PREDICTION OF ORGANIC CHEMICAL LEACHATE CONCENTRATION FROM SOIL SAMPLES

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ABSTRACT

Volatile organic compound (VOC) contamination of soil is common in the United States. Once soil becomes contaminated, precipitation may infiltrate through the soil and carry contaminants downward into the groundwater. Understanding VOC leaching from soil is important because groundwater is the primary source of drinking water for about 50 percent of the United States and VOCs are known to negatively affect human health. Methods are needed to assess how VOCs leach from soil. In order to model mass transport of VOCs at sites where subsurface contamination is present, their desorption processes must be understood.

Quantification of desorption rates will allow use of the advection dispersion equation with a time varying influent boundary condition and other simple models. An empirical leach rate relation is developed based upon basic soil parameters. It can be used to evaluate VOCs leaching from a body of soil.

Constant head reservoirs were developed and used to conduct column desorption studies using four VOCs - toluene, methylene chloride, trichloroethylene, and m-xylene - and three soils - topsoil, sand, and clay. In addition, batch isotherm studies were performed on the same soils and chemicals. A gas chromatrograph was used to analyze samples.

An empirical leach rate constant relation was statistically developed from curve fits to the column data. The leach rate curve fits were not continuous functions and reached asymptotic concentrations above zero. Long term and short term leach rates had distinctively different rates. The difference in the long and short term leach rates and the lack of a single continuous function describing leach rates would suggest different rate limiting process control desorbtion over time.

The empirical leach rate relation will help consultants and regulators assess the impact of VOC contaminated soil on groundwater quality, and quantify potential human health risks.

ACKNOWLEDGMENTS

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CHAPTER 1

INTRODUCTION

1.1 VOLATILE ORGANIC COMPOUND CONTAMINATION

Volatile organic compounds (VOC) are hazardous to human health and the environment. EPA developed a priority pollutant list of substances which may be carcinogenic, mutagenic, or teratogenic, or are known to have toxic effects on humans or aquatic organisms. A number of VOCs are present on the priority pollutant list. Listed pollutants include trichloroethylene, toluene, and methylene chloride. These compounds are also common soil and groundwater contaminants.

Sites with VOC contaminated soil and groundwater are ubiquitous in the United States. The number of contaminated sites may be attributed to the widespread use of solvents and petroleum products which contain VOCs, combined with a lack of understanding of the significant risks associated with VOCs. Consequently handling practices and safeguards were often inappropriate and resulted in soil and groundwater contaminated with VOCs.

Laws were enacted to address growing concerns over contaminated soil and groundwater. These laws include the Safe Drinking Water Act (SDWA), Toxic Substances Control Act (TSCA), Resource Conservation and Recovery Act (RCRA), and Comprehensive Environmental Response Compensation and Liability Act (CERCLA) on the national level, and Department of Industry Labor and Human Relations regulation 10

(DILHR 10) in the state of Wisconsin. These laws regulate a wide range of activities including investigation and remediation of soil and groundwater contamination.

VOC releases to the subsurface may follow a number of different scenarios. In the past, spent solvents were kept in unlined waste lagoons or poured on the soil surface as a means of disposal. Other releases include accidental spills and leaks from underground storage tanks (USTs). In any scenario, once VOCs are released to the soil, precipitation may infiltrate into the soil and leach the VOCs downward through the vadose zone and into the groundwater in underlying aquifers. Groundwater containing the leached VOCs may then be used for human consumption creating a health risk or alternatively may discharge to surface waters and contaminate them.

1.2 PRESENT MODELING PROBLEMS

Methods to evaluate VOC leaching from contaminated soil are needed to assess potential human health risks and identify remedial strategies. Several models are currently used to evaluate VOC mass transport and may be used to model VOC leaching from soil at contaminated sites. However, in order to use these models a leach rate must be quantified. In addition, the models can be costly and time consuming to apply.

The partial differential form of the advection-dispersion equation is the theoretical contaminant mass transport model. The equation may be used to model VOC movement through the vadose zone into groundwater. However, application of this equation in this scenario requires a time varying influent boundary condition which quantifies VOC leach

rates. Determining leach rates for a specific site and calibrating and running the model on the computer is time consuming and costly.

Analytical solutions to the advection dispersion equation have been developed by van Genuchten (1981). To apply these solutions to VOCs leaching from a body of soil, a leach rate constant is also required. Again, VOC leach rates have not been quantified. Use of these equations would also require computer modeling which may be time consuming and costly.

VOC leach rates need to be quantified so that models that are presently available can be used. In addition, a simplified method to evaluate VOCs leaching from soil would save both time and money.

1.3 OBJECTIVES

The objectives of this research are to:

(1) Conduct a literature search of research on VOC mass transport and modeling in the subsurface

(2) Develop a constant head influent reservoir that minimizes VOC losses.

(3) Perform desorption studies and use the results of these studies to adapt an empirical leach rate model, developed by Rodgers and Associates (1988) for low level nuclear waste containment facilities, to VOCs leaching from soil.

(4) Perform batch isotherm and desorption studies using four VOCs - methylene chloride, trichloroethylene, toluene, and m-xylene - and three soils - sand, clay and topsoil.

(5) Develop a VOC leach rate predictive equation based on the results of these studies.

1.4 EXPECTED RESULTS AND BENEFITS

The literature search will help current understanding of subsurface mass transport processes. The constant head influent reservoir may be useful to others investigating VOC mass transport. The leach rate predictive equation will be useful to regulators and consultants assessing the human heath risks of VOC contaminated sites.

CHAPTER 2

LEACHING OF VOLATILE ORGANIC COMPOUNDS IN THE SUBSURFACE

VOCs released to the subsurface will be sorbed to soils, degraded biologically and/or chemically, volatilized through soil pore space and leached further down by gravitational flow. Contaminant physical properties, subsurface conditions, physical processes, and infiltration rates will affect subsurface leaching and mass transport. Current understanding of the complex processes affecting subsurface contamination is limited.

2.1 VOLATILE ORGANIC COMPOUNDS

Volatile organic compounds are a common subsurface contaminant. VOCs are widely used as solvents and are found in fuels such as gasoline. EPA's priority pollutant list identifies 129 toxic substances that are believed to be harmful to the environment and may effect human health. The list contains 31 organic compounds which are purgable and may be considered volatile (Environmental Testing and Certification Corp., 1989).

2.1.1 VOC Properties

The physical properties of a VOC are a function of its structure (Reid, 1987) Compound properties in turn will affect its fate in the subsurface. The following properties and partitioning coefficients affect VOC fate in the subsurface (Hern, 1987).

Solubility (S) is the concentration of a contaminant that will form a saturated solution in water at a given temperature. Solubility gives an indication of a compound's tendency to partition into soil pore water. VOCs typically have low solubilities (about 1000

mg/L or less). Because of their low solubility, VOCs are often referred to as hydrophobic. The hydrophobic nature of many VOCs will result in significant partitioning of VOCs to the solid phase (soil), in order to escape the aqueous phase.

Vapor pressure (Vp) is the vapor pressure exerted by the gaseous phase of a compound in equilibrium with its liquid or solid phase at a given temperature. Vapor pressure indicates the tendency of a compound to be present in the vapor phase. VOCs typically have relatively high vapor pressures; hence, they are referred to as volatile compounds. Due to their high vapor pressures, VOCs may partition significantly to the vapor phase from either the solid or liquid phase.

Henry's constant (Hc) is the ratio of the equilibrium concentration in the liquid phase and the concentration in the vapor phase.

K_{ow} is the octanol water partition coefficient. It is the ratio of the concentration of a compound in octanol over its concentration in water at equilibrium.

K_{oc} is the organic carbon/water partition coefficient. It is the ratio of the concentration of a compound sorbed to carbon divided by the concentration in the water at equilibrium.

Specific gravity (SG) is the density of a compound relative to the density of water. Compounds that are denser than water, specific gravity greater than 1 will sink and those less dense than water, specific gravity less than 1, tend to float.

Viscosity (V) is a measure of the internal friction of a fluid. The more viscous the fluid (higher viscosity), the more resistant it is to flow. Thus high viscosity substances will

tend to become immobile in the soil due to their resistance to flow. VOCs typically have low viscosities (less than water).

Priority pollutant VOC and their properties are listed in Table 2-1.

2.1.2 Non-Aqueous Phase Liquid (NAPL)

VOCs may be introduced to the subsurface in solvents, fuels, oils, or process chemicals. Thus, VOC may be present in mixtures, or as a pure phase. When the substance contaminating soil is immiscible in water, it may be described as a nonaqueous phase liquid (NAPL). Generally, the presence or absence of a NAPL may be identified by determining whether a compound is present above its solubility limit. NAPLs can be characterized as single compounds or complex mixtures and may not consist exclusively of VOCs.

For NAPLs where the lighter fraction VOCs are a small part of a heavier NAPL fraction containing longer chain aliphatics, VOC may leach from the NAPL by dissolution into the soil pore water (Weber, 1991). Thereafter, VOCs may leach independently of the NAPL.

NAPL leaching properties may be different than the properties of its individual components. The density, viscosity, solubility and the vapor pressure of the NAPL differ from those for a specific compound within the NAPL. In a sense, the physical properties of the NAPL are a composite of the properties of the different compounds that it contains.

Table 2-1
Properties of Volatile Compounds/Purgable Organics on EPA's Priority Pollutant List

Compound	Molecular Weight[1] (g/mol)	Specific Gravity[1]	Reference Temp. (C)	Viscosity[2] (mNsm^{-2})	Reference Temp. (C)	Vapor Pressure[1] (mm Hg)	Reference Temp (C)	Solubility[1] (mg/L)	Reference Temp. (C)	Henry's Constant[1] (atm m3/mol)	Reference Temp. (C)	Log Kow[1]
Acrolein	56.06	0.841	20	0.35	20	2.10E+02	20	2.08E+05	20	4.40E-06	25	-0.09
Acrylonitrile	53.06	0.806			20	1.37E+02	30	7.35E+04	NA	8.80E-05	NA	-0.92
Benzene	78.11	0.8765	20	0.649	15	9.50E+01	25	1.78E+03	20	5.55E-03	25	2.13
Toluene	92.14	0.8669	20	0.623	20	2.80E+01	25	5.15E+02	20	5.92E-03	25	2.69
Ethylbenzene	106.17	0.867	20	0.669	20	1.00E+01	25.9	1.52E+02	20	8.04E-03	25	3.15
Carbon tetrachloride	153.82	1.594	20	0.965	20	1.13E+02	25	8.00E+02	20	2.93E-02	25	2.73
Chlorobenzene	112.56	1.1058	20	0.799	20	1.18E+01	25	4.88E+02	25	3.93E-03	25	2.84
1,2 Dichloroethane	98.96	1.2351	20	0.887	15	7.90E+01	25	8.69E+03	20	1.18E-03	25	1.45
1,1,1 Trichloroethane	133.4	1.339	20	0.903	15	1.00E+02	20	4.40E+03	20	4.08E-03	25	2.47
1,1 Dichloroethane	98.96	1.1757	20	0.505	25	2.34E+02	25	5.50E+03	20	5.87E-03	25	1.79
1,1 Dichloroethylene	96.94	1.218	20	0.358	20	5.91E+02	25	2.10E+02	25	2.29E-02	25	1.48
1,1,2 Trichloroethane	133.4	1.4397	20	0.119	20	2.50E+01	25	4.50E+03	20	9.61E-04	25	2.17
1,1,2,2 Tetrachloroethane	167.85	1.5953	20	1.844	15	4.00E+00	25	2.90E+03	20	3.80E-04	20	2.39
Chloroethane	64.51	0.8978	20	0.279	10	1.01E+03	20	5.74E+03	20	6.92E-03	20	1.43
2 Chloroethyl vinyl ether												
Chloroform	119.38	1.4832	20	0.596	15	1.60E+02	20	9.30E+03	25	3.39E-03	25	1.97
1,2 Dichloropropane	112.99	1.156	20	0.865	20	4.20E+01	20	2.70E+03	20	2.68E-03	25	2.28
1,3 Dichloropropene	110.97	1.217	20			4.30E+01	NA	2.70E+03	NA	3.55E-03	NA	1.41
Methyene chloride	84.93	1.3266	20	0.449	15	4.29E+02	25	1.67E+04	25	3.19E-03	25	1.25
Methyl chloride	50.49	0.9159	20	0.0106	20	3.80E+03	20	6.36E+03	20	8.22E-03	24.8	0.91
Methyl bromide	173.83	2.497				4.00E+01	23.3	1.17E+04	15			
Bromoform	252.73	2.8899	NA	2.152	15	5.60E+00	25	3.20E+03	30	5.32E-04	25	2.3
Dichlorobromomethane												
Trichlorofluromethane	137.38	1.494	17.2	0.42	25	6.87E+02	20	1.10E+03	25	5.83E-02	25	2.53
Dichlorodiflouromethane	120.91	1.1834	57	0.26	25	4.25E+03	20	2.80E+02	25	3.90E-01	25	2.16
Chlorodibromomethane												
Tetrachloroethylene	165.83	1.6227	20	1.932	15	1.90E+01	25	1.50E+02	25	2.69E-02	25	2.53
Trichloroethylene	131.39	1.4642	20	0.566	20	7.70E+01	25	1.10E+03	25	1.17E-02	25	2.53
Vinyl chloride	62.5	0.9106	20			2.58E+03	20	1.10E+03	25	2.78E-02	20	0.6
trans-1,2-Dichloroethylene	96.94	1.2565	20	0.423	15	3.31E+02	25	6.00E+02	20	6.67E-03	25	1.48
bis(Chloromethyl) ether												

References:
(1)EPA, 1992.
(2)Dean, 1992

2.2 SUBSURFACE CONDITIONS

The types of soil that may be present in the subsurface are variable from site to site. Conditions at any given site are often heterogeneous and unpredictable.

