Table 6-12 gives the regression coefficients obtained for this plot. Figure 6-22 shows that the volatilization rate constant is not only a function of area/volume, but also depends on the initial PCE concentration. In order to determine this relationship, the slopes and intercepts of each curve were plotted against concentration. The best fit equation was then determined for each case as shown in Appendix E. The best fit Eq. 6-10a gives the volatilization rate of aqueous PCE for sandy loam.

$$k_{SL} = 10^{((0.64-0.012C_1)(A/V)+0.023C_1-1.32)} \qquad (6\text{-}10a)$$

Table 6-12 Regression Coefficients for Volatilization Rate Constant Versus A/V for Aqueous PCE in Sandy Loam Soil

CONCENTRATION mg/kg	SLOPE	INTERCEPT	r^2
6.75	0.5704	-1.1620	1.000
13.51	0.4635	-0.9961	1.000
20.27	0.4128	-0.8478	1.000

However, Eq. 6-10a was simplified by neglecting the effect of PCE concentration. As shown in Appendix E, the resulting equation of best fit for for volatilization for all concentrations is:

$$k_{SL} = 10^{(0.482(A/V)-1.00)} \qquad (6\text{-}10b)$$

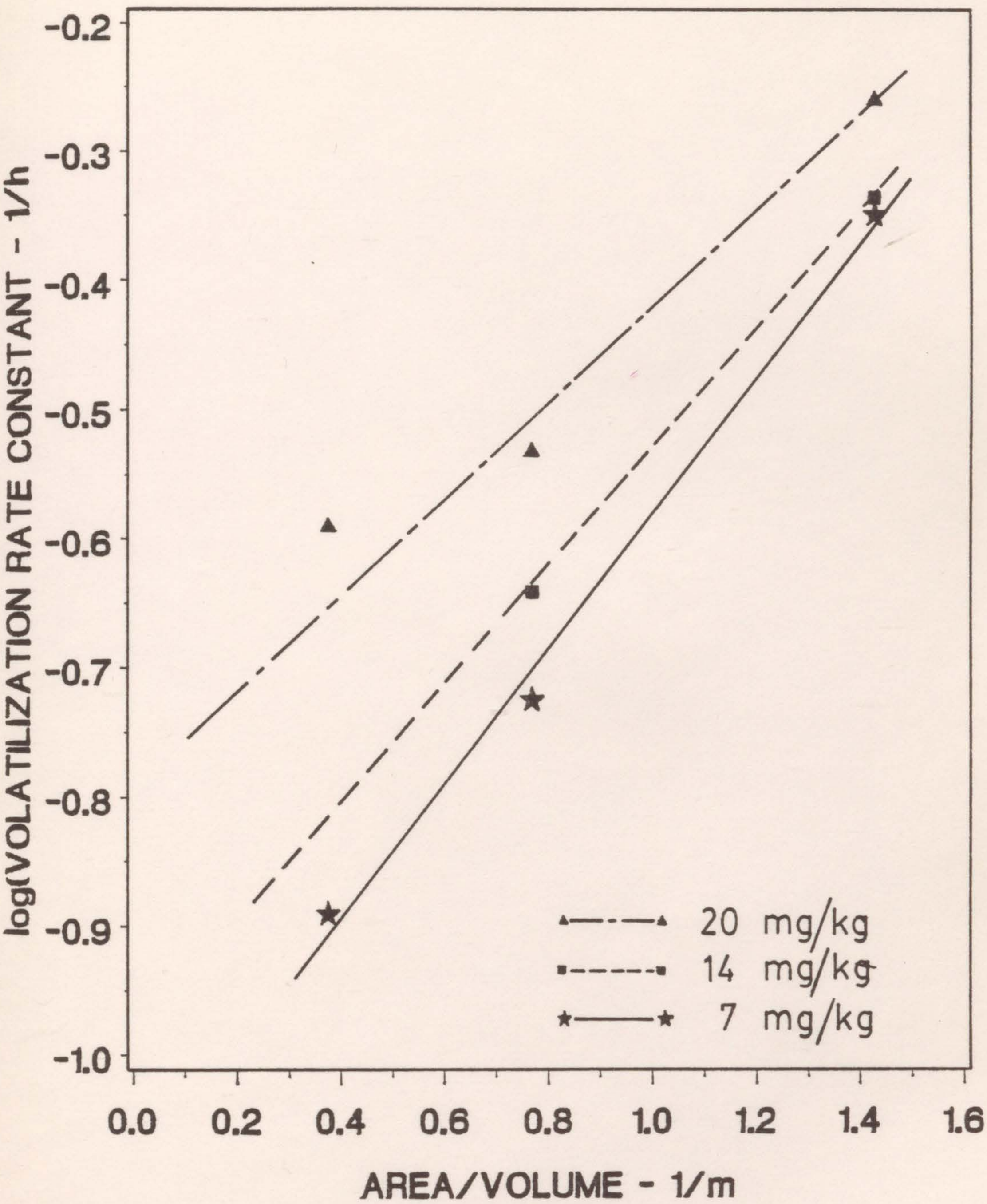


Figure 6-22 VOLATILIZATION RATE CONSTANT VS AREA TO VOLUME RATIO FOR AQUEOUS PCE IN SANDY LOAM SOIL

where

k_{SL} = volatilization rate constant for aqueous PCE from sandy loam soil, 1/h,

C_1 = initial concentration of PCE in soil, mg/kg,

A = cross-sectional area, m^2,

V = volume, m^3.

Substituting k_{SL} into the general volatilization equation developed for water, Eq.4-12, Eq. 6-11 was obtained to calculate the concentration of PCE remaining in the soil at time t.

$$\log(C_2/C_1)_{SL} = -k_{SL}t \tag{6-11}$$

where

C_1, C_2 = initial and final concentration of PCE in soil, mg/kg,

t = time, h.

6.2.3.2 Organic Top Soil

Figures 6-23 to 6-25 show semi-log plots of the results obtained from the experiments with organic top soil. Table 6-13 gives the regression coefficients obtained, for these plots.

The regression data in Table 6-13 were analyzed in the same manner as for the sandy loam data. The volatilization rate constants (slope) were plotted against area to volume ratio using semi-log graph paper, as shown in Fig. 6-26.

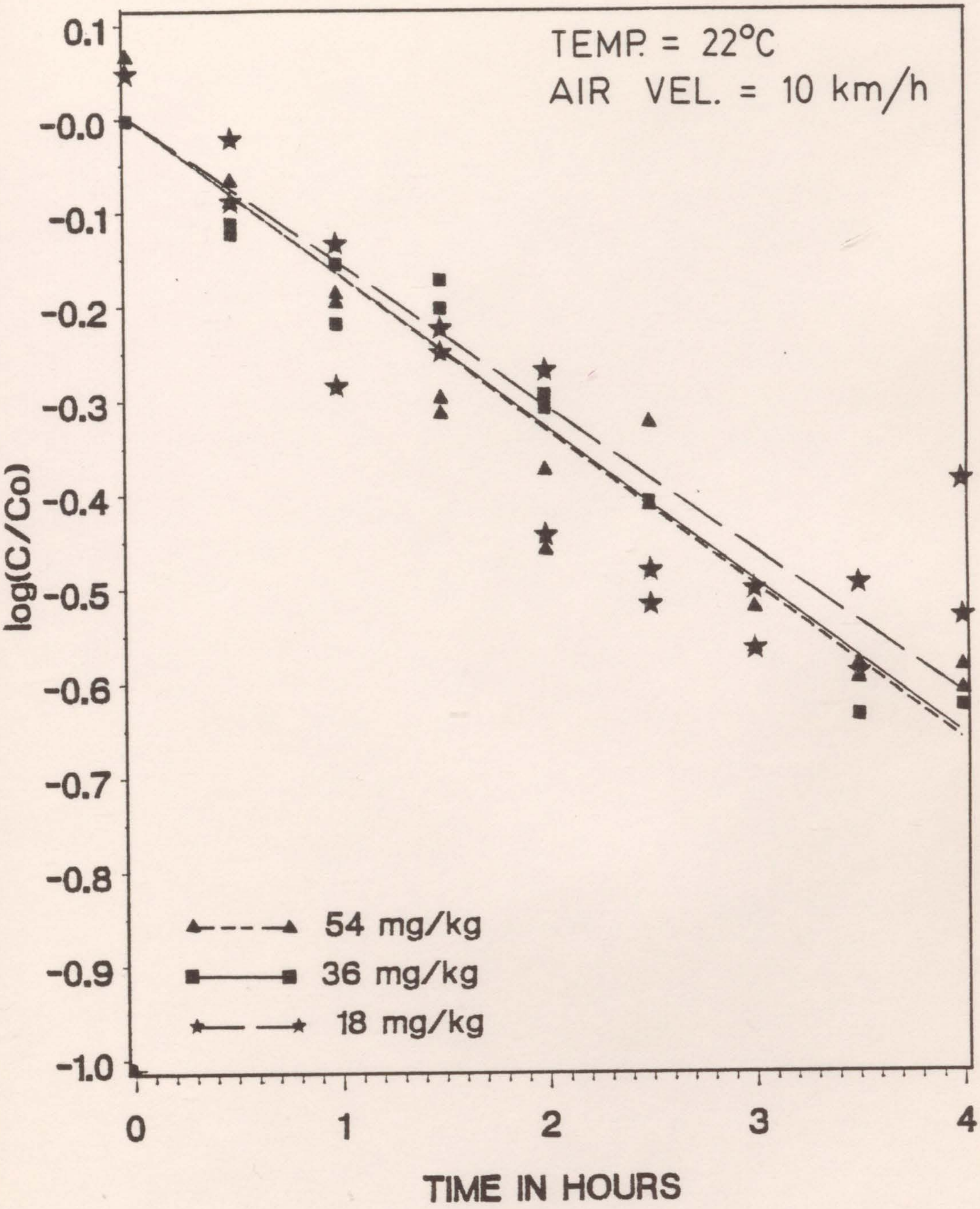


Figure 6-23 VOLATILIZATION OF AQUEOUS PCE FROM ORGANIC TOP SOILS--AREA/VOLUME=0.377 (1/m)

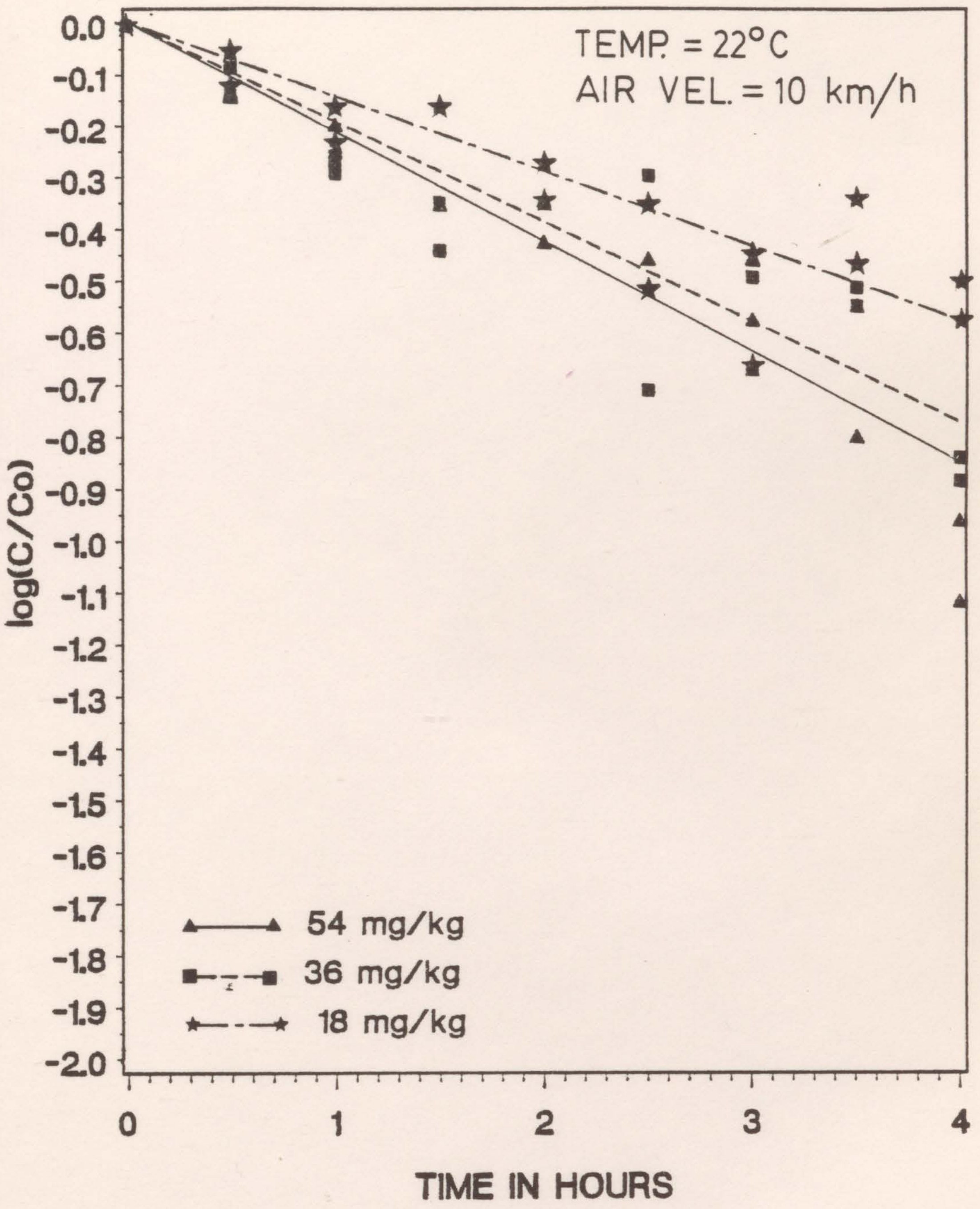


Figure 6-24 VOLATILIZATION OF AQUEOUS PCE FROM ORGANIC TOP SOIL--AREA/VOLUME=0.77 (1/m)

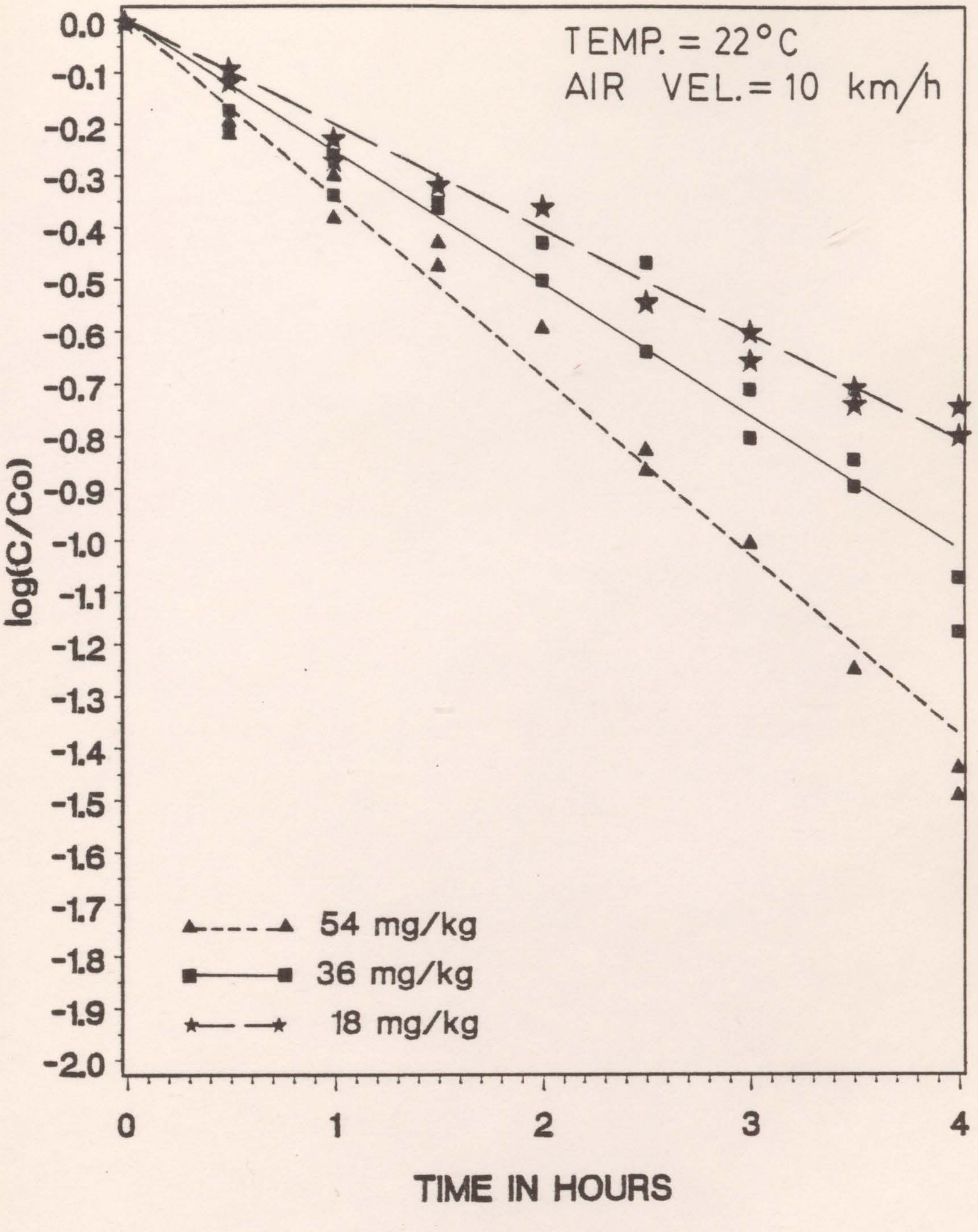


Figure 6-25 VOLATILIZATION OF AQUEOUS PCE FROM ORGANIC TOP SOIL--AREA/VOLUME=1.429 (1/m)

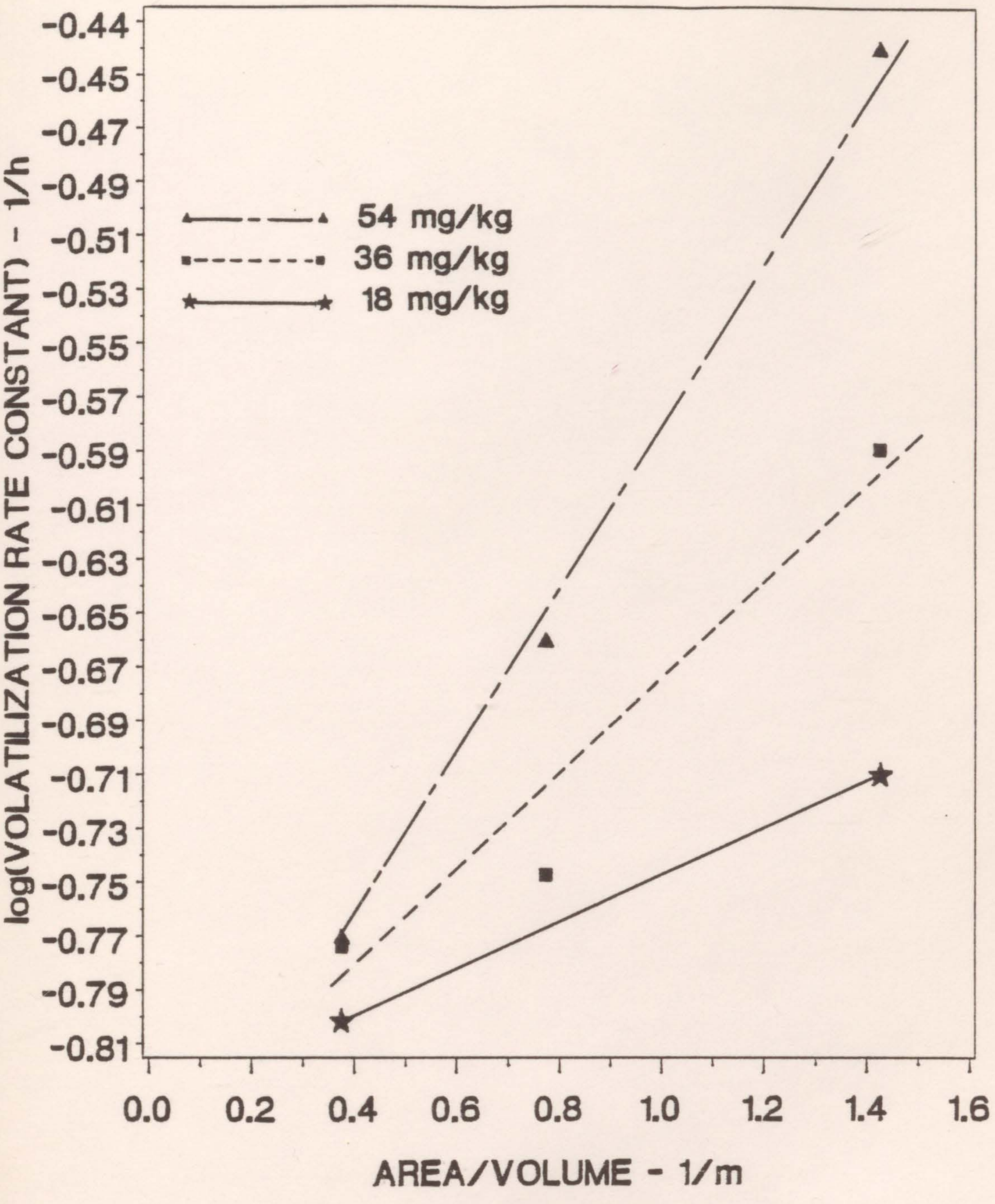


Figure 6-26 VOLATILIZATION RATE CONSTANT VS AREA TO VOLUME RATIO FOR AQUEOUS PCE IN ORGANIC TOP SOIL

Table 6-14 gives the regression coefficients. The following best fit equations were obtained with and without PCE concentration as a variable,

$$k_{ORG} = 10^{((0.006C_1-0.034)(A/V)-0.0015C_1-0.799)} \quad (6\text{-}12)$$

$$k_{ORG} = 10^{((0.006C_1-0.034)(A/V)-0.853)} \quad (6\text{-}13)$$

where

k_{ORG} = volatilization rate constant of aqueous PCE from organic top soil, 1/h

C_1 = initial concentration of PCE in soil, mg/kg,

A = area/volume ratio, 1/m.

Using k_{ORG} in Eq. 4-12, the concentration of PCE remaining in organic top soil at time t is given by:

$$\log(C_2/C_1) = -k_{ORG}t \quad (6\text{-}14)$$

where

C_1, C_2 = initial and final concentration of PCE in soil, mg/kg,

t = time, h.

Table 6-13 Regression Coefficients for Aqueous PCE Volatilization from Organic Top Soil

CONCENTRATION mg/kg	AREA/VOLUME 1/m	SLOPE	r^2
18.02	0.377	-0.1581	0.8841
	0.77	-0.1332	0.8188
	1.429	-0.1942	0.9863
36.04	0.377	-0.1655	0.9642
	0.77	-0.1787	0.8830
	1.429	-0.2548	0.9578
54.08	0.377	-0.1694	0.9408
	0.77	-0.2170	0.8870
	1.429	-0.3555	0.9881

Table 6-14 Regression Coefficients for Volatilization Rate Constant Versus A/V for Aqueous PCE in Organic Top Soil

CONCENTRATION mg/kg	SLOPE	INTERCEPT	r^2
18.02	0.0849	-0.8331	1.000
36.04	0.1712	-0.8385	1.000
54.08	0.3060	-0.8865	1.000

6.2.4 Volatilization of Pure PCE from Soil

Experiments were conducted on the two soils to determine the volatilization of pure PCE spilled on them.

6.2.4.1 Sandy Loam Soil

The data collected for the volatilization of pure PCE from soil are plotted on semi-log paper in Figure 6-27. The regression coefficients for the best fit are shown in Table 6-15.

Only one mass of PCE was tested for volatilization. The relationship between the area to volume ratios and corresponding volatilization rate constants was determined for this mass from Figure 6-28. The resulting Eq. 6-15 can be used to calculate the volatilization rate as a function of area to volume ratio.

$$k_{PSL} = 10^{(0.210(A/V)-2.439)} \tag{6-15}$$

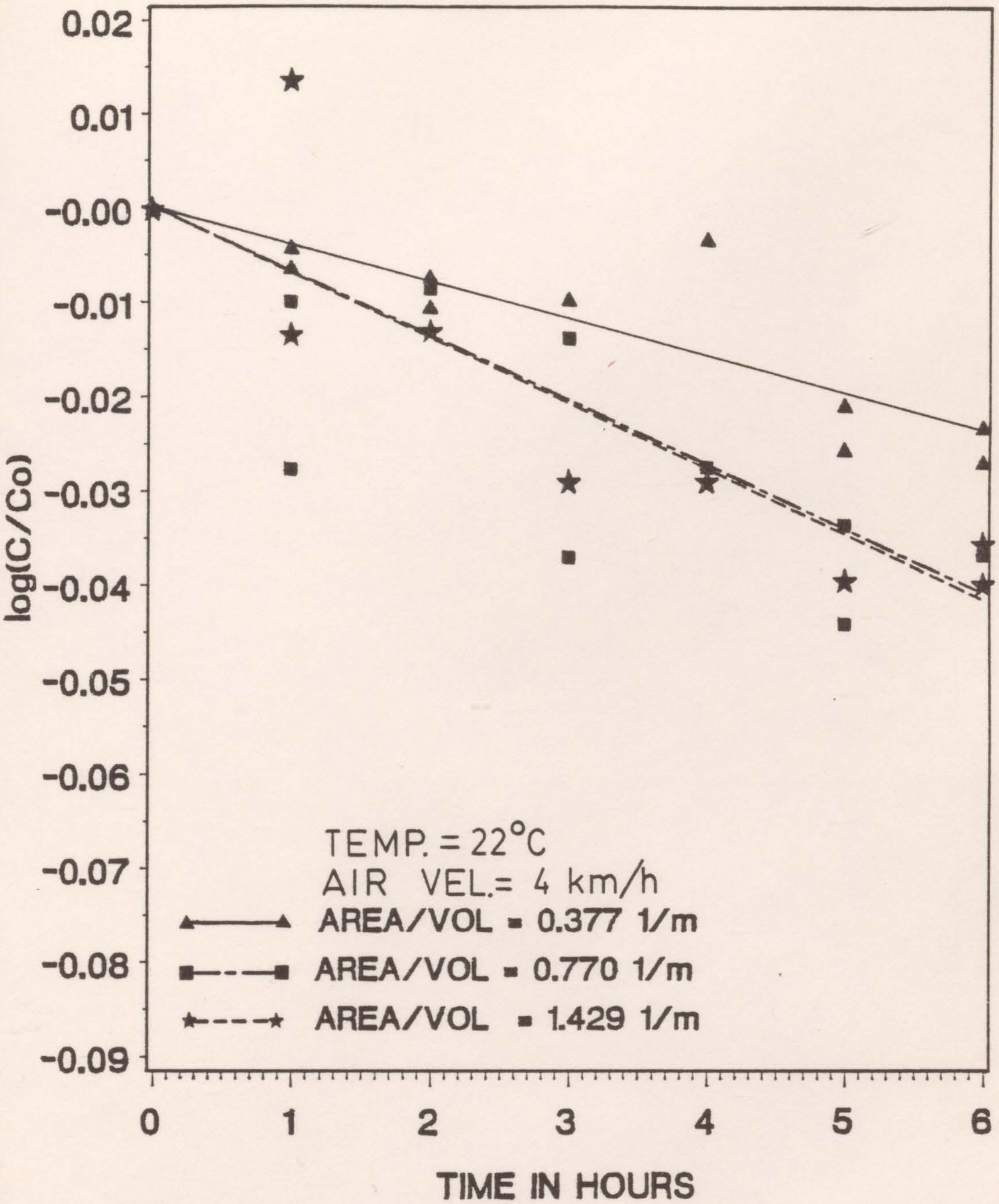


Figure 6-27 VOLATILIZATION OF PURE PCE FROM SANDY LOAM SOIL--0.292 mg/kg APPLIED

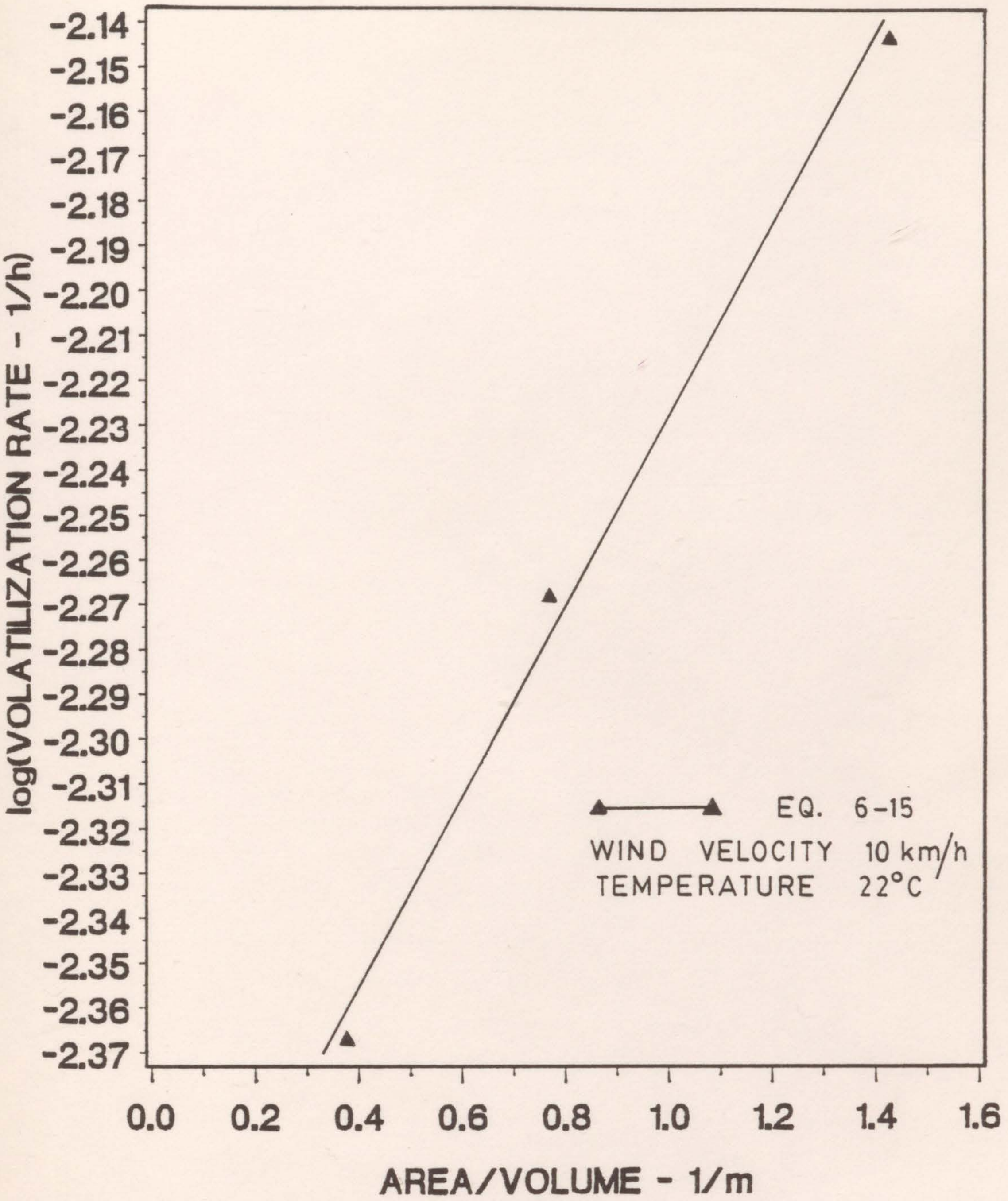


Figure 6-28 VOLATILIZATION RATE VS AREA TO VOLUME RATIO FOR PURE PCE ON SANDY LOAM SOIL

where

k_{PSL} = volatilization rate constant of pure PCE in sandy loam soil, 1/h

A = cross-sectional area, m^2,

V = volume, m^3.

The corresponding equation for pure PCE volatilization from sandy loam soil is:

$$\log(C_2/C_1)_{PSL} = -k_{PSL}t \qquad (6\text{-}16)$$

where

C_1, C_2 = initial and final concentrations of PCE in soil, mg/kg,

t = time, h.