The subsurface can be generalized into three distinct zones, the vadose, water table, and saturated zones. The vadose zone is the unsaturated area above the water table. The water table zone is the area just above the water table where the capillary fringe causes saturated conditions. The saturated zone is the area below the water table. VOCs released to the subsurface will initially reside near the ground surface. Over time, infiltration from precipitation will leach VOCs downward through the vadose zone into the water table and saturated zones. Water flow in the vadose zone may be saturated or unsaturated, depending on site specific conditions. Saturated leaching may occur when a surface depression filled with water is above the contaminated mass of soil. More typically, leaching will occur under unsaturated conditions with moisture contents, hydraulic conductivity and hydraulic head that are highly variable with depth. VOC leaching may also occur in the vapor phase as gas migrates within the vadose zone by advection and dispersion.

2.2.1 Flow in the Vadose Zone

In order for water to flow downward in the vadose zone the hydraulic head needs to decrease with depth. Vadose zone leaching is governed by the opposing forces of elevation head (or in essence, gravity pulling interstitial water downward) and capillary suction caused

by surface tension. It follows that the total potential head (matric potential) is:

$$H = z + (\psi) \qquad\qquad (2\text{-}1)$$

where z = elevation head; and ψ = suction head.

As moisture content increases the suction decreases. Suction head is negative. Thus, flow will occur from high moisture content to low moisture content, and more generally over the total hydraulic gradient from high to low potential or total head.

For fluid flow in the saturated zone there are two fundamental parameters, K (hydraulic conductivity) and n (porosity). In the unsaturated zone these parameters become k (unsaturated hydraulic conductivity) and θ (moisture content).

Moisture content is a measure of the amount of water in a given volume of soil by either weight or by volume. Moisture content is significant because it has a direct effect on unsaturated zone hydraulic conductivity. For unsaturated soils in the vadose zone, their moisture content may be assumed to be at field capacity (Ong, 1990). When the moisture content exceeds the field capacity of the soil, gravity will overcome capillary surface tension forces and the interstitial water will move downward through the soil column. Thus, the moisture content of vadose zone soil is analogous to the effective porosity of saturated zone soils. The volumetric moisture represents the pore volume of the soil available for flow. It follows that unsaturated hydraulic conductivity is a function of moisture content and will decrease as moisture decreases (van Gnutchen, 1980).

Unsaturated hydraulic conductivity is a measure of the ability of soil to carry a liquid or gas. Hydraulic permeability decreases with moisture content (van Gnuchten, 1980). van Gnutchen's model may be used to predict unsaturated hydraulic (van Gnuchten, 1980).

2.3 CONTAMINANT PHASE DISTRIBUTION

Once VOCs (or NAPLs) are released to the subsurface, VOCs will distribute into the solid, liquid, gas, or pure phase. The number of phases available is a function of the moisture content of the soil. Saturated and unsaturated conditions correspond to NAPL 3-phase and 4-phase flow respectively. Under saturated conditions compounds may not be present in the vapor phase. NAPLs may be distributed in the soil pore space in three different phases:

Solid Phase - Contamination attaches to the soil solid

Liquid Phase - Contamination is dissolved in the soil pore water

Pure Phase - Contamination is present in its pure phase in the soil pores

Figure 2-1 shows three phase distribution of contamination in the soil pore. Under unsaturated conditions (4-phase flow) the NAPL may be present in the soil pore space in the above three phases and in the vapor phase where contamination is present in the vapor phase in the soil pore space. Figure 2-2 shows 4-phase distribution in the soil pore. Due to the complexities involved with modeling a NAPL phase it is sometimes neglected as a simplifying assumption. If the NAPL phase is neglected the distribution in four phases may be modeled as follows (Hern et al, 1987):

$$C_t = \rho_b C_s + \theta C_l + a C_g \qquad (2-2)$$

where C_t = total quantity of chemical per soil volume; C_s = sorbed VOC concentration

($\mu g/gm$); C_l = dissolved VOC concentration ($\mu g/cm^3$); C_g = VOC vapor density ($\mu g/cm^3$

air); ρ_b = soil bulk density (gm/cm^3); θ = volumetric water content (cm^3/cm^3); and a =

Volumetric air content (cm^3/cm^3).

Hern further modifies equation 2-2 to simplify its solution to:

$$C_t = Rs\ Cs = Rl\ Cl = Rg\ Cg \qquad (2\text{-}3)$$

where:

$$Rs = C_t/C_s = (\rho_b + \theta)/K_d + a\ Hc/K_d \qquad (2\text{-}4)$$

$$Rl = Ct/C_l = \rho_d\ K_d + \theta + a\ K_d \qquad (2\text{-}5)$$

$$Rg = C_t/C_g = \rho_d\ K_d/Hc + \theta/Hc + a \qquad (2\text{-}6)$$

also where Rs = fraction of total concentration in the solid phase; Rl = fraction of total

concentration in the liquid phase; Rg = fraction of total concentration in the liquid phase;

and Hc = Henry's Constant (dimensionless); and K_d = solid/liquid equilibrium partition

coefficient (mL/gm).
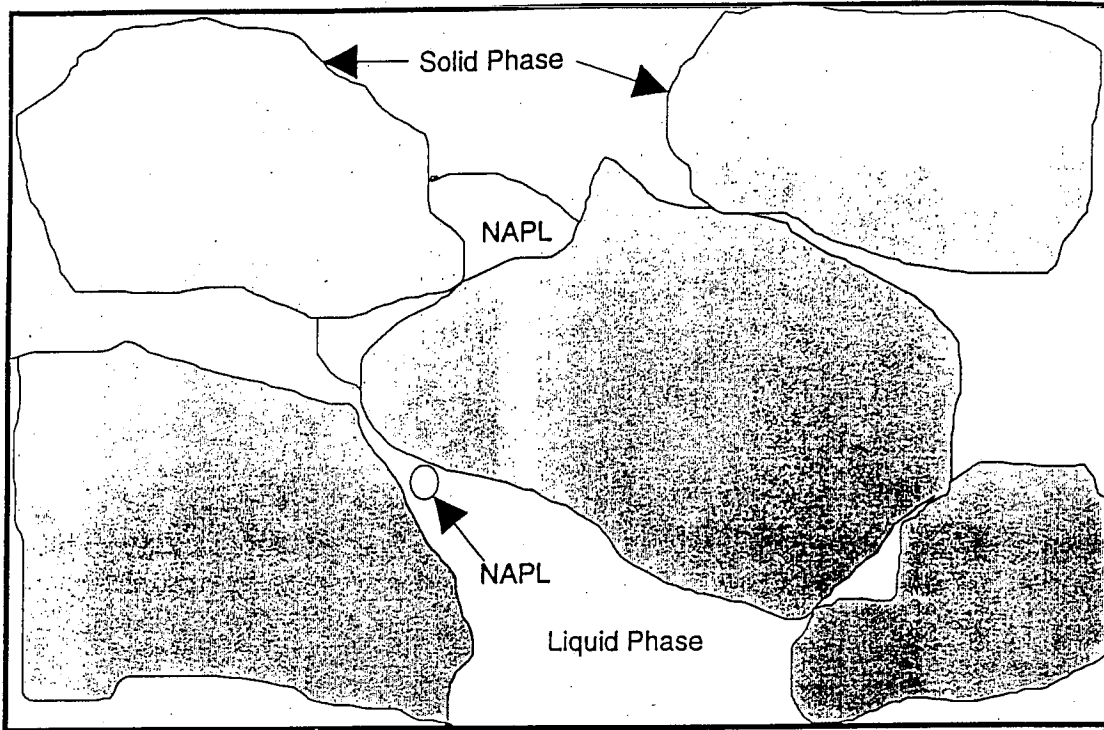
Figure 2.1 Three Phase Contaminant Distribution
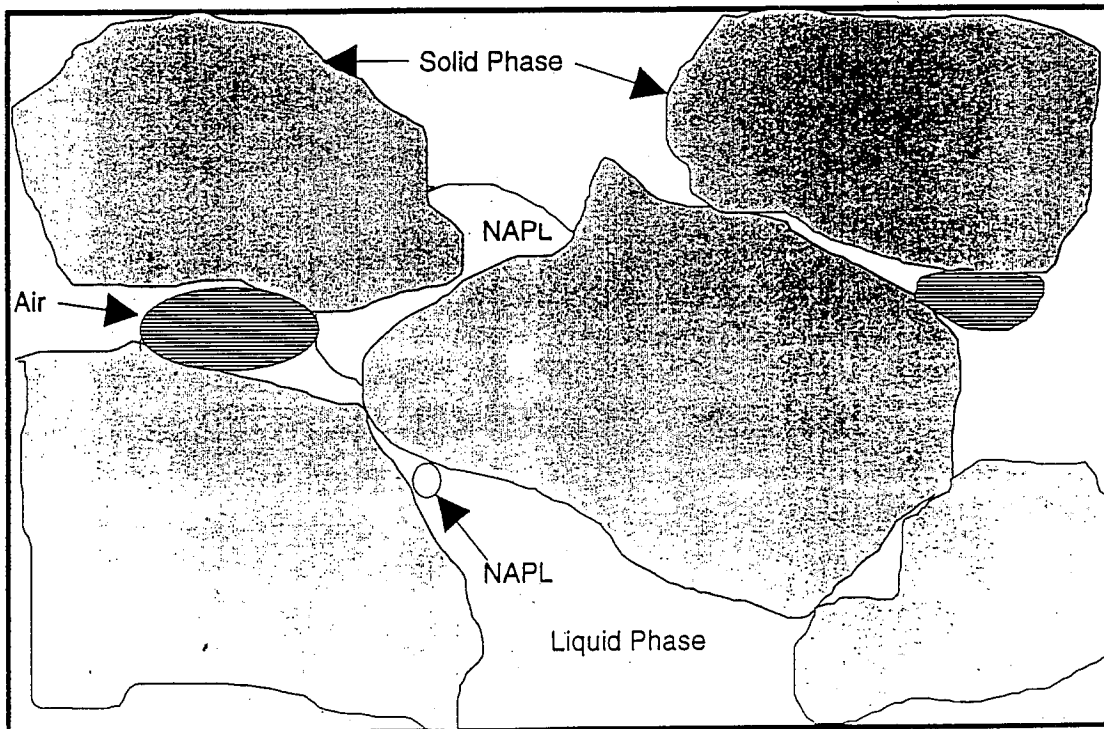
Figure 2.2 Four Phase Contaminant Distribution

2.4 BIOLOGICAL DEGRADATION

Contaminants in the soil may undergo natural degradation in the subsurface under favorable conditions. Indigenous bacteria are capable of degrading organic compounds through direct metabolism. Metabolism refers to the processes microorganisms use to obtain energy from substrate. Microorganisms' secrete enzymes which degrade the substrate/compounds which may then be sorbed through the cell wall. The microorganisms use the compounds to generate cell mass and maintain bodily functions. The compounds are degraded to intermediaries or may undergo complete minirilization to carbon dioxide and water.