Table 6-15 Regression Coefficients for the Volatilization of Pure PCE from Sandy Loam Soil-- 0.292 mg/kg Applied

AREA/VOLUME 1/m	SLOPE	r^2
0.377	-0.0043	0.9348
0.77	-0.0054	0.7224
1.429	-0.0070	0.8068

6.2.4.2 Organic Top Soil

Figure 6-29 shows the volatilization data for pure PCE volatilization from organic top soil. It can be seen that the data points are quite scattered, giving poor correlation

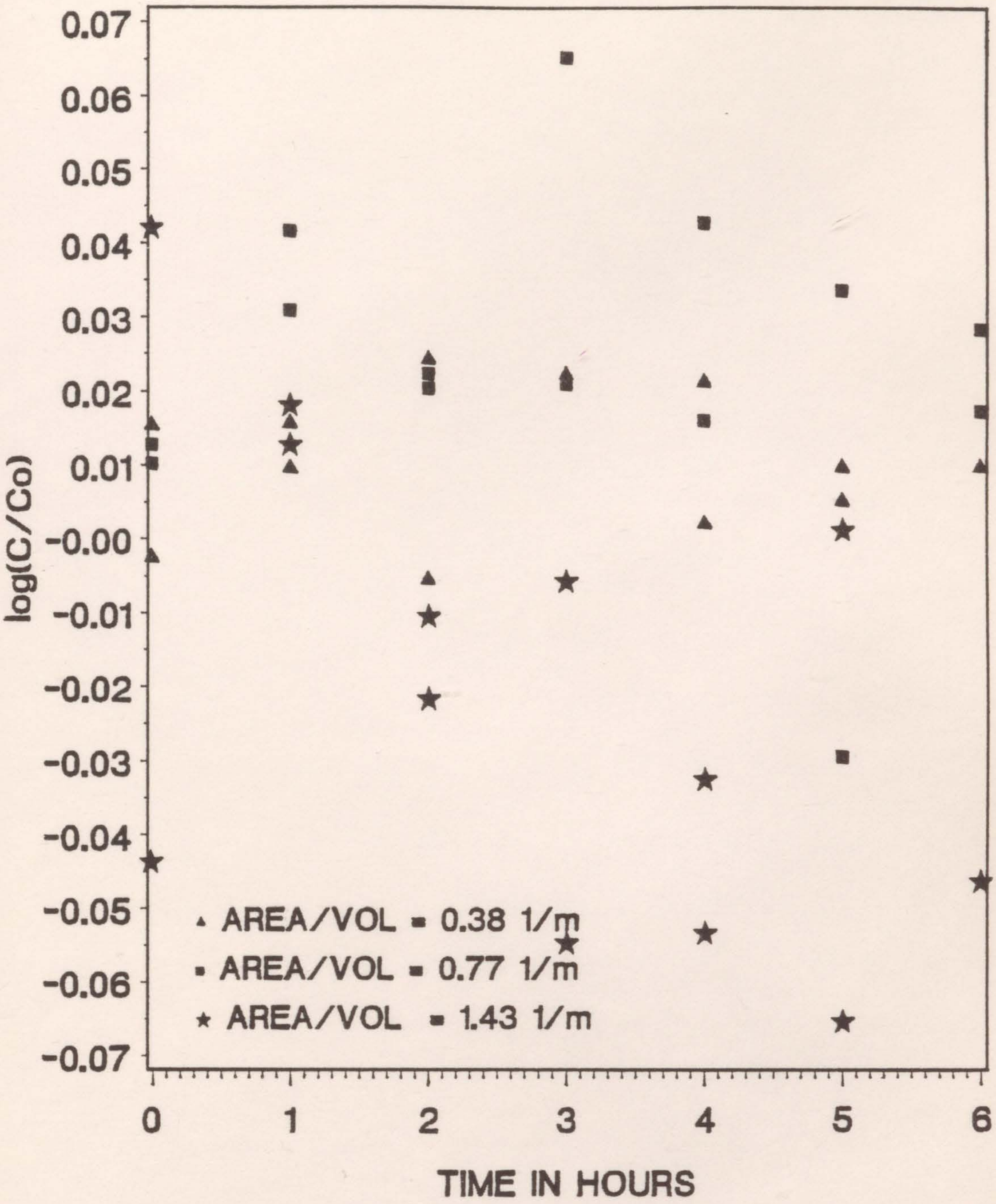


Figure 6-29 VOLATILIZATION OF PURE PCE FROM ORGANIC TOP SOIL --0.492 mg/kg APPLIED

coefficients. The values of r^2 varied between 0.0009 and 0.3318. These tests were repeated twice and similar results were obtained. Therefore, no equation for volatilization of PCE from organic top soil could be determined.

6.3 Perfusion Apparatus

Degradation of PCE in soil was evaluated both for sandy loam soil and organic top soil using the perfusion apparatus. Several runs were completed with and without airflow. The tests were conducted on both sterilized and unsterilized soils.

6.3.1 Sandy Loam Soil

To determine whether degradation under spill conditions would occur, the concentrations in the perfusion flask, measured daily, are plotted in Fig. 6-30 for initial PCE concentration of 11.25 mg/L, with air flow. Figure 6-31 presents a similar run without air flow. Results from another run, performed with an initial PCE concentration of 120.0 mg/L, with air flow is shown in Fig. 6-32.

The data were analyzed using semi-log regression to determine the rate coefficients for various runs. The results are given in Table 6-16.

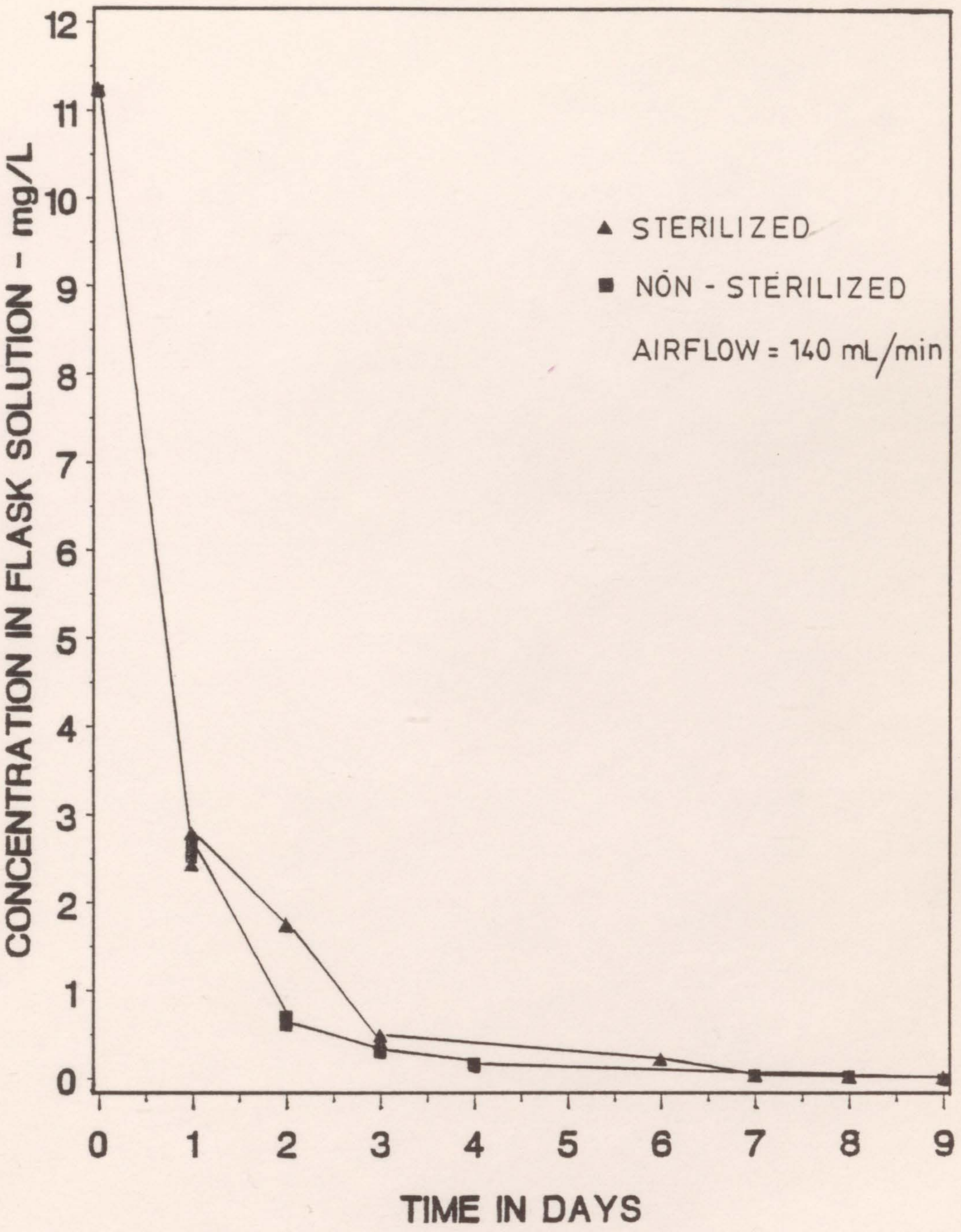


Figure 6-30 PERFUSION OF AQUEOUS PCE AT 11.25 mg/L THRU SANDY LOAM SOIL--WITH AIRFLOW

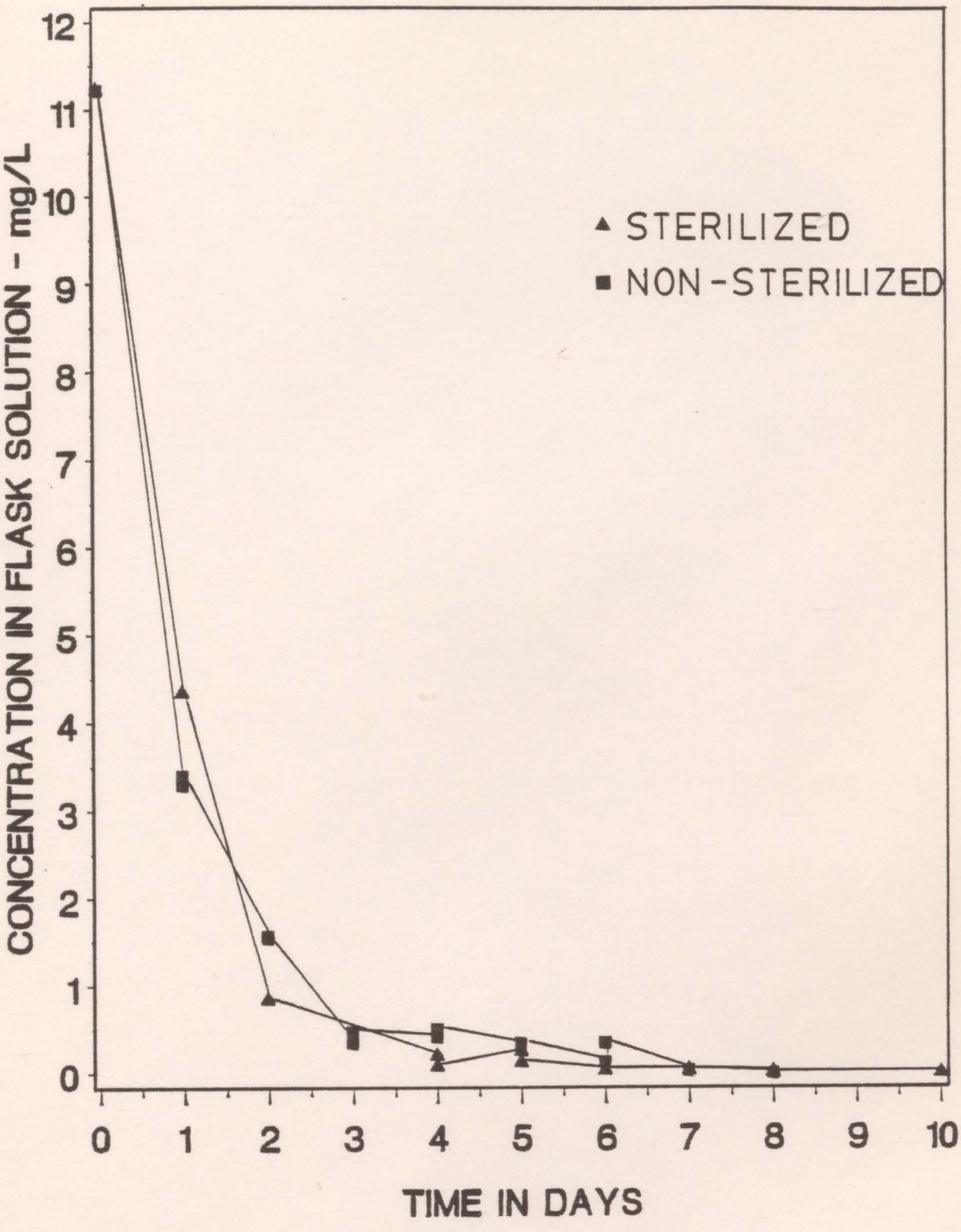


Figure 6-31 PERFUSION OF AQUEOUS PCE AT 11.25 mg/L THROUGH SANDY LOAM SOIL--WITHOUT AIRFLOW

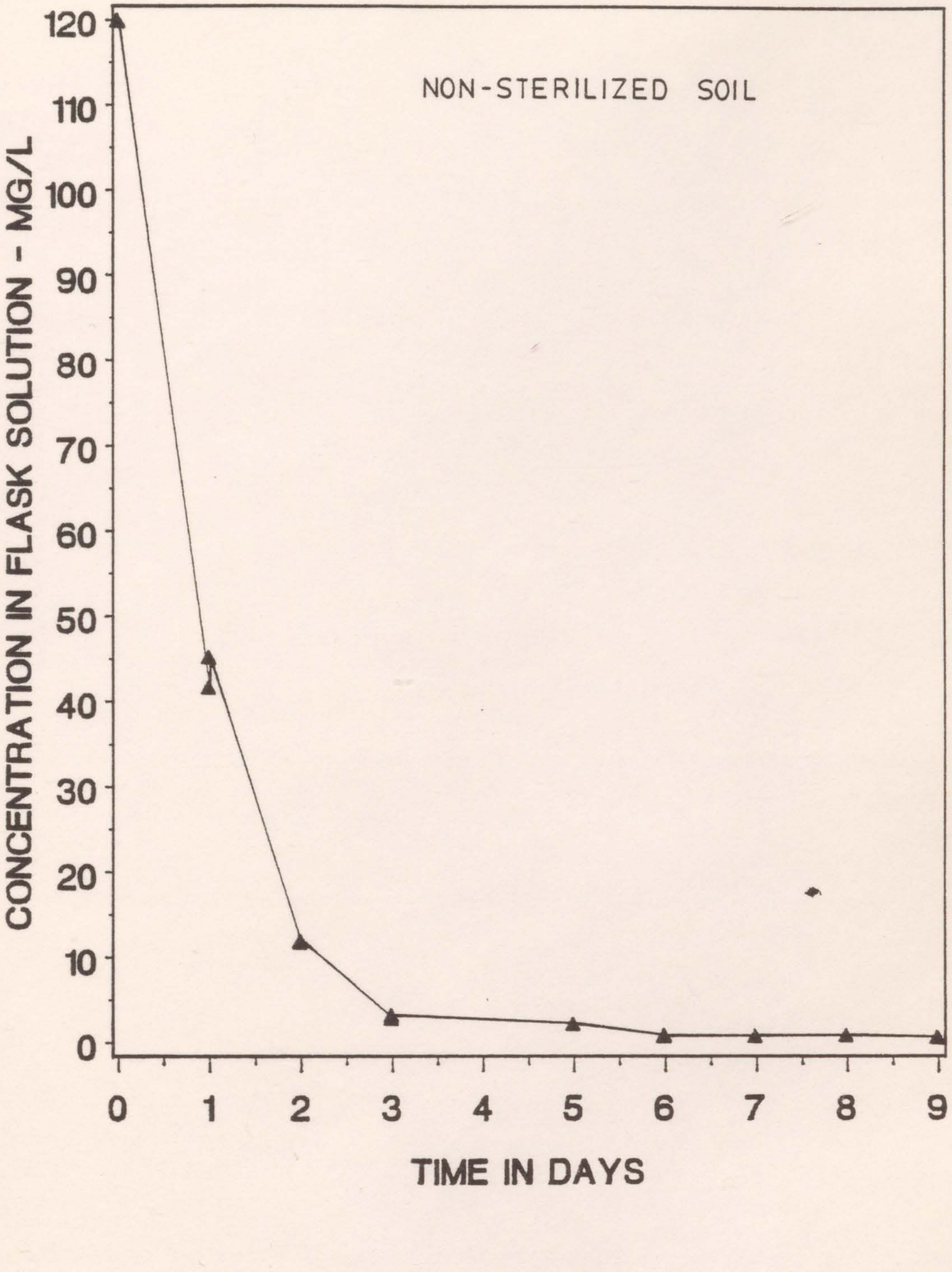


Figure 6-32 PERFUSION OF AQUEOUS PCE AT 120.00 mg/L THROUGH SANDY LOAM SOIL--WITHOUT AIRFLOW

6.3.2 Organic Top Soil

Organic top soil was tested in the perfusion apparatus without airflow for two different initial concentrations, 11.25 mg/L and 120.0 mg/L. The results obtained can be seen in Figs. 6-33 and 6-34 respectively. Table 6-17 contains the semi-log regression data.

Table 6-16 Regression Data for Sandy Loam Soil in the Perfusion Apparatus

RUN	STERILIZED SOIL	SLOPE	INTERCEPT	r^2
11.25 mg/L with airflow	no	-0.3337	1.0277	0.9209
	yes	-0.3450	1.0376	0.9765
11.25 mg/L without airflow	no	-0.3216	1.0446	0.9811
	yes	-0.3426	1.0355	0.9011
120.0 mg/L without airflow	no	-0.3111	2.0440	0.8587

Table 6-17 Regression Data for Organic Top Soil in the Perfusion Apparatus

RUN	STERILIZED SOIL	SLOPE	INTERCEPT	r^2
11.25 mg/L without airflow	no	-0.2453	1.0484	0.9462
	yes	-0.2201	1.0484	0.9124
120.0 mg/L without airflow	no	-0.2548	2.0586	0.8762

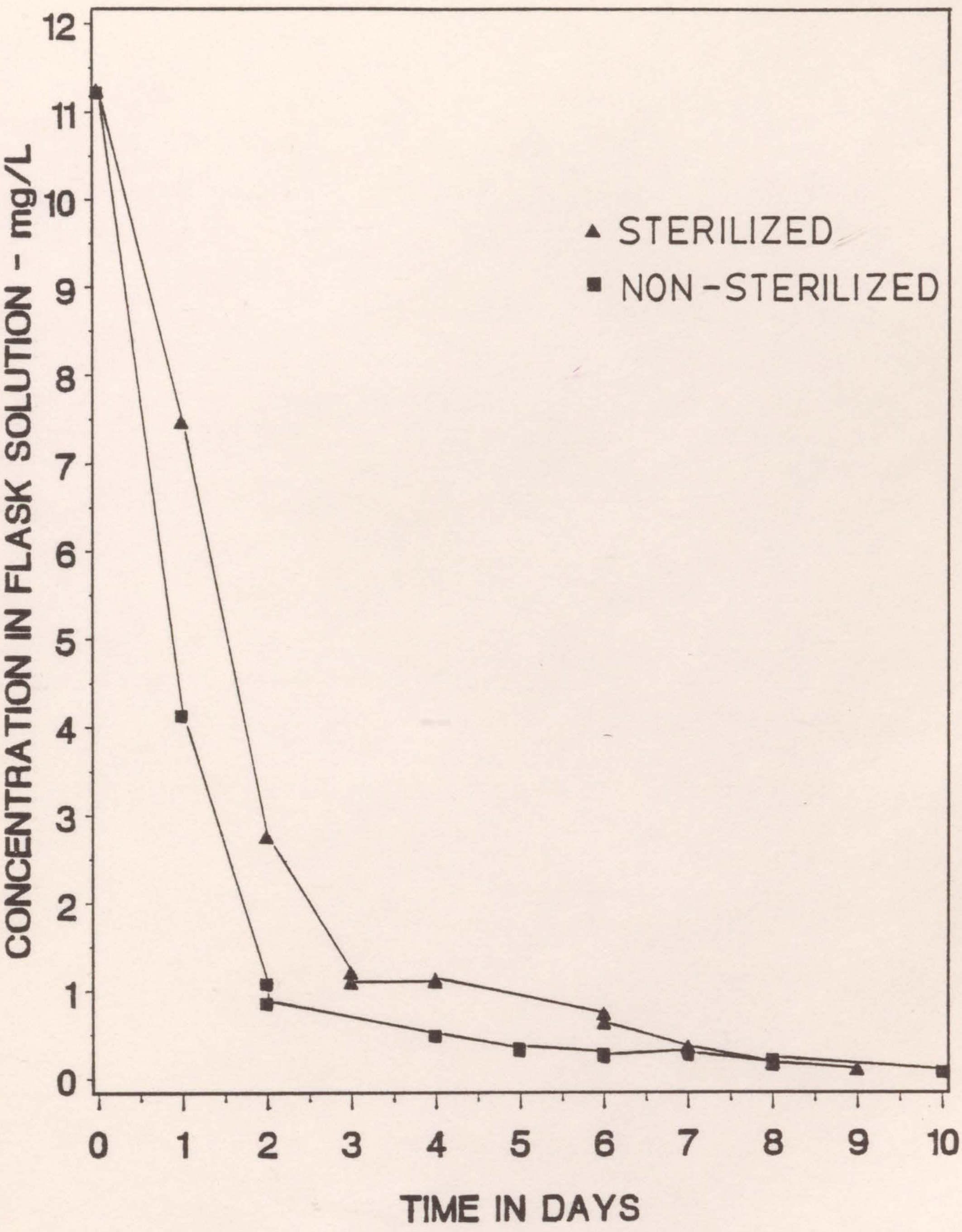


Figure 6-33 PERFUSION OF AQUEOUS PCE AT 11.25 mg/L THROUGH ORGANIC TOP SOIL--WITHOUT AIRFLOW

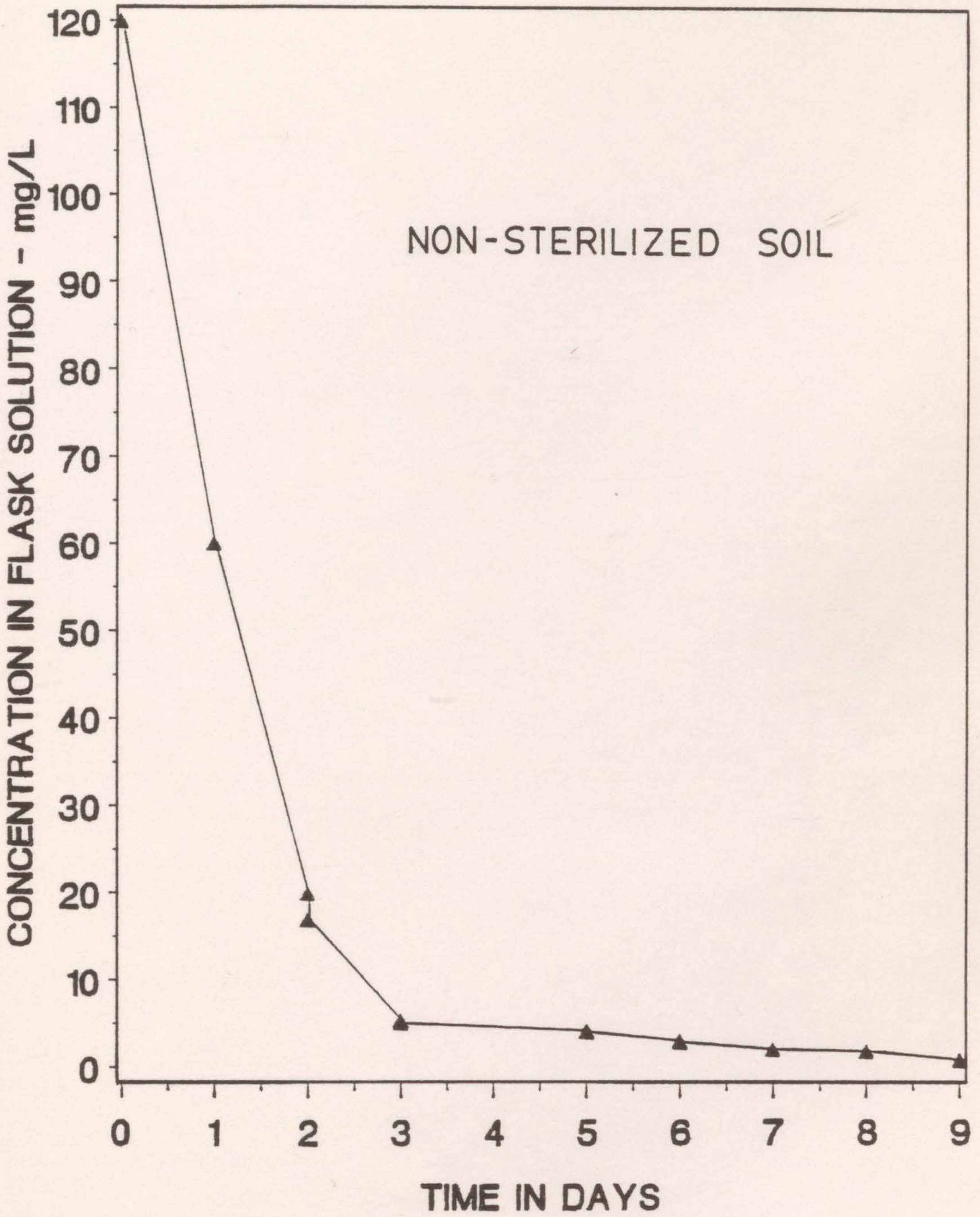


Figure 6-34 PERFUSION OF AQUEOUS PCE AT 120.00 mg/L THROUGH ORGANIC TOP SOIL--WITHOUT AIRFLOW

6.3.3 Prediction of Adsorption With the Perfusion Apparatus

As theoretically derived in Section 4.4, the ratio of pumping rate, Q, to volume of perfusate, V_ℓ, should approach the adsorption rate. The values for Q and V_ℓ were set at 1130 mL/d and 570 mL respectively for all the runs. The ratio of Q to V_ℓ, Q/V_ℓ, equalled 1.98 1/d.

The calculated adsorption rates listed in Tables 6-16 and 6-17 were first converted from $\log_{10}$ to $\log_e$ and then the following average rates of adsorption were determined for each type of soil.

$$K'_{AVESL} = 0.76 \text{ 1/d} \quad \text{with } s = \pm 4.3\%$$

$$K'_{AVEORG} = 0.55 \text{ 1/d} \quad \text{with } s = \pm 7.5\%$$

where

K'_{AVESL} = adsorption rate constant for sandy loam soil,
K'_{AVEORG} = adsorption rate constant for organic top soil,
s = standard deviation.

6.4 Column Studies

Sandy loam and organic top soil columns were analyzed for the movement of PCE and Cl^-. Chlorides were used as a tracer to determine the flow through time of water in the respective soils.

6.4.1 PCE in Column Effluent

The column studies involving PCE had a duration of 104 days. The effluent was measured daily for the first 45 days and then every second day thereafter. Figures 6-35 to 6-38