In general for natural degradation to occur a minimum amount of substrate, nutrients, an electron acceptor, and water must be present. While nutrients are necessary, they are typically readily available in the subsurface and do not limit degradation. Electron acceptors may be oxygen, nitrate, sulfate, carbon dioxide, ferric iron and manganese. Oxygen is typically the most efficient electron acceptor; however, when oxygen is not available, nitrate sulfite and carbon dioxide will be used, and degradation rates will be typically slow. Water must be present as bacteria will only uptake the substrate or compounds dissolved in water.

Degradation may occur under aerobic, anaerobic or anoxic conditions. The degradation rates of compounds vary depending on these conditions. BTEX compounds are typically readily degraded under aerobic conditions. Chlorinated aliphatic compounds may be resistant to natural degradation under aerobic conditions and may degrade much more

slowly than nonchlorinated compounds, (Wilson, 1983). Cometabolic degradation may be more conducive to degradation of chlorinated compounds. Cometabolism occurs when enzymes secreted by bacteria to degrade a target substrate also degrade an untargeted compound. An example of a cometabolic bacteria would be methanotrophic bacteria. These bacteria will utilize compounds such as methane and cometabolize chlorinated organic compounds such as trichloroethylene (Bouwer, 1983). When concentrations of organic compounds are too high they may become inhibitory to biological growth, and degradation may not occur.

2.4.1 Required Conditions

Critical factors affecting biological degradation and favorable conditions required for aerobic degradation in the vadose zone were reported by the Wisconsin Department of Resources (WDNR, 1993):

(1) Soil moisture content: 25-85% of field capacity (50-80 % is optimal)

(2) Soil temperature: greater than 10°C

(3) Soil pH: 5-9 (6-8 is optimal)

(4) Permeability: Greater than 10^{-3} cm/s

(5) Electron acceptor: Oxygen in soil gas 2-5% and air filled pore space of 10%.

(6) Microbes present: Heterotrophic bacteria greater than 1000 cfu/gram

(7) Contaminant level: For petroleum hydrocarbon contamination gasoline range organics (GRO) less than 500 ppm, diesel range organics (DRO) less than 1000 ppm.

(8) Availability of nutrients: C:N:P ranging from 100:10:1 to 100:1:0.5. TON greater

than 1.5%.

2.4.2 Degradation Model

Biological degradation may be assumed to follow a first order loss process:

$$C = C_0 \, e^{-\lambda t} \qquad\qquad (2\text{-}8)$$

where C = concentration at some time t (mg/Kg); C_0 = initial concentration (mg/Kg); λ =

decay rate constant (1/day); and t = time (day).

Degradation may be accounted for by using the same term in the advection-dispersion

equation that would be used for leaching.

2.4.3 Degradation Rates

Degradation half lives for priority pollutant VOC for solid, liquid and air phases are listed

in Table 2-2 (Howard, 1991). These half lives listed are typically but not exclusively a

result of biological degradation. In some cases half lives represent degradation based on

hydrolysis, if a given degradation process was faster than biological degradation it was used.

Air phase degradation will not occur biologically but as a result of photooxidation by

hydroxyl radicals and ozone (Howard, 1991).

Table 2.2 - VOC Degradation Half Lives			
Compound	Soil (days)	Groundwater (days)	Air (days)
Acrolein	7-28	14-56	0.14-1.4
Acrylonitrile	7-28	14-56	54-548
Benzene	5-16	10-730	2.09-20.9
Toluene	4-22	7-28	0.43-4.3
Ethylbenzene	3-10	6-228	0.36-3.6
Carbon tetrachloride	180-365	7-365	668-6680
Chlorobenzene	68-150	136-300	3-30.4
1,2-Dichloroethane	100-180	100-365	12.2-122
1,1,1-Trichloroethane	140-273	140-546	8.2-82
1,1-Dichloroethane	32-154	64-154	10.3-103
1,1-Dichloroethylene	28-183	56-132	4.1
1,1,2-Trichloroethane	135-365	135-730	8.2-82
1,1,2,2-Tetrachloroethane	45	45	8.9-89
Chloroethane	7-28	14-56	6.7-67
2 Chloroethyl vinyl ether			
Chloroform	28-180	56-1825	26-260
1,2 - Dichloropropane	167-1278	334-2592	2.7-27
1,3 - Dichloropropene	5.5-11.3	5.5-11.4	0.2-3.3
Methylene chloride	7-28	14-56	
Methyl chloride	28-56	14-56	61-613
Methyl bromide	7-28	14-38	68-680
Bromoform	28-180	56-365	54-541
Dichlorobromomethane			
Trichlorofluromethane	180-365	365-730	15-147
Dichlorodiflouromethane	28-280	56-365	88-876
Chlorodibromomethane			
Tetrachloroethylene	180-365	365-730	16-160
Trichloroethylene	180-365	321-1642	1.1-11.3
Vinyl chloride	28-180	56-2850	9.7-97
1,2 - trans Dichlorethylene	28-180	56-2850	1.1-11.9
bis (Chloromethyl) ether	0.00044-0.0044	0.00044-0.0044	0.008-0.08

Howard classifies the half life reaction rates from resistant to fast as follows:

Fast: 1-7 days

Moderately Fast   7-28 days

Slow   28-180 days

Resistant   180-365 days

2.5 VOLATILIZATION

Volatilization refers to the loss of VOCs from the vadose zone through volatilization. Under unsaturated conditions, VOCs may partition into the vapor phase. Any soil pore void space not taken up by either water or NAPL will allow for a contaminant vapor phase. VOC may volatilize from either the pure, solid, or aqueous phases. Once contamination is present in the vapor phase it may migrate by diffusion, following Fick's Law through the boundary layer at the ground surface or be carried to the ground surface by pressure gradients caused by changes in atmospheric pressure (Massmann et al, 1992). Once gas migrates past the surface boundary layer it may be carried away by the wind into the atmosphere.

2.5.1 Vapor Phase Partitioning

For single compounds, concentrations in the pore space vapor phase may be estimated using Henry's constant. Henry's constant (Hc) is the ratio of the concentration in the liquid phase and the concentration in the vapor phase for dilute solutions. Henry's constant is

based on Henry's Law which states that the equilibrium concentration of a compound

dissolved in water is proportional to its partial pressure in the vapor phase (Mackay, 1981):

$$Hc = P_i/C_l \qquad (2\text{-}9)$$

where P_i = partial pressure (atm); C_l = liquid phase concentration (mg/L); and

Hc = Henry's constant (atm/mole fraction).

Henry's constant is a function of solubility and vapor pressure and is strongly influenced

by temperature (Mackay, 1981). It is often used as a measure of the volatility of a

compound and may be used to quantify the partitioning of a compound between the liquid

and vapor phase (Mackay, 1981). Henry's constants for VOCs are relatively high thus

significant partitioning of VOCs from the aqueous phase to the vapor phase may occur.

For multicomponent mixtures and when NAPLs are present the vapor phase

concentration may be predicted using Raoult's Law. Raoult's Law states (Reid, 1987):

$$Cv = Vp_iX_iMW/(RT) \qquad (2\text{-}10)$$

where C_v = concentration of pure component vapor (mg/L); Vp_i = pure component vapor

pressure at temperature t (atm); X_i = mole fraction of the component in the liquid phase (X =

1 for single compound); MW = molecular weight (mg/mole); R = Universal gas constant

(0.0821 L-atm/mole-K); and T = absolute temperature of residual (K).

2.5.2 Vapor Phase Mass Transport

Atmospheric pressure changes are expected with changing weather patterns. Storms and precipitation events are generally associated with low pressure. Due to rapid changes in ambient air pressure caused by these events, pressure gradients into and out of the soil are created. Ambient air may intrude more than 10 feet during a storm event (Massmann, 1992). Air intrusion will cause advective and dispersive transport of the vapor phase contaminants. In addition, as fresh air intrudes VOC will partition into the air from the solid and liquid phases. As the "fresh" air leaves the subsurface following a storm event VOC in the air will be released to the atmosphere. The result is a net loss of VOC from the subsurface system.

Massmann contends contaminant will migrate as a vapor phase following a capillary tube model. Gas may migrate as a result of two mechanisms:

1. Diffusive flow, where gradients in gas concentrations and partial pressures will induce contaminant vapor phase to migrate from higher concentrations to lower concentrations. Diffusive flow may be slowed by Knudsen diffusion where gas molecule collides with the capillary tube.

2. Pressure flow, where pressure gradients in the capillary tube induce gasses to flow from high to low pressure. Viscous flow and slip flow are microscale mechanisms of pressure flow induced by viscous resistance and the slide of molecules along capillary walls.

When the gas permeability of the porous media is greater than 10^{-10} cm^2, Massmann suggests single component gas fluxes can be modeled using the classical advection-dispersion equation that is used for solute transport in saturated groundwater systems.

$$(RT)N_{tj} = D_j,\text{mix } \Delta P_j + BkP_j\Delta P/\mu \qquad (2\text{-}11)$$

where N_{tj} = total molar gas flux for species (mol L^{-2} t^{-1}); D_j = effective diffusion coefficient for component j (L^{2}t^{-1}); ΔP = pressure gradient (M L^{-1} t^{-2}); and μ = gas viscosity (M L^{-1} t^{-1}). Massmann found this method of predicting vapor phase flux rates overestimates flux rates for low permeability materials, and underestimates flux rates for high permeability materials.

2.5 LIQUID PHASE MASS TRANSPORT PROCESSES

Liquid phase transport of VOC in the subsurface have two components, advection and dispersion.

2.5.1 Advection and Dispersion

Advection and dispersion are physical processes responsible for the movement and mixing of contaminants in porous soil media and do not include reactions. These physical processes include advection, dispersion and diffusion. Dispersion and diffusion processes are often combined and called hydrodynamic dispersion.

Advection refers to transport of a contaminant by the advective interstitial velocity of water flowing through the soil. The contaminant travels with the fluid at fluid velocity.

Hydrodynamic dispersion represents mixing processes which include both dispersion and diffusion.

Dispersion is caused by three microscale advective processes at the pore scale (known as mechanical dispersion). The first process induces dispersion of the contaminant due to the differing velocities in fluid flowing through a pore. Resistance at the edges of the pore slows the fluid down. The variation in velocity causes mixing. The second process causes mixing through variations in the velocity between pores where smaller pores have higher velocity and larger pores have lower velocity. This follows Bernoulli's equation for fluid flow and conservation of energy. The first two processes result in longitudinal dispersion. The third process is called tortuosity which causes mixing as a result of the pore geometry which allows for different paths of travel. Some paths are longer than others and this causes mixing. This process is responsible for longitudinal, transverse and vertical dispersion.

Diffusion refers to molecular diffusion which is assumed to follow a Normal or Frickian distribution. The contaminant mixes by moving over a concentration gradient from high to low in an effort to minimize energy. The advective processes typically dominate diffusion except in low hydraulic conductivity and velocity situations.

Unsaturated Flow

Unsaturated flow follows the classic advection-dispersion equation (Hern, 1987):

$$\partial C_t / \partial t = \partial / \partial Z [D \partial^2 C_t / \partial Z^2 - v C_t] - S_s \quad (2\text{-}12)$$

where Ct = total concentration and may be obtained from equation 2-3; Ss = first order

degradation rate constant (gm/cm^3/day); z = vertical distance (cm); and v_e = effective

velocity (cm/day). For solute transport equation 2-12 becomes:

$$\partial Ct/\partial t + Ss = \partial/\partial Z[D^{SOIL}_E\partial 2C_l -Hc[\partial h/\partial Z+1]C_l] \qquad (2\text{-}13)$$

Unsaturated zone mass transport is analogous to saturated zone mass transport except that

VOC may also exist in the vapor phase. Unsaturated zone transport is a function of the

infiltration rate, gravity and capillary forces. It may be conservatively assumed that the

volumetric moisture content corresponds to the effective porosity of the soil in the vadose

zone. This accounts for soil pore space that does not contain water in the vadose zone.