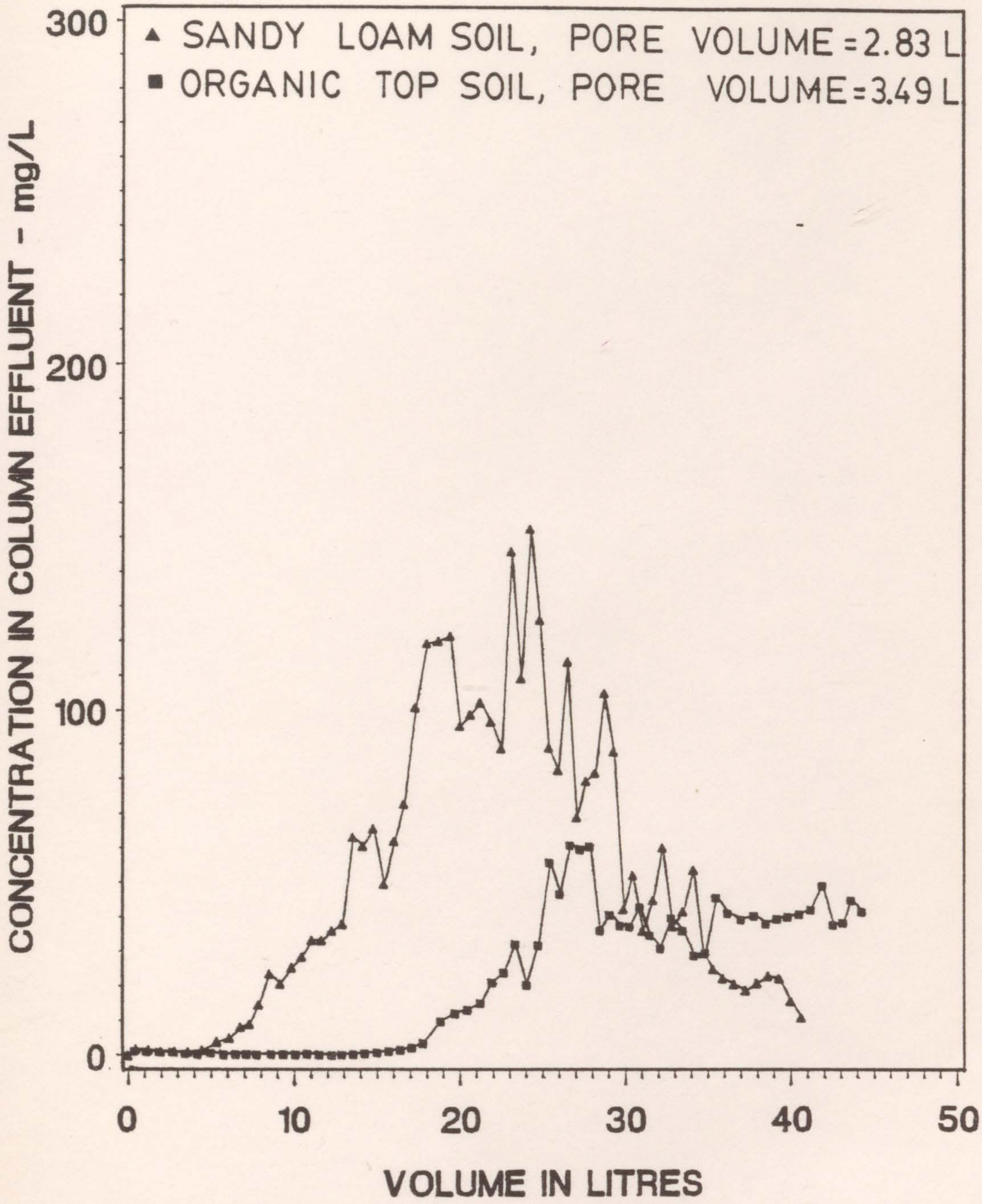


Figure 6-35 BREAKTHROUGH CURVE FOR PCE IN 0.8 m COLUMN

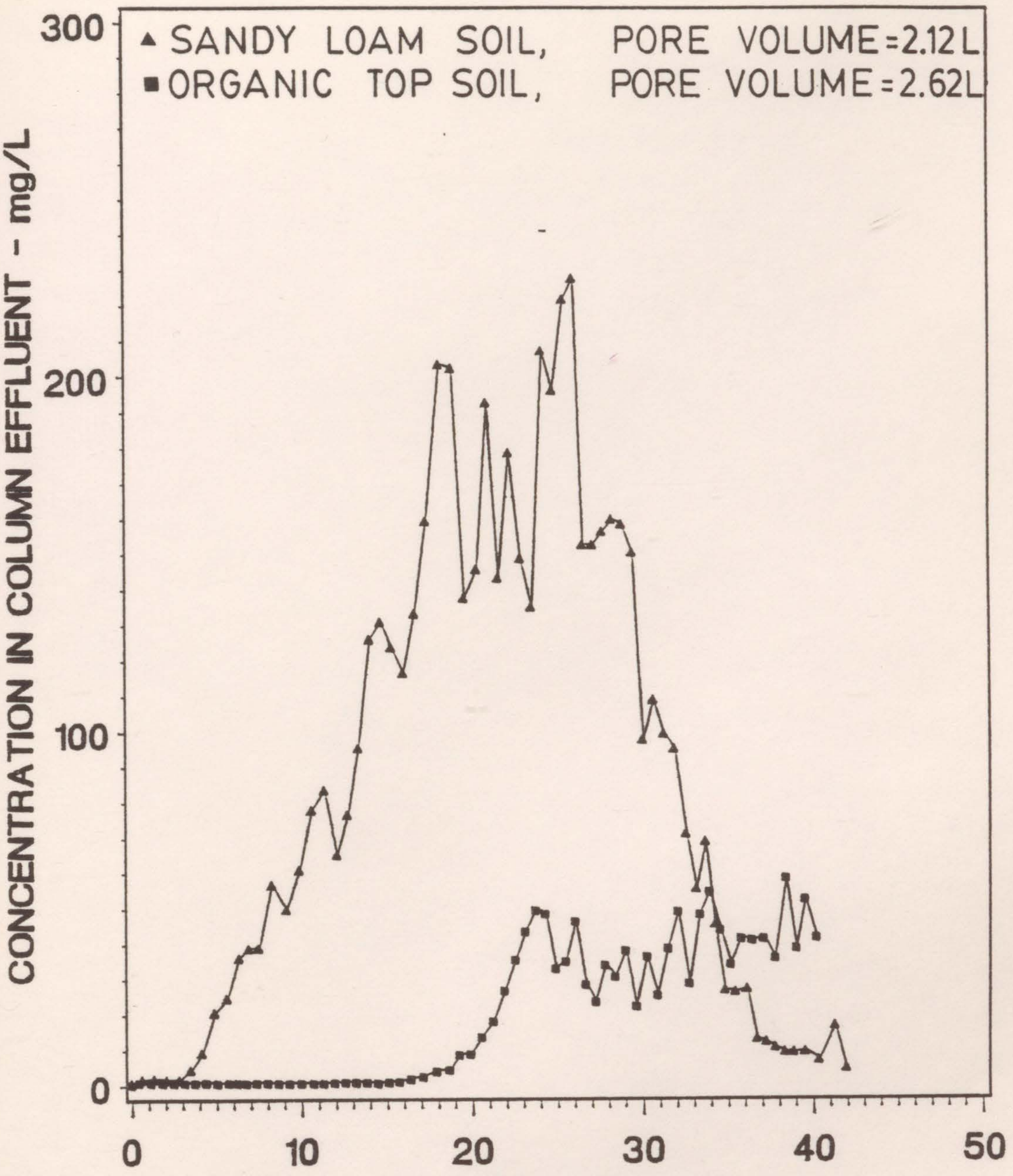


Figure 6-36 BREAKTHROUGH CURVE FOR PCE IN 0.6 m COLUMN

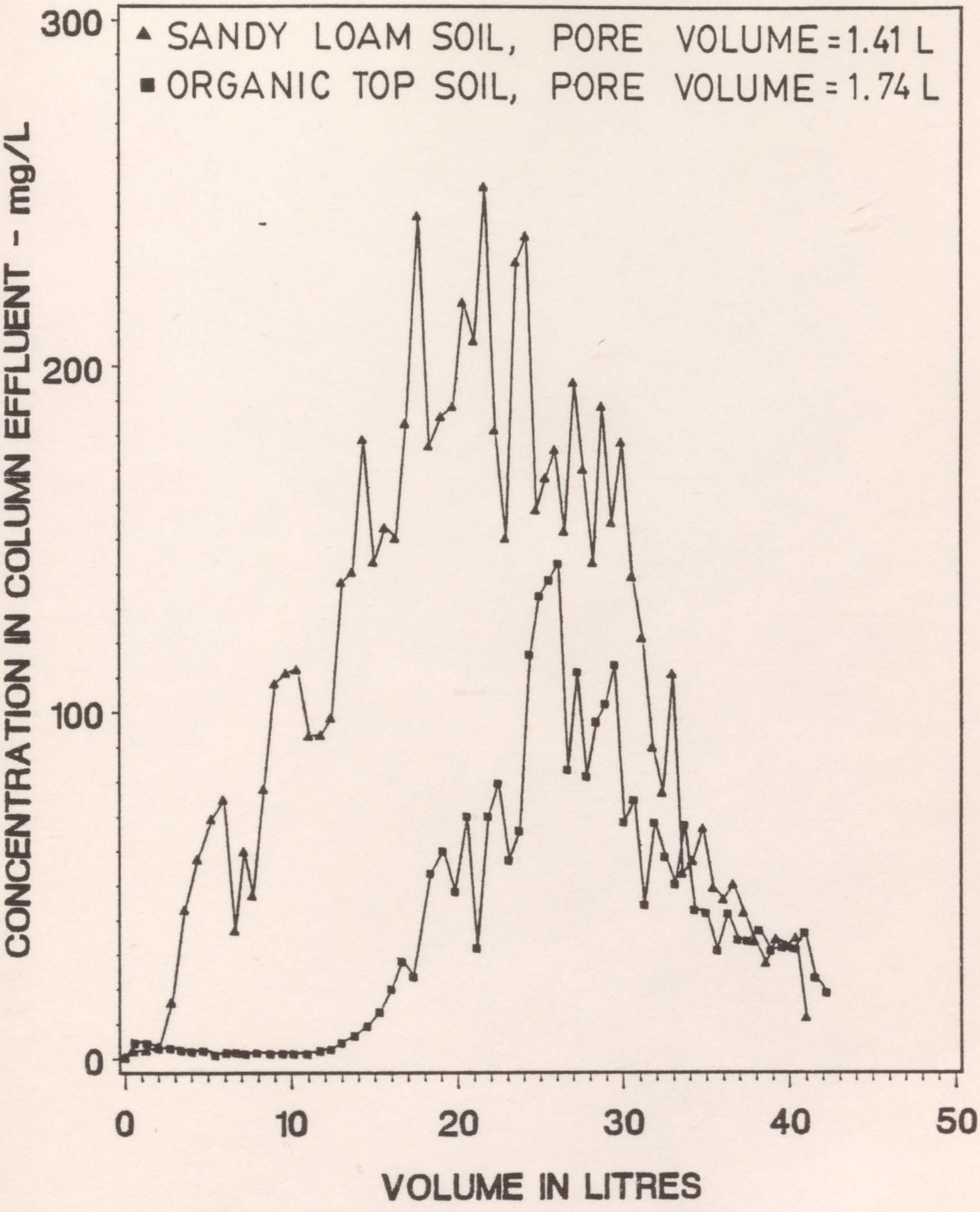


Figure 6-37 BREAKTHROUGH CURVE FOR PCE IN 0.4 m COLUMN

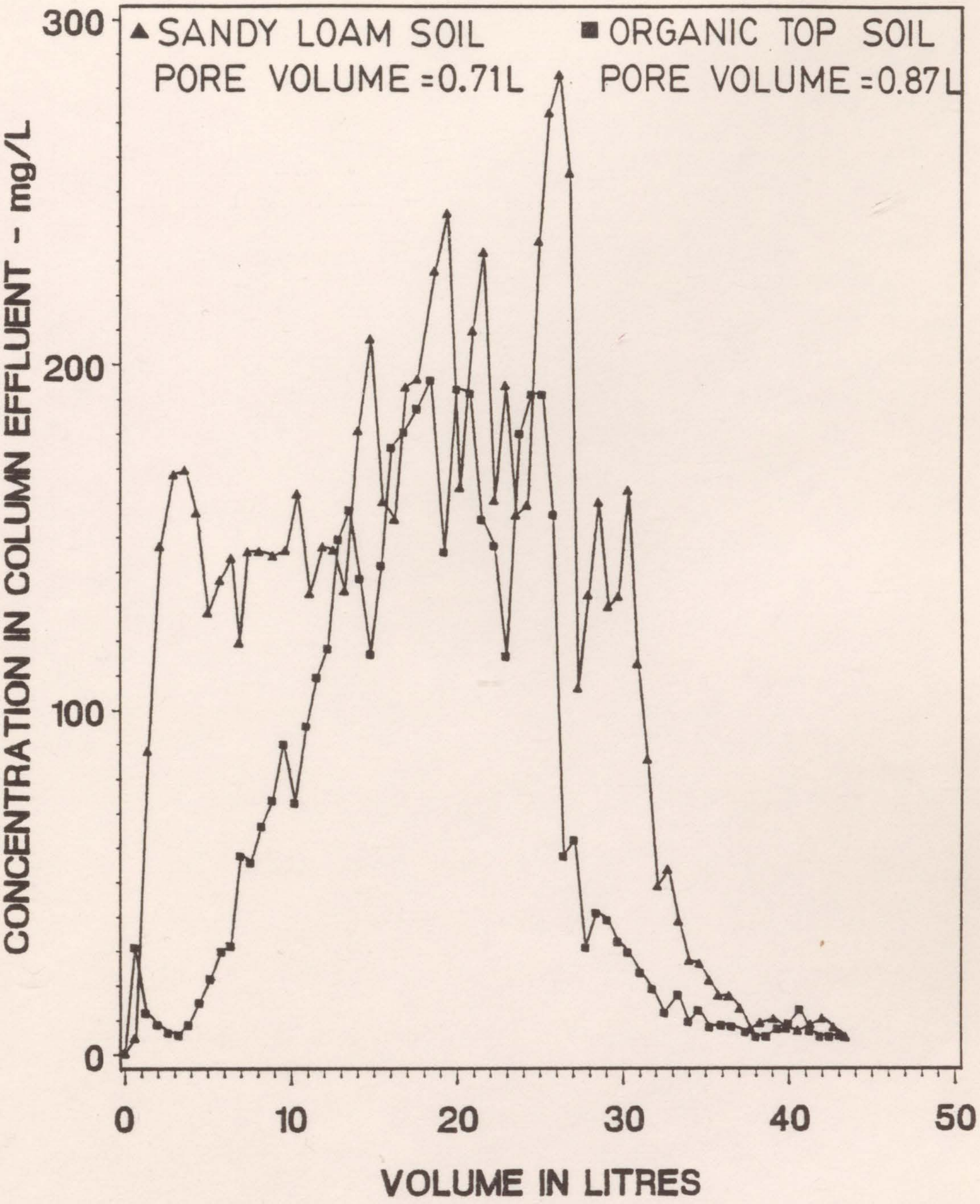


Figure 6-38 BREAKTHROUGH CURVE FOR PCE IN 0.2 m COLUMN

show the concentration variations for each soil profile with respect to throughput volume. Each figure presents the two different soils for easy comparison.

6.4.2 Chlorides in Column Effluent

The column studies using Cl^- had a duration of eight days. The effluent was measured three times daily. Figures 6-39 to 6-42 show the concentration variations for each soil profile, with each figure presenting both soil types.

6.4.3 Breakthrough Volumes

For comparison of experimental data with the theory presented in Section 4.4, the breakthrough curves in Figs. 6-35 to 6-42 were analyzed to determine the throughput volumes for initial breakthrough and exhaustion. However, it should be noted that the maximum concentration value used for C_o was 150 mg/L. Any concentration above 150 mg/L was considered to be influenced by the presence of pure PCE that had migrated through the entire soil column. The corresponding breakthrough volumes, V_t, have been tabulated in Table 6-18 for PCE and in Table 6-19 for chlorides. The average throughput volume per unit soil length, V_t/L and their respective correlation coefficients, are also shown in these tables.

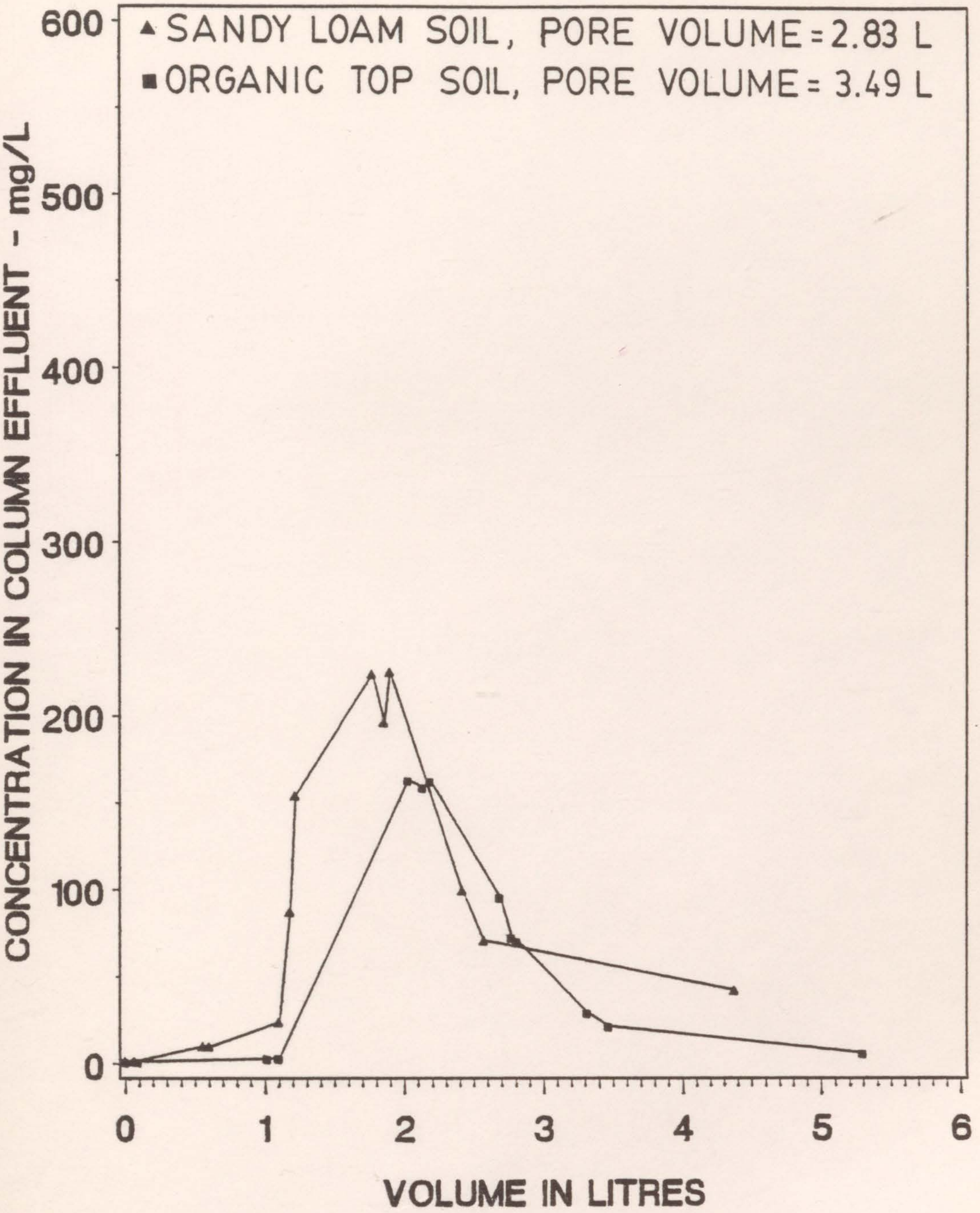


Figure 6-39 BREAKTHROUGH CURVE FOR CHLORIDES IN 0.8 m COLUMN

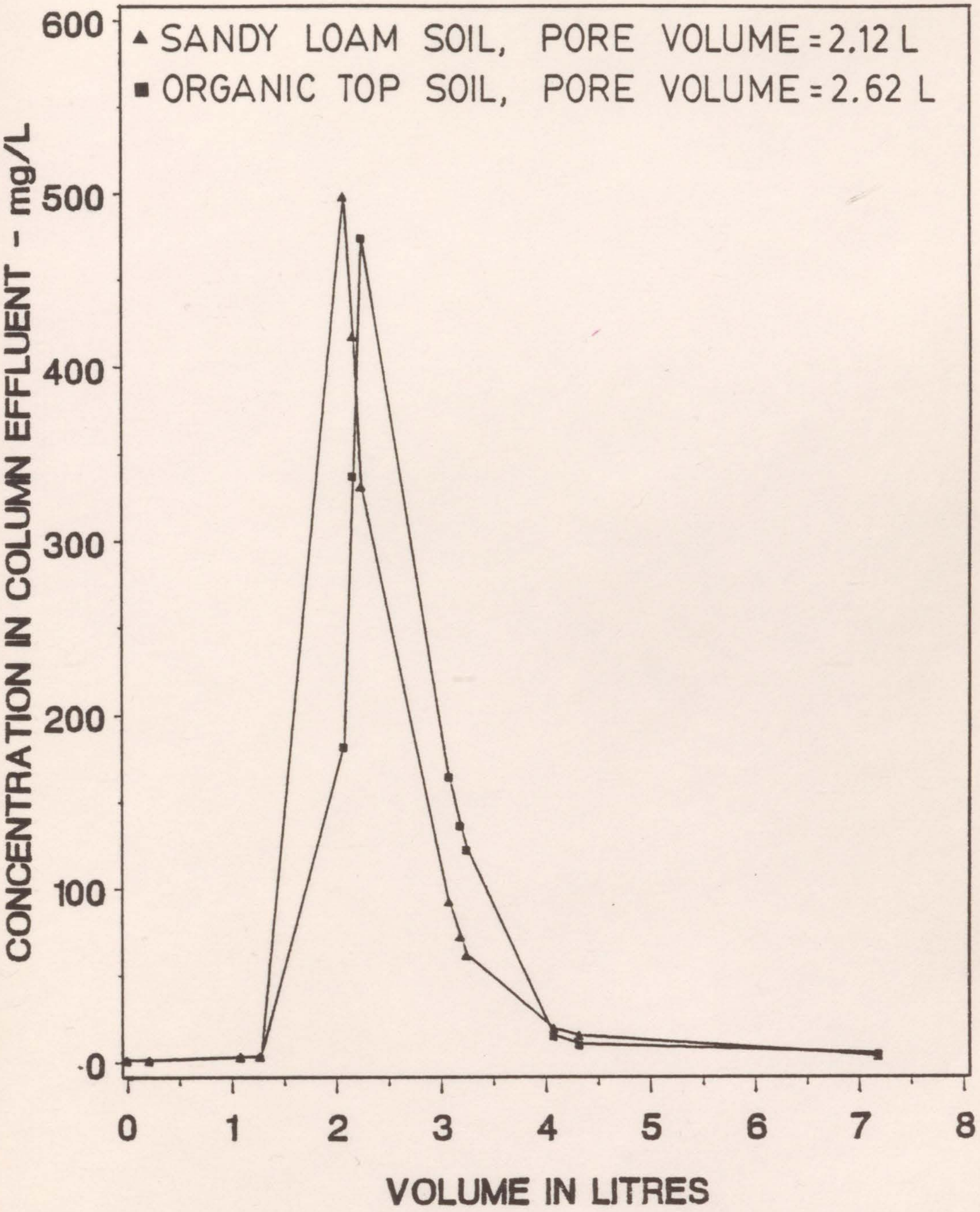


Figure 6-40 BREAKTHROUGH CURVE FOR CHLORIDES IN 0.6 m COLUMN

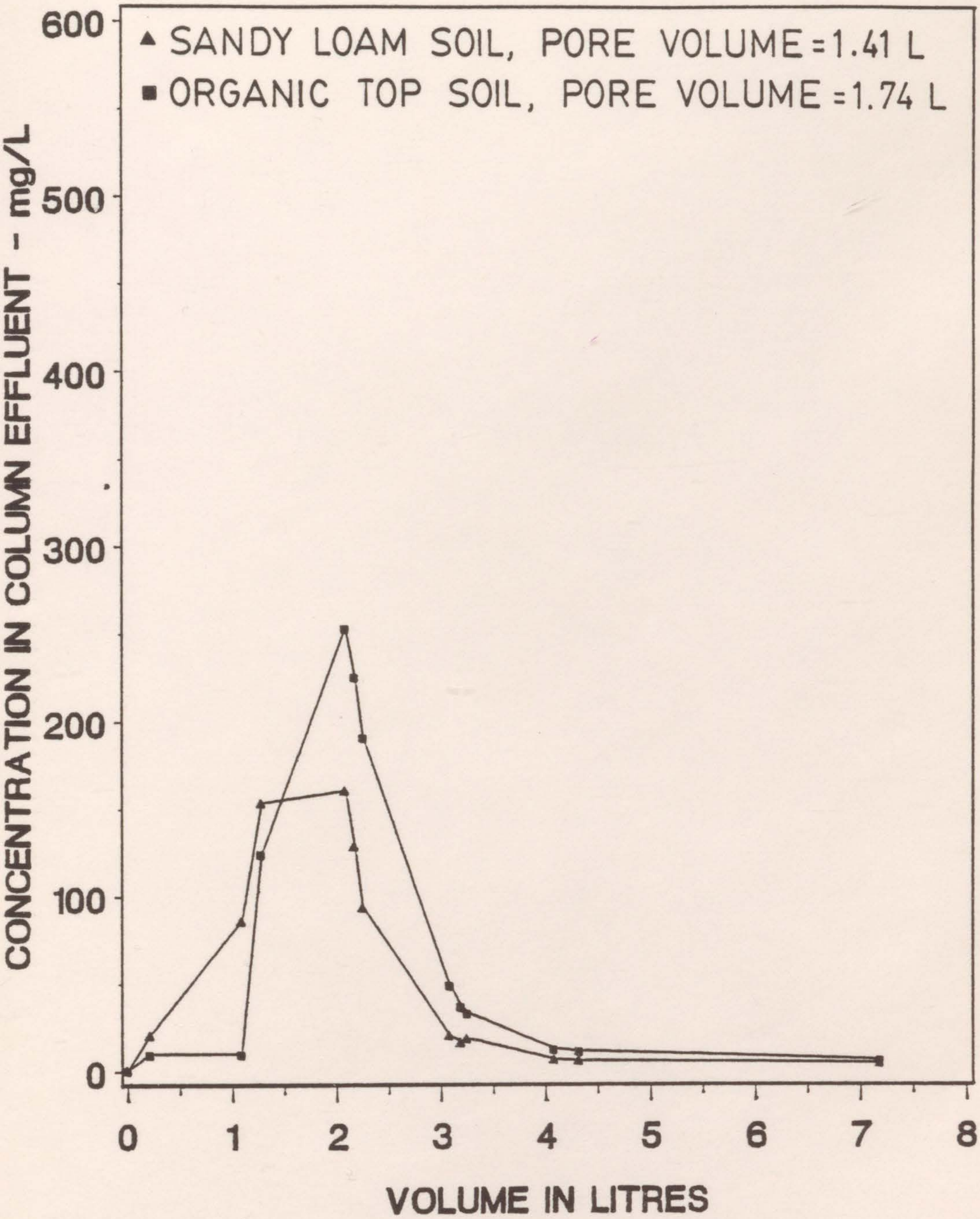


Figure 6-41 BREAKTHROUGH CURVE FOR CHLORIDES IN 0.4 m COLUMN

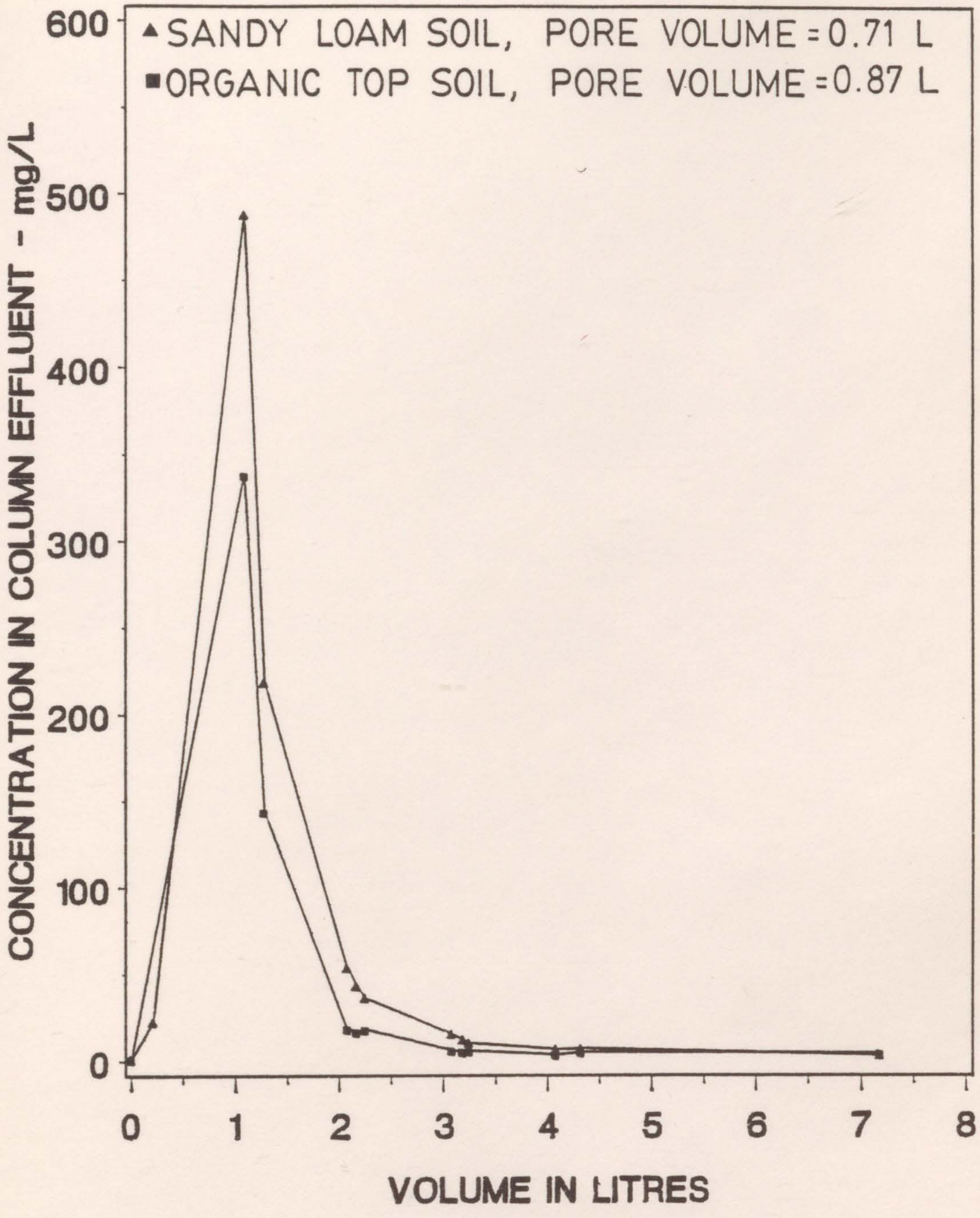


Figure 6-42 BREAKTHROUGH CURVE FOR CHLORIDES IN 0.2 m COLUMN

Table 6-18 Breakthrough Volumes for PCE

SOIL PROFILE	SANDY LOAM SOIL		ORGANIC TOP SOIL	
	V_t for $0.05C_o$	V_t for $0.95C_o$	V_t for $0.05C_o$	V_t for $0.95C_o$
m	10^{-3} m^3	10^{-3} m^3	10^{-3} m^3	10^{-3} m^3
0.0	0	0	0	0
0.2	0.8	2.1	3.2	12.5
0.4	2.3	13.8	-	-
0.6	3.9	17.0	16.4	23.5
0.8	6.5	23.4	17.8	26.7
V_t/L, m^3/m	0.0075	0.0287	0.0239	0.0357
r^2	0.9448	0.9682	0.9568	0.9728

Table 6-19 Breakthrough Volumes for Chlorides

SOIL PROFILE	SANDY LOAM SOIL		ORGANIC TOP SOIL	
	V_t for $0.05C_o$	V_t for $0.95C_o$	V_t for $0.05C_o$	V_t for $0.95C_o$
m	10^{-3} m^3	10^{-3} m^3	10^{-3} m^3	10^{-3} m^3
0.0	0	0	0	0
0.2	0.10	0.54	0.11	0.60
0.4	0.30	0.63	0.59	1.08
0.6	0.70	1.18	0.70	1.26
0.8	0.76	1.65	1.16	1.99
V_t/L, m^3/m	0.00099	0.00199	0.00136	0.00240
r^2	0.9622	0.9528	0.9667	0.9457

The reciprocal of V_t/L can be used to determine the penetration depth of the chemical front when multiplied by the volume of water added to the spill site, V_t. Furthermore, with velocity defined as length/time or $L/(V_t/Q)$, the various front velocities were determined by multiplying L/V_t by Q. However, it is important to note that the empirical equations given in Table 6-20 for both soils and solutes, were developed for an application rate of 650 mL/d.

Several other observations can also be made from Figs. 6-35 to 6-38. As mentioned earlier, concentrations above 150 mg/L in samples were influenced by the presence of pure PCE chemical. If one assumes that the occurrence of concentrations in excess of 150 mg/L result from the penetration of pure PCE, equations can be developed which would roughly predict this movement. However, it must be emphasized that pure PCE may have penetrated and broken through the soil columns earlier. The PCE was then dissolved in the water present, keeping the concentration below 150 mg/L. The equations for pure PCE penetration are given in Table 6-20.

6.4.4 PCE Concentrations Adsorbed on Soil

After the columns were taken out of operation, they were disassembled and soil samples taken at various core depths. These soil samples were analyzed for the PCE concentrations still adsorbed on the soil and the results are shown in Figs. 6-43 and 6-44.

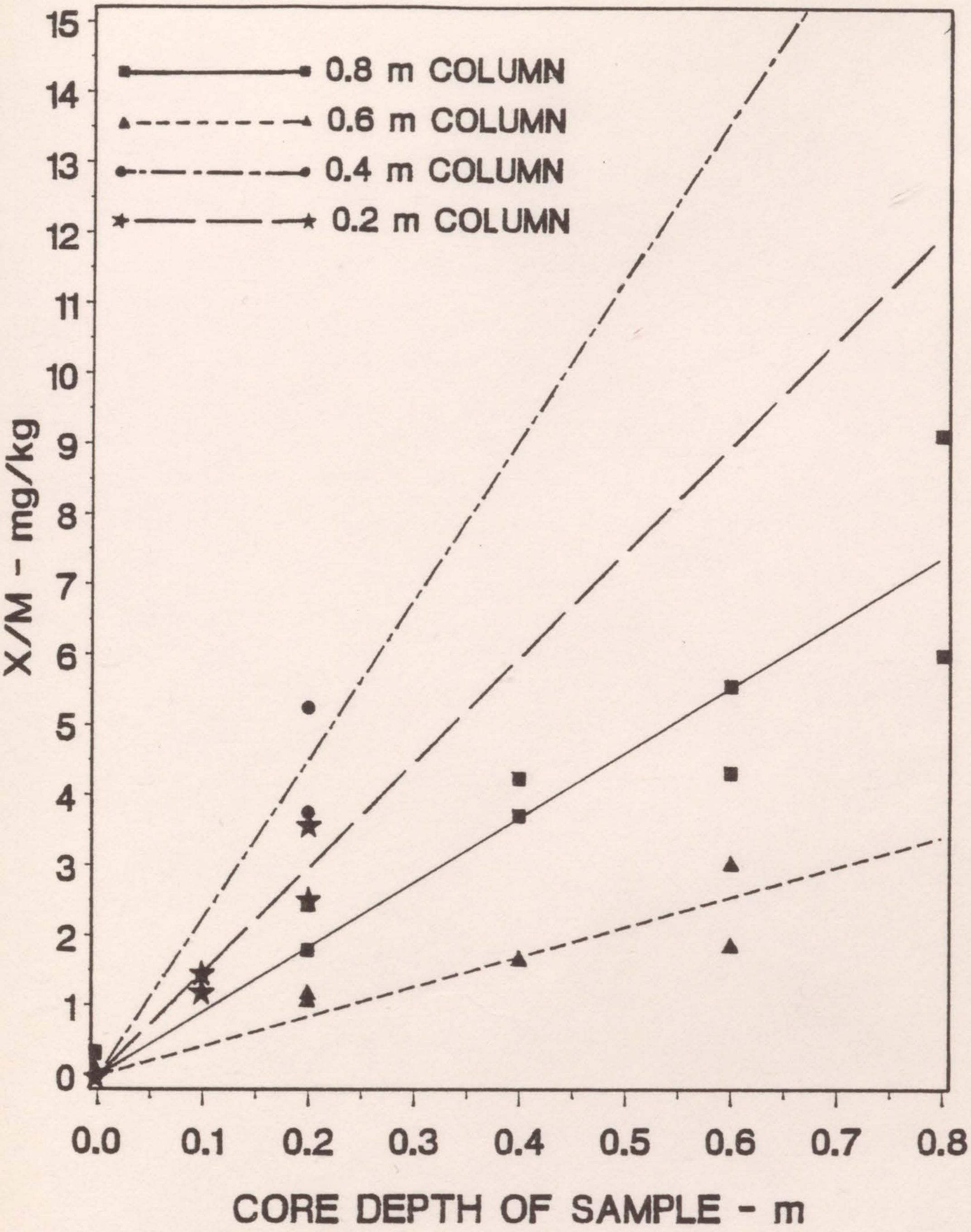


Figure 6-43 PCE CONCENTRATIONS ADSORBED ON SANDY LOAM SOIL COLUMN

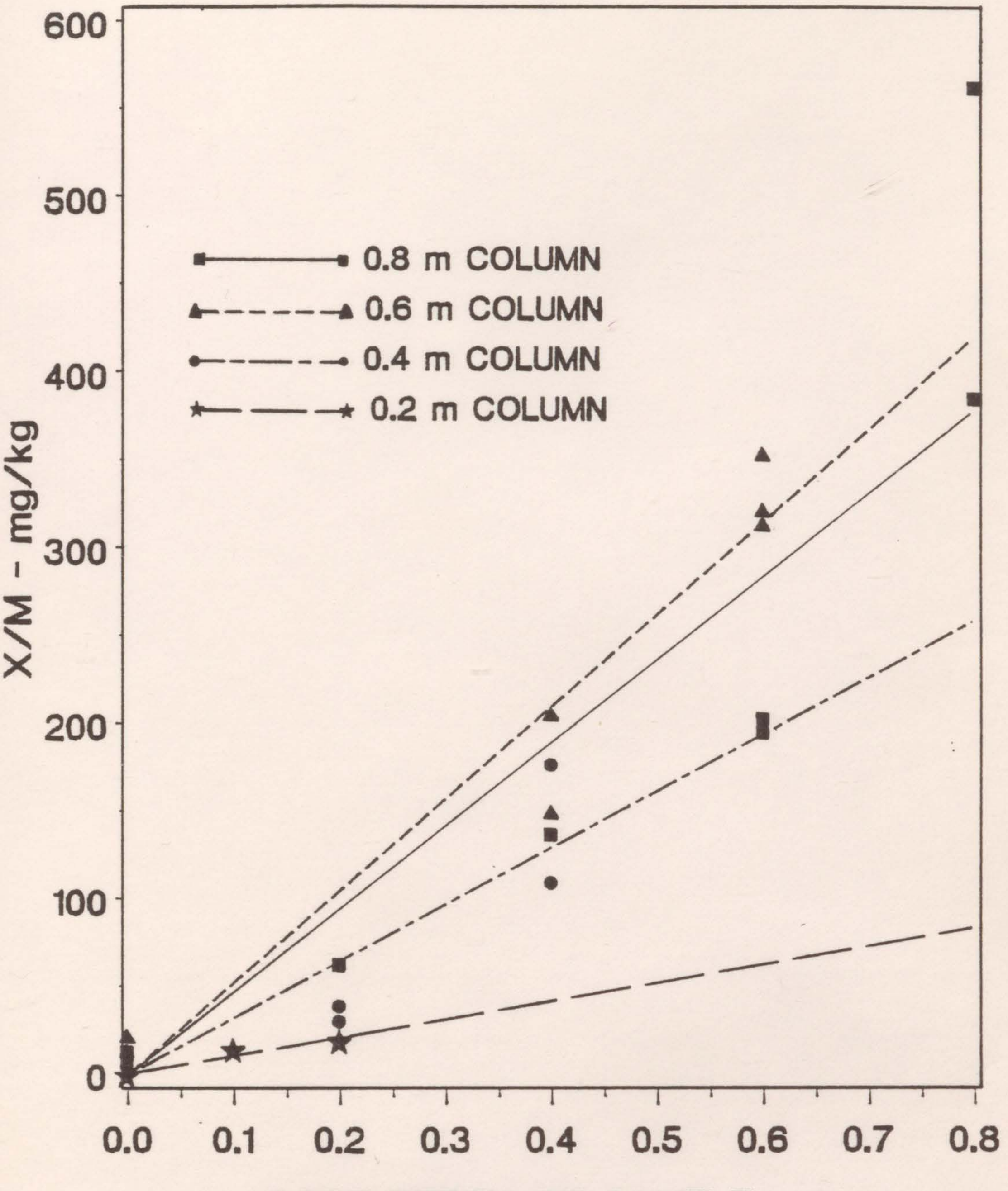


Figure 6-44 PCE CONCENTRATIONS ADSORBED ON ORGANIC TOP SOIL COLUMN

Table 6-20 Breakthrough and Exhaustion Equations as a Function of Time and Volume for Columns at Field Capacity

BREAKTHROUGH of DISSOLVED PCE and CHLORIDES

$$BT_{SLP} = 133.3V_t = 0.084t$$

$$BT_{ORGP} = 41.84V_t = 0.026t$$

$$BT_{SLCl} = 1010V_t = 0.636t$$

$$BT_{ORGCl} = 735.3V_t = 0.463t$$

EXHAUSTION of DISSOLVED PCE and CHLORIDES

$$EX_{SLP} = 34.84V_t = 0.022t$$

$$EX_{ORGP} = 28.01V_t = 0.018t$$

$$EX_{SLCl} = 502.5V_t = 0.317t$$

$$EX_{ORGCl} = 416.7V_t = 0.263t$$

BREAKTHROUGH of PURE PCE

$$PBT_{SL} = 0.018t$$

$$PBT_{ORG} = 0.009t$$

BT_i = depth at which concentration equals $0.05C_o$, m
EX_i = depth at which concentration equals $0.95C_o$, m
SLP = subscript for dissolved PCE in sandy loam soil
ORGP = subscript for dissolved PCE in organic top soil
SLCl = subscript for Cl^- in sandy loam soil
ORGCl = subscript for Cl^- in organic top soil
PBT_{SL} = migration of pure PCE in sandy loam soil, m
PBT_{ORG} = migration of pure PCE in organic top soil, m
V_t = volume of moisture added to spill, m^3
t = time, days

6.5 Mathematical Models

Two models were presented in Chapter Four, one for unsaturated moisture movement and the other for contaminant transport in unsaturated soil. The unsaturated moisture movement model has been solved for a sandy loam soil since the data were available. The contaminant model was calibrated for both the soils used in the column experiments.