Saturated Flow

For saturated zone flow, the advection and dispersion processes are combined in the

advection-dispersion equation. For one dimensional saturated flow through homogeneous

isotropic soil under steady state uniform flow, the equation is (Dominico, 1990):

$$\partial C/\partial t = D\partial 2C/\partial x2 - v\partial c/\partial t \qquad (2\text{-}15)$$

where C is the VOC concentration (mg/L), t is the time (day), D is the hydrodynamic dispersion coefficient (m^2/day), x is the distance (m), and v is the seepage or linear velocity (m/day).

The one dimensional advection-dispersion equation can be modified to include the desorption reaction by adding a term to account for changes in mass in the solid phase. The equation is given below:

$$\partial C/\partial t = D\partial^2 C/\partial x^2 - v\partial c/\partial t - (\rho/n)\partial S/\partial t \qquad (2\text{-}16)$$

where ρ is the bulk density (g/m^3), n is the porosity, and S is the concentration in the solid ($\mu g/Kg$).

Use of this partial differential equation to model the leaching of VOCs from a body of soil into an aquifer, requires that the decaying (Cauchy) influent boundary condition, or leach rate, be quantified. The leach rate constant quantifies VOC changes in the solid phase over time.

The concentration of a VOC in the solid phase is considered a function of concentration in the aqueous phase as follows:

$$-\partial S/\partial t = \partial S/\partial C \; \partial C/\partial t \qquad (2\text{-}17)$$

where $\partial S/\partial C$ represents the partitioning of VOC between the solid and liquid phases, and:

$$\partial S/\partial C = K_d \qquad\qquad (2\text{-}18)$$

2.6.2 Sorption/Desorption Reactions

The reactions VOCs undergo in the subsurface have a direct effect on the migration of VOCs through the soil. Sorption is considered to be the primary reaction affecting VOC migration. The reaction tends to retard VOC movement through soil. Sorption refers to the reaction that results from the attraction of the sorbate (VOC) to the sorbent (soil) and results in an increased concentration of the sorbate at the interface between solid and liquid phase. The sorbate may also travel inner passages of the sorbent and attach to sites there. The sorption/desorption reaction VOCs undergo in the subsurface is considered to be a reversible, equilibrium, surface reaction. The reaction is reversible because the forward sorption reaction, where the VOC is attracted to a site on the soil matrix, is mirrored by the reverse desorption reaction. It is equilibrium because the reaction is assumed to occur quickly compared to the transport processes of dispersion and advection The reaction is a surface reaction because the relatively easily broken bonds occur at the surface of the substances involved.

A. Sorption Forces

Sorption results from a variety of attractive forces where one force may be dominant (Weber, 1991). Weber indicated interactions between the dipole moments of sorbate and

sorbent molecules are the primary mechanisms underlying sorption. Weber categorized adsoprtion forces in three categories, chemical, electrostatic, and physical (Weber, 1983).

1. Chemical sorption refers to the interactions caused by covalent and hydrogen bonding of the solute to the sorbate.

2. Electrostatic sorption results from the attraction of charged molecules to the charged surface of the sorbent through ion-ion and ion-dipole forces.

3. Physical sorption is a result of van der Waals forces which consist of London dispersion forces and hydrophobic bonding. London forces are caused by rapidly fluctuating dipole and quadrupole moments resulting from the movement of electrons in their orbitals. Hydrophobic bonding is a result of thermodynamic gradients caused by repulsion of the sorbate from solution to the sorbent. The sorbent-solute interactions are preferred to the solute-water interactions. Physical sorption van der Waals forces are thought to predominate for sorption of VOC.

B. Equilibrium Partitioning (K_d) Model

VOC sorption is assumed to occur to the organic carbon fraction of the soil and where partitioning of VOC between soil and water will follow a Freundlich linear isotherm. VOC sorption (equilibrium partitioning) is typically modeled using a Freundlich isotherm ($1/n = 1$):

$$C_s = K_d \, C_l \qquad\qquad (2\text{-}19)$$

where K_d is the equilibrium partition coefficient (L/Kg), C_s is the equilibrium concentration (mg/Kg) in the solid phase and C_l is the concentration (mg/L) in the liquid phase.

Karickhoff (1979) has shown partitioning of VOCs from the liquid to the solid phase will occur preferentially to the organic matter in the soil. In particular, the fraction of organic carbon (f_{oc}) in the soil is considered to be the best predictor. The equilibrium partition coefficient may be calculated from the following relationship (Karickhoff, 1979);

$$K_d = f_{oc} K_{oc} \hspace{3cm} (2\text{-}20)$$

where f_{oc} = fraction of organic carbon in the soil.

K_{oc} is a function of either a compounds solubility, S, or its octanol-water partition coefficient, K_{ow}. Piwoni et al. (1989) found that organic chemicals partition between octanol and water in approximately the same way they partition between water and soil organic carbon and developed the relationship:

$$\log K_{oc} = 0.22 + 0.69 \log K_{ow} \hspace{2cm} (2\text{-}21)$$

where K_{oc} = organic carbon-water partition coefficient, and K_{ow} = octanol-water partition coefficient.

The model has often been shown to be a good predictor of VOC sorption phenomena (Schwartzenbach et al., 1981). However it has not always been accurate. While it does appear sorption of VOC will be dominated by sorption to the organic sites, there are exceptions and difficulties with this approach and its assumptions.

The assumptions of the model are:

(1) VOCs will partition to the organic sites on the soil matrix.

(2) VOC partitioning follows a linear isotherm (Freundlich $1/n=1$), which also assumes equilibrium, i.e., sorption reaction is fast compared to transport processes, and thus a local equilibrium assumption is valid.

(3) Desorption is a two dimensional surface reaction.

(4) Partitioning of the organic chemicals between soil/water is similar to partitioning of the organic chemicals between water and octanol.

2.6.3 Sorption Modeling Problems

1. Organic fraction sorption constraints: Research has shown that partitioning of VOCs is not always limited to the organic fraction of the soil. While partitioning typically occurs to the organic fraction there are exceptions. Problems may be encountered during modeling VOC partitioning to soil organic carbon when the organic carbon content of the soil is very low. A study by Schwartzenbach and Westall (1981) found that when the organic content of the soil is below 0.1% the specific surface and mineralogical character of the surface are more significant in predicting VOC sorption. Ball (1991) reported that in low organic content soil (<0.1%) "certain minerals may play important roles in sorption." When the

organic carbon content of soil is low, using the organic content of the soil may be a poor predictor.

2. Equilibrium Issues: The local equilibrium assumption is used implicitly in the K_d model and in the development and use of the leach rate model. Both models are based on VOC/soil equilibrium partitioning (isotherms). This approach assumes the desorption reaction is at local equilibrium or fast compared to mass transport processes. Transport processes are assumed to be rate limiting. The literature suggests this may not always be true. In particular, the time it takes to reach desorption equilibrium can be quite long. Ball (1991) found that TCE can take years to reach desorption equilibrium. Pavlostathis and Jaglal (1991) found that "TCE requires extended equilibration times for desorption to occur". Bahr (1989) found indications that desorption was the rate limiting step during a field test at a contaminated site in Ottawa, Canada. "It is becoming increasingly apparent that sorption and desorption rates may be sufficiently slow to impact solute transport in groundwater environments" (Ball, 1991). If desorption is the rate limiting step then the local equilibrium assumption is invalid. We cannot assume that enough time has passed to allow concentrations in the solid and liquid phases to equilibrate given the rate of transport processes.

Other research suggests that under natural gradients nonequilibrium sorption may not be limiting relative to transport processes. One report indicated that it was only under induced gradients that nonequilibrium effects might be seen (Brusseau et al, 1991). When modeling desorption of VOCs, particularly in the lab where high gradients may be used, the local equilibrium assumptions may not hold.

Reasons for the K_d model's departure from local equilibrium assumptions are given below:

(1) Colloidal fraction: Results from an experiment by Gschwend and Wu (1985) suggested that if sorption to non-settling microparticles and organic macromolecules is taken into account the K_d model is an excellent predictor. This result is not generally accepted, because it is difficult to explain the reason for long desorption times (relative non-equilibrium) by the colloidal theory. Organics sorbed to colloidal particles would be removed from the system, by advective transport, over the long desorption time frames making it impossible for them to have any effect on long term desorption outcomes. We actually expect organic colloidal particles to increase the effective velocity of contaminant transport. The importance of considering non-settling organic particles is not considered a concern in this experiment. Such issues were addressed by flushing the soil samples under a high gradient prior to the sorption/desorption studies.

(2) Diffusion: Sorption models can be either two dimensional or three dimensional. Equilibrium isotherm models assume two dimensional surface adsorption. Adsorption is the increase in concentration of the VOC at the internal and external surfaces of a solid. It is a two dimensional surface reaction. The two dimensional model assumes organics sorb to the surface of the solid or the liquid in the solid/liquid interface (diffuse layer). Three dimensional sorption, absorption, occurs when organics sorb to the three dimensional volume that is the solid and/or the liquid at the solid/liquid interface (diffuse layer). This model allows for diffusion to internal sites on the solid. It is believed that the three dimensional absorption, which includes a diffusion process, may be the cause of the slow

sorption equilibration times. Brusseau et al. (1991) found that an intraorganic matter diffusion model best explained macro- and micro-scopic deviations from equilibrium. Pavlostathis and Jaglal (1991) found that soil contaminated (primarily) with TCE for long periods of time was resistant to desorption. It appeared to be a case of three dimensional desorption, where diffusion became the rate limiting process. Sorption/desorption then is dependent on the contact time of the solid with the contaminated aqueous phase. The proposed leach rate model is based on two dimensional desorption. If VOCs have long contact time with the soil, the leach rate model may over predict VOC desorption rates.

(3) Linear isotherm assumption issues: There are problems with using a linear isotherm to predict partitioning. Dominico and Schwartz (1990) claimed that a linear isotherm does not adequately describe sorption of VOCs to soil, particularly at high concentrations. The proposed leach rate model assumes the concentration in the solid phase increases indefinitely with the liquid phase. If there are a finite number of sites this is not possible and the model will over predict concentrations in the solid phase and under predict concentrations in the liquid phase. It may be that the linear isotherm does not completely model VOC desorption. The Langmuir isotherm model may be appropriate in this case. Using this isotherm model, the sorptive capacity would be linear at low concentrations and then flatten (sorption effectively stopping) at high concentrations (maximum sorption capacity). This would be a more effective approach if a maximum sorptive capacity exists. The proposed leach rate model does not provide for this outcome.

A second problem is that linear equilibrium partitioning assumes desorption occurs at one rate. One explanation of the long desorption times is that there are two reactions occurring

at different rates. Desorption from the surface of the solid which occurs relatively quickly and diffusion from micropores or from inside the solid which occurs much more slowly. At some point diffusion may become the primary process. This observation was noted in a report by Estes et al. (1988). It may not be possible to account for the kinetic effects of the slow diffusive processes with a linear assumption. It may not be correct to assume a linear or continuous function for the desorption of VOCs.

2.7 TIME RELEASE LOSS MODEL

The processes involved in VOCs leaching from soil may involve too many complex and interactive processes to allow modeling.

2.7.1 Model Scenarios

The proposed model assumes VOCs released from soil can be considered to follow two different bracketing loss processes. The release can be gradual over time or a complete instantaneous pulse release. The instantaneous release is a worst possible case scenario. The gradual release over time is considered to be most representative of VOC leaching from soil.