6.5.1 Unsaturated Moisture Model

The moisture movement in sandy loam soil was simulated for a one time release of water to the soil with the water table at 4.0 m. The soil was initially at field capacity, $\theta=0.243\ m^3/m^3$, with one exception, the capillary fringe. In the capillary fringe the moisture content was corrected such that head and moisture tension equalled zero, as drainage is rapid in the capillary fringe. Simulation was started by saturating the first 0.80 m of soil with water, $\theta=0.335\ m^3/m^3$, and releasing it. The moisture content at the soil surface was held constant at field capacity for the first 1000 minutes. After this time the moisture content at the surface was reduced to the level at which plant wilting occurs, $\theta=0.100\ m^3/m^3$, to induce evaporation. The data used in the simulation were obtained from Remson _et_ _al_., [1965], where the values represent one time drainage of soil. Figures 6-45 and 6-46 contain the output from the simulation runs for two different time steps.

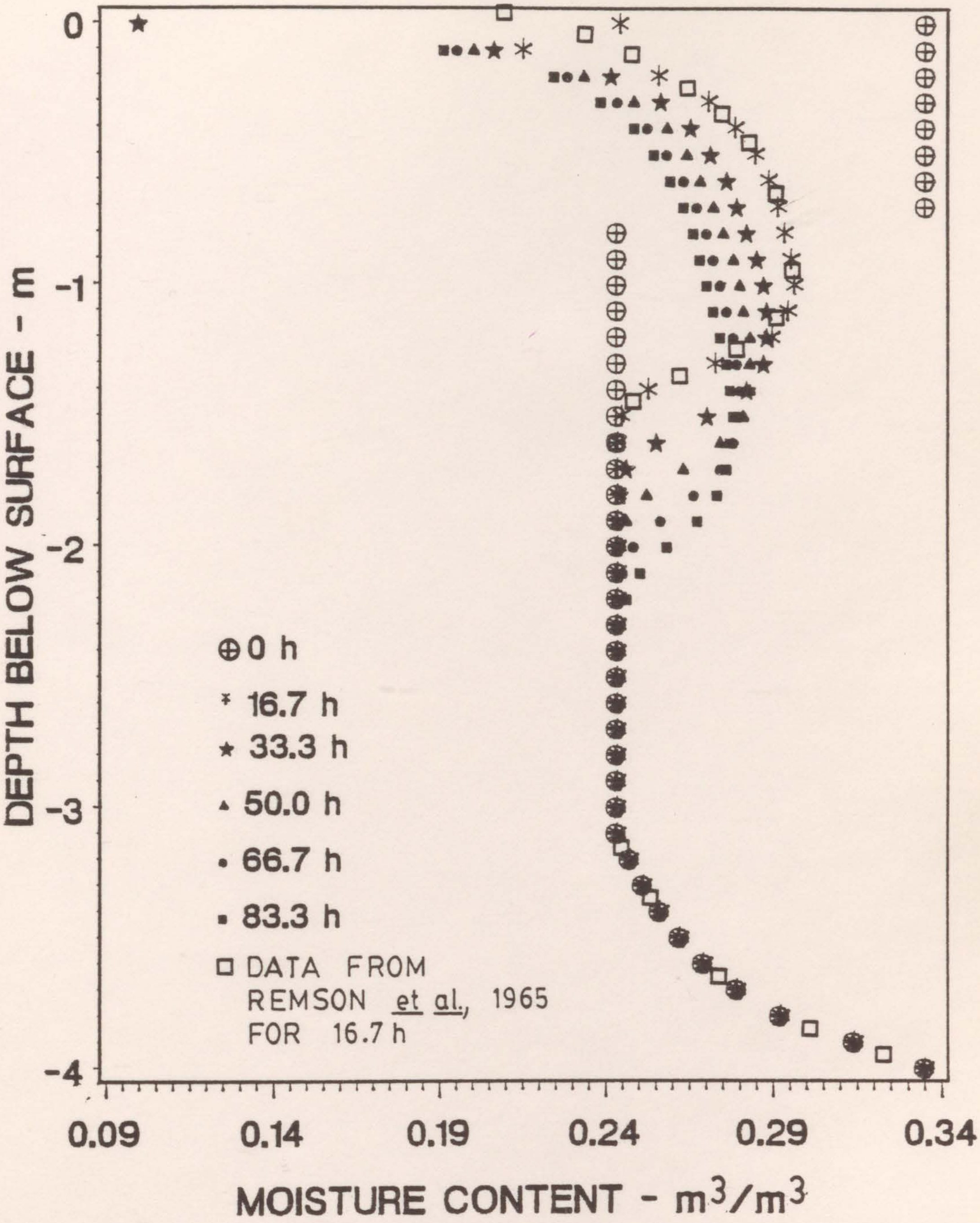


Figure 6-45 UNSATURATED MOISTURE PROFILE IN SANDY LOAM SOIL - DT=10 min

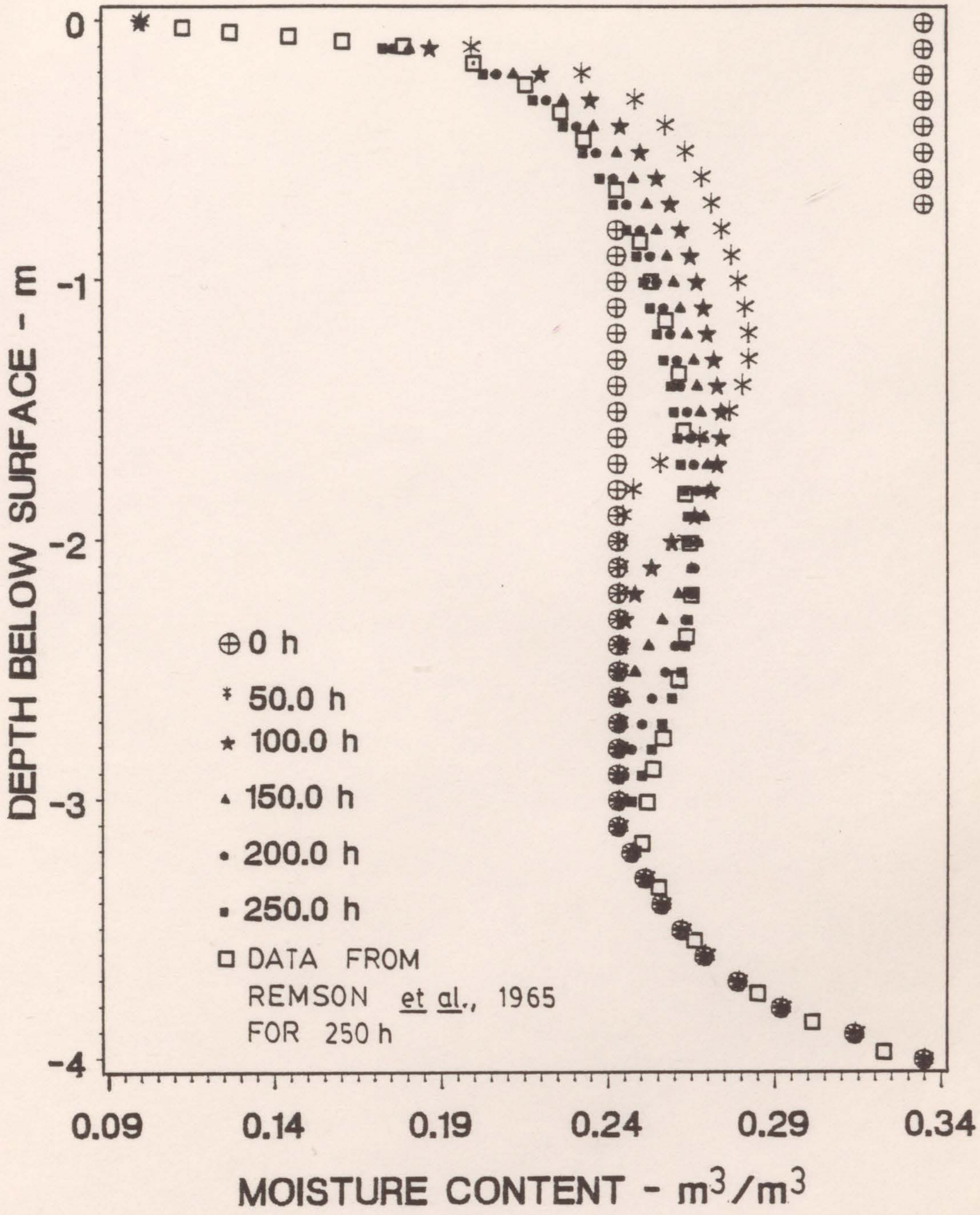


Figure 6-46 UNSATURATED MOISTURE PROFILE IN SANDY LOAM SOIL - DT=30 min

6.5.2 Contaminant Model Parameters

Accurate coefficients were required to properly calibrate the contaminant transport model. Table 6-21 lists the coefficients used for both soils.

6.5.2.1 Velocity of Fluids

When steady infiltration occurs in unsaturated soil, with no storage at the surface, $dH/dz=i=1$ [Baver, 1972]. Now from Darcy's Law, $Q=KAi$, under a steady infiltration rate $Q=KA$. Since capillary conductivity, K, equals bulk velocity, v, $v=Q/A$. However, actual seepage velocity, v_s, must account for pore structure, giving $v_s=v/n_p$. Furthermore, by assuming that the water content in the unsaturated soil is free water [Palmer, 1987], unsaturated interstitial seepage velocity is given by $v_{is}(\theta)=v_s/\theta$.

With the rainfall intensity applied to all columns being 76 mm/d, $v_{is}(\theta)$ for the sandy loam and organic top soil were calculated to be 0.677 and 0.446 m/d respectively. The actual measured $v_{is}(\theta)$ from the chloride tracer studies for the sandy loam soil and organic top soil were 0.636 and 0.463 m/d respectively. For the model simulation runs these measured velocities were used.

In order to determine vapour velocity, v_v, the relative velocity approach was used. The vapour velocity was set equal to the moisture velocity as the columns were being operated under steady state conditions. However, the sign of

Table 6-21 Parameters Used in the Model Simulations

PARAMETER	UNITS	SANDY LOAM SOIL	ORGANIC TOP SOIL
v_w	m/d	0.636	0.463
v_v	m/d	-0.636	-0.463
v_i	m/d	0.068	0.020
D_w	m^2/d	$6.49x10^{-5}$	$6.49x10^{-5}$
D_{mech}	m^2/d	$1.44x10^{-4}$	$1.44x10^{-4}$
D_a	m^2/d	$2.16x10^{-4}$	$2.16x10^{-4}$
D_{air}	m^2/d	$1.77x10^{-2}$	$1.77x10^{-2}$
D_v	m^2/d	$3.70x10^{-4}$	$4.28x10^{-4}$
Di	m^2/d	$1.44x10^{-4}$	$1.44x10^{-4}$
moisture content	m^3/m^3	0.262	0.327
vapour content	m^3/m^3	0.162	0.195
immiscible fraction		10%	10%
K_p	m^3/kg	$5.19x10^{-3}$	$14.46x10^{-3}$
K_H		0.543	0.482
K_i		11055	11055
density	kg/m^3	1500	1000
porosity		0.450	0.555
solubility	kg/m^3	0.150	0.150

the PCE vapour velocity was opposite in sign to the moisture velocity, as the vapour moved upwards toward the soil surface.

The immiscible fluid velocity, v_i, was observed to have a significant impact on the model predictions. As a result, the immiscible front velocity was used to calibrate the model breakthrough times. By using the empirical breakthrough equations in Table 6-20, the times could be calculated at which 7.5 mg/L (5 % of saturation) of PCE would appear at a depth z. Computer runs were then made to predict the model breakthrough times at 0.1 m intervals for different v_is. These model predicted times were then compared to the times predicted from the column breakthrough equations. The difference between the two times was squared and the sum for all the depths calculated. The correct velocity was then selected by choosing the v_i with the smallest sum of the squared value.

6.5.2.2 Dispersion Terms

Aqueous dispersion of PCE in soil is influenced both by molecular diffusion and mechanical dispersion [Palmer, 1987]. The molecular diffusion coefficient was calculated using Eq. 6-17 which is valid for any type of fluid [Reid and Sherwood, 1966].

$$D_{fluid} = \frac{13.2 \times 10^{-5}}{(\mu_{fluid})^{1.4}(MV)^{0.589}} \qquad (6\text{-}17)$$

where

D_{fluid} = diffusion into a fluid, cm^2/s,

μ_{fluid} = viscosity of fluid the chemical is diffusing into (solvent), cP,

MV = molar boiling volume of the chemical, cm^3/g.

The mechanical dispersion coefficient was determined by using the chloride tracer data. Since the chlorides are non-reacting, the only parameters required for the transport model were advection and dispersion. With advection or velocity measured in the laboratory, the value for the dispersion coefficient was determined by running computer simulations for various depths and calculating the correct value.

The immiscible dispersion parameter was set equal to the value for aqueous PCE, as the infiltrating water acted as the driving mechanism.

Vapour diffusion into the atmosphere was determined using Eq. 6-17, with the value for the air viscosity. After calculating D_{air}, it was corrected to account for pore structure using Eq. 6-18 [Jury et al., 1983].

$$DA = (n^{10/3}/n_p^{\,2})D_{air}, \qquad (6\text{-}18)$$

where

DA = diffusion corrected for porosity, m^2/s

n = volumetric air content, m^3/m^3

n_p = soil porosity.

6.5.2.3 Decay Rates

Since PCE has been reported to be completely non-biodegradable for the conditions studied [Darcel, 1984, Wilson and McNabb, 1983 and Palmer 1987], the decay rates for all phases were assumed to be zero.

6.5.2.4 Partition Coefficients

The linear partition coefficients for the two soils were taken from the isotherm results.

Henry's Law Constant was used to determine the volatilization partition coefficient. However, these coefficients were adjusted to account for the humic matter present in the soil [Namkung and Rittmann, 1987].

The partition coefficient between the pure chemical and water was calculated using the following relation [Briggs, 1981]:

$$\log K = 1 - \log WS \tag{6-19}$$

where

K = partition of chemical between itself and water,

WS = molar water solubility, moles/L.

6.5.2.5 Volumetric Parameters

Volumetric parameters include moisture content, air content and immiscible content. The moisture content was measured. The immiscible content was estimated as a percentage of the moisture content and the computer program would then calculate it. This estimate was written as an input variable. The vapour content was then calculated so that all the volumetric contents equalled the porous volume of the medium, 6-21.

6.5.2.6 Physical Constants

Constants such as density and porosity were measured using standard soil measurement techniques and have been placed in Table 6-21.

6.5.2.7 Initial Conditions

The spill situation simulated involves the spilling of pure PCE on the soil surface, with the entire soil profile having field capacity moisture content. This moisture content was not varied during the simulation run. Immediately after the PCE was spilled the precipitation began which caused a dissolved chemical front and an immiscible chemical front to percolate down the soil profile. Based on the column breakthrough theory presented in Section 4.5, the computer model was calibrated to calculate the time required for a chemical concentration that is 5% of the chemical's solubility limit, to appear at a depth z below the soil surface.

6.5.3 Model Predictions

Table 6-22 lists the empirical breakthrough equation and contaminant transport model breakthrough times for both soils, using the coefficients given in Table 6-21. Figures 6-47 and 6-48 present the comparison between the measured breakthrough concentrations and those predicted by the contaminant transport model. Figs. 6-49 and 6-50 show the measured and model predicted effluent concentrations for times exceeding the breakthrough time.

6.5.4 Sensitivity Tests for Contaminant Model Coefficients

When using a numerical model, accuracy of the results must be ensured. Accuracy of the model was determined by running sensitivity tests on the coefficients used in the simulations to determine which coefficient had the greatest impact on the simulation values. Table 6-23 shows the sensitivity test results for the contaminant transport model developed.

Table 6-22 Breakthrough Times at Various Depths

DEPTH	BREAKTHROUGH TIME			
	Sandy Loam Soil		Organic Top Soil	
m	EB day	CTM day	EB day	CTM day
0.4	4.78	4.33	15.18	13.59
0.5	5.83	5.71	18.97	18.00
0.6	7.18	7.10	22.77	22.47
0.7	8.38	8.50	26.56	27.00
0.8	9.57	9.92	30.36	31.56

EB = breakthrough times calculated from empirical breakthrough equations

CTM = breakthrough times predicted from contaminant transport model

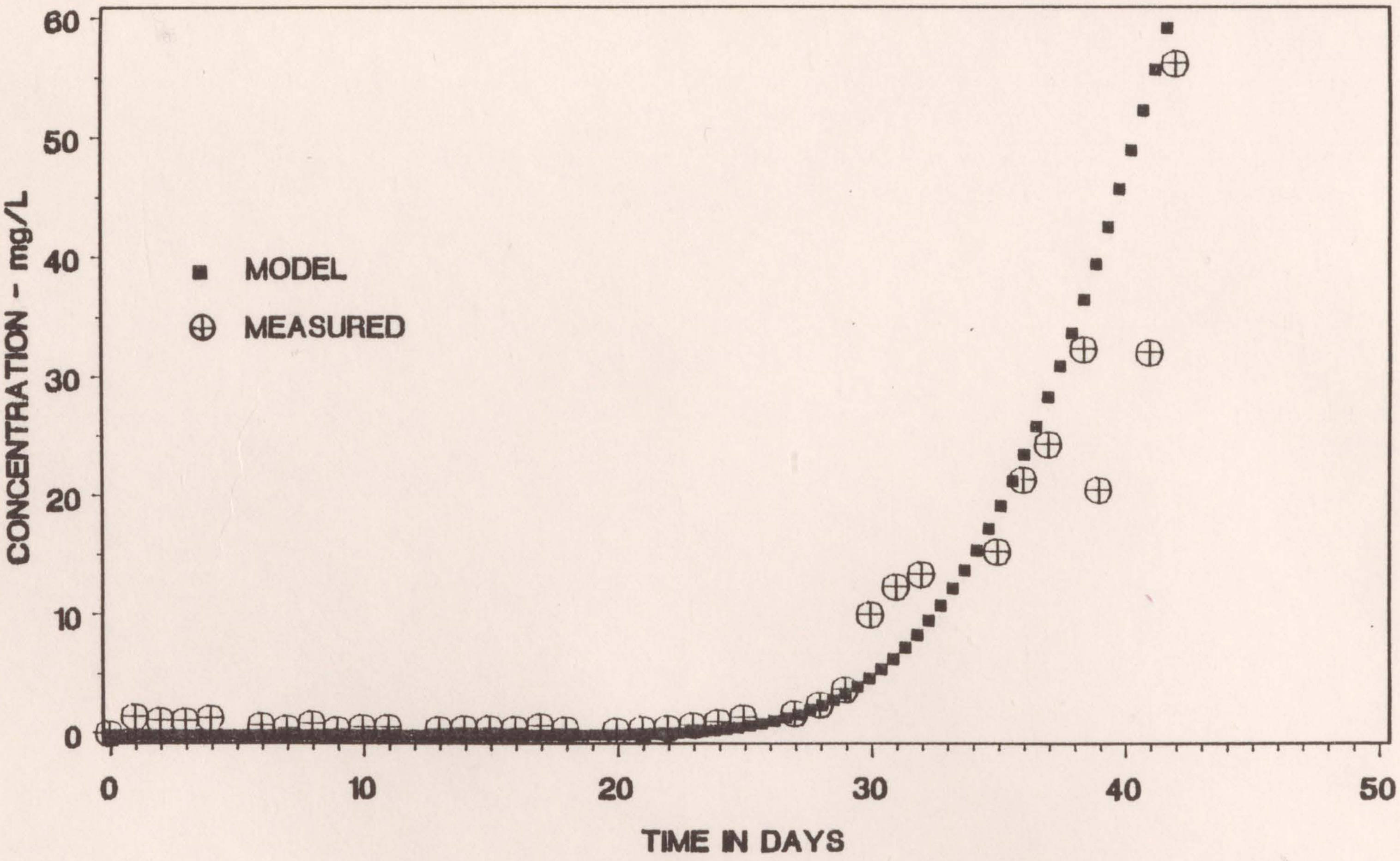


Figure 6-47 BREAKTHROUGH CONCENTRATIONS IN ORGANIC SOIL FOR 0.8 m LONG COLUMN

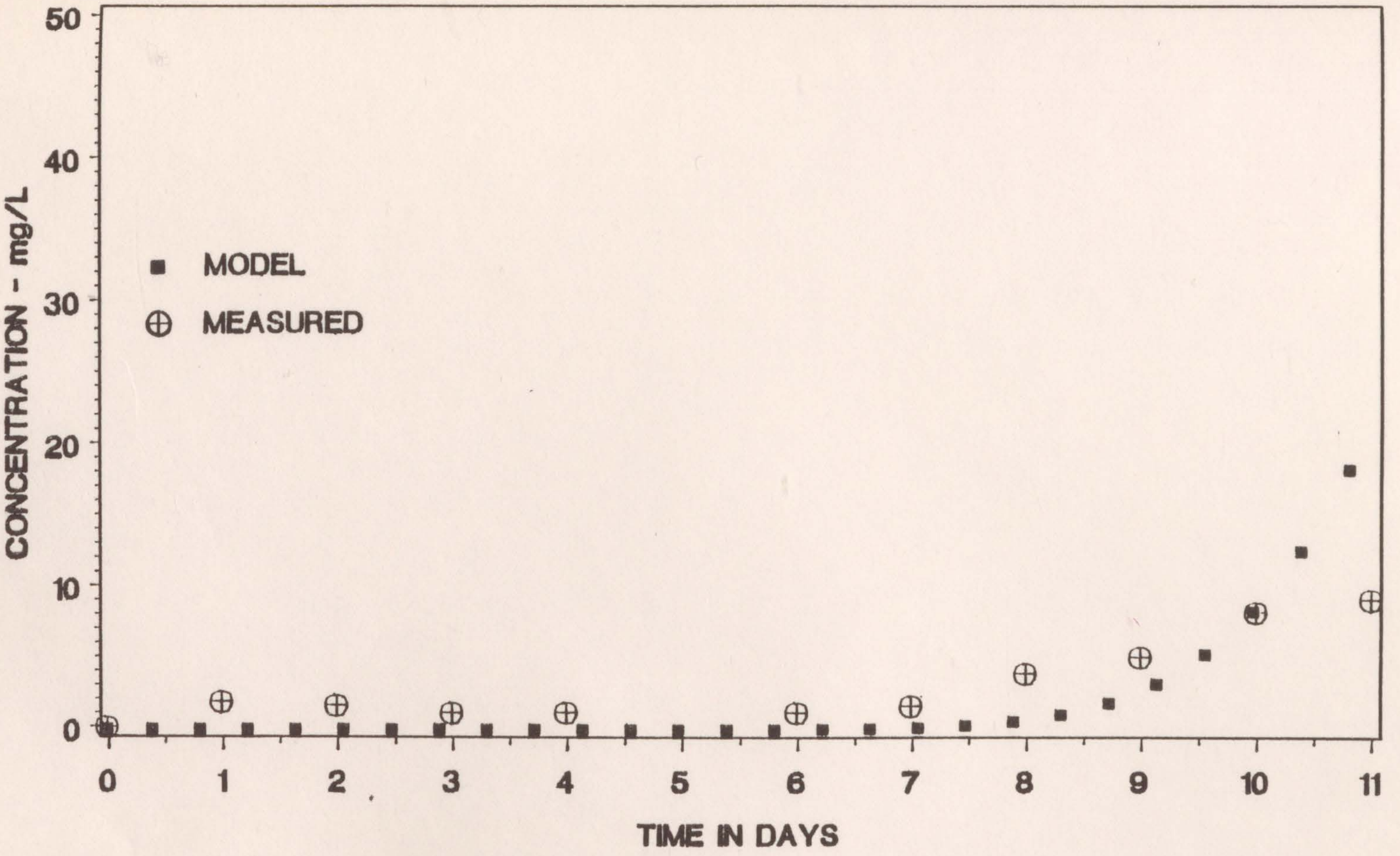


Figure 6-48 BREAKTHROUGH CONCENTRATIONS IN SANDY LOAM SOIL FOR 0.80 m LONG COLUMN

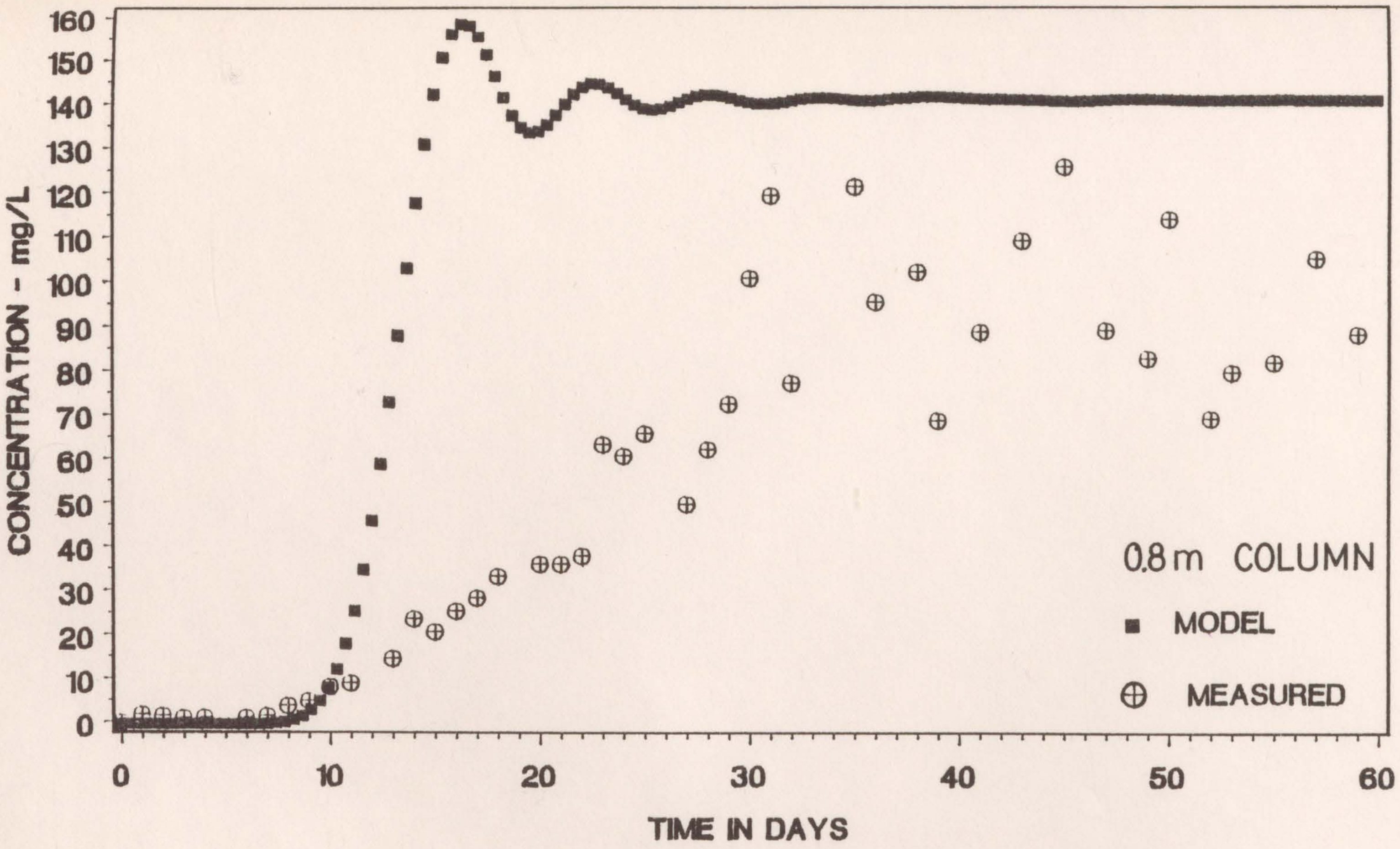


Figure 6-49 BREAKTHROUGH CONCENTRATIONS IN SANDY LOAM SOIL

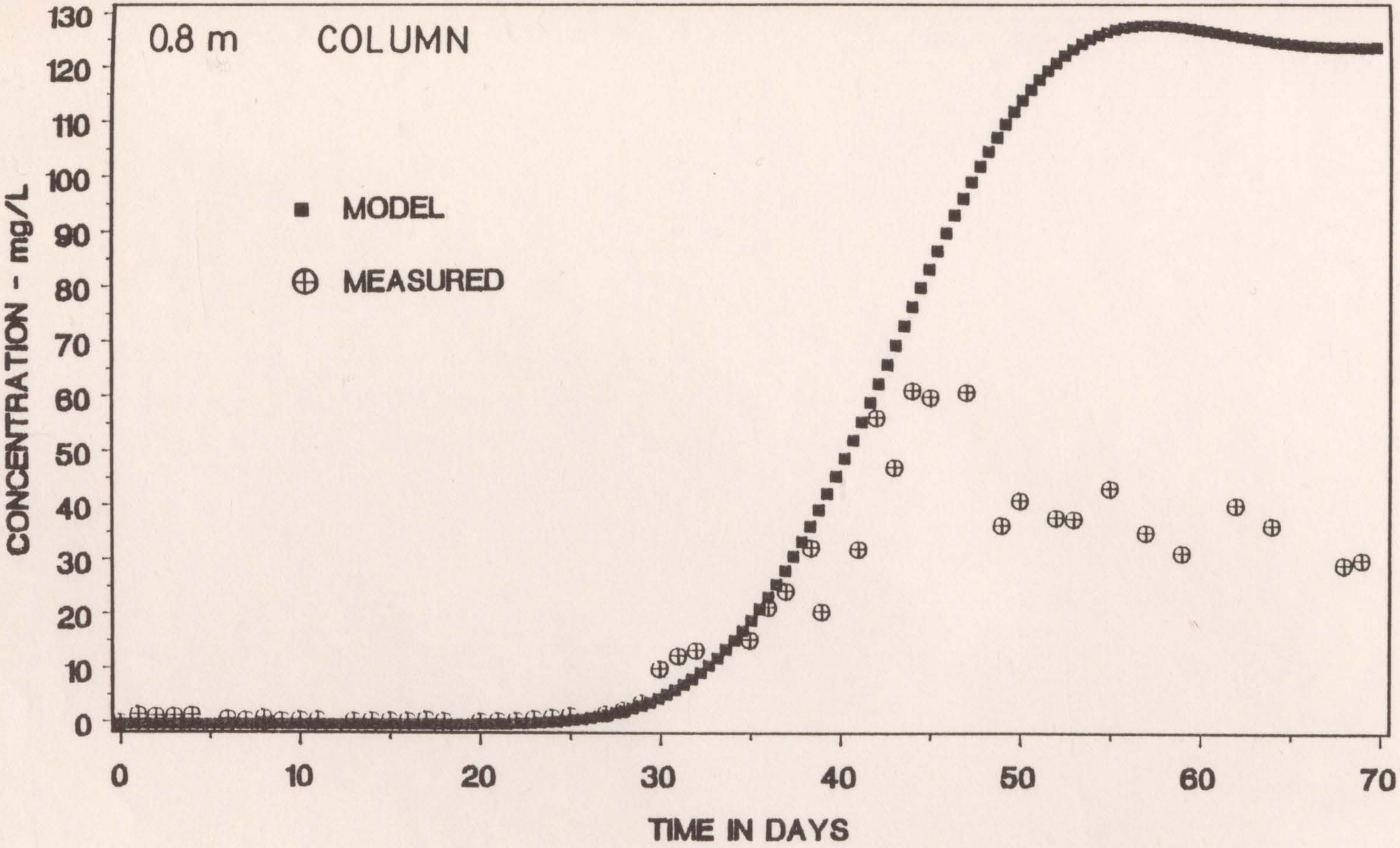


Figure 6-50 BREAKTHROUGH CONCENTRATIONS IN ORGANIC SOIL

Table 6-23 Sensitivity Results for Contaminant Model for Sandy Loam Soil - 0.6 m Column, Breakthrough at 7.10 days

COEFFICIENT	T	P	T	P	T	P
D_a (2.16×10^{-4})	10^{-3}	7.10	10^{-2}	7.08	10^{-5}	7.10
D_i (1.44×10^{-4})	10^{-3}	5.85	10^{-5}	7.29	-	-
D_{air} (1.77×10^{-2})	10^{-1}	7.10	10^{-3}	7.10	-	-
V_w^* (0.634)	6.34	6.77	0.063	7.13	-	-
V_v^* (-0.634)	6.34	6.77	0.063	7.13	-	-
V_i (0.068)	0.066	7.25	0.069	6.96	0.130	3.79
	0.677	B.U.	0.014	CFNA	0.086	5.60
% Immiscible (10)	15	7.04	25	7.00	35	6.98
	5	7.25	-	-	-	-
K_p (5.19)x10^{-3}	15.19	7.46	25.19	7.81	250.2	CFNA
K_H (0.543)	0.443	7.10	0.343	7.08	0.243	7.08
	0.643	7.10	0.843	7.10		
K_i (11055)	9754	7.12	12755	7.08	-	-
DT (30)	5	7.06	15	7.07	90	7.19
	300	7.71	350	B.U.		

(####) - actual value for coefficient
T - value of coefficient used in model
P - predicted time of breakthrough, d
* - values were changed simultanteously
B.U. - model was unstable
CFNA - chemical concentration at depth z has not yet attained 5% of solubility limit

CHAPTER SEVEN

DISCUSSION

7.1 Adsorption and Desorption of PCE by Granular Media

The results presented in the previous Chapter on adsorption and desorption are discussed in the following sections.

7.1.1 Adsorption

Tables 6-1 and 6-2 clearly show that the adsorption of PCE in aqueous solutions on different media is well represented by the Freundlich Isotherm. The applicability of this isotherm is confirmed by the excellent correlation coefficient values, r^2, where the worst case has an r^2 of 0.9387. The use of the Freundlich Isotherm to explain adsorption of various chemicals on soil is well documented, [Walker, 1984, La Poe, 1982, Dzombak and Luthy, 1984, Roy and Griffin, 1985 and Karickhoff *et al*., 1979]. It successfully describes multilayer adsorption on surface sites which is the phenom- enon that occurs in soil. However, care must be taken to ensure that these isotherms are not extrapolated outside their experimental range, as they are valid only for this range.

In fitting the adsorption data to the Freundlich Isotherm, one obtains values for an isotherm slope, $1/n_f$, and an equilibrium constant indicative of adsorption, K_f. The greater the value of K_f, the greater is the adsorptive capacity of that medium. The slope indicates whether the medium in question can effectively be used as an adsorbent. A smaller value of $1/n_f$ combined with a larger K_f value represents a more efficient adsorption medium [Reynolds, 1984]. Table 6-1 confirms these facts, where GAC has the smallest $1/n_f$ value and the largest K_f value. When compared to values reported by Sakoda et al. [1987], a K_f of 130 to 390 $(mg/kg)(L/mg)^{1/n_f}$ with a $1/n_f$ of 0.77, the type of GAC used in these experiments is determined to be better suited for adsorption of PCE.

At the other end of the effectiveness of adsorption is sandy loam soil. While it has the second smallest $1/n_f$, it also has the lowest K_f, giving the least effective adsorption. A similar trend was observed by Friesel et al. [1984], and they have reported a K_f of 0.9 $(mg/kg)(l/mg)^{1/n_f}$ and a $1/n_f$ of 0.70 for a sandy subsoil. The other two media exhibit K_f and $1/n_f$ values consistent with those reported in the literature [La Poe, 1985 and Friesel et al., 1984].

Since PCE is moderately hydrophobic, it repels water and attaches itself onto a solid surface, in this case on to the surface of the media tested. The amount of PCE adsorbed varies with the nature of the medium as indicated by the different K_f values determined. It is observed that an increase in the K_f value is related to a corresponding increase in the values of surface area, CEC and organic carbon content (Tables 3-1 and 3-2). Of the three parameters, it is believed that the organic carbon content has the greatest impact on adsorption. Karickhoff et al. [1979] have shown that hydrophobic chemicals readily adsorb on organic carbon. CEC is the next most important parameter. However, Felsot and Dahm [1979] have observed that the correlation between adsorption and CEC is related more to the organic content of the CEC than to the CEC itself. Furthermore, in all the studies reporting CEC and adsorption, no attempt has been made to correlate between adsorption and CEC [Kaufman et al., 1981, Lee et al., 1979, Means et al., 1980 and Rogers et al., 1980]. Instead they have reported the importance of higher organic carbon contents associated with the higher CEC. The third parameter affecting adsorption is the specific surface area. It should be noted that very little work can be found on linking adsorption to particle size. Various researchers have shown that adsorption is mostly affected by the organic carbon content of the medium [Walker, 1984, Karickhoff et al., 1979 and Schwarzenbach and Westall, 1981].

7.1.2 Desorption

Figures 6-1 to 6-4 also indicate the desorption isotherms for each adsorbent. The desorption isotherms for organic top soil, peat moss and GAC are all below their respective adsorption isotherms. This indicates that each of these media has the ability to retain PCE on their surface due to the various binding mechanisms referred to in the literature review. However, it appears from Fig. 6-1 that, for the sandy loam soil the desorption isotherm is shifted above the adsorption isotherm. What this indicates is that the sandy loam soil has no ability to retain any PCE and will release it when a suitable solvent (water) is present. The reason for the slight shift in the isotherm is based solely on the fact that total equilibrium for desorption and adsorption must not have been reached. La Poe [1985] has shown that for the adsorption and desorption isotherms to coincide for a mineral soil like sandy loam soil, the true equilibrium times must be determined. He states further that the adsorption equilibrium time for mineral soils is long term, as the humic materials attached to the mineral fraction exhibit a slow rate of adsorption. Once this true equilibrium time is attained, the two isotherms will yield a single reversible isotherm.

Figures 6-1 to 6-4 also show the curve which depicts the mass of chemical retained after the desorption process. It can be seen that these new adsorption curves do not exactly follow the adsorption isotherm. This can be attributed to two main factors [La Poe, 1985 and Vaccari, 1988]. One of the factors is the complex problem of hysteresis which is always associated with soil-water systems. The other being the possible errors in the experimental procedure in conducting the desorption studies.

As stated earlier, all sorbents except sandy loam soil had the ability to retain PCE. This ability is related directly to the organic carbon present in the soil [Roy and Griffen, 1985] and the strength of the bonds developed between the sorbent and sorbate. GAC is a good example as it can develop strong bonds on the activated surface and also has a high organic carbon content.

When using the Freundlich Isotherm to explain desorption, K_f is replaced with K_{fd}, as seen in Table 6-2. It should be noted however, that the K_{fd} coefficients for the organic soil and peat moss were multiplied by a factor calculated in the desorption equilibrium time study. This was necessary as the desorption equilibrium times were determined after the desorption isotherms were established. Initially the desorption isotherms were evaluated using the adsorption equilibrium times. However, this was discovered to be incorrect as desorption is a slower process than adsorption [La Poe, 1985]. Therefore, in evaluating the equilibrium desorption times, it was determined that the desorption for the organic top soil and peat moss increased 5% and 12.5% respectively. Using these values each K_{fd} value was corrected to correspond to the new desorption equilibrium time.

Table 6-2 shows that GAC has the largest K_{fd}, indicating that it releases the greatest amount of PCE. However, one must keep in mind that it also adsorbed the greatest amount of PCE. Therefore, it would be useful to compare the ratio of K_f to K_{fd} to indicate how strongly the chemical is retained by the adsorbent. Table 7-1 gives these ratios for all the media tested.

Table 7-1 K_f/K_{fd} for Different Media

MEDIUM	K_f/K_{fd}
Sandy loam Soil	2.07
Organic Top Soil	5.54
Peat Moss	6.57
GAC	23.5

It is obvious that the higher the ratio between K_f and K_{fd}, the greater would be the retention of the chemical by the medium. When the ratio approaches 1.0, the medium in question has reversible adsorption, as in the case of sandy loam soil. Furthermore, if the slopes in the adsorption and desorption isotherms were identical, it would be possible to calculate the percentage of chemical that would be desorbed, by taking the inverse of the above ratio and multiplying by 100.

7.1.3 Desorption According to Regulation 309

The Ministry of the Environment, Ontario [1985], has included a test in Regulation 309 to determine the quality of leachate for various solid wastes. The test basically involves lowering the pH of the solid waste to 5.0 ± 0.2 for 24 hours and analyzing the leachate. Table 6-3 gives the

Freundlich coefficients determined according to this test. K_{fd} for the organic soil has been adjusted to account for the increased desorption determined in the equilibrium time desorption study.

As Table 6-3 indicates, there are two sets of data. In the first batch, the pH values were higher than the desired limits because of the soil's buffering capacity. Furthermore, no acid could be added to the desorption tubes as required by the test protocol, because PCE would have been lost through volatilization. Therefore, larger amounts of acid were added initially in the second batch to compensate for the buffering capacities.

No data are provided for peat moss and GAC in Table 6-3. The peat moss was acidic and its pH was already below Regulation 309 limits. Therefore, no desorption tests were performed on this soil. The data obtained with GAC did not provide an isotherm. However, as Fig. 6-4 indicates the values did fall on the desorption isotherm obtained with the DDI water, indicating no increase in desorption. The tests were repeated twice and both times the results had clustered in the same region.

The results of desorption according to Regulation 309, indicate that desorption is independent of pH for the soils tested. This can be seen by comparing the desorption coefficients in Table 6-2 and 6-3, where the K_{fd} and $1/n_{fd}$ values are identical. Therefore, for PCE, it is not necessary to perform a leachate study with an acidic solution, but rather just with DDI water. Furthermore, this leads one to believe that if PCE is spilled on soil in an area subjected to acid rain, the migration of the PCE into the ground would only be a function of the type of soil present and its desorption characteristics.

7.1.4 Adsorption - Desorption With Different Size Particles

The isotherm coefficients determined for different size particles, Table 6-4, were evaluated for the same equilibrium times as used for the composite samples. The results for graded sizes of the sandy loam soil are considerably different when compared to the composite sample, indicating the possibility of different equilibrium times for the various particle sizes. The lower K_f values are indicative of the lower organic carbon contents measured for each size, Table 3-1, when compared to the composite organic carbon content. The surface area available for adsorption is inversely related to particle size [Weber, 1972]. This is no indication that an increase in specific area, i.e. smaller particles, increases the K_f. Weber [1972] has suggested that the only time surface effects become a factor in adsorption, is when large organic particles are broken up and interior surfaces are exposed. This increased surface area of the organic fraction resulted in increased adsorption.

The organic soil exhibited the same trend as the sandy loam soil, i.e., no increase in adsorption is observed with a decrease in particle size. However, it is noticed that the

K_f values are consistent with the value determined for the composite sample. This can be directly attributed to the relatively constant equilibrium times that must have existed and also to the similar organic carbon contents measured in the composite sample and the various particle sizes, Table 3-1.

As can be seen from Table 6-5 and Figs. 6-6 to 6-11, there is no difference in desorption between different particle sizes and the composite sample. This indicates that desorption is mainly a function of organic carbon content. The sandy loam soil has a desorption isotherm higher than the adsorption isotherm, indicating that equilibrium had not been reached; while the organic soil indicates the ability to retain PCE at the same ratio as obtained with the composite sample. No comparison with published data could be made as research on similar desorption studies is lacking.

7.1.5 Soil-Water Partition Coefficient

The soil-water partition coefficient, K_{OC}, values are used to help in the classification of a chemical's mobility in soil. This parameter is independent of soil/sediment type but has a constant value for each chemical [Hamaker and Thompson, 1972]. Table 6-6 shows the values calculated for organic top soil and peat moss. K_{OC} values were not evaluated for sandy loam soil or GAC as their isotherm slopes were not close to unity [Roy and Griffin, 1985]. The K_{oc} values for PCE determined in this study and other investigators are given in Table 7-2.

Table 7-2 shows considerable variations in reported K_{oc} values. This is consistent with reported observations on the use of K_{oc} to predict mobility of chemicals in soils [Lyman et al., 1982]. It is believed that if K_{oc} values for a given chemical are within an order of magnitude, they are acceptable. Therefore, the K_{oc} values determined in this study are within the accepted norm. The mean value of the K_{oc} values listed in Table 7-2 is 375, indicating that PCE can be classified as having medium mobility.

Table 6-7 presents the K_{oc} values for organic soil sieved to various sizes. Using the above criteria, these values are acceptable and indicate that PCE should be considered a chemical having medium mobility in the soil.

Table 7-2 Reported K_{oc} Values for PCE

SOURCE	K_{oc}*
This study (organic soil)	123
This study (peat moss)	534
Schwarzenbach and Westall, 1981	247
Roy and Griffin, 1985	303
La Poe, 1985 (mineral soil)	337
La Poe, 1985 (peat)	707
Mean =	375

* K_f used to determine K_{oc} based on C_e in mg/L and X/M in mg/kg

7.1.6 Adsorption of Pure PCE by Granular Media

The residual saturation values reported in Table 6-8 indicate that when the media tested are dry, they can adsorb significant quantities of pure PCE. After the PCE has been adsorbed by the medium, the PCE will be released for a long time. This is a result of PCEs low solubility which allows the percolating water to transport only a small portion of PCE at a time, and its slow desorption kinetics.

There is a significant difference in adsorption between the air dried medium and that of the adsorption isotherms, as seen in the following calculation. This difference is significant as it indicates that air dried medium like peat moss can be applied to a spill site to adsorb the chemical.

Mass of peat moss = 10,000.0 mg
Maximum solubility in water = 150.0 mg/L
Maximum mass adsorbed by peat moss from saturated solution using adsorption isotherm = 206.0 mg
Maximum mass of pure PCE adsorbed by peat moss using residual saturation value given in Table 6-8 = 77,630.0 mg
Difference in two adsorbed masses = 77,424.0 mg

7.1.7 Application of Isotherm Data

The adsorption and desorption isotherms indicate that granular media high in organic carbon content, like peat moss and activated carbon, can effectively retain PCE that has been adsorbed. The value of K_f/K_{fd} indicated the relative retention capacity. When this ratio increases, the amount of

PCE retained by the soil is larger. This information has a direct application at a spill site when the soil is high in moisture content. An appropriate medium like peat moss or GAC can be applied to the spill to prevent or minimize the migration of the chemical. This application is enhanced further by examining the residual saturation capacities of the various media. When a spill occurs and the moisture content at the spill site is low, a medium like peat moss can be directly applied to the spill. Not only does peat moss have a great affinity for the chemical, approximately eight times its body mass, peat moss is also relatively cheap. Once the chemical spill is contained, the contaminated medium can be collected and disposed of in an acceptable manner for hazardous wastes.

When applying a medium to a spill site, the time required to reach maximum adsorption must also be considered. This time can be obtained from the adsorption equilibrium time, t_e. For a smaller value of t_e, the chemical will be adsorbed faster and thus the spread of the chemical will be minimized. In this study, peat moss has the smallest t_e of six hours. Using this information along with the residual saturation data, peat moss is considered to be well suited for application to contain a spill. The adsorption by peat moss at a spill can be enhanced further by applying amounts in excess of the calculated values.

Another application of the adsorption isotherms would be in the calculation of the affected area. If the mass of spilled chemical is known, the mass of contaminated soil can be determined. Using the density of the medium, its volume can be calculated. This volume then can be excavated and disposed of in a proper manner.

7.2 Volatilization of PCE from Water and Soil

The results presented in the previous chapter on volatilization are discussed in the following sections.

7.2.1 Volatilization of PCE from Stagnant Water

The volatilization data indicate that PCE in aqueous solution volatilizes very rapidly. From Eq. 6-3, it can be determined that for an area/volume of 81 1/m, only 2.7% of the initial mass will remain after 4.5 hours. This rapid volatilization has been observed by others as well [Mackay and Yeun, 1983, Dillinget al., 1975 and Namkung and Rittmann, 1987]. The volatilization of PCE is rapid as it has one of the highest Henry's Law Constants (23.0×10^{-3} atm-m^3/mol) for volatile organic chemicals, VOCs. The partial pressure of any compound increases with an increase of the Henry's Law Constant [Yurteri et al., 1987]. However, other factors have also been shown to affect the volatilization rate.

Table 6-9 shows that the volatilization rate constant increased with an increase in area to volume ratio, for each concentration tested. This relationship was investigated and the resulting Eq. 6-1 gives the volatilization rate constant as a function of area/volume. It is seen that Eq. 6-1 is independent of initial PCE concentration and all the volatilization rate constants and area to volume ratios, A/V, correlate nicely into one equation, with a correlation coefficient, r^2 of 0.9537. The importance of A/V has been reported by other researchers also [Abdel-Gawad, 1985 , NRC, 1971, AWWA, 1971 and Dilling, 1971]. For larger bodies of water, A/V approaches 1/d, where d is depth in meters.

However, it should be noted that Eq. 6-1 is valid for a wind velocity of approximately 10 km/h and and an ambient temperature of 22°C. This is important as others have indicated that volatilization of VOCs increases with the wind velocity and temperature [Kilzer _et_ _al_., 1979, Spencer, _et_ _al_., 1982, Mackay and Yeun, 1983].

By substituting Eq. 6-1 into the volatilization rate equation, Eq. 4-12, Eqs. 6-2 and 6-3 were derived. These two equations can be used to determine the PCE concentration or mass remaining in the stagnant water after time ,t, in hours. Other equations have been developed [Dilling _et_ _al_., 1975 and Mackay and Yeun, 1983], but those are for dilute solutions and usually employed a stirrer to aid the volatilization process. Equations 6-2 and 6-3 are valid for aqueous PCE concentrations up to the solubility limit. No turbulence was provided other than a low wind velocity.

7.2.2 Flux of PCE into Stagnant Water

The flux experiments indicate that PCE does diffuse from a pure pool of submerged PCE into stagnant water. Equation 6-7 has been developed to explain this mass transfer. This equation is time dependent, and gives the accumulated mass of PCE, mg, diffused into the water at any time, t, in days.

If C_F in Eq. 6-8 is compared to Eq. 4-16e, it can be seen that the empirical equation obtained from the data has the same form as the theoretical derivation, thereby confirming the approach used to obtain Eq. 6-8. Further comparison enables one to calculate the values for C_i and K_{OLPCE}. The saturation concentration at the interface, C_i, of 89 mg/L is only 60% of the solubility limit, which may be considered low. However, experience in the laboratory had indicated that, when the standards were being mixed at a concentration of 112.5 mg/L, the PCE and DDI water had to be mixed vigorously for twelve hours to completely dissolve the PCE. Since the flux experiment was conducted without turbulence at the PCE-water interface, a C_i of 89 mg/L is quite acceptable. No comparison of the value for K_{OLPCE}, 0.006 m/h, is possible because no values are reported in the literature for similar situations.

As Figure 6-17 indicates, the maximum measured concentrations in the bulk liquid in the flux experiment approached 37 % of its maximum solubility of 150 mg/L. Maximum solubility was not obtained because of the lack of turbulence and simultaneous volatilization of the PCE from the surface.

An equilibrium condition had been reached after approximately twelve days when the mass diffusing into the water was equal to the mass volatilizing from the water surface.

Figure 6-17 shows the comparison of the empirical equation for C_L and the model equation for C_{LT} to the experimental data. As can be seen, the the model equation can predict the data satisfactorily, indicating that the values for liquid film coefficients K_{OLWF}, of 0.004 m/h, and K_{OLPCE}, of 0.006 m/h, used in the model are correct. Proper values for these coefficients are necessary as the equation for X_F depends on the equation for C_{LT} to which adjustments are made for volatilization.

The differences between K_{OLW}, 0.009 m/h, and K_{OLWF}, 0.004 m/h, values should be noted. These liquid film coefficients describe similar conditions and as such should be identical. K_{OLW} was obtained from the volatilization data, where as K_{OLWF} was obtained from the flux data. A closer evaluation of K_{OLW} and k_W, may provide the explanation. Theoretically when A/V approaches zero no volatilization should occur. The plot of k_W versus A/V, Fig. 6-16, shows this was not the case. Therefore, another factor must be influencing volatilization at lower A/V values. Also, the intensity of the turbulence on the water surface in these two different types of experiments was not necessarily the same.

The literature on volatilization of PCE from water revealed that stirrers were used in all the studies to simulate moving water [Matter-Mueller <u>et</u> <u>al</u>., 1981 and MacKay and

Yuen, 1983]. The K_{OLW} values obtained with the use of stirrers in the experiment will be greater as the overall volatilization rate will be greater and can not be compared with the results obtained in this study.

Figure 6-18 indicates the total flux rate of PCE into stagnant water after correcting Eq. 6-5b for volatilization losses. Equation 6-7 was developed to represent this mass flux. The total mass of PCE fluxed in fifteen days is determined by integrating Eq. 6-7. For the conditions used in the laboratory, the mass fluxed was 2000 mg or 1.23 mL of PCE giving a flux rate of 0.028 kg/m^2/d or 0.017 mm/d. This flux rate is slow when compared to that of 0.96 kg/m^2/d in flowing water having a velocity of 0.1 to 0.2 m/s [Canada-Ontario, 1986].

As stated previously, Eq. 6-7 was developed for an area to volume ratio of 2.00. Since spill situations may have different area to volume ratios, a method must exist to modify the X_F equation for the corresponding A/V. Since K_{OLPCE} is independent of A/V, a new C_F equation can be obtained by using the A/V ratio for the actual situation being studied. Once the new C_F equation is determined, the appropriate X_F equation can be derived. The new X_F equation is then integrated and the corresponding flux rate determined. Another method is to find C_{LT} first and then using the computer program in Appendix D to determine X_F.

7.2.3 Application of Flux and Volatilization from Water

When the spill situation involves PCE dissolved in water, the results indicate that the PCE will volatilize very quickly into the atmosphere. Therefore, if water containing PCE is released accidentally and it does not immediately percolate into the ground, one can allow it to volatilize into the atmosphere. Such remedial actions have been recommended by the EPA Emergency Response Team for a chemical such as PCE and for the conditions described above [Turpin, 1987].

Even though the volatilization rate from water is quite rapid, the rate of flux movement into water, when a continuous supply exists, is slow. A good example is a pool of PCE that has settled at the bottom of a reservoir. If there is no turbulence, a significant amount of time will be required for the PCE to dissolve into the water. Therefore, sufficient time will be available to take proper remedial actions. Proper response can involve pumping out the submerged pool of PCE directly, so that no concentrated sources remains. Once this is done, the remaining traces of PCE will volatilize into the atmosphere.

7.2.4 Volatilization from Soil

The volatilization of dissolved and pure PCE from soil is discussed in the following sections.

7.2.4.1 Volatilization of Aqueous PCE

As Figs. 6-19 to 6-21 for sandy loam soil and Figs. 6-23 to 6-25 for organic top soil indicate, volatilization is a function of area to volume ratios. In both soils, the volatilization rate constant increases with an increase in area to volume ratio. However, when the k value for sandy loam soil at a concentration of 20 mg/kg is compared to the k value for organic top soil at 18 mg/kg, it is observed that the volatilization rate from sandy loam soil is greater than that for the organic top soil. This difference in volatilization rate is attributed to several factors; however, the most significant factor is the organic carbon content. With the organic carbon content of the organic top soil being significantly higher than that of the sandy loam soil, a larger portion of the adsorbed PCE is retained. The higher the retention of the chemical the slower will be the rate of volatilization. Similar trends have been reported with other chemicals [Spencer et al., 1982, Hamaker, 1972 and, Spencer and Cliath, 1974]. Hamaker [1972] has suggested that as the adsorption increases, mobility and therefore diffusion rates are decreased, thereby reducing volatilization. The decrease in volatilization is related to the change in Henry's Law Constant [Yurteri et al., 1987 and Dupont and Reineman, 1987]. As the presence of salts and humic matter increases, Henry's Law Constant decreases, thereby reducing the vapour pressure of the chemical.

Another factor affecting volatilization is bulk density of the soil [Farmer et al., 1973 and Spencer et al., 1982]. When the bulk density of the soil is small, it is easier for the chemical to diffuse to the surface. For the soils studied, sandy loam soil and organic top soil, the densities were 1500 kg/m^3 and 1000 kg/m^3 respectively. Thus, it is expected that the aqueous PCE would volatilize at a faster rate from the organic top soil. However, the opposite was the case in this study indicating that the higher organic carbon content was the dominant factor in volatilization of aqueous PCE from soil.

In determining a relationship between the volatilization rate and area to volume ratio, it is observed that volatilization is not only a function of area/volume, as was determined for water, but also depends on the PCE concentration. As Eqs. 6-10a and 6-12 indicate, a linear relationship can be used to account for PCE concentration. The additional parameter in the volatilization equation is due to the soil properties. The water can be assumed to be mixed more uniformly when compared to a soil profile. When a chemical is present in soil, the surface layers will volatilize first setting up concentration gradients [Spencer and Cliath, 1974, Dupont and Reineman, 1987 and Spencer et al., 1982]. After the surface layer has volatilized, the remaining PCE in the soil profile must first diffuse to the surface. This diffusion is dependent on factors such as adsorption and bulk density.

Equations 6-10a and 6-12 were simplified, as explained in the Results and Analysis Chapter, to make them easier to use. In the simplification process, k_{SL} becomes independent of concentration, Eq. 6-10b, whereas k_{ORG} is adjusted for concentration, Eq. 6-13. The differences in k_{SL} and k_{ORG} values are noted in Figs. 6-22 and 6-27. For sandy loam soil, the curves are parallel, whereas for the organic top soil they converge to one point. These differences are attributed to the differences in soil properties. For this reason, two separate correlations for volatilization rates are presented. Equation 6-11 for sandy loam soil and Eq. 6-14 for organic top soil.

The correlation equations for soils are based on data collected over a four hour period. This is the longest duration available due to the batch procedure used. After four hours, the soil in the vials exhibited marked increase in dryness. Since the headspace technique depended on a consistent matrix, samples beyond this time period could not be relied upon. A more sophisticated method, using better control on moisture and temperature, is required to perform a volatilization study over a longer period of time. Furthermore, it should be recognized that the volatilization equations for aqueous PCE application on soil were developed at a temperature of 22°C and a wind velocity of 10 km/h.

7.2.4.2 Volatilization of Pure PCE from Soil

As Fig. 6-27 indicates, there is scatter in the data on the volatilization of pure PCE from sandy loam soil . This is reflected in the correlation coefficients calculated. The relatively poor values of correlation coefficient can be attributed to the low rate of volatilization exhibited by the soil for the duration studied.

The wind velocity was reduced, as compared to that used in the previous volatilization studies, in order to simulate spill conditions in the column. With the top of the soil mantle being 0.1 - 0.9 m below the top of the column, the air movement across the soil surface was quite low. Rainfall simulators further reduced the air movement. Therefore, the simulated wind velocity for the pure PCE was reduced to approximately 4 km/h at the entrance point to the fume hood.

Equation 6-16 calculates the amount of PCE remaining in sandy loam soil after time t. The equation is valid for the mass of PCE applied and the soil having a moisture content at field capacity. At this concentration, the volatilization rate is given as a function of the area to volume ratio. Since it was desired to maintain field capacity moisture in the samples, the maximum duration of the test was six hours. A longer duration, as compared to the aqueous PCE study, was used because the pure chemical assisted in keeping the samples moist for a longer period. It should be recognized that this equation is valid for a temperature of 22°C.

As indicated in Chapter Six no correlation was available for volatilization of pure PCE from organic top soil. When the slopes of the data sets in Figure 6-28 are considered, it is seen that they vary from 0.0001 to 0.001 per hour. These volatilization rates are slower than the ones determined for the sandy loam soil 0.004 to 0.007 per hour. Slower rates of volatilization are expected whenever the organic carbon content is higher. It is obvious that the measurement of the volatilization rate for PCE from organic soil requires a more sophisticated apparatus or methodology.

7.2.4.3 Application of Soil Volatilization Equations

The results of this study show that PCE in an aqueous phase volatilizes rapidly. Therefore, in the case of a spill where the soil has enough moisture to dissolve the entire amount of PCE, it is expected that the spilled chemical will disappear quickly through volatilization. In such circumstances there may not be sufficient time available to excavate the contaminated soil. It would be advisable to cordon off the area and allow the chemical to volatilize.

However, if one considers a massive spill, where most of the pure PCE is adsorbed by the soil, the volatilization rate will be quite slow as compared to the previous scenario. Under such circumstances sufficient time would exist to excavate the contaminated area. Furthermore, a soil like the organic top soil or peat moss could be applied to the spill area. Not only would the PCE be prevented from migrating into the groundwater, but also no appreciable volatilization of chemical would occur.

7.2.5 Comparison of Volatilization Rate Constants

When the volatilization rate constant of PCE from water is compared with the volatilization rate constant of pure PCE from sandy loam soil for an A/V of 2.0 1/m, a factor of approximately 3.5 is noticed. The volatilization rate constant for water, k_W, is 0.045 1/h, while for sandy loam soil, k_{PSL}, is 0.01 1/hr. This indicates that volatilization data obtained from water cannot be used for wetted soils, a fact observed by others [Kilzer _et_ _al_., 1979, and Spencer _et_ _al_., 1982]. In fact, Spencer _et_ _al_. [1982] observed, that for organic chemicals less volatile than PCE, there is a difference of the order of ten in volatilization rates.

The volatilization rate constants of the aqueous PCE solutions applied to the soils tested were higher than those for water. With an aqueous concentration of 112.5 mg/L and a A/V of 2.0 1/m, k_W was 0.045 1/h. Identical concentrations in soils at their respective field capacities are 20 mg/kg in sandy loam soil and 54 mg/kg in organic top soil, Appendix E. The resulting volatilization rate constants, k_{SL} and k_{ORG}, are 0.87 1/h and 0.124 1/h respectively. The higher volatilization rate constants from the soils are due to the higher surface areas present. For a chemical mixed in water, the only film exposed to the atmosphere is the surface.

However, for the soils all the particles have surfaces exposed to the atmosphere. When one considers the sandy loam soil, the particles have a surface area of approximately 22,000 m^2/kg. This is a considerable increase in film surface exposure for a similar gross area to volume ratio as used with water. This increase in actual film area will result in a higher volatilization rate constant.

The volatilization rate constant for the sandy loam soil is approximately seven times that of the organic top soil. Even though the study concerned itself with the chemical mass in the field capacity moisture, the soil properties still affected the volatilization rate constant. The higher organic carbon content in the organic top soil increased its tendency to be adsorbed. Therefore, it's ability to volatilize was reduced.

7.3 Perfusion Experiments

The perfusion experiments were initially set up to evaluate the degradation of PCE under spill conditions. After conducting several runs it was observed that the data collected could also be used to predict adsorption.

7.3.1 Degradation

The sandy loam soil was tested in the perfusion apparatus both with and without airflow. Runs with airflow included air scrubbers to determine if the volatilizing PCE could be measured. However, no PCE was detected in the scrubber water, even with the GC set at maximum sensitivity. Consequently, gas samples were drawn from the air tube leaving the apparatus and from the headspace directly above the soil surface. In both instances, the results concurred with that of the air scrubber, i.e., no detectable PCE was observed. From these results it was concluded that the volatilization rate in the perfusion apparatus was negligible. However, realizing that PCE was highly volatile, the apparatus was modified by removing the inlet and outlet air lines. The sandy loam soil was retested with the air lines removed. Figures 6-30 and 6-31 show no difference in observations. Furthermore, the rate constant values obtained for these two tests were very close as given in Table 6-17. Therefore, for the perfusion apparatus used in these experiments, volatilization losses were considered to be negligible.

Although the soils were biologically active, the curves and the resulting rates in Figs. 6-30, 6-31 and 6-33 indicate that biodegradation was not a significant factor. Many researchers have indicated that PCE does not degrade in an aerobic environment even at concentrations lower than those used here [Vogel and McCarty, 1985, Wilson and Wilson, 1985 and Namkung and Rittmann, 1987].