2.7.2 Theoretical Development

A simple model of the time release and instantaneous loss process can be evaluated as a first order kinetic model with the rate of change of pollutant in the soil over time as follows:

$$dQ_d/dt = -(\lambda_1 + \lambda_d)Q_d \qquad (2-22)$$

where Q_d = amount of pollutant in the soil (g); λ_1 = leach rate constant of a pollutant from the soil to the groundwater (day^{-1}); λ_d = decay rate constant for the pollutant in the soil (day^{-1}); and t = time (day). Solving equation 2-8 yields:

$$Q_d(t) = Q_{do}\, e^{-(\lambda_1+\lambda_d)t} \qquad (2\text{-}23)$$

where Q_{do} = initial pollutant mass at t = 0 (g). Total initial pollutant mass is given by:

$$Q_{do} = A\, h\, C_s\, \rho_b \qquad (2\text{-}24)$$

where A = area of contamination (m0^2); h = depth of contamination (m); C_s = concentration in the soil (mg/Kg); and ρ_b = bulk density of the soil (g/cm^3). The release rate is given by:

$$r = Q_d(t)\lambda_1 \qquad (2\text{-}25)$$

where r = release rate (g/day). Substituting $Q_d(t)$ from equation 2-23 into equation 2-25 yields:

$$r = [Q_{do} \, e^{-(\lambda_1 + \lambda_d)t}]\lambda_1 \qquad (2\text{-}26)$$

Integrating the release rate from zero to infinity yields the total pollutant release as follows:

$$T = Q_{do}\lambda_1 \,/(\lambda_1 + \lambda_d) \qquad (2\text{-}27)$$

where T = total pollutant released (g). Only the leach rate constant is needed to assess mass leached from a body of soil into an aquifer.

If asymptotic conditions are observed in leaching concentration declines, and only leaching decay is considered, equation 2-23 becomes:

$$Q_d(t) = (Q_{do} - Q_{df}) \, e^{-(\lambda_1)t} + Q_{df} \qquad (2\text{-}28)$$

where Q_{df} = asymptotic concentration (mg/L).

2.8 LEACH RATE CONSTANT PREDICTIVE MODEL

Rodgers and Associates Engineering Corporation (1988) developed an empirical leach rate model to assess leaching of radioactive waste from a cement lined low level radioactive waste repository:

$$\lambda_1 = 86400P/100h(\theta + \rho_b K_d) \qquad (2\text{-}29)$$

where P = percolation rate of water through soil (cm/sec); θ = volumetric water content

(cm^3 water/cm^3 waste); ρ_b = soil dry bulk density (g/cm^3); K_d = equilibrium partition

coefficient between soil and pollutant (L/Kg); h = soil thickness (m); and λ_1 = leach rate

constant (day-1).

This relationship adapted for VOCs leaching from a body of soil becomes:

$$\lambda_1 = Pa/h(\theta + \rho_b K_d) \qquad (2\text{-}30)$$

where Kd = the equilibrium partition coefficient of the pollutant between the solid and liquid

phase (L/Kg); and a = constant determined by regression analysis.

The soil dry density, volumetric moisture content, percent organic matter, and percolation

rate are relatively easily obtained. The percent organic matter in the soil is divided by 1.7 to

obtain the organic carbon fraction in the soil (Brady, 1974). The equilibrium partitioning

coefficient can be determined from the relations developed by Piwoni, et al. (1989).

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 VOCs Studied

Four VOCs were studied: methylene chloride (MC), trichloroethylene (TCE), toluene (TOL), and m-xylene (MX). These compounds are representative of some of the VOCs encountered at contaminated sites. The compounds selected cover a wide range of octanol-water partition coefficients, solubility's and Henry's constants, and therefore a wide range of rates of VOC leaching can be theoretically represented based on Hassett et al. (1983). Table 3.1 shows the properties of these compounds.

Table 3.1 Properties of VOCs Used in Study				
Properties	**MC**	**TCE**	**TOL**	**MX**
Density at 20C (g/mL) [a]	1.32	1.456	0.866	0.864
Boiling Point (C) [a]	39.8	86.9	110.6	139
Solubility (mg/L) [a]	16700	1100	515	198
Henry's Constant (atm m^3/mol) [b], [c]	0.093	0.00913	0.00637	0.00704
Octanol-Water Coefficient (log Kow) [b], [c]	0.91	2.38	2.73	3.26

References: (a) Verschueren et al, 1983. (b) EPA, 1986. (c) Lyman, 1990.

Methylene chloride (MC)

Methylene chloride is a chlorinated aliphatic compound. This compound is primarily used in paint strippers, aerosol formulations, and as an extraction solvent in making decaffeinated coffee. A carcinogen, its toxic effects act primarily on the central nervous system. It may be found at industrial sites. This compound would be expected to leach from soil at a faster rate than the other compounds studied based on its K_{ow}.

Trichloroethylene (TCE)

Trichloroethylene is a chlorinated aliphatic compound. It is a common solvent used in metal finishing degreasing operations and dry cleaning. It may be found at contaminated industrial sites or dry cleaning operations. This compound is toxic and affects the central nervous system. Based on its K_{ow}, TCE should leach faster than TOL and MX, but more slowly than MC.

Toluene (TOL)

Toluene is an aromatic compound. Its structure consists of a benzene ring with one methyl group. It is a petroleum derivative used primarily in gasoline, but is also found in naphtha and asphalt. Toluene may be found at leaky underground storage tank (LUST) sites where gasoline is present. It exhibits low toxicity effects. Based on its K_{ow}, TOL should leach faster than MX, but more slowly than TCE and MC.

m-Xylene (MX)

m-Xylene is an aromatic compound. Its structure consists of a benzene ring with two methyl groups. It is derived from petroleum, and used primarily in gasoline. This compound is also used in the manufacture of isophthalic and as a solvent. It may be found

at LUST sites where gasoline is present. m-Xylene is a mild irritant and only mildly toxic. The leach rate of this compound is expected to be the slowest of the compounds studied.

3.1.2 Soils Studied

Three types of soil were studied: topsoil, clay, and sand. These soils are expected to represent a range of soils that might be encountered at a contaminated site. Table 3.2 shows the basic parameters for these soils.

The sand was collected from a Lake Michigan beach. It was clean and fine grained, and had a very low organic content.

The clay has been used in previous studies at the University of Wisconsin (Heim, 1992). It was brownish orange in color and contained some small gravel. It had a low organic content.

The topsoil was collected from a barrow pit located in the Arboretum in Madison, Wisconsin. It was collected near the soil surface in a woods and appeared to be a loam containing high amounts of humus.

| Table 3.2 Properties of Soils								
Soil Type	Sand (%)	Silt (%)	Clay (%)	Particle Density (g/cc)	Organic Matter (%)	Organic Carbon (%)	CEC[1]	pH
Sand	99	1	0	2.62	0.2	0.12	0	6.3
Clay	34	42	24	2.36	0.6	0.35	26	7.2
Topsoil	51	37	12	2.18	7.2	4.24	37	7.2

1) = cation exchange capacity

3.2 EXPERIMENTAL APPARATUS

3.2.1 Apparatus Development

Various pump and reservoir configurations were tested during development of the experimental apparatus. Configurations using pumps proved ineffective due to fluctuations in pressure head during testing. Therefore, a cylindrical glass reservoir was tested. The unevenness of the walls of the cylinder caused variability in the friction between the piston seal and the cylinder wall. This, in turn, created variability in the rate of piston travel over the length of the cylinder. The variability of piston movement made flow rates vary, the device could not achieve a consistent flow rate. A precision bored cylinder was finally tested and produced a relatively constant flow rate.

3.2.2 Apparatus Description

Figure 3.1 shows the influent reservoir developed for the experiment. A precision bored cylinder 4 inches in diameter and 2 feet in length was used. A machined aluminum bottom plate and piston with Teflon seals provided barriers to VOC volatilization. The cylinder was laid on its side to maintain constant elevation head. A pulley and weight system applied a constant force (2.2 lb.) to the end of the piston rod. This force slightly exceeded the resisting friction force of the seal and maintained positive pressure on the system. The positive pressure helped minimize air leaving solution and facilitated piston movement. Any air in the reservoir or lines would both decrease the pressure head and allow VOCs to volatilize out of solution. Copper and Teflon lines were used between the reservoir and soil samples to minimize losses of VOCs. Previous experience has shown that tubing capable of carrying 10 times the expected flow will not restrict flow. Approximate flows were computed and this rule of thumb adhered to in sizing the lines (3/16" OD). Teflon bags were connected to the effluent side of the soil sample. Sample ports were placed at the influent and effluent sides of the soil samples. Three apparatus were built, allowing 9 to 12 soil samples to run simultaneously. Figure 3.2 shows the experimental apparatus developed.
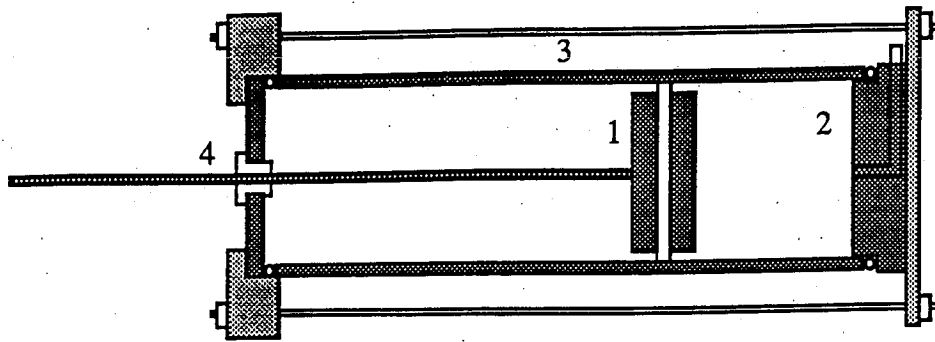
1. Piston with Teflon Seal
2. Bottom Plate with Teflon Seal
3. Precision Bored Annodized Aluminum Cylinder
4. Piston Rod with Teflon Guide
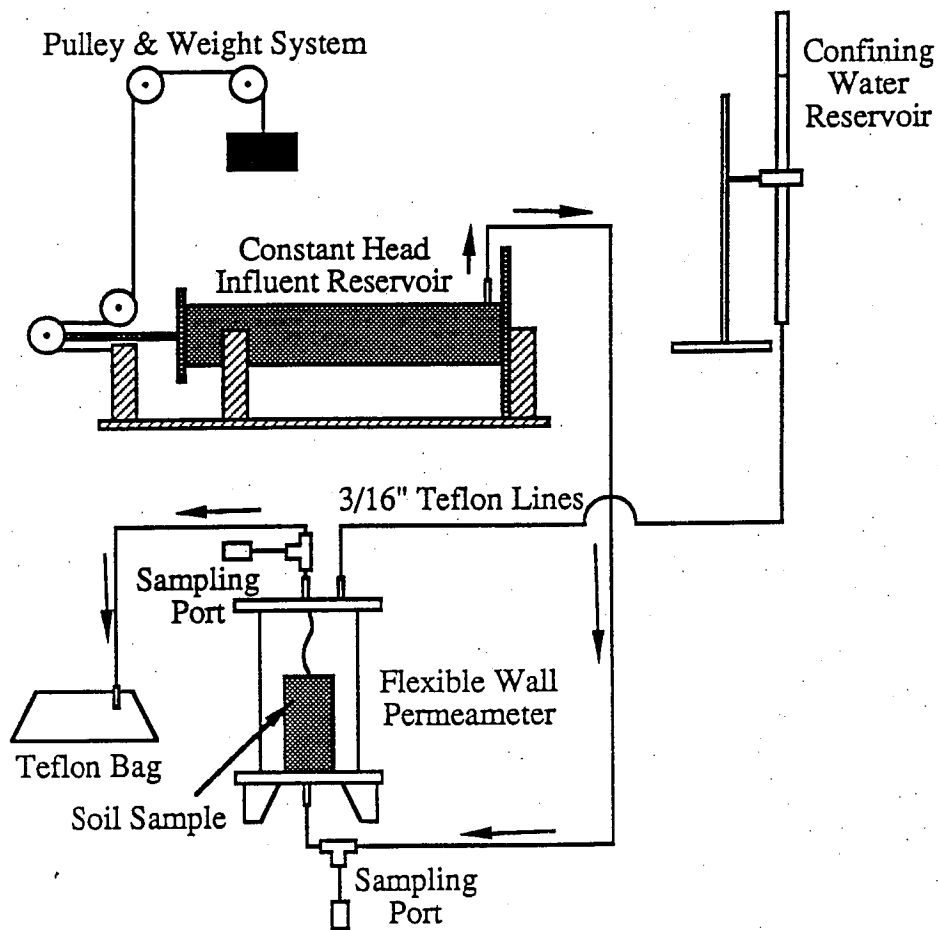
Figure 3.1 Influent Reservoir Apparatus

Figure 3.2 Experimental Appratus

3.3 ANALYTICAL METHODS

3.3.1 Gas Chromatography and Program

A Vavarian Model 3600 Gas Chromatograph (GC) with a flame ionization detector (FID) was used to analyze samples from both column and batch studies. The GC was equipped with a Supelco VOCOL glass capillary column 60 m in length, 0.75 mm ID, with a film thickness of 1.5 μm. Various concentrations of VOC were run on the GC to determine the column and detector temperatures, and holding times that would allow for identification of the different compound response peaks, and quantification of concentrations over a range between 1 to 100 mg/L. The times at which the test compounds eluted from the GC were individually identified at this time. The GC program settings are shown below:

GC Program First Column Experiment

Attenuation: 1-12

Carrier Gas: Helium @ 3 cc/min

Initial Column Temperature: 130 C

Initial Column Hold Time: 5 min

Final Column Temperature: 230 C

Initial Injector Temperature: 50 C

Initial Injector Hold Time. 0.5 min

Final Injector Temperature: 230 C

Detector Temperature: 250 C

GC Program Second Column and Batch Experiments

Attenuation: 1-12

Carrier Gas: Helium @ 3 cc/min

Initial Column Temperature: 60 C

Initial Column Hold Time: 5 min

Final Column Temperature: 230 C

Initial Injector Temperature: 60 C

Initial Injector Hold Time. 1 min

Final Injector Temperature: 230 C

Detector Temperature: 250 C

GC Program Batch Experiment Carbon Disulfide Extractions

Attenuation: 1-11

Carrier Gas: Helium @ 3 cc/min

Initial Column Temperature: 80 C

Initial Column Hold Time: 5 min

Final Column Temperature: 230 C

Initial Injector Temperature: 80 C

Initial Injector Hold Time. 1 min

Final Injector Temperature: 230 C

Detector Temperature: 250 C

3.3.2 Calibration/Standard Curves

The primary standard curves used in the analyses are shown in Appendix A. Three

different calibration curves were used during the experiments. One standard curve for the

first column experiment, a second standard curve for the second column experiments, and a

third carbon disulfide/VOC standard curve for the batch experiment extractions. The first standard curve was based on the analyses of 5 samples at each concentration level: 2, 10, 25, 50, and 100 mg/L. The second standard curve was based on the analyses of 5 samples at each concentration level: 4, 10, 40, and 100 mg/L. The carbon disulfide-VOC standard curve was based on analyses of 5 samples at each concentration level; 2, 50, 100, and 400 mg/L. A linear curve was fitted to the data using a least square regression. The curves were not forced through the origin in the regression. A 99.7% confidence interval was computed for all three standard curves. The standard curves were used to quality control results. Data with corresponding standard detections outside of this 99.7% confidence interval were considered to be outside control limits and these results were typically not used.

3.3.3 Sample Handling and Analysis

Samples were kept in 2 mL glass vials sealed with Teflon lined septa and refrigerated prior to analysis. Samples were typically analyzed within a week of the time they were taken.

Standards were run every 10 samples. GC analytic results were evaluated by comparing the detected standard concentrations to the known standard concentration. Results corresponding to standards outside the 99.7% confidence interval of the standard curves were considered outside of acceptable control limits and thrown out. In some cases samples were analyzed on the automated sampler. These samples were purged with air as part of the automated sampling procedure. Thus, when these analyses were out of control there were no alternative samples and the results were accepted. In other cases the concentration of the standard was orders of magnitude above the concentrations of several of the VOCs while being close to the concentrations of other VOCs. Bias at the lower concentrations may not have been accurately assessed.

When concentrations in samples were high and when carbon disulfide samples were analyzed, blank samples containing water were run between samples to flush residual VOCs out of the column that might otherwise cause false positive detections.

3.4 OVERALL EXPERIMENTAL METHODS

The leach rate model was developed from the results of three types of experiments:

1. Soil column desorption studies which were used to determine contaminant leaching characteristics over time.

2. Batch studies to determine soil/water equilibrium partition coefficients (K_d) for different pairings of VOCs and soil types.

3. Soil parameter studies to determine soil organic content, density, bulk density, and volumetric moisture content.

4. Potassium bromide tracer studies to determine an approximate effective velocity, effective porosity, and dispersion/diffusion coefficient for several soil columns.

3.5 FIRST COLUMN STUDY EXPERIMENTAL METHODS

The purpose of the first sorption/desorption studies was to determine the mass of VOC lost from the soil column over time. A mass balance based on influent and effluent concentrations was to be used to determine the VOC mass in the soil.

3.5.1 Sample Preparation

Initial preparation of samples entailed homogenizing the soils used in samples. The soil was dried, mixed, and passed through a #6 (3.35 mm) sieve. Twigs and small roots were removed by hand from the topsoil. Moisture contents of the topsoil and clay were checked and water was added to the soils corresponding to known and assumed optimum water contents following suggestions given by Heim (1992). The moisture in the soil was then

allowed to equilibrate and moisturized soil was placed in double sealed plastic bags for approximately 1 week prior to sample preparation.

The soil was then compacted in a Proctor mold. Compaction efforts were varied to produce a wide range of permeabilities. A certain amount of trial and error was involved in determining the correct compaction effort for the desired permeability. Permeabilities were briefly checked using a falling head test to ensure the range of permeabilities desired were achieved.

Soil samples 2 inches high and 4 inches in diameter were placed in a flexible wall permeameter (Figure 3.3). A bronze porous stone was placed at each end of the samples. The samples were then wrapped in 3 inch wide Teflon tape, sealed with silicone caulk, covered with a latex sock, and sealed with two rubber o-rings. Compacted samples were placed in flexible wall permeameters and leakage to the confining water was checked under high gradients.

3.5.2 Experimental Conditions

Soil samples were contaminated with a constant influent VOC solution of 100 mg/L and 10 mg/L toluene, m-xylene, methylene chloride and trichloroethylene. Solutions were passed through six clay columns with hydraulic conductivities ranging from 10^{-4} cm/sec to 10^{-6}, and four topsoil columns with hydraulic conductivities ranging from 10^{-4} to 10^{-6} cm/sec. Hydraulic gradients were between 1 and 6, except for column C6 which had gradients of 16 to 18 due to its low permeability. The experimental conditions are summarized in Table 3.3.

Brozen Porous Stone

Sealing Ring

Latex Sock

Soil Sample

Teflon Tape
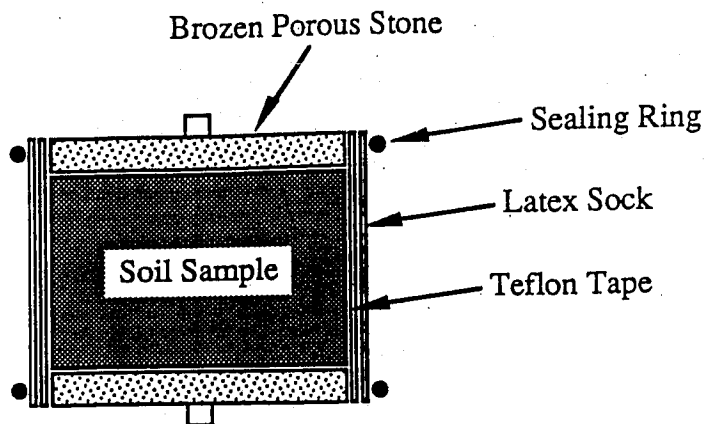
Figure 3.3 Prepared Soil Sample

3/16" O.D. Teflon Line

Stopper with
Teflon Seal

Flexible Wall
Permeameter

Target Organic
Chemical Solution

Soil Sample

Faucet

Venturi
Device

Carbon Columnn Traps

Hot Plate
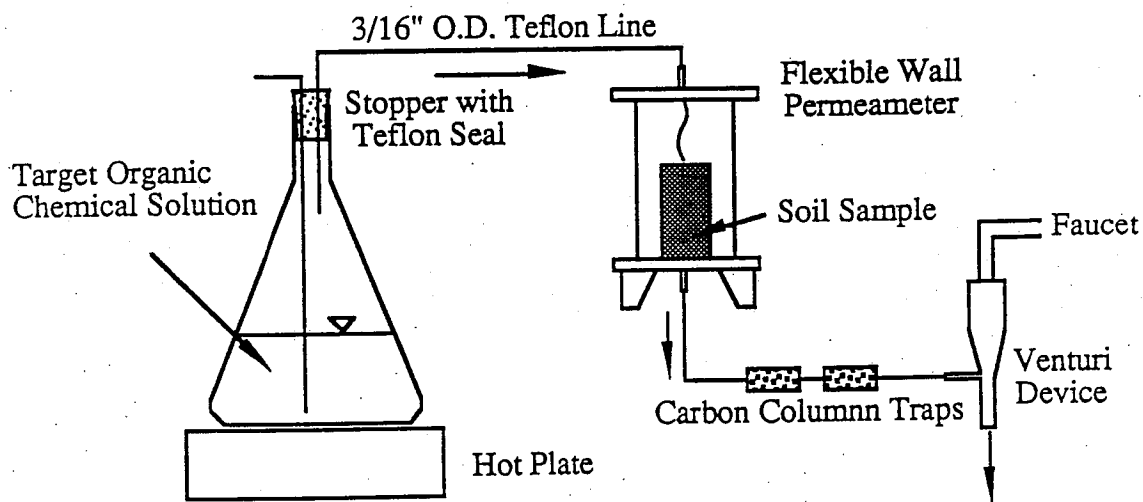
Figure 3.4 Contamination Apparatus Using Organic Chemical Vapor

Table 3.3 - Experimental Conditions					
Column	Soil Type	Sample Height (in)	Sample Diameter (in)	Gradient (in./in.)	Hydraulic Conductivity (cm/sec)
C3-1	Clay	2	4	5.75	6.44E-5
C5-1	Clay	2	4	2	2.84E-4
C6-1	Clay	2	4	18.5	4.91E-6
T4-1	Topsoil	2	4	1	5.92E-4
S1-2	Sand	2	4	1	1.41E-4

3.5.3 First Column Study Data Collection

Samples were taken approximately three times a day from the influent and effluent sides of the samples. The weights of the effluent bags were taken at the time of the samples. In this way concentration versus time and flow (weight was converted to volume of flow assuming the density of water was 1g/mL) were known, and breakthrough curves developed.

Once breakthrough of the soil columns was reached, flow was maintained until the influent concentrations equaled effluent concentrations for at least four consecutive samples. At this time, flow of the VOC solution was stopped and influent and effluent valves closed for four days. This allowed the VOC concentrations to equalize within the sample. The liquid phase concentration in the soil column was then checked and desorption experiments

started. A solution of 50% deionized water and 50% tap water was passed through the samples. Sampling followed the earlier sampling procedure.

3.5.4 Experimental Problems

During the four day equilibration period, the thermostat in the temperature controlled room containing the experimental apparatus broke. Temperatures in the room reached and may have exceeded 113 degrees fahrenheit for 1 to 2 days. A check of the VOC concentrations determined more than 60% of the contaminant mass in some samples volatilized during the temperature increase. In spite of the losses, desorption experiments were performed until sample effluent concentrations were in the part per billion range. Data from columns C3-1, C4-1, C5-1, C6-1, and T4-1 (four clay and one topsoil column) appeared to be unaffected, the remaining data was lost.

3.6 SECOND COLUMN STUDY EXPERIMENTAL METHODS

The purpose of the second desorption studies was to obtain additional data to make up for the data lost and if possible to perform mass balances on VOC lost from the samples over time. The initial mass of VOC in the sample was determined by a mass balance based on the difference between mass of VOC passed through the sample, and the mass of VOC extracted from a carbon trap on the effluent side of the column. An uncontaminated solution was then passed through the sample to model VOC leaching.

3.6.1 Experimental Apparatus

Because of the problems in the first column study a second column study was performed. A second method to introduce VOCs into the soil samples was developed. This method contaminated the samples quickly (5 minutes) and the mass of VOC in the sample could be determined from a mass balance. Soil samples were prepared and placed in flexible wall

permeameters as shown in Figure 3.3. A vaporization chamber was placed on the influent side of the sample and two 2-stage carbon tubes were placed on the effluent side followed by a water venturi device that produced a vacuum. Figure 3.4 shows the second contamination apparatus. A known mass of VOCs were placed in the high temperature vaporization chamber, and a fine mist formed was drawn through the sample. VOC that was not sorbed to the soil was collected in the carbon trap. Carbon disulfide was then used to extract the VOC from the carbon. The difference between the initial VOC mass in the vaporization chamber and the mass extracted from the carbon was assumed to be the mass in the samples. After the soil columns were contaminated, the influent and effluent valves were closed, and the VOCs were allowed to equilibrate in the sample for four days.