When the soil was autoclaved for this study, the larger particles were possibly broken down, especially the organic top soil. By breaking the soil into smaller particles, more surface sites were exposed for increased adsorption capabilities [Dao et al., 1982 and Sparling and Cheshire, 1979]. This increased adsorption capacity resulted in a higher rate constant as seen in Tables 6-16 and 6-17.

7.3.2 Adsorption

The theory developed to predict adsorption in the perfusion apparatus, Section 4.4 indicates that the rate of adsorption is directly related to the pumping rate and the perfusate volume. However, for both the soils tested, the results deviated from the theory. From the column breakthrough analysis in Section 4.5.1, it is estimated that the sandy loam soil in the perfusion apparatus should adsorb 3100 mg/kg before breakthrough occurs. The corresponding value for the organic top soil was 14900 mg/kg. However, for both soils in the perfusion study the maximum mass of PCE applied was considerably less: 128 mg/kg for sandy loam soil and 170 mg/kg for the organic top soil.

The difference between the theoretical adsorption rate, Q/V_ℓ, and actual adsorption rate, K'_i, in the perfusion experiment can be attributed to several factors. With the columns in the perfusion apparatus being relatively short, short circuiting of the fluid can occur, resulting in a slower adsorption rate. This trend was observed for both the sandy loam and organic top soils, with K'_{AVESL} and K'_{AVEORG} values being less than Q/V_ℓ. The lower rate constant for the organic top soil can be related to its higher porosity. In a soil with a high porosity, more channels will exist thus providing more short circuiting routes in a short column. Therefore, for better application of the perfusion apparatus to adsorption studies, longer soil cores should be used to minimize short circuiting.

It can be observed from Figs. 6-30, 6-31 and 6-33 that the data points for sterilized soils are above the values obtained using unsterilized soil, indicating higher adsorption rates for sterilized soil. This trend was expected because sterilized soil particles break up during autoclaving and expose more surface area for adsorption. Such a behaviour also explains the higher standard deviation calculated for the organic soil adsorption rate, Section 6.3.3, with the organic soil having more organic matter. The organic matter is expected to break up more easily than the mineral substances. Therefore, the organic soil having more organic matter will provide a greater increase in contact area for adsorption to occur.

7.4 Column Studies

As derived in Section 4.5.1, the adsorption of dissolved PCE by the soil columns was directly related to the V_t values listed in Table 6-18. It is observed from the table that the V_t values corresponding to $0.05C_o$, Figs. 6-35 to 6-38, required to evaluate the V_t/L values at chemical breakthrough for both soils, correlate quite well with the lowest r^2 being 0.9448. Similarly, the exhaustion V_t/L values at 0.95 Co also produced good correlation.

These high correlations confirm the theory used to develop the empirical expressions listed in Table 6-20, which calculate the breakthrough depths as functions of time or water volume. The empirical equations determine the time or volume of water required to obtain a specific dissolved concentration of PCE at a depth z from the soil surface. The equations apply to conditions where PCE is spilled and adsorbed by the soil, and followed by precipitation which may transport the PCE into the groundwater.

The data collected from column studies indicate that the front velocity of dissolved PCE was retarded by its interaction with the soil, mainly through adsorption. The second equation in Table 6-20 for each data set, expresses the front velocity of the dissolved chemical in m/d. It can be seen that this velocity in the organic top soil is approximately one-third of the velocity in sandy loam soil. As expected, the higher the organic carbon content of the soil, the greater was the reduction in dissolved front velocity. However, it should be noted that even in the sandy loam soil columns the dissolved PCE front velocity was retarded through adsorption on the soil, when compared to the Cl^- velocity.

The non-reacting velocity was determined through the use of Cl^- ions, which were non-reactive and conservative. The Cl^- data in Figs. 6-39 to 6-42 and Table 6-19 indicated that the PCE front velocity in the sandy loam soil column was one-eighth of the Cl^- front velocity, whereas in the organic top soil column it was one-eighteenth.

In further analyzing Figs. 6-35 to 6-38, it becomes apparent that in the case of shorter column lengths, pure PCE has percolated through. This was especially evident for the three sandy loam columns of 0.2, 0.4 and 0.6 m in length. Since the method of PCE analysis was developed for concentrations between 5 and 150 mg/L, any concentration in excess of the saturation concentration, 150 mg/L, must have contained some pure PCE. For the organic column, only two columns, 0.2 and 0.4 m length columns had exhibited this trend.

Two equations in Table 6-20 were developed to roughly approximate the velocity of the pure PCE through the soil columns. These equations give only a rough estimation since they do not account for the small fraction of pure PCE which had penetrated and subsequently was dissolved in the water present in the soil. The empirical equations indicate that the velocities were 0.018 and 0.009 m/d for the sandy loam soil and organic top soil respectively. Considering the characteristics of the two soils, this reduction in velocity could be attributed to the higher organic carbon content of the organic top soil.

After the pure chemical front has passed, a residual concentration remains in the soil. Subsequently, this adsorbed chemical would be dissolved gradually by the percolating water passing through the soil and transported down the soil profile. The length of time that the residual saturation lingers depends mainly on the volume of water passed and the adsorption properties of the soil. For the soil columns used in this study, the residual saturation concentrations remaining after 104 days at various depths of the core are plotted in Figs. 6-43 and 6-44.

Figure 6-43 for the sandy loam column indicates that the majority of the PCE has been desorbed. This is also observed in Figure 6-35 where the PCE concentration for the sandy loam soil approached zero after 40 L of water had passed. However, a different behaviour was observed for the organic top soil, after passing a similar volume of water. When the organic soil was analyzed, there still existed relatively large concentrations of PCE on the soil surface as indicated by Fig. 6-44. Furthermore, the effluent concentrations in Fig. 6-35 were still quite high, hovering around 45 mg/L. These steady effluent concentrations were expected since the organic soil desorbs PCE slowly as indicated by the determined desorption equilibrium times.

Since the precipitation rates were identical for both soils, the different trends between the soils indicate that residual saturations of PCE adsorbed on soil is an important controlling parameter for the behaviour of a spilled chemical in the soil. Soils high in organic carbon, like organic top soil have a high residual saturation potential, Table 6-8, and a low tendency to desorb the chemical. Therefore, the penetration of the chemical will be minimal if no excessive rainfall occurs. Thus, such soils will allow sufficient time to remove the contaminated soil and minimize the leaching of the chemical into the groundwater.

7.5 Numerical Models

Numerical models were developed to predict the behaviour of moisture and contaminants in the subsurface. The contaminant model was calibrated to predict the breakthrough time for a desired concentration at a depth z.

7.5.1 Moisture Movement Model

In simulating the moisture movement for unsaturated sandy loam soil, it is demonstrated that the differential equations developed in this thesis are verified. Furthermore, the Crank-Nicolson finite differencing approach is an effective method for analysis when dispersion coefficient, capillary conductivity and moisture tension values are altered according to the moisture content present. The results obtained in Figs. 6-45 and 6-46 show good agreement with the data reported in the literature [Remson et al., 1975].

Freeze [1979] and Bresler [1973] have stated that the implicit technique of Crank-Nicolson is the best way to model vertical unsteady-unsaturated flow. This method is adequate for handling the complexities associated with non-uniform conditions and changing moisture contents. Considering that the moisture content, dispersion coefficient and capillary conductivity values are recalculated in this method at each time step, the model converges quickly even when a low tolerance limit is used. Furthermore, numerical dispersion is minimized, making the application more suitable for unsaturated flow.

However, the accuracy of the desired model depends on the accuracy of the measurements of the dispersion coefficient, capillary conductivity and moisture tension coefficient. The measured data should also include the effect of hysteresis since it is an important factor for moisture movement in soil [Freeze and Cherry, 1979]. Ideally, soil data should be provided for all expected conditions, i.e., from air dried to saturated soils.

7.5.2 Calibration of Contaminant Transport Model

As mentioned previously, the model was calibrated to predict the time at which a certain concentration appeared at a depth z. This time is considered to be the critical time for a spill situation because it is important in the determination of the maximum penetration of the chemical. By having an indication of the distance travelled in a specified time, the depth of soil requiring excavation will be known. Furthermore, the time available for remedial action before the chemical reaches the groundwater can be determined. These times are critical, as no chemical must reach the groundwater, where cleanup becomes very difficult and costly.

Another restriction on the model application concerns the depth. As seen in Table 6-22, only column data measured below 0.4 m was used to calibrate the model. This distance was beyond the initial penetration of the pure chemical calculated from the residual saturation data. The model was calibrated to account for the pure chemical that was transported down the soil profile with the moisture flux. A similar approach has been used by the U.S.EPA in developing the Regulatory and Investigative Treatment Zone Model, RITZ [Nofziger et al., 1987 and Short, 1985]. In fact, they have totally neglected the immiscible phase of the transport model and have assumed that the chemical front becomes stationary and the only movement is through the dissolved phase. However, this study shows that the immiscible phase cannot be ignored.

The final comment concerns the coefficients of dispersion, capillary conductivity and moisture content used in model calibration. Both the theoretical development and the unsaturated moisture model indicate that these three coefficients are all interrelated and vary simultaneously, affecting the moisture movement through the soil. However, in the experiments conducted in the laboratory, the moisture content was held constant, restricting the model to a constant moisture content. The effect of changing moisture conditions and thus the soil hydraulic properties can be incorporated in the next generation contaminant transport model.

7.5.3 Simulation of PCE Transport in Soil

The values in Table 6-22 indicate that the breakthrough times obtained from the empirical breakthrough equations and contaminant transport model compare satisfactorily. Both sets of breakthrough times indicate that for the identical mass of chemical spilled, the organic top soil exhibited a greater retardation of the chemical as compared to sandy loam soil. This was expected due to the higher adsorption potential of the soil and the lower aqueous phase velocity.

For comparison of measured PCE concentrations to those simulated by the contaminant model, Figs. 6-47 and 6-48 indicate that the model satisfactorily predicts the effluent concentrations for the 0.8 m soil column. Similar results were obtained while checking other column lengths. With both the predicted model breakthrough times and the simulated effluent concentrations in agreement with actual observations, it is believed that the contaminant transport model developed in this study is calibrated within the stated restrictions.

In comparing the results between the simulation runs for the sandy loam and organic top soils, it can be concluded that the parameter having a significant impact was the fluid velocity of the aqueous PCE. The chloride tracer study indicated that the dispersion terms were identical for both the soils and the only hydraulic difference was the interstitial velocity. With the applied rates of precipitation kept identical for all the columns, the differences in velocity existed because of the difference in soil porosities and moisture contents. Therefore, when using the model in the field, careful and accurate measurements of the moisture content and porosity are required. In this study, the theoretical and actual velocities for both soils were within 7% of each other.

The other important velocity term required in the simulation is the immiscible front velocity. As stated in Section 7.4.1 a rough estimate of v_i can be made by conducting a column study. Unfortunately, this would not be feasible for a spill in site specific soil considering the time involved in conducting the study. Since the theoretical and actual velocities were within 7% of each other, the velocity coefficients in Table 6-21 were compared. It is noticed that v_i is 1/10 and 1/20 of v_w for sandy loam soil and organic top soil respectively. These values indicate the possibility of a relationship existing between v_i and v_w. Further research is needed to determine this relationship for a broad range of chemicals and soils. With this information, the contaminant transport model can be applied to a large number of spill situations.

Figures 6-49 and 6-50 provide a comparison between the concentrations predicted by the numerical model and the concentrations actually measured. It can be seen that the model over predicts the chemical concentrations observed in the effluent after the occurrence of initial breakthrough. This suggests that the model does not fully describe the entire transport process occurring in the soil columns. Therefore, before the model can be used to fully describe the transport process, it has to be modified and further experimental work is required to collect the necessary calibration data.

In order to determine some of the reasons why the contaminant model does not properly predict concentration past the initial breakthrough, a mass balance was done on all the columns, Table 7-3. These values show that in the majority of the columns, over half of the PCE is unaccounted for. The experimental set-up used to conduct the column studies was an open system and this allowed the PCE to volatilize into the atmosphere. Therefore, it is suggested that a closed system be developed to gather information on the mass of chemical volatilized from the soil columns. This data can then be used in the model to account for the volatilization losses of the chemical spilled at the soil surface. Another area for improvement concerns the measurement technique of PCE in the effluent. The headspace technique chosen is accurate for dissolved concentrations of PCE below solubility, 150 mg/L. However, when the concentrations exceed this value, pure PCE is expected to be present in the sample, requiring a different analytical procedure to analyze the concentrations. By properly analyzing the chemical concentrations in the effluent, an accurate mass balance can be conducted to determine how much chemical has passed through the soil. In doing so, the model can be calibrated to predict the breakthrough times and equally as important, determine the fraction of the spilled chemical that is transported into the groundwater.

Table 7-3 Mass Balance of PCE in the Soil Columns

COLUMN	Mass Spilled mg	Mass Measured mg	Theoretical* Mass Adsorbed mg	Mass Unaccounted mg
Sandy Loam Soil 0.8 m	16220	3161	1336	11723
Organic Top Soil 0.8 m	16220	1865	10608	3747
Sandy Loam Soil 0.6m	16220	5137	1002	10081
Organic Top Soil 0.6m	16220	1569	7956	6696
Sandy Loam Soil 0.4 m	16220	6910	668	8642
Organic Top Soil 0.4 m	16220	2828	5304	8088
Sandy Loam Soil 0.2m	16220	7030	334	8856
Organic Top Soil 0.2m	16620	4114	2652	9454

* Based on Freundlich Adsorption Isotherms

Finally, the use of a non-reactive type of column should be used for this kind of study. After the studies were completed, the soil was removed from the Plexiglas columns. All of the columns showed spot marks on the inside wall where the spilled pure PCE was applied to the soil, indicating that a fraction of the spilled PCE had reacted with the Plexiglas, the material of the column.

7.5.4 Sensitivity Analysis

From the sensitivity data in Table 6-23, it can be determined that the coefficients which had the greatest impact on the contaminant transport model were v_i and D_i. Even a slight change in v_i greatly affected the output results; emphasizing that care should be exercised when evaluating v_i. In fact, the system became unstable when the v_i value was to large. This is expected due to the high impact that the pure chemical has on concentrations measured in water. Varying the values of D_i also had an impact on the breakthrough time. When D_i was increased by one magnitude, the breakthrough time decreased by 18 % (1.25 days). The D_i of PCE was assumed to be identical to the dispersion coefficient for water, as the percolating water was the driving force down the soil profile. Additional research will be required to verify this assumption.

Changes in D_a, whether one or two magnitudes larger or smaller, appeared to have no affect on the breakthrough time. This indicates that dispersion for Dense Non Aqueous

Phase Liquid, DNAPL, substances could be ignored with respect to the dissolved phase transport. Similar observations have been reported by other investigators [Schwarzenbach and Westall, 1981 and Enfield, 1985], including the RITZ Model [Short, 1985].

The advection data in Table 6-23 indicate that the advection term for the aqueous phase can be changed without significantly affecting the breakthrough times. The results for v_w further reinforce the importance of determining v_i and D_i for the immiscible phase.

It is noticed from the sensitivity analysis that an increase or decrease in the volumetric immiscible phase content of PCE moderately affected the breakthrough time. Therefore, the assumption that the immiscible content was 10% of the aqueous phase is reasonable.

Variations in the values of various partition coefficients, K_p, K_H and K_i, had no a significant impact on the breakthrough times. As expected, the higher was the adsorption capacity, K_p, the shorter was the breakthrough time. The value of K_H had no substantial affect on the breakthrough time indicating that volatilization from within the soil core was minimal.

Reasonable changes in time interval, DT, did not affect the breakthrough time. However, when DT was large, such as 350 min, the model became unstable. Successful simulation with large DT values is directly related to the use of the

Crank-Nicolson approach for solving differential equations. Larger DT values reduce the number of iterations and hence less computer time is required.

The distance steps, DZ, were not checked for sensitivity as v_i was determined for a chosen value of DZ. It is granted that a finer grid with a smaller value for DZ would produce a more accurate solution. However, when DZ is too small, excessive computer time is used. Therefore, a DZ of 0.05 m was chosen as a compromise of all factors. Furthermore, for the more complex model of unsaturated moisture movement, tests indicated that a DZ value of 0.05 m was quite satisfactory.

7.6 Application of Results to Spill Situations

Some of the possible spill scenarios have been considered in this section and appropriate remedial actions based on the research work are suggested.

If pure PCE is spilled into a small body of water or a lake having very low turbulence, theoretical equations developed from the flux experiments can be applied, after substituting the appropriate values for the variables. Since the flux rate of pure PCE into a stagnant water column is found to be low, the proper remedial action will be to pump out the pool of chemical from the bottom of the water body as soon as possible.

In a situation where the PCE is in aqueous form, no special remedial actions are required. The PCE will quickly volatilize into the atmosphere as shown by the volatilization experiments. The rate of volatilization of PCE and consequently the change in PCE concentration in solution can be determined from the equations presented in this thesis.

The third scenario may involve a situation where pure PCE is spilled on an impervious surface or soil. If the PCE accumulates on the surface or percolates very slowly into the soil subsurface, the most appropriate remedial action will be to apply peat moss to the spill site directly. This relatively cheap material will quickly adsorb the PCE and prevent its further migration. The mass of peat moss required to adsorb a given mass of spill can be determined from the equations presented. When this adsorption of the chemical is complete, the PCE laden peat moss can be disposed of in a manner acceptable to the regulatory agency. The remaining traces of PCE can then be allowed to volatilize into the atmosphere. However, if the PCE penetrates into the soil surface, the column studies have shown that the PCE will migrate slowly down the soil profile. Since there will be no biodegradation of PCE in the natural soil environment, it will persist in the environment for a very long time. Consquently, it is important to remove the chemical before it can contaminate the aquifer. The results indicate that the immiscible phase front will have a large impact on the observed dissolved PCE concentrations. Therefore, it becomes imperative that the immiscible phase be removed quickly as possible from the soil by excavation of the spill site.

CHAPTER EIGHT

CONCLUSIONS

Based on the investigations conducted on the fate of perchloroethylene in soil-water environments, the following conclusions are drawn:

1. The headspace technique using a gas chromatograph equipped with a flame ionization detector to analyze PCE in water and soil is fast, reliable and accurate for the concentration range analyzed, 5 to 120 mg/L.

2. The adsorption-desorption processes of PCE on various granular media are well represented by the Freundlich Isotherm. All isotherms were linear for the range of concentrations studied. The organic carbon partition coefficient indicates that PCE has medium mobility in soil.

3. The organic carbon content of the medium was the governing factor in the adsorption-desorption process. Adsorption and retention potential of the medium increases with an increase in organic carbon content. The retention ratio indicates that GAC is ideal for adsorbing dissolved PCE.

4. Peat moss, amongst all the media tested, exhibited the highest residual saturation value for PCE at eight times of body mass.

5. Desorption studies conducted with a pH of 5.0 indicate no increase in mobility of PCE in soil.

6. Mass flux studies show that the flux of submerged PCE into stagnant water can be approximated using a first order equation. Studies also indicate that the mass transport of PCE into stagnant water is very low.

7. Volatilization of PCE from water was quite rapid. The rate equation obtained indicates that the area to volume ratio, A/V, is a critical factor in the volatilization of PCE from stagnant water.

8. Studies indicate that the water content in a soil matrix plays an important role in the volatilization of PCE from soil. The unsaturated soils exhibited higher volatilization rates of aqueous PCE when compared to those from water alone. However, in the case of pure PCE spilled on unsaturated soil the volatilization rate is lower than that from water.

9. The soil column studies confirm the empirical equations developed using column breakthrough theory. The presence of organic carbon in soil retards the migration of PCE under a spill condition.

10. The Crank-Nicolson implicit finite differencing scheme was successfully applied to the unsaturated moisture movement and contaminant transport models. This scheme allows easy modification of the governing differential equations and is numerically stable for a wide range of time and distance steps.

11. The contaminant transport model was calibrated to predict breakthrough times and concentrations of PCE at any depth z. The model also confirmed that the immiscible phase transport of the chemical was important.

12. Results from the perfusion study show that under spill conditions PCE was not biodegradable. The perfusion apparatus also demonstrated some promise for evaluating adsorption under field conditions.

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NOMENCLATURE

A = cross-sectional area, m^2

A_f = volume of feed solution applied/h, mL

b = constant for Langmuir Isotherm

B = volumetric phase content constant in transport model

C = pollutant concentration, mg/L

C_a = pollutant concentration in aqueous phase, mg/L

C_e = pollutant concentration leaving soil, mg/L

C_i = pollutant concentration in pure form, mg/L

C_s = pollutant concentration in adsorbed phase, mg/kg

C_o = initial concentration of pollutant, mg/L

C_v = pollutant concentration in vapour phase, mg/L

C_G = bulk gas phase concentration, mg/L

C_{is} = saturation concentration of the chemical, kg/m^3

C_{sb} = concentration of volatilizing material at top of
= soil layer, μg/L

C_{SG} = gas phase concentration at interface, g/m^3

C_l = concentration of volatilizing material in air, μg/L

C_L = bulk liquid phase concentration, kg/m^3

C_{SL} = liquid phase concentration at interface

D = constant for dispersion coefficients in transport model

D_a = dispersion coefficient through soil, m^2/h

D_f = μg of compound/mL of feed solution

D_{fluid} = diffusion of fluid, cm^2/s

D_i = dispersion of pure chemical through soil, m^2/h

D_o = vapour diffusion coefficient in air, cm^2/d

D_G = diffusion coefficient through gas, m^2/h

D_L = diffusion coefficient through liquid, m^2/h

D_{OL} = overall diffusion coefficient, m^2/h

D_v = diffusion of vapour through soil, m^2/h

F = mass flux, g/m^2/d

F_v = fractional material applied that volatilized

f_{oc} = fraction of organic carbon

H = Henry's Laws Constant, m^3-atm/kg

j = mass flux rate, kg/m^2/d

J = vapour flux from soil surface, ug/cm^2/d

k = volatilization rate, 1/h

K = capillary conductivity, m/d

K_x = capillary conductivity in x-direction, m/d

K_y = capillary conductivity in y-direction, m/d

K_z = capillary conductivity in z-direction, m/d

K_f = adsorption equilibrium constant for Freundlich Isotherm, m^3/g

K_{fd} = desorption equilibrium constant for Freundlich Isotherm, m^3/g

K_G = gas film mass transfer coefficient, m/h

K_H = Henry's Law Constant, m^3-atm/mole

K_{OLW} = overall liquid film mass transfer coefficient at water-air interface from batch volatilization studies, m/h

K_{OLWF} = overall liquid film mass transfer coefficient at water-air interface from flux experiment, m/h

K_{OLPCE} = overall liquid film mass transfer coefficient at chemical-water interface, m/h

K_{OL} = overall liquid film coefficient, m/h

K_{OL1} = overall liquid film coefficient at chemical-water interface, m/h

K_{OL2} = overall liquid film coefficient at water-chemical interface, m/h

k_W = volatilization rate from water, 1/h

k_{SL} = volatilization rate from sandy loam soil, 1/h

k_{ORG} = volatilization rate from organic top soil, 1/h

k_{PSL} = volatilization rate of pure PCE from sandy loam soil, 1/h

K_{oc} = partition coefficient between aqueous phase and organic carbon

K_{ow} = octanol/water partition coefficient

K_i = partition coefficient between the chemical and water

K_p = linear partition coefficient, m^3/g

L = soil depth, m

M = mass of adsorbent, g

MV = molar boiling volume, cm^3/g

n_f = constant for Freundlich Adsorption Isotherm

n_{fd} = constant for Freundlich Desorption Isotherm

n = volumetric air content, m^3/m^3

n_p = porosity of soil

p_i = partial pressure, atm

P_a = soil air filled porosity, cm^3/cm^3

P_t = total soil porosity, fraction

P_v = atmospheric partial pressure, atm

Q = recirculation rate, m^3/h

Q^* = mass of adsorbed solute per unit mass of adsorbent

q = flow per unit area, m^3/m^2

R = universal gas constant, atm-m^3/mole°K

S = solubility of chemical, μmol/L

S_A = surface area of column, cm^2

T_e = equilibrium temperature, °K

t = time, days

t_e = equilibrium time for adsorption, days

t_{ed} = equilibrium time for desorption, days

$t_{1/2}$ = volatilization half life, min

U = constant for all decay terms in transport model

V = volume, m^3

V_ℓ = bulk liquid volume in flask, m^3

V_t = throughput volume, m^3

v_a = advection of dissolved chemical through soil, m/h

v_c = constant for advection in contaminant transport

v_i = advection of pure chemical through soil, m/h

v_v = advection of gaseous chemical through soil, m/h

v_x = velocity component in the x-direction

v_y = velocity component in the y-direction

v_z = velocity component in the z-direction

X = mass of solute, mg

X_F = mass of solute fluxing into water, kg

X_L = mass of solute in water, kg

X_V = mass of volatilized from water, kg

z = distance from soil surface, m

θ = moisture content, m^3/m^3

Φ = immiscible phase content, m^3/m^3

μ_s = decay rate for adsorbed chemical, 1/h

μ_a = decay rate for aqueous chemical, 1/h

μ_v = decay rate for vapour phase chemical, 1/h

μ_{fluid} = viscosity of fluid, cP

ρ = density of water, kg/m^3

γ = density of soil, kg/m^3

APPENDIX A

A.1 Spill Volume for Column Experiments

The adsorption isotherms were used to determine the volume of PCE that should be spilled on the columns to ensure breakthrough. Assuming that the percolating water will attain a maximum concentration of 150 mg/L (saturation), it can be calculated how much chemical will be adsorbed by the soil.

For a sandy loam column, 0.8 m in length, the following data apply:

Mass of soil = 9.425 kg

C_e = 150 mg/L

Density of PCE = 1622 mg/L

Adsorption Isotherm: $X/M = 5.19(C_e)^{0.66}$

Therefore,

$X/M = 141.71$ mg/kg

or

$X = 141.71 \times 9.425$

$= 1336$ mg

Volume of PCE = Mass/Density

= 1336/1622

= 0.824 ml

Therefore, if 824 µL of pure PCE was applied to the long sandy loam column, none should appear in the effluent if desorption is neglected. For the organic top soil column, similar calculations indicate that 6.187 mL of PCE would suffice.

In deciding on the spill volume to be used for all the columns, another factor must also be considered. Since the the columns are located inside the environmental laboratory, occupational exposure limits should be met. These limits are 1340 mg/m^3 for the Short Term Exposure Limit, STEL, and 335 mg/m^3 for the Time Weighted Average, TWA [Cheminfo, 1987]. While satisfying STEL for initial and TWA for the long term exposure, 10 ml of PCE could be applied. This volume ensured an excess of PCE, especially for the shorter columns, and still satisfied the exposure limit criteria.

Appendix B

B.1 Centrifuge Settings

The centrifuge settings to settle particles 0.05 μm or greater were determined using the following Stokes equation [Black, 1982]:

$$t = \frac{\mu_{fluid} \log_{10}(R/D)}{3.81 N^2 r^2 (deltS)} \qquad (B\text{-}1)$$

where

t = spin time, sec,

μ_{fluid} = fluid viscosity, poise,

R = distance from hub to bottom of container, cm,

D = distance from hub to top of solution, cm,

N = revolutions per second,

r = size of particles to be settled out, cm,

deltS = change in specific gravity.

For the sandy loam tested, the following values were used:

$n = 1.002$ cP $= 0.01002$ P,

$R = 11$ cm,

$D = 9.5$ cm,

$N = 4000$ RPM $= 66.67$ RPSec,

$r = 0.05$ μm $= 5\text{x}10^{-6}$ cm,

deltS $= 2.65-1 = 1.65$.

Using the above data, the required spin time is 911.5 sec, for sandy loam soil or 15.2 min. For organic top soil, the spin time is 30 min.

Appendix C

C.1 Adsorption-Desorption Coefficients

For K_f and K_{fd} values, the batch equilibrium data were regressed to determine the slope and intercept. The batch equilibrium data consisted of the equilibrium PCE concentration, mass of sorbent, volume of sorbate and volatilization losses, for different concentrations of PCE. Table C-1 lists the adsorption data used to calculate the adsorption of PCE by sandy loam soil, while Table C-2 gives the desorption data for the same soil.

Table C-1 Adsorption Data for Sandy Loam Soil

Initial Conc. mg/L	Conc. after Correction for Volatilization mg/L	C_e mg/L *	Conc. Adsorbed mg/L **	Mass Adsorbed mg #	Relative Mass Adsorbed mg/kg ##
22.5	22.05	12.82	9.23	129	26
22.5	22.05	13.01	9.04	127	26
45.0	44.10	25.76	18.34	257	52
45.0	44.10	25.79	18.31	256	52
67.5	65.48	44.23	21.25	298	60
67.5	65.48	44.53	20.95	293	60
90.0	86.40	60.61	25.79	361	74
90.0	86.40	61.39	25.01	350	71
112.5	106.88	74.37	32.51	455	93
112.5	106.88	75.80	31.08	435	89

* C_e was measured in a subsample of the supernatant

** Concentration adsorbed is difference between corrected concentration and C_e

\# Mass adsorbed is concentration adsorbed times volume of solution used in adsorption study. For sandy loam 14.0 mL were used.

\#\# determined by dividing mass adsorbed by dry mass of adsorbent used. For sandy loam soil 4.92 g (dry basis) was used.

Table C-2 Desorption Data for Sandy Loam Soil

Initial Conc. mg/L	C_e Conc. mg/L *	Concentration Desorbed Vol.%	Concentration Desorbed mg/L **	Mass Desorbed mg #	Relative Mass Desorbed mg/kg ##
22.5	4.44	2.0	4.53	57	12
22.5	4.33	2.0	4.42	55	11
45.0	8.54	2.0	8.71	109	22
45.0	5.92	2.0	6.04	76	15
67.5	12.4	3.0	12.78	160	33
67.5	vial broken				
90.0	17.87	4.0	18.61	233	47
90.0	15.95	4.0	16.61	208	42
112.5	27.17	5.0	28.60	358	73
112.5	22.99	5.0	24.11	301	61

* C_e was measured in a subsample of the supernatant.

** Concentration desorbed is Ce corrected for volatilization losses. The magnitude of correction depended on initial concentration when adsorption began. For example 112.5 mg/L was used for adsorption, volatilization losses were 5%. Therefore, same vial in the desorption experiment was corrected by 5% for volatilization losses

\# Mass desorbed is concentration desorbed times volume of DDI used in desorption study. For sandy loam soil 12.5 mL were used.

\#\# Relative mass desorbed is determined by dividing mass desorbed by mass of adsorbent used. For sandy loam 4.92 g (dry basis) was used.

Appendix D

D.1 Derivation of Empirical Flux Equations

The following approach was taken to develop an empirical equation for flux.

D.1.1 Concentration and Mass of PCE Flux in Water

It was desired to represent the flux of PCE through a column of water with an empirical equation. As can be seen in Figure 6-17, PCE flux in stagnant water exhibits a pattern similar to oxygen uptake by wastewater. Using this analogy, the Thomas method for BOD coefficient determination was used [Steel and McGhee, 1979].

The time, t, in days, divided by concentration, mg/L, and raised to the power 1/3, $(t/\mathrm{Conc})^{1/3}$, values were plotted against t in Figure D-1 and regressed for a straight line. The slope and intercept of the line was set equal to the following terms;

$$(K_1L)^{-1/3} = \text{intercept} = 0.36197 \qquad \text{(D-1)}$$

$$K_1^{2/3}/6L^{1/3} = \text{slope} = 0.02367 \qquad \text{(D-2)}$$

Equations D-1 and D-2 are solved for K_1 and L to obtain the following equation:

$$C_L = L(1-e^{-K1t}) \qquad \text{(D-3)}$$

or

$$C_L = 53.75(1-e^{-0.3923t}) \qquad \text{(D-4)}$$

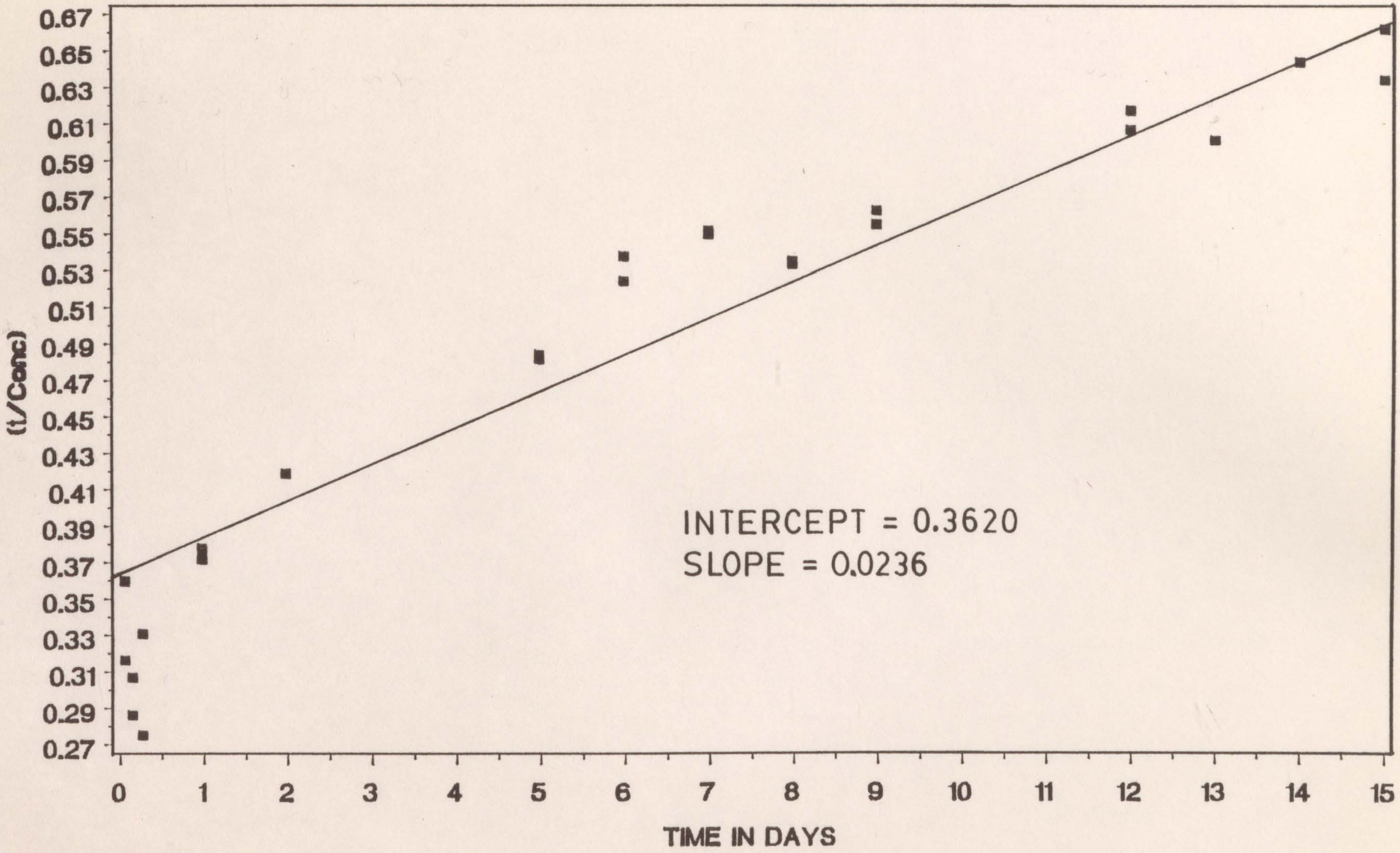

Figure D-1 DATA TO DETERMINE FLUX COEFFICIENTS

where

C_L = concentration in water, mg/L,

t = time, d.

C_L gives the concentration of PCE in a body of water containing a pool of submerged pure PCE. However, a more desirable term would be the mass of PCE present in the water, X_L, mg at time t. Therefore, Eq. D-4 was modified to give mass present in water. With a volume of 2 L, the mass flux into a body of water is given by

$$X_L = 107.5(1-e^{-0.3923t}) \qquad \text{(D-5)}$$

D.1.2 Total Flux of PCE into a Body of Water

The total flux, X_F, leaving a pool of pure PCE into a body of stagnant water, is defined as:

$$X_F = X_L + X_V \qquad \text{(D-6)}$$

where X_V is the mass of PCE leaving body of water, mg.

X_V was determined by computing volatilization losses during a time step, DELT, when the concentration in the water was C_L and mass was X_L. The first step involved the determination of average value of X_L, AVEXL, for the time step chosen to be equal to 0.25 d. The average volatilization rate was determined from Eq. 6-1, where A/V was 2.0 1/m.

The mass of PCE lost through volatilization was calculated by setting AVEXL to X_1 and determining the value for X_2 from Eq. 6-3 with t equal to time step used. The mass lost through volatilization is then written as:

$$X_V = \text{AVEXL} - X_2 \qquad \text{(D-7)}$$

With X_V determined, X_F can be calculated using Eq. D-8. Since X_V is based on the average mass present for any time step, Eq. D-8 can be rewritten as:

$$X_F = X_V + \text{AVEXL} \qquad \text{(D-8)}$$

A computer program was written to calculate the necessary mass flux values. It should be noted that a time step less than 0.25 d gave results identical to those obtained with 0.25 d. Table D-1 has a listing of the program, while Table D-2 gives the output.

Using the X_F and corresponding time values in Table D-2, an empirical equation for X_F was determined:

$$X_F = 178.38(1-e^{-0.2752t}) \qquad \text{(D-9)}$$

Table D-1 Program to Calculate XF

```
      DIMENSION TIME(400),AVEXL(400)
      DIMENSION XF(400),XV(400),XL(400)
      INTEGER T
C     CALCULATION OF MASS PRESENT IN LIQUID
      T=0
10    T=T+1
C     DELT IS IN HOURS
      DELT=6
C     TIME IS IN DAYS
      TIME(T)=(T-1)*DELT/24.0
      XL(T)=107.5*(1.0-EXP(-0.3923*TIME(T)))
      ARVOL=4.09167/2.0
      IF(TIME(T).LT.15)GO TO 10
C     CALCULATION OF VOLATILZATION LOSSES EACH TIME STEP
C     IT IS NUMBER OF MASSES CALCULATED
C     XV IS MASS IN GRAMS LOST THROUGH VOLATILZATION
      XV(1)=0
      AVEXL(1)=0
      IT=T-1
      DO 20 I=1,IT
      AVEXL(I+1)=(XL(I)+XL(I+1))/2.0
      X2=AVEXL(I+1)*10**(-(10**(0.0112*ARVOL-1.3654))*DELT)
20    XV(I+1)=AVEXL(I+1)-X2
      DO 40 I=1,T
40    XF(I)=XV(I)+AVEXL(I)
C     CALCULATING TOTAL MASS (AREA UNDER CURVE)
      TOT=0.0
      DO 41 I=1,IT
41    TOT=TOT+((XF(I+1)+XF(I))/2.0)*(DELT/24)
      TOMASS=TOT/1000
      WRITE(*,100)
100   FORMAT(’0’,7X,’TIME’,8X,’XL’,8X,’AVEXL’,7X,’XV’,8X,’XF’)
      WRITE(*,101)
101   FORMAT(8X,’DAYS’,2(8X,’MG’),2(9X,’MG’))
      WRITE(*,102)
102   FORMAT(1X)
      DO 50 I=1,T
50    WRITE(*,103)TIME(I),XL(I),AVEXL(I),XV(I),XF(I)
103   FORMAT(5F11.2)
      WRITE(*,104)TIME(T)
104   FORMAT(’0’,’TOTAL MASS FLUXED AFTER’,F5.1,1X,’DAYS’)
      WRITE(*,105)DELT,TOMASS
105   FORMAT(1X,’WITH DELT’,F6.2,1X,’HRS IS’,F6.1,1X,’GRAMS’)
      STOP
      END
```

Table D-2 Output for Mass Flux Program

TIME DAYS	XL mg	AVEXL mg	XV mg	XF mg
.00	.00	.00	.00	.00
.25	10.04	5.02	2.34	7.36
.50	19.15	14.59	6.81	21.40
.75	27.40	23.27	10.85	34.13
1.00	34.88	31.14	14.52	45.66
1.25	41.67	38.28	17.85	56.12
1.50	47.82	44.74	20.86	65.60
1.75	53.39	50.61	23.60	74.20
2.00	58.45	55.92	26.07	81.99
2.25	63.03	60.74	28.32	89.06
2.50	67.18	65.11	30.36	95.47
2.75	70.95	69.07	32.20	101.27
3.00	74.36	72.66	33.88	106.54
3.25	77.46	75.91	35.40	111.31
3.50	80.27	78.86	36.77	115.64
3.75	82.81	81.54	38.02	119.56
4.00	85.12	83.96	39.15	123.11
4.25	87.21	86.16	40.18	126.34
4.50	89.10	88.16	41.11	129.26
4.75	90.82	89.96	41.95	131.91
5.00	92.38	91.60	42.71	134.31
5.25	93.79	93.09	43.40	136.49
5.50	95.07	94.43	44.03	138.47
5.75	96.23	95.65	44.60	140.26
6.00	97.29	96.76	45.12	141.88
6.25	98.24	97.76	45.59	143.35
6.50	99.11	98.67	46.01	144.68
6.75	99.89	99.50	46.39	145.89
7.00	100.60	100.25	46.74	146.99
7.25	101.25	100.92	47.06	147.98
7.50	101.83	101.54	47.35	148.88
7.75	102.36	102.09	47.60	149.70
8.00	102.84	102.60	47.84	150.44
8.25	103.28	103.06	48.05	151.11
8.50	103.67	103.47	48.25	151.72
8.75	104.03	103.85	48.42	152.27
9.00	104.35	104.19	48.58	152.77
9.25	104.65	104.50	48.73	153.22
9.50	104.91	104.78	48.86	153.64
9.75	105.15	105.03	48.98	154.01
10.00	105.37	105.26	49.08	154.35
10.25	105.57	105.47	49.18	154.65
10.50	105.75	105.66	49.27	154.93
10.75	105.92	105.83	49.35	155.18
11.00	106.06	105.99	49.42	155.41

Table D-2 Continued

11.25	106.20	106.13	49.49	155.62
11.50	106.32	106.26	49.55	155.80
11.75	106.43	106.37	49.60	155.97
12.00	106.53	106.48	49.65	156.13
12.25	106.62	106.57	49.69	156.27
12.50	106.70	106.66	49.73	156.40
12.75	106.78	106.74	49.77	156.51
13.00	106.84	106.81	49.80	156.61
13.25	106.91	106.88	49.83	156.71
13.50	106.96	106.93	49.86	156.79
13.75	107.01	106.99	49.89	156.87
14.00	107.06	107.03	49.91	156.94
14.25	107.10	107.08	49.93	157.01
14.50	107.14	107.12	49.95	157.06
14.75	107.17	107.15	49.96	157.12
15.00	107.20	107.19	49.98	157.16

TOTAL MASS FLUXED AFTER 15.0 DAYS
WITH DELT 6.00 HRS IS 2.0 GRAMS

Appendix E

E.1 Relating Volatilization to Concentration

The following approach was taken to determine correlations for volatilization from different soils.

E.1.1 Sandy Loam Soil

As indicated in Figure 6-22, the volatilization rate concstant is not only a function of area/volume, but also initial PCE concentration in the aqueous phase. To determine the relationship, the slopes and intercepts for each concentration in Table 6-12 were plotted in Figs. E-1 and E-2. The data points were regressed linearly and the following equations were obtained:

$$m_{SL} = 0.6397-0.0117C_1 \quad (r^2=0.9593) \qquad \text{(E-1)}$$

$$Int_{SL} = 0.0232C_1-1.3159 \quad (r^2=0.9990) \qquad \text{(E-2)}$$

where

m_{SL} = slope (volatilization) from Fig. E-1,

Int_{SL} = intercept from Fig. E-2,

C_1 = concentration in soil, mg/kg.

Combining Eqs. E-1 and E-2, the equation for k_{SL} can be written as:

$$k_{SL} = 10^{((0.640-0.012C_1)(A/V)) + 0.023C_1-1.316} \qquad \text{(E-3)}$$

Equation E-3 requires the initial concentration of PCE in soil. Therefore an attempt was made to simplify it. From the data in Table 6-14 it is further observed that both the slopes and intercepts can be averaged. In doing so, Eq. E-4 is obtained which gives k_{SL} independent of C_1.

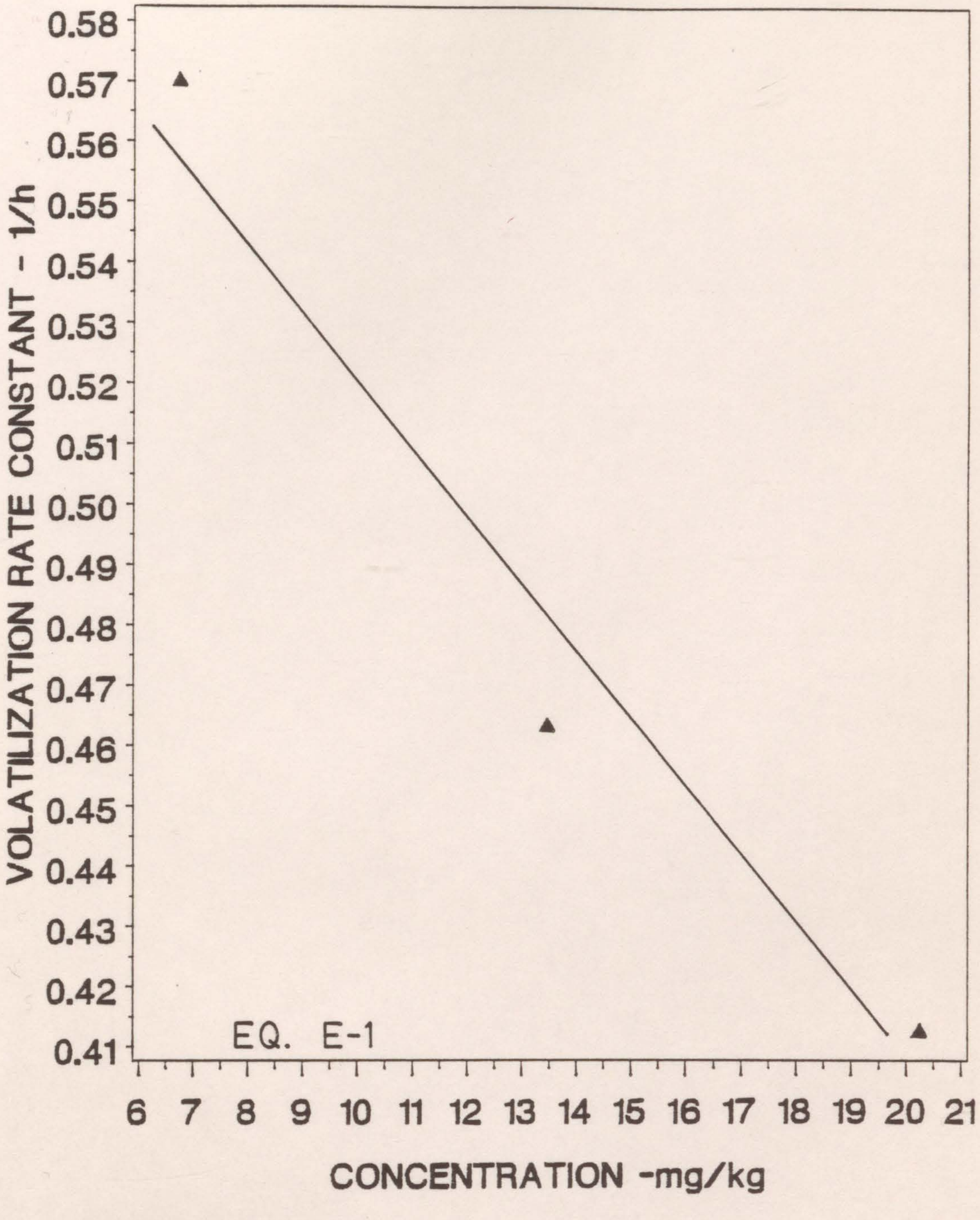

Figure E-1 VOLATILIZATION RATE CONSTANT VS CONCENTRATION FOR AQUEOUS PCE IN SANDY LOAM SOIL

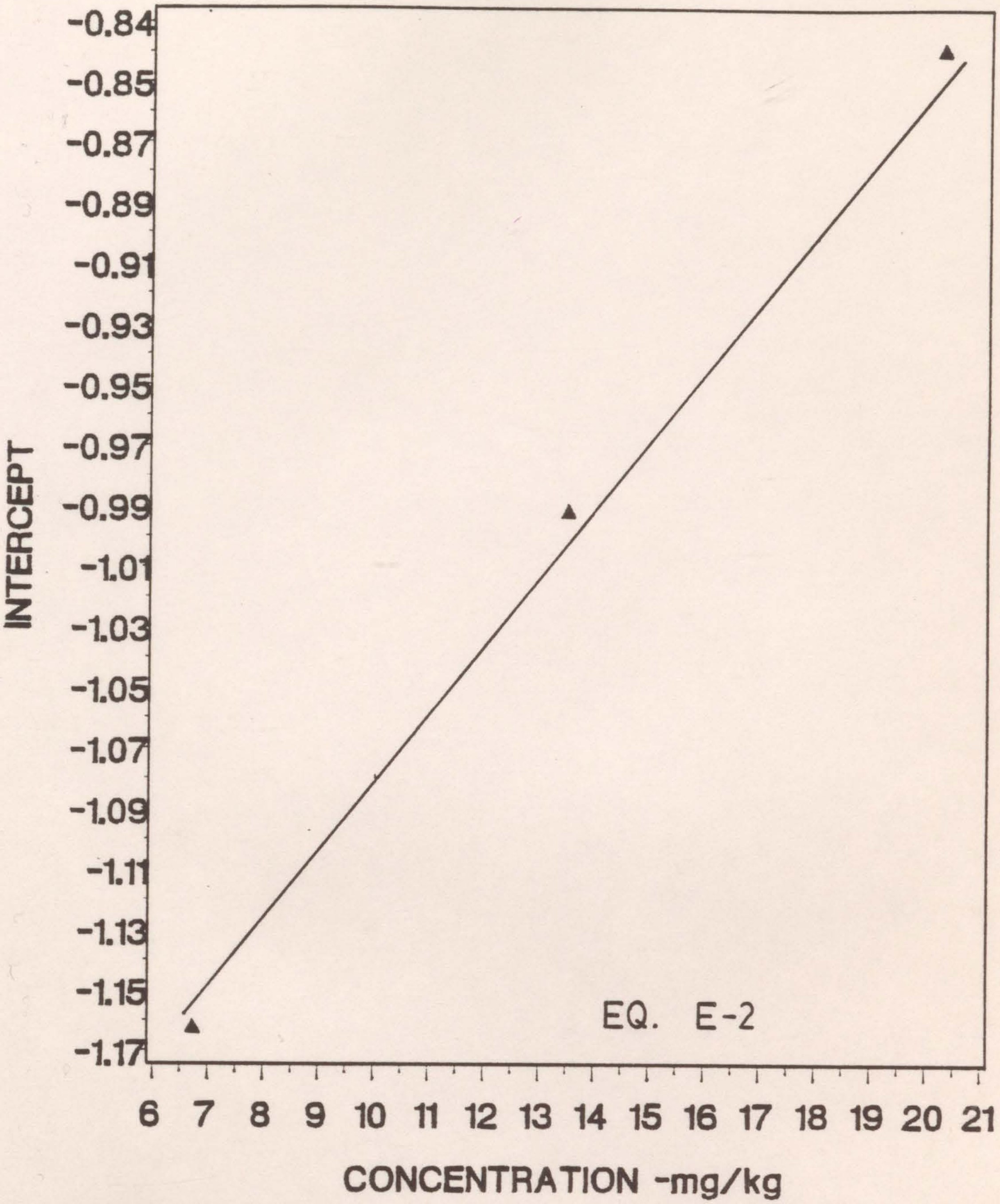

Figure E-2 INTERCEPT VS CONCENTRATION FOR AQUEOUS PCE IN SANDY LOAM SOIL

$$k_{SL} = 10^{(0.4822(A/V)-1.002)} \qquad \text{(E-4)}$$

In order to check whether Eq. E-4 is a valid approximation of Eq. E-3, concentration ratios at various times were calculated using both rate equations and are plotted in Fig. E-3. This plot indicates that the simplified rate equation is a good approximation of the original equation.

E.1.2 Organic Top Soil

The data in Table 6-14 were processed in the same manner as for the sandy loam soil. The results are plotted in Figs. E-4 and E-5. The following equations were obtained by using the regression data:

$$m_{ORG} = 0.0061C_1-0.0337 \quad (r^2=0.9843) \qquad \text{(E-5)}$$

$$Int_{ORG} = -0.0015C_1-0.7993 \quad (r^2=0.8252) \qquad \text{(E-6)}$$

The resulting rate equation for k_{ORG} is

$$k_{ORG} = 10^{((0.006C_1-0.034)(A/V)-0.0015C_1-0.799)} \qquad \text{(E-7)}$$

Again, Eq. E-7 is dependent on concentration in the soil. On analyzing the data in Table 6-15, it becomes apparent that only one simplification can be made. The intercept values can be averaged, but the slope values exhibit large variations. Therefore the new k_{ORG} equation is:

$$k_{ORG} = 10^{((0.006C_1-0.034)(A/V)-0.8527)} \qquad \text{(E-8)}$$

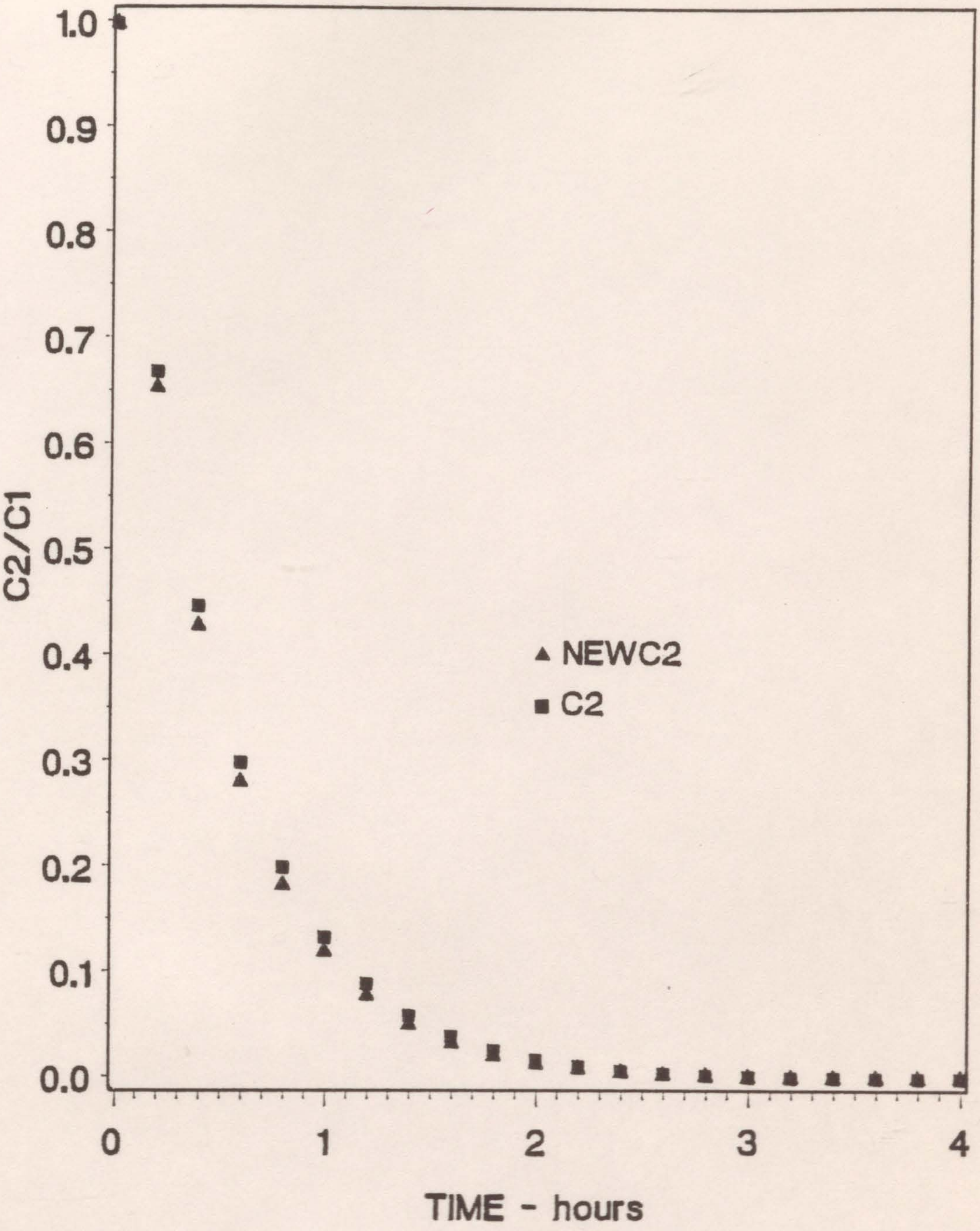

Figure E-3 NORMALIZED CONCENTRATION VS TIME FOR AQUEOUS PCE IN SANDY LOAM SOIL

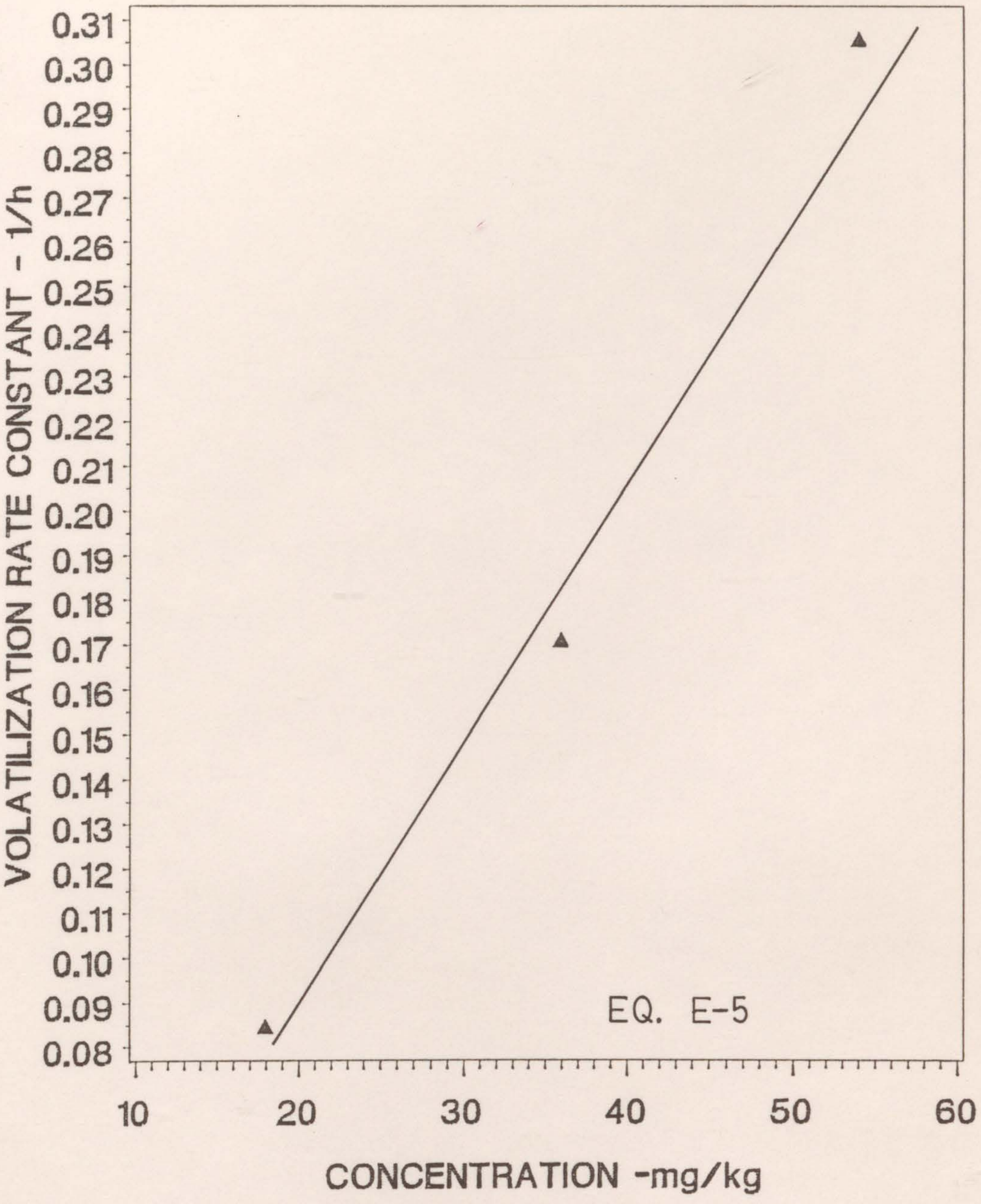

Figure E-4 VOLATILIZATION RATE CONSTANT VS CONCENTRATION FOR AQUEOUS PCE IN ORGANIC TOP SOIL

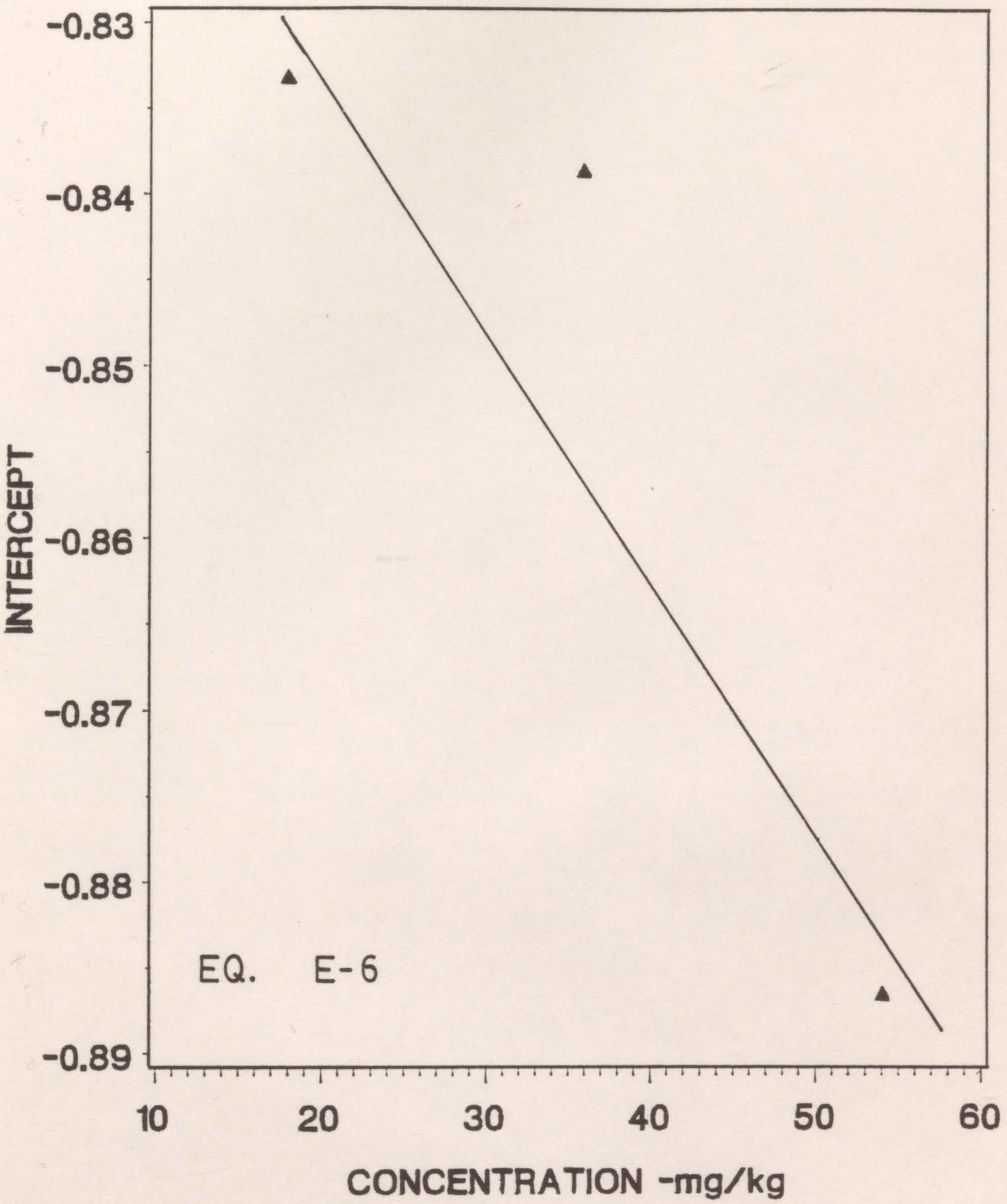

Figure E-5 INTERCEPT VS CONCENTRATION FOR AQUEOUS PCE IN ORGANIC TOP SOIL

By plotting the normalized concentration values using both rate equations in Fig. E-6 it is concluded that no significant difference exists between the simplified and the original equations for k_{ORG}.

E.2 Volatilization Rate Constants

For a proper comparison of the volatilization rates from water and soil, similar conditions must be used for both area/volume and initial aqueous concentration. Using an initial liquid concentration of 112.5 mg/L, the corresponding concentrations in soil for aqueous PCE are calculated below.

Sandy loam soil had a field capacity of 18 percent. Therefore if 1 L of water is applied to dry sandy loam soil, 5.556 kg of soil would be required to attain the proper moisture content. The mass of PCE present in the 1 L solution at 112.5 mg/L is 112.5 mg. If one assumes a uniform distribution of the PCE when applied to the soil, a concentration of 112.5/5.556 = 20.27 mg/kg would be attained. Using this concentration and an area/volume of 2.0 1/m in Equation 6-7, k_{SL} is 0.870 1/h.

When performing the aqueous PCE volatilization study for organic top soil, the soil had a moisture content of 48 percent. Following the steps of calculations performed for sandy loam soil, k_{ORG} is 0.124 1/h.

The volatilization rate from water surface, k_W, corresponding to a concentration of 112.5 mg/L and area/volume of 2.0 1/m is calculated from Eq. 6-1 as 0.045 1/h.