3.6.2 Experiment and Data Collection

The second column experiments used the same procedures as the first column experiments. Mass balances were not performed on columns for the second column studies.

3.7 Tracer Study

The purpose of this study was to determine the effective velocity and porosity and dispersion/diffusion coefficients of several of the samples. This study was performed during the initial contamination of the soil samples. A tracer, potassium bromide, was spiked to the influent reservoir for samples T4-1, C5-1, and C6-1.

After initially flushing the sample at high gradients (dh/dl) to remove colloidal particles, a pulse input of 10 ppm potassium bromide tracer was passed through the soil columns and samples of the influent and effluent were taken over time. The samples were analyzed using Beckman System Gold liquid chromatograph (HPLC). The HPLC system consisted of a Beckman Model 126 solvent module, a Shimadzu CTO-6A column, and a Shimadzu CDD-6A conductivity detector. Potassium bromide was used as the tracer because the bromide

anion should not be affected by the cation exchange of the clay soil. It is assumed that the tracer is nonreactive so the tracer mass transport is not retarded by sorption processes. Dispersion of nonreactive tracers is typically assumed to follow a Normal or Fickian distribution. Over time, a relation to statistical parameters is seen in the breakthrough curve. The longitudinal dispersion can be found from the breakthrough curve for a pulse input using:

$$D_L = \sigma_t^2 v^2/2t' \qquad (3\text{-}1)$$

where D_L is the longitudinal dispersion (m^2/day), σ_t is a statistical parameter of the breakthrough curve:

$$\sigma_t = \Gamma/2.354 \qquad (3\text{--}2)$$

and Γ = difference between the times at $C/C_0 = 0.5$; $v = x/t'$ = average linear velocity or effective velocity (m/day); x = column length (m); and t' is the mean breakthrough time (day).

Once the effective velocity was determined, the effective porosity was computed following Darcy's Law:

$$v_e = ki/n_e \qquad (3\text{--}3)$$

where k = hydraulic conductivity (m/day); I = hydraulic gradient over the sample (m/m); and n_e = the effective porosity.

Longitudinal dispersivity can also be found from the relation:

$$a_L = D_L/v \qquad\qquad (3\text{--}4)$$

where a_L = longitudinal dispersivity (m).

Since the dispersivity of the columns is assumed to have little impact on application of the leach rate model, dispersivity was found for only one clay sample. It is included to establish test conditions.

3.8 BATCH EXPERIMENT

The purpose of the batch experiments was to determine the equilibrium partition coefficient (K_d) for the different soil/VOC pairings. The K_d values obtained in this experiment were used as variables to compute predicted leach rates using the leach rate model.

3.8.1 Preliminary VOC Loss Analysis

Preliminary tests were performed to determine VOC volatilization and sorption losses for three types of 50 mL centrifuge tubes: polyethylene, stainless steel, and Teflon. Solutions ranging from 2 to 100 mg/L toluene, methylene chloride, trichloroethylene, and m-xylene were placed in the tubes and tumbled for 24 hours. Samples were then taken from the tube supernatant and analyzed on the GC. Results indicated the Teflon tubes had the lowest loss (<3%). The high losses found in the polypropylene tubes (<50%) and stainless steel tube (<80%), made them incompatible with attempting to close a mass balance.

3.8.2 Soil-VOC Mass Determination

Computations to determine the appropriate soil to solution ratio were then performed using methylene chloride as a worst case. The mass of VOC sorbed to the soil had to be high enough so that differences in the final concentrations in the soil and solution could be measured. The calculated VOC and soil masses were then added to the Teflon tubes in a preliminary test to verify that actual mass change in the soil and liquid phases approximated computed changes and was measurable. After one adjustment, acceptable results were obtained.

3.8.3 Batch Experiment

The batch experiment method followed ASTM D34. Soil samples weighing 15 g (topsoil), 25 g (clay), and 50 g (sand) were placed in 50 mL Teflon centrifuge tubes. The remaining tube volume was filled with 100, 40, 10, and 1 mg/L solutions of toluene, trichloroethylene, methylene chloride, and m-xylene. The tubes were then tumbled for 24 hours on a Millipore rotary agitator to provide end-over-end rotation. After 24 hours the tubes were centrifuged in a Beckman Model J2-21 Centrifuge Rotor at 10,000 RPM for 20 minutes. Supernatant samples were taken and placed in Teflon sealed 2 mL glass vials and analyzed on the GC along with samples containing the initial solution. This allowed for a mass balance between influent and effluent concentrations. The difference in the mass of VOCs in the liquid phase was assumed to equal the mass of VOC in the soil phase.

3.9 SOIL AND SOIL SAMPLE PARAMETER EXPERIMENTS

The objective of these studies was to determine soil density, bulk density, hydraulic conductivity, volumetric water content, and fraction of organic matter. Other parameters that characterize the soils were also determined.

3.9.1 Organic Matter

Representative samples of the sand, topsoil, and clay were analyzed by the UW Extension Physical Plant Lab. The lab determined the cation exchange capacity (CEC), pH, percent organic matter, and the percent of sand, silt and clay in the soils. Results of the analytic report are shown in Appendix B. The fraction of organic carbon in the soil was determined by dividing the percent organic matter by 1.7.

3.9.2 Dry Bulk Density and Volumetric Water Content

After column studies were completed the samples were carefully measured and weighed. The samples were then placed in a 100 degree centigrade oven for 2 weeks. The samples were then weighed. Based on the volume of the soil prior to drying and the weight of the dry soil, dry bulk densities were computed. Based on the difference between the wet weight of the sample and the dry weight of the sample the volumetric water content of the sample was computed.

3.9.3 Hydraulic Conductivity (K)

Initially, falling head tests were used to compute estimated sample hydraulic conductivities. Hydraulic conductivity typically decreases over the term of a hydraulic conductivity experiment until influent and effluent flows equilibrate and the actual equilibrium K is reached. For this reason the initial falling head tests are gross estimates of K and were only used to preselect a wide range of hydraulic conductivities in the samples. The hydraulic conductivities used to determine the leach rate equation were computed based on the average flow rate, hydraulic gradient, and the cross sectional area of the sample. Significant decreases in hydraulic conductivity were not seen over time.

3.9.4 Soil Particle Density

Soil particle densities were determined to characterize the soils and check the results of other soil parameter tests. Three 200 mL volumetric flasks were weighed, filled with water to the fill mark, deaired using a vacuum, and weighed again. The flasks were then dried, and approximately 50 grams of dry soil was placed in the flasks. The remaining volume was filled with water. The flasks were deaired and weighed again. Soil densities were computed based on the difference in flask weights and the mass of soil added. The densities were then corrected for temperature effects on water density.

CHAPTER 4

RESULTS

4.1 TRACER STUDY RESULTS

The effective velocity, effective porosity, and dispersion coefficients found from the tracer studies are summarized in Table 4-1. The effective porosities determined from experimental data appear to be in error. The highest porosity a sample may have approaches unity, the pore space cannot exceed the overall volume of the sample. Thus, samples may not have porosities greater than one. The error in the effective porosities also calls into question the other results. It may be the tracer used was not conservative. This would decrease the effective velocity, and the porosity would increase. The diffusion coefficient and dispersivity would be effected as well.

Table 4.1 - Tracer Study Results						
Column	t' (s)	V_e (cm/s)	n_e (mL/mL)	σ_L (s)	D_L (cm^2/s)	α_L (cm)
T4.1	15053	3.4×10^{-4}	1.74	3542	4.8×10^{-5}	0.142
C5.1	15720	3.2×10^{-4}	1.77	1888	1.2×10^{-5}	0.036
C6.1	54280	9.4×10^{-5}	0.97	3759	1.2×10^{-6}	0.012

4.2 SOIL PARAMETER STUDY RESULTS

Soil parameter study results are shown in Table 4.2. The soil parameters determined from laboratory analysis are within the range of values found in the literature. The soil

particle densities and void ratios are consistent with those found in previous studies (Das, 1985 and Dominico et al., 1990). The high organic content of the topsoil was expected based on its observed high humic content.

Table 4.2 Properties of Selected Soils							
Soil Type	Particle Size Dsitribution			Particle Density (g/cc)	Organic Matter (%)	Organic Carbon (%)	CEC	pH
	Sand	Silt	Clay					
Sand	99	1	0	2.62	0.2	0.12	0	6.3
Clay	34	42	24	2.36	0.6	0.35	26	7.2
Topsoil	51	37	12	2.18	7.2	4.24	37	7.2

4.3 BATCH ISOTHERM TEST RESULTS

4.3.1 Data Evaluation

Initial tube supernatant concentrations (mg/L) were plotted against extracted solid phase concentrations (µg/gm). A line following a Freundlich linear isotherm was fitted to the data by linear regression and forced through the origin. The slope of the line was set equal to K_d, the equilibrium partition coefficient. The curve fits developed from the batch study data are shown in Appendix D.

4.3.2 Equilibrium Partition Coefficients

The equilibrium coefficients found from the batch experiments are summarized in Table 4.3. The K_d values determined from the batch experiments were not consistent with the general trend expected based on prediction of partitioning coefficients from the octanol

water partition coefficient and soil organic content. The K_d for TCE was greater than the K_d for TOL. This is not expected given the Kds predicted following Hassett et at. (1983). However, a comparison of the batch study equilibrium partition coefficients and the coefficients predicted following Piwoni et al. (1989), show the coefficients are approximately the same (Table 4.3). Coefficients predicted using Piwoni's relation in Karickhoff's model are within an order of magnitude of the values determined from the batch studies. Deviation from predicted partitioning may be a result of the variability of humic components of the soil samples, variability of the GC analyses and other experimental errors.

Table 4-3 Summary of Equilibrium Partition Coefficients (K_d)						
	Experimental			**Predicted**		
Compd.	**Sand**	**Clay**	**Topsoil**	**Sand**	**Clay**	**Topsoil**
MC	0.121	0.304	0.138	0.014	0.042	0.51
TCE	0.957	0.835	2.23	0.113	0.326	4.0
TOL	0.733	1.01	2.37	0.144	0.421	5.1
MX	1.92	1.98	6.44	0.234	0.628	8.27

4.3.3 Batch Study Mass Balance

A mass balance was conducted on the K_d test results for each compound and clay. Mass balances were computed based on the influent concentration of VOC, the supernatant concentration of VOC, and the mass of VOC in the soil based on the carbon disulfide extractions. The percent errors of the closure of the mass balance found computed by computing the perecnt change in total mass in versus total mass out. The errors ranged from

about +30% to -11%. Given the variability of the GC and the experimental method this was considered reasonable.

4.3.4 Batch Study Evaluation of Losses

Losses were checked during batch experiments. Tubes containing the original solution (100 mg/L) were placed in the tumbler with the other batch tubes, then sampled and analyzed, to determine if losses occurred. No losses were found for methylene chloride and m-xylene. Losses for toluene were less than 1%. Trichloroethylene had the highest loss (1.8%). These losses are negligible and are not expected to have affected the outcome of the batch experiments.

4.4 COLUMN STUDY RESULTS

4.4.1 Data Evaluation

A computer program was written and used to derive time increments and volume of flow from the base data. The desorption time increment and concentration data were then plotted. The concentration changes over time by desorption are shown in Appendix E. The desorption curves followed the decreasing trends typically found in other VOC desorption studies in the literature. In addition, concentrations generally approached asymptotic values.

The variability in the GC analyses complicated data evaluation. In some cases, abrupt changes in decreasing concentration trends occurred. These abrupt changes are believed to be an artifact of GC variability and are apparent in the standard curves. In evaluating the data, standards were used to confirm control for the samples analyzed. In several instances

during analysis with the automated sampler samples were close to but outside three standard deviations from the mean. Because there was no alternative these data were used but may be considered questionable.