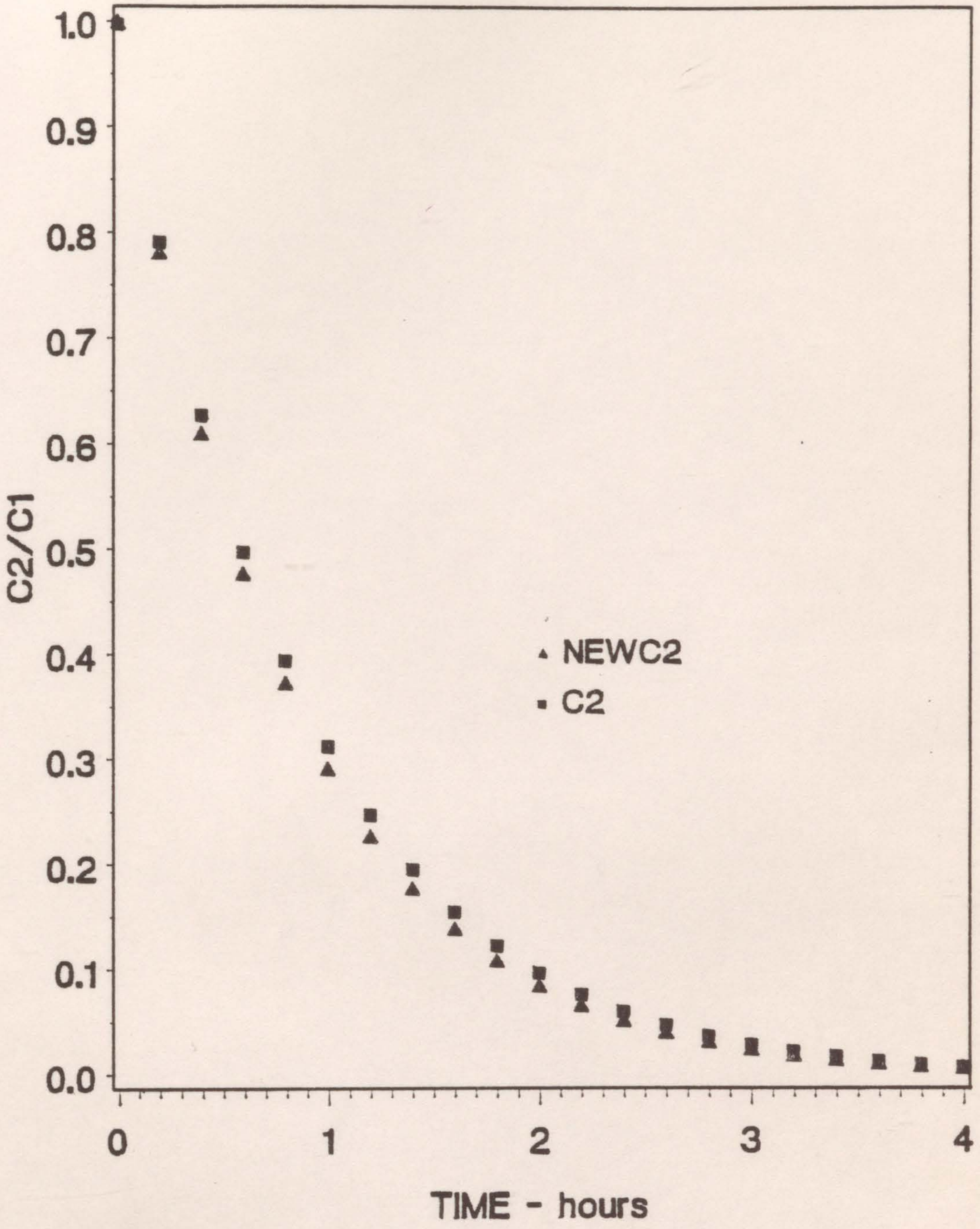

Figure E-6 NORMALIZED CONCENTRATION VS TIME FOR AQUEOUS PCE IN ORGANIC TOP SOIL

Appendix F

F.1 Computer Program to Simulate Unsaturated Moisture Movement

```
C
C     EVALUATION OF VERTICAL MOISTURE MOVEMENT USING THE
C     CRANK NICKOLSON APPROACH WITH NO FLUX
C
      EXTERNAL PRESD,NEWD,GREDUC
      REAL*8 M(41,2),FCC(41),CC(41,41),MSAT,MROOT,MFIELD,MC(41,6)
      REAL*8 MCAP,DT,DZ,FUNC,R1,R2,W(40),D(40),K(40),DAO,DBO
      REAL*8 DAN,DBN,KA,KB,TIME,DIS(41),VERT,MOS(41,2),TDAYS(6)
      REAL*8 DA,DB,DIFF(41),SHI(40),DISCAP,M1,M2,C1,C2,DEP
      INTEGER T,T1,TT,Z,TOTALT,ZTOT,ZZ
      OPEN(4,FILE='SOIL.DAT')
      DZ=20.0
      DT=30.0
      TOTALT=501
      N6=100
      MSAT=0.335
      MROOT=0.100
      MFIELD=0.243
      VERT=1.0
C
C     CONSTANTS FOR CAPILLARY MOISTURE EQUATIONS
C
      M1=-13.513514
      C1=1.750827E05
      M2=-38.461538
      C2=1.193777E13
      ZTOT=400/DZ+1
      LEVEL=ZTOT-1
      MMM=ZTOT-2
      R1=DT/(2.0*DZ**2)
      R2=DT/(2.0*DZ)
C
C     SETTING OF INITIAL MOISTURE CONDITIONS
C
C     WATER SPILL (MOISTURE @ SATURATION)
C
      N1=70.0/DZ+1
      DO 2 Z=1,N1
      MC(Z,1)=MSAT
2     M(Z,1)=MSAT
C
C     INTERMEDIATE ZONE (MOISTURE @ FIELD CAPACITY)
C
      N2=N1+1
      N3=300/DZ+1
      DO 3 Z=N2,N3
      MC(Z,1)=MFIELD
3     M(Z,1)=MFIELD
C
```

```
C     PARTIAL CAPILLARY (MOISTURE CLOSE TO SATURATION)
C
      N4=N3+1
      DO 4  Z=N4,LEVEL
      DEP=Z-1
      DISCAP=DABS(DEP*DZ-400.0)
      MCAP=DLOG10(DISCAP/C1)/M1
      MC(Z,1)=MCAP
4     M(Z,1)=MCAP
C
C     READING IN K(M), D(M) AND SHI(I) VALUES FOR DIFFERENT
C     MOISTURE CONTENTS FOR SANDY LOAM
C
      WRITE (*,281)
281   FORMAT('1',11X,'SOIL PROPERTIES FOR SANDY LOAM')
      WRITE (*,8)
      WRITE (*,9)
8     FORMAT('0','M-CM3/CM3',4X,'D(M)-CM2/MIN',6X,'K(M)-CM/MIN',
     &6X,'SHI(M)-CM')
9     FORMAT(1X)
      DO 6 I=8,34
      READ (4,300) W(I),D(I),K(I),SHI(I)
300   FORMAT(F3.2,E8.2,E8.2,F10.1)
6     WRITE (*,7) W(I),D(I),K(I),SHI(I)
7     FORMAT(2X,F4.2,8X,F10.7,6X,E12.3,6X,F10.2)
C
C     SETTING CC MATRIX TO ZERO
C
      DO 20 J=1,MMM
      DO 20 I=1,MMM
20    CC(I,J)=0.0
C
C     DETERMINATION OF MOISTURE CONTENT, WHERE T=1 AND T=T+1 ARE
C     THE ONLY MOISTURE CONTENTS STORED
C
      TDAYS(1)=0.0
      TT=0
      DO 10 T1=1,TOTALT
      T=T1-TT
      TIME=(TT)*DT
      IF(TIME.GT.1000)GO TO 770
      M(1,T+1)=MFIELD
      GO TO 771
770   M(1,T+1)=MROOT
771   M(ZTOT,T)=MSAT
      M(ZTOT,T+1)=MSAT
      MC(ZTOT,1)=MSAT
      L=0
C
C     INITIAL DETERMINATION OF DIFFUSION COEFFICIENT
C
      DO 11 Z=2,LEVEL
      CALL PRESD(Z,T,M,D,K,DAO,DBO,KA,KB,LEVEL)
      DA=DAO
      DB=DBO
      FUNC=M(Z-1,T)*R1*DA+M(Z,T)*(1-R1*(DA+DB))+M(Z+1,T)*R1*DB-
     &VERT*R2*(KB-KA)
```

```
      ZZ=Z-1
      IF(ZZ.EQ.1)GO TO 183
      IF(ZZ.EQ.MMM)GO TO 184
C
C     FCC IS FORCING FUNCTION
C     CC(Z,Z-1)=M(Z-1,T);CC(Z,Z)=M(Z,T);CC(Z,Z+1)=M(Z+1,T)
C
      FCC(ZZ)=FUNC
      CC(ZZ,ZZ-1)=-R1*DA
      CC(ZZ,ZZ)=1.0+R1*(DA+DB)
      CC(ZZ,ZZ+1)=-R1*DB
      GO TO 11
183   FCC(ZZ)=FUNC
      CC(ZZ,ZZ)=1.0+R1*(DA+DB)
      CC(ZZ,ZZ+1)=-R1*DB
      GO TO 11
184   FCC(ZZ)=FUNC
      CC(ZZ,ZZ-1)=-R1*DA
      CC(ZZ,ZZ)=1.0+R1*(DA+DB)
11    CONTINUE
      CALL GREDUC(FCC,CC,MMM)
C
C     SETTING MOISTURES AFTER TIME T+1, ACCOUNTING FOR CAPILLARY ZONE
C
      DO 15 II=1,MMM
      N7=N3-1
      IF(II.GT.N7)GO TO 115
      M(II+1,T+1)=FCC(II)
      GO TO 15
115   DEP=II
      DISCAP=DABS(DEP*DZ-400.0)
      MCAP=DLOG10(DISCAP/C1)/M1
      M(II+1,T+1)=MCAP
15    CONTINUE
C     N IS USED IN ACCURACY TEST OF MOISTURE
C     L INDICATES WHICH PASS T+1 IS AT
C
      N=1
60    L=L+1
C     RECALCULATION OF DIFFUSION COEFFICIENT FOR T+1 STEP
C
      DO 21 Z=2,LEVEL
      CALL PRESD(Z,T,M,D,K,DAO,DBO,KA,KB,LEVEL)
      CALL NEWD(Z,T,M,D,K,DAN,DBN,KA,KB,LEVEL)
      DA=(DAO+DAN)/2.0
      DB=(DBO+DBN)/2.0
      FUNC=M(Z-1,T)*R1*DA+M(Z,T)*(1-R1*(DA+DB))+M(Z+1,T)*R1*DB-
     &VERT*R2*(KB-KA)
C
C     FORCING FUNCTION
C
      ZZ=Z-1
      IF(ZZ.EQ.1)GO TO 283
      IF(ZZ.EQ.MMM)GO TO 284
      FCC(ZZ)=FUNC
      CC(ZZ,ZZ-1)=-R1*DA
      CC(ZZ,ZZ)=1.0+R1*(DA+DB)
```

```
      CC(ZZ,ZZ+1)=-R1*DB
      GO TO 21
283   FCC(ZZ)=FUNC
      CC(ZZ,ZZ)=1.0+R1*(DA+DB)
      CC(ZZ,ZZ+1)=-R1*DB
      GO TO 21
284   FCC(ZZ)=FUNC
      CC(ZZ,ZZ-1)=-R1*DA
      CC(ZZ,ZZ)=1.0+R1*(DA+DB)
21    CONTINUE
      CALL GREDUC(FCC,CC,MMM)
C
C     SETTING MOISTURES AFTER TIME T+1, ACOUNTING FOR CAPILLARY ZONE
C
      DO 215 II=1,MMM
      N7=N3-1
      IF(II.GT.N7)GO TO 1215
      MOS(II,N)=M(II+1,T+1)
      M(II+1,T+1)=FCC(II)
      GO TO 215
1215  DEP=II
      DISCAP=DABS(DEP*DZ-400.0)
      MCAP=DLOG10(DISCAP/C1)/M1
      MOS(II,N)=M(II+1,T+1)
      M(II+1,T+1)=MCAP
215   CONTINUE
      N=2
C
C     IF L=1, FIRST PASS FOR T+1 MOISTURE
C
      IF(L.EQ.1)GO TO 60
      YY=0.0
C
C     CHECKING ACCURACY OF MOISTURE CONTENT
C
      DO 50 I=1,MMM
      DIFF(I)=DABS(MOS(I,2)-MOS(I,1))
      IF(DIFF(I).LT.0.001)GO TO 50
      MOS(I,1)=MOS(I,2)
      YY=1.0
50    CONTINUE
      IF(YY.EQ.1.0)GO TO 60
C
C     SETTING OF CALCULATED MOISTURE OF T+1 TO T
C
      DO 49 Z=1,ZTOT
49    M(Z,T)=M(Z,T+1)
      TT=TT+1
      IF(TT.EQ.101)GO TO 70
      IF(TT.EQ.201)GO TO 71
      IF(TT.EQ.301)GO TO 72
      IF(TT.EQ.401)GO TO 73
      IF(TT.EQ.501)GO TO 74
      GO TO 75
70    LL=2
      GO TO 77
71    LL=3
```

```
      GO TO 77
72    LL=4
      GO TO 77
73    LL=5
      GO TO 77
74    LL=6
77    CONTINUE
C
C     M IS MOISTURE CONTENT AT T+1
C     MC USED TO STORE MOISTURE CONTENT FOR DESIRED TIME INTERVAL
C
      DO 76  Z=1,ZTOT
      TDAYS(LL)=TIME/60.0/24.0
76    MC(Z,LL)=M(Z,T+1)
75    CONTINUE
10    CONTINUE
      WRITE (*,80) DT,DZ
80    FORMAT(’1’,4X,’MOISTURE AFTER RELEASE IN MINUTES/DAYS, WITH DT=’,
     &F5.1,1X,’MIN. AND DZ=’,F5.1,1X,’CM.’)
      WRITE(*,40)(TDAYS(J),J=1,6)
40    FORMAT(’0’,7X,’Z-CM’,6F10.2)
      WRITE (*,82)
82    FORMAT(1X)
      DO 83 Z=1,ZTOT
      DIS(Z)=(Z-1)*DZ
83    WRITE(*,84) DIS(Z),(MC(Z,J),J=1,6)
84    FORMAT(7X,F5.1,6F10.3)
      STOP
      END
      SUBROUTINE NEWD(Z,T,M,D,K,DAN,DBN,KA,KB,LEVEL)
C
C     CALCULATION OF DIFFUSION AT TIME STEP T+1
C
      REAL*8 M(41,2),D(40),K(40),D4,D5,D6,C1,C2,C3,DAN
      REAL*8 DBN,KA,KB
      INTEGER Z,T,ZTOT
      C1=100.0*(M(Z-1,T+1))
      L1=C1
      C2=100.0*(M(Z,T+1))
      L2=C2
      C3=100.0*(M(Z+1,T+1))
      L3=C3
      D4=D(L1)+(D(L1+1)-D(L1))*(C1-1.0*L1)
      D5=D(L2)+(D(L2+1)-D(L2))*(C2-1.0*L2)
      D6=D(L3)+(D(L3+1)-D(L3))*(C3-1.0*L3)
      KA=K(L1)+(K(L1+1)-K(L1))*(C1-1.0*L1)
      KB=K(L3)+(K(L3+1)-K(L3))*(C3-1.0*L3)
      DAN=(D4+D5)/2.0
      DBN=(D5+D6)/2.0
      RETURN
      END
      SUBROUTINE PRESD(Z,T,M,D,K,DAO,DBO,KA,KB,LEVEL)
C
C     CALCULATION ON DIFFUSION AT TIME T
C
      REAL*8 M(41,2),D(40),K(40),D1,D2,D3,C1,C2,C3,DAO
      REAL*8 DBO,KA,KB
```

```
      INTEGER Z,T,ZTOT
      C1=100.0*(M(Z-1,T))
      L1=C1
      C2=100.0*(M(Z,T))
      L2=C2
      C3=100.0*(M(Z+1,T))
      L3=C3
      D1=D(L1)+(D(L1+1)-D(L1))*(C1-1.0*L1)
      D2=D(L2)+(D(L2+1)-D(L2))*(C2-1.0*L2)
      D3=D(L3)+(D(L3+1)-D(L3))*(C3-1.0*L3)
      KA=K(L1)+(K(L1+1)-K(L1))*(C1-1.0*L1)
      KB=K(L3)+(K(L3+1)-K(L3))*(C3-1.0*L3)
      DAO=(D1+D2)/2.0
      DBO=(D2+D3)/2.0
      RETURN
      END
      SUBROUTINE GREDUC (FCC,CC,NEQNS)
      REAL*8 FCC(41),CC(41,41),A,B
C
C     REDUCTION OF MATRIX WITHOUT PIVOTING
C
      MM=0
      DO 85 I=2,NEQNS
      MM=MM+1
      A=CC(I,I-1)
      B=CC(I-1,I-1)
      DO 86 J=MM,NEQNS
      CC(I,J)=CC(I-1,J)*A-CC(I,J)*B
86    CONTINUE
85    FCC(I)=FCC(I-1)*A-FCC(I)*B
C
C     BACK SUBSITUTION FOR CONCENTRATIONS
C     ***NOTE***
C     FORCE VECTOR IS DESTROYED
C
      I=NEQNS
      FCC(I)=FCC(I)/CC(I,I)
78    I=I-1
      FCC(I)=(FCC(I)-CC(I,I+1)*FCC(I+1))/CC(I,I)
      IF(I.NE.1)GO TO 78
C
C     RESTORE CC MATRIX TO ZERO
C
      DO 15 J=1,NEQNS
      DO 15 I=1,NEQNS
15    CC(I,J)=0.0
      RETURN
      END
```

Table F-1 Sandy Loam Soil Properties for Moisture Model
[Remson *et al*., 1965]

	D	K	Ψ
	cm2/min	cm/min	cm
.08	1.00E-7	1.0E-13	-100000.0
.09	9.00E-6	1.0E-10	-10000.0
.10	2.30E-4	1.8E-09	-6400.0
.11	6.40E-4	3.4E-09	-5000.0
.12	1.30E-3	6.0E-09	-3800.0
.13	2.30E-3	1.1E-08	-3000.0
.14	3.70E-3	3.1E-08	-2450.0
.15	5.50E-3	9.4E-08	-2025.0
.16	8.40E-3	2.0E-07	-1700.0
.17	1.15E-2	3.6E-07	-1440.0
.18	1.60E-2	6.2E-07	-1200.0
.19	2.20E-2	1.0E-06	-960.0
.20	3.00E-2	1.9E-06	-770.0
.21	4.00E-2	3.3E-06	-560.0
.22	5.20E-2	6.2E-06	-360.0
.23	6.90E-2	1.2E-05	-200.0
.24	8.70E-2	2.5E-05	-99.0
.25	1.10E-1	5.6E-05	-50.0
.26	1.48E-1	1.1E-04	-37.5
.27	2.01E-1	2.1E-04	-29.0
.28	2.95E-1	4.2E-04	-23.0
.29	4.50E-1	7.6E-04	-18.2
.30	7.50E-1	1.4E-03	-14.4
.31	1.85E 0	3.5E-03	-10.0
.32	3.60E 0	7.0E-03	-7.0
.33	6.00E 0	1.3E-02	-4.8
.34	1.00E 1	3.0E-02	-1.0

F.2 Contaminant Transport Simulation Program

```
C
C     EVALUATION OF VERTICAL CHEMICAL MOVEMENT USING THE
C     CRANK NICKOLSON APPROACH
C
      EXTERNAL GREDUC
      REAL*8 C(41,2),FCC(41),CC(41,41),MSAT,MROOT,MFIELD,CONC(41,20)
      REAL*8 DT,DZ,FUNC,KP,MOIST,NA,DW,DV,VW,VV,LENGTH,A,D,V,TIME
      REAL*8 DIS(41),TDAYS(20),DP,VP,Y,CO,DENS,KH,BREAK,DIFF,DAVP
      REAL*8 IMUL,KL,DI,VI,U,UP,UW,US,UV,UI,ACONC,POROS,PERPUR,DTT,DZZ
      INTEGER T,T1,TT,Z,TOTALT,ZTOT,ZZ,SOIL
      OPEN(4,FILE='CHEMORG.DAT')
      READ(4,*)SOIL,POROS,DENS,MOIST,KP,KH,PERPUR,KL
C
C     ALL INPUT DATA ARE SI UNITS, KG,M AND DAYS EXCEPT FOR DISTANCE
C     STEPS AND TOTAL LENGTH OF PROFILE SIMULATION. THEY ARE IN CM, BUT
C     PROGRAM CONVERTS THEM TO METERS
C
C     SOIL IDENTIFIES SOIL TYPE, 1 FOR SANDY LOAM, 2 FOR ORGANIC
C     POROS IS POROSITY OF SOIL
C     MOIST IS VOLUMETRIC MOSITURE CONTENT IN UNIT VOLUME OF SOIL
C     PERPUR IS PERCENTAGE OF FLUID CONSIDERED TO BE PURE CHEMICAL
C
C     DW IS DISPERSION OF AQUEOUS FLUID IN SOIL
C     DEVAP IS DIFFUSION OF CHEMCIAL INTO AIR
C     DI IS DISPERSION OF IMMISCIBLE FLUID IN SOIL
C
      READ(4,*)DW,DVAP,DI,VW,VV,VI,CO
      READ(4,*)UW,US,UV,UI
      IMUL=PERPUR*MOIST
      NA=POROS-MOIST-IMUL
C
C     DV IS DIFFUSION OF CHEMICAL INTO AIR, CORRECTED FOR TORUOSITY
C
      DV=(NA**(10/3)/POROS**2)*DVAP
      IF(SOIL.EQ.1)WRITE(*,500)
      IF(SOIL.EQ.2)WRITE(*,501)
500   FORMAT(1X,'PCE PENETRATION IN SANDY LOAM SOIL')
501   FORMAT(1X,'PCE PENETRATION IN ORGANIC TOP SOIL')
      WRITE(*,502)
502   FORMAT('0','******SOIL CHARACTERISTICS******')
      WRITE(*,503)
503   FORMAT('0','**DISPERSION COEFFICIENTS--M2/DAY**')
      WRITE(*,504)DW,DV,DI
504   FORMAT(1X,'MOISTURE',E10.3,3X,'VAPOUR',E10.3,3X,'PURE PCE',E10.3)
      WRITE(*,505)
505   FORMAT('0','**VELOCITY OF VARIOUS PHASES (ADVECTION)--M/DAY**')
      WRITE(*,506)VW,VV,VI
506   FORMAT(1X,'AQUEOUS',F8.4,3X,'VAPOUR',F8.4,3X,'PURE PCE',F8.4)
      WRITE(*,507)
507   FORMAT('0','**VOID VOLUMES OF THE VARIOUS PHASES--M3/M3**')
```

```
      WRITE(*,508)MOIST,NA,IMUL
508   FORMAT(1X,'AQUEOUS',F8.4,3X,'VAPOUR',F8.4,3X,'PURE PCE',F8.4)
      WRITE(*,509)
509   FORMAT('0','**DECAY RATES--1/DAY**')
      WRITE(*,510)UW,US,UV,UI
510   FORMAT(1X,'AQUEOUS',F5.2,3X,'ADSORBED',F5.2,3X,'VAPOUR',F5.2,3X,
     *'PURE PCE',F5.2)
      WRITE(*,511)
511   FORMAT('0','**PARTITION COEFFICIENTS**')
      WRITE(*,512)KP,KH,KL
512   FORMAT(1X,'KP',F7.3,1X,'M3/KG',3X,'KH',F7.3,3X,'KL',F8.1)
      WRITE(*,513)
513   FORMAT('0','**PHYSICAL CONSTANTS**')
      WRITE(*,514)POROS,DENS
514   FORMAT(1X,'POROSITY',F6.3,3X,'DENSITY',F7.1,1X,'KG/M3')
      READ(4,*)DZZ,DTT,L,TOTALT,NN
C
C     DZZ AND L ARE IN CENTIMETERS
C     DT IS IN MINUTES
C     NN IS FREQUENCY OF PRINTING
C
      DT=DTT/(60*24)
      DZ=DZZ/100.0
      LENGTH=L/100.0
      WRITE(*,515)
515   FORMAT('0','**MODEL PARAMETERS**')
      WRITE(*,516)DZZ,DTT
516   FORMAT(1X,'DZ',F5.1,1X,'CM',4X,'DT',F5.1,1X,'MIN')
      WRITE(*,517)
517   FORMAT('0','**LENGTH OF SOIL PROFILE BEING SIMULATED**')
      WRITE(*,518)LENGTH
518   FORMAT(1X,'SOIL DEPTH',F6.2,1X,'M')
      WRITE(*,519)
519   FORMAT('0','**SOLUBILITY OF CHEMICAL IN WATER AT ROOM TEMP.**')
      WRITE(*,520)CO*1E+03
520   FORMAT(1X,'CO',F6.1,1X,'MG/L')
      ZTOT=L/DZZ+2
      LEVEL=ZTOT-1
      NEQNS=LEVEL-1
C
C     CONSTANTS USED IN PROGRAM
C     BREAK IS BREAKTHROUGH CONCENTRATION IN MG/L
C
      READ(4,*)BREAK
      A=MOIST+DENS*KP+NA*KH+IMUL*KL
      D=MOIST*DW+DV*NA*KH+IMUL*KL*DI
      V=-MOIST*VW-NA*VV*KH-IMUL*VI*KL
      U=-MOIST*UW-US*DENS*KP-NA*UV*KH-UI*KL*IMUL
      UP=U/A
      DP=D/A
      VP=V/A
      Y=(DT*DP)/(2.0*DZ**2.0)
C
C     SETTING OF INITIAL CONCENTRATION CONDITIONS
C
      C(1,1)=CO
      CONC(1,1)=CO*1.0E+03
```

```
      DO 2 Z=2,ZTOT
      C(Z,1)=0
2     CONC(Z,1)=0
C
C     SETTING CC MATRIX TO ZERO
C
      DO 20 J=1,NEQNS
      DO 20 I=1,NEQNS
20    CC(I,J)=0.0
C
C     DETERMINATION OF CHEMICAL CONCENTRATION, WHERE T=1 AND T=T+1 ARE
C     THE ONLY CHEMICAL CONTENTS STORED
C
      TDAYS(1)=0.0
      T1=0
      N=1
      DO 10 TT=2,TOTALT
      T=TT-T1
      C(ZTOT,T)=C(LEVEL,T-1)
      DO 21 Z=2,LEVEL
      FUNC=C(Z,T-1)+Y*(C(Z-1,T-1)+C(Z+1,T-1)-2.0*C(Z,T-1))+
     *VP*DT/(2*DZ)*(C(Z+1,T-1)-C(Z-1,T-1))+UP*DT*C(Z,T-1)
C
C     FORCING FUNCTION
C
      ZZ=Z-1
      IF(ZZ.EQ.1)GO TO 283
      IF(ZZ.EQ.NEQNS)GO TO 284
      FCC(ZZ)=FUNC
      CC(ZZ,ZZ-1)=-Y
      CC(ZZ,ZZ)=1.0+2.0*Y
      CC(ZZ,ZZ+1)=-Y
      GO TO 21
283   FCC(ZZ)=FUNC
      CC(ZZ,ZZ)=1.0+2.0*Y
      CC(ZZ,ZZ+1)=-Y
      GO TO 21
284   FCC(ZZ)=FUNC
      CC(ZZ,ZZ-1)=-Y
      CC(ZZ,ZZ)=1.0+2.0*Y
21    CONTINUE
      CALL GREDUC(FCC,CC,NEQNS)
      DO 22 Z=1,NEQNS
22    C(Z+1,2)=FCC(Z)
C
C     SETTING OF CALCULATED CONCENTRATIONS OF T+1 TO T
C
      DO 49 Z=2,ZTOT
49    C(Z,T-1)=C(Z,T)
C
C     CONVERTING CONCENTRATIONS TO MG/L AND STORING VALUES FOR PRINTING
C
      ACONC=C(LEVEL,1)*1.0E+03
      DIFF=DABS(BREAK-ACONC)
      IF(DIFF.GT.0.375)GO TO 60
      TIME=(TT-1)*DTT/60.0/24.0
60    T1=T1+1
```

```
      COUNTR=(TT/NN)/N
      IF(COUNTR.NE.1)GO TO 10
      DO 70 Z=1,ZTOT
      CONC(Z,N+1)=C(Z,1)*1.0E+03
70    TDAYS(N+1)=(TT-1)*DTT/60.0/24.0
      N=N+1
10    CONTINUE
C
C     PRINTING CALCULATED VALUES
C
      WRITE(*,75)BREAK,TIME
75    FORMAT('0','BREAKTHROUGH CONCENTRATION OF',F6.3,1X,'OCCURS AT',
     *F6.2,1X,'DAYS')
      WRITE (*,79)(TDAYS(I),I=1,N)
79    FORMAT('0',7X,'Z-M',2X,6F10.3)
      WRITE(*,80)
80    FORMAT(1X)
      DO 81 Z=1,ZTOT
      DIS(Z)=(Z-1)*DZ
81    WRITE(*,40)DIS(Z),(CONC(Z,I),I=1,N)
40    FORMAT(1X,7F11.3)
      STOP
      END
      SUBROUTINE GREDUC (FCC,CC,NEQNS)
      REAL*8 FCC(41),CC(41,41),A,B
C
C     REDUCTION OF MATRIX WITHOUT PIVOTING
C
      MM=0
      DO 85 I=2,NEQNS
      MM=MM+1
      A=CC(I,I-1)
      B=CC(I-1,I-1)
      DO 86 J=MM,NEQNS
      CC(I,J)=CC(I-1,J)*A-CC(I,J)*B
86    CONTINUE
85    FCC(I)=FCC(I-1)*A-FCC(I)*B
C
C     BACK SUBSITUTION FOR CONCENTRATIONS
C     ***NOTE***
C     FORCE VECTOR IS DESTROYED
C
      I=NEQNS
      FCC(I)=FCC(I)/CC(I,I)
78    I=I-1
      FCC(I)=(FCC(I)-CC(I,I+1)*FCC(I+1))/CC(I,I)
      IF(I.NE.1)GO TO 78
C
C     RESTORE CC MATRIX TO ZERO
C
      DO 15 J=1,NEQNS
      DO 15 I=1,NEQNS
15    CC(I,J)=0.0
      RETURN
      END
```

```
PCE PENETRATION IN ORGANIC TOP SOIL

******SOIL CHARACTERISTICS******

**DISPERSION COEFFICIENTS--M2/DAY**
MOISTURE  .216E-03   VAPOUR  .428E-03   PURE PCE  .144E-03

**VELOCITY OF VARIOUS PHASES (ADVECTION)--M/DAY**
AQUEOUS   .4630   VAPOUR  -.4630   PURE PCE   .0200

**VOID VOLUMES OF THE VARIOUS PHASES--M3/M3**
AQUEOUS   .3270   VAPOUR   .1953   PURE PCE   .0327

**DECAY RATES--1/DAY**
AQUEOUS  .00   ADSORBED  .00   VAPOUR  .00   PURE PCE  .00

**PARTITION COEFFICIENTS**
KP   .014 M3/KG   KH   .482   KL 11055.0

**PHYSICAL CONSTANTS**
POROSITY  .555   DENSITY 1000.0 KG/M3

**MODEL PARAMETERS**
DZ  5.0 CM    DT 45.0 MIN

**LENGTH OF SOIL PROFILE BEING SIMULATED**
SOIL DEPTH   .80 M

**SOLUBILITY OF CHEMICAL IN WATER AT ROOM TEMP.**
CO 150.0 MG/L

BREAKTHROUGH CONCENTRATION OF 7.500 OCCURS AT 31.78 DAYS

       Z-M        .000      6.219     12.469     18.719     24.969     31.219

       .000    150.000    150.000    150.000    150.000    150.000    150.000
       .050       .000    125.479    136.348    132.587    133.497    133.441
       .100       .000     84.627    138.359    133.994    132.676    133.680
       .150       .000     41.568    123.950    138.592    132.227    133.331
       .200       .000     15.716     92.609    138.689    134.783    132.287
       .250       .000      4.790     57.500    125.946    139.028    132.348
       .300       .000      1.218     30.123    100.508    138.810    135.111
       .350       .000       .265     13.560     70.049    128.401    138.898
       .400       .000       .050      5.334     42.881    107.411    138.909
       .450       .000       .008      1.860     23.281     80.658    130.675
       .500       .000       .001       .582     11.323     54.464    113.297
       .550       .000       .000       .165      4.980     33.252     89.799
       .600       .000       .000       .043      1.997     18.479     65.018
       .650       .000       .000       .010       .735      9.410     43.163
       .700       .000       .000       .002       .250      4.414     26.274
       .750       .000       .000       .000       .080      1.946     15.208
       .800       .000       .000       .000       .021       .671      6.645
       .850       .000       .000       .000       .020       .662      6.584
Stop - Program terminated.
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VITA AUCTORIS

Richard Gustav Zytner was born on September 18, 1958 in Leamington, Ontario, Canada. He graduated from Leamington District Secondary School in June, 1977 and entered the University of Windsor, Windsor, Ontario in September, 1978. In June, 1982 he graduated with a Bachelor of Applied Science Degree in Civil Engineering and received the Board of Governor's Medal.

He obtained his Master of Applied Science degree in Civil Engineering, from the University of Windsor in June 1984. Immediately thereafter, he was accepted into the Faculty of Graduate Studies at the University of Windsor in a program leading to the degree of Doctor of Philosophy in Civil Engineering. This included a 10 month visit to the University of Stuttgart, West Germany, as a research scholar.