4.4.2 Column Study Mass Balance

Mass balances on VOC following sorption and desorption were performed on column C6-1. Table 4-4 summarizes the mass balance following the sorption phase of the column study.

Table 4.4 Mass Sorbed versus Kd Predicted Mass Sorbed Column C6-1						
Compound	Batch Study Kd	Equilibrium Concentration (mg/L)	Soil Mass (gm)	Mass Gain By Kd (mg)	Mass Gain By Sorption (mg)	Error (%)
MC	0.304	95.8	745.1	21.7	104.6	+79
TCE	0.835	75.8	745.1	47.2	195.2	+75.8
TOL	1.01	78.8	745.1	59.3	242.6	+75.5
MX	1.98	75.9	745.1	112.0	299.6	+62.6

Mass balances following the sorption phase indicated increasing amounts of mass were retained by the soil for MC, TCE, TOL, and MX respectively. Generally a good correlation was found between the mass in the soil following the sorption study and the K_d values found from the batch studies. Percent errors were computed for mass predicted from K_d values and mass retained following the sorption study. Percent errors ranged from about +62% to +79%. A sample was collected following the column C6.1 desorption study and a mass

balance on the VOC mass in the soil versus the total mass gain or loss over the course of the sorption/desorption experiments was performed. The overall mass balance results are summarized in Table 4-5.

Table 4.5 Overall Mass Balance Column C6-1 and All Compounds					
Compound	Total Mass Gain Sorption Study (mg)	Total Mass Lost Desorption Study (mg)	Residual Mass Extracted from Soil (mg)	Mass Gain/Loss (mg)	Error (%)
MC	104.6	115.3	0	-10.7	-10.2
TCE	195.2	111.7	81.9	1.6	0.8
TOL	242.6	89	83.6	70	28.8
MX	299.6	88	226.8	-15.2	-5.1

Percent errors were computed for the total mass gained from the sorption study versus the total mass lost from the desorption study and the mass remaining in the soil following the desorption study. Percent errors ranged from about +30% to -10%. Residual mass in the sample at the conclusion of the desorption phase increased from MC, TCE, TOL, and MX, respectively. Masses into and out of the column were computed on a flow weighted basis.

4.5 LEACH RATE MODEL RESULTS

4.5.1 Data Evaluation

The following step wise approach was used to compute leach rate constants.

1. Initially data for each compound-soil sample pair desorption time versus concentration data was plotted. Then curves were fit to the data by computer by varying the leach rate constant parameter and observing curve match up.

2. Leach rate constants were predicted using the Rodgers and Associates equation and the sample parameters - hydraulic conductivity, partitioning coefficients, volumetric water content, and dry density, developed form the other experimental studies.

3. A least squares regression was performed on the curve fit leach rates and the leach rates predicted with the Rodgers and Associates equation, and a slope and intercept value were determined.

4. The slope and intercept values were applied to the Rodgers and associates equation to calibrate it to the column study desorption curve data.

A substantial amount of time was spent attempting to fit exponential and various other curves to the desorption curve data. Ultimately exponential curves approaching asymptotic concentrations provided the best fit.

The leach rate predictive equation is shown below:

$$\lambda_l = 105/h(\theta + \rho_b K_d) + 1.0E\text{-}05 \tag{4-1}$$

where λ_l = leach rate constant (mg/kg); P = percolation rate (cm/second); θ = volumetric water content (cm^3 of contaminated water/cm^3 of contaminated soil); h = depth of

contamination (m); K_d = partition coefficient between soil and pollutant (L/kg); and ρ_b = soil dry bulk density (gm/cm^3).

The observed leach rates and the predicted leach rates are correlated. The observed leach rate versus predicted leach rate curve fit is shown in Figure 4-1. The statistical parameters used in fitting the curve are shown in Appendix E. A summary of the predicted leach rates and the parameters used to compute them, the observed leach rates, and the leaching curves fitted to the column desorption data are shown in Appendix E.
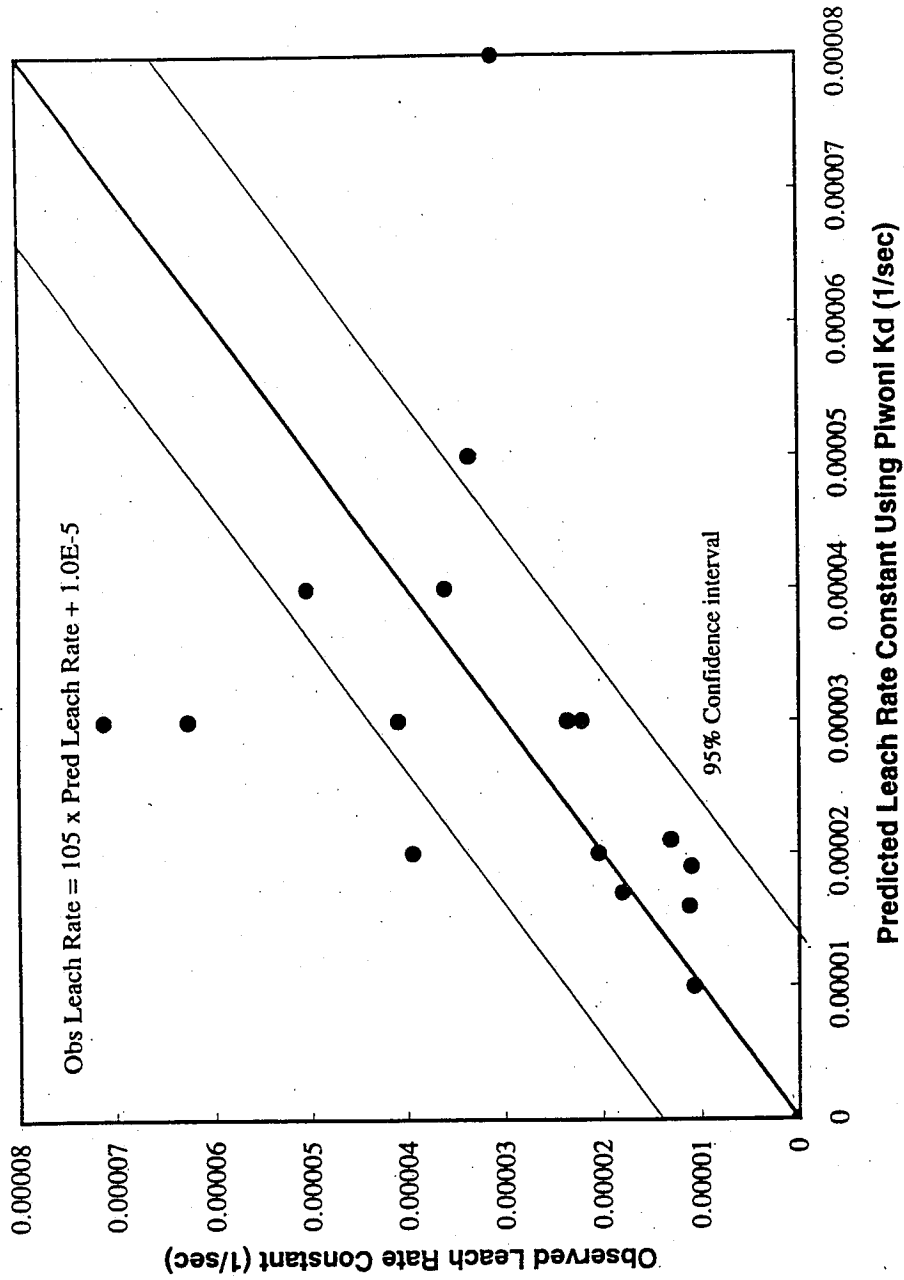
Figure 4.1 Leach Rate Observed versus Predicted Using Piwoni Kd

CHAPTER 5

CONCLUSIONS

5.1 CONCLUSIONS

From a series of laboratory column sorption/desorption tests, the following conclusions

can be drawn:

1. Desorption of VOCs occurs at two distinct rates. Initial short term desorption occurs at a

faster rate than long term desorption. The initial rapid rate of desorption may be caused by

desorption of VOCs from the surface of the solid. Long term desorption may be a result of

intraparticle diffusion and diffusion of VOCs from micropores to macropores, and occurs at

a slow rate. This may indicate that sorption is not a reversible reaction.

2. Current VOC mass transport theory is not consistent with the experimental results. The

long term desorption rate of VOCs did not increase as solubility decreased. Contrary to

present understanding, the higher solubility VOCs had slower the long term desorption rates.

Results repeatedly show that the long term desorption rate for methylene chloride is slower

than the long term desorption rate for m-xylene. Current mass transport theory incorrectly

predicted relative desorption rates.

3. Current theory correctly predicts the short term desorption of VOCs (the first 12 hours of

desorption). The rate of short term desorption increased as VOC solubility increased.

4. An inversion of the desorption rates was observed at some point in time (4 to 24 hours).

At this time, desorption rates that initially increased as solubility increased, increased as

solubility decreased. It is believed this inversion occurs because of a fundamental change in the physical mechanisms of VOC desorption. There is no specific explanation for the apparent inversion as a function of solubility. There is, however, a general explanation for the phenomena. Short term desorption will occur primarily from the surface of the solid. This type of desorption occurs at a rapid rate. Once desorption from the surface of the solid has occurred, desorption from within micropores and organic matter occurs.

5. While desorption rates were observed to invert as a function of solubility, the desorption rates for the different compounds were close in value in some samples. This may be a result of nonequilibrium desorption due to high rates of flow through the samples.

6. The observed two rate desorption is consistent with the findings of Pavlostathis et al. (1992). Pavlostathis found initial desorption rates were faster than the long term desorption rates. The slow rates of desorption for lower solubility VOCs is consistent with Ball's (1992) findings, where extended desorption times were seen for VOCs with solubilities of less than 150 mg/L. Pavlostathis (1992) also observed long desorption times for trichloroethylene.

7. Losses of VOCs from the soil will range from 25-80% during short term desorption. Losses are a function of VOC solubility, advective velocity, and soil organic content.

8. The leach rate model developed by Rodgers and Associates for nuclear waste facilities is applicable to VOC desorption from soil. The leach rate predicted using this model and the leach rate observed during experiments show reasonable correlation.

9. The proposed leach rate model only applies to the compounds, concentrations, and soils tested. It is likely the model can be extended to other VOCs, soil types, and conditions, based on the correlation seen in the various VOC-soil conditions tested.

10. VOCs leaching from soil do not always follow simple exponential decay. The leaching of VOCs followed exponential decay but often reached asymptotic conditions over time. The asymptotic exponential decay model provided the best fit to the data.

11. Because the proposed model has not been tested at the field scales caution should be exercised in its use in the field.

12. The proposed leach rate model has not been tested in either the partial differential form of the advection-dispersion equation or Van Gnutchen's solutions to that equation. While the leach rate should be applicable, caution should be exercised if it is used.

13. Batch isotherm partitioning studies may not accurately model partitioning because of the short time frames typically used.

14. The variability of GC analyses was substantial. When standard curve samples were analyzed, the difference between the high and low concentrations detected was as much as 25%. This analytic variability created problems during data interpretation.

CHAPTER 6

RECOMMENDATIONS

6.1 RECOMMENDATIONS

The following recommendations are made:

1. Use of the proposed leach rate model in both the advection-dispersion equation and Van Genutchen's solution to the advection-dispersion equation should be tested and evaluated, by comparing proposed model predictions with actual field results..

2. Experiments should be undertaken to verify this research and increase the range of compounds, concentrations, and soil conditions to which the model may be applied.

3. The viability of the model for field use should be determined. Extrapolation of the model to the field scale has not been investigated. Laboratory results may not be duplicated in the field due to large scale heterogeneities in the soil and other factors. Before the model is applied in the field, studies to verify model applicability should be performed.

4. Future research should investigate how the leaching process will be affected by soil wetting cycles and volatilization of the compounds into the gas phase. The water passing through the soil may create irregular pulses each time it rains. These issues were not addressed in this research.

5. Standard samples should be as close as possible to the expected sample concentration. This will minimize the effect of GC variability when standard corrections are applied.

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and suspended solids - I, *Water Resources*, Vol. 17, No. 10, pp. 1433-1441.

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528.

APPENDIX A

STANDARD CURVES

Conc. = 0.00154(Area Count) + 1.90;UCL = .00134;LCL = .00182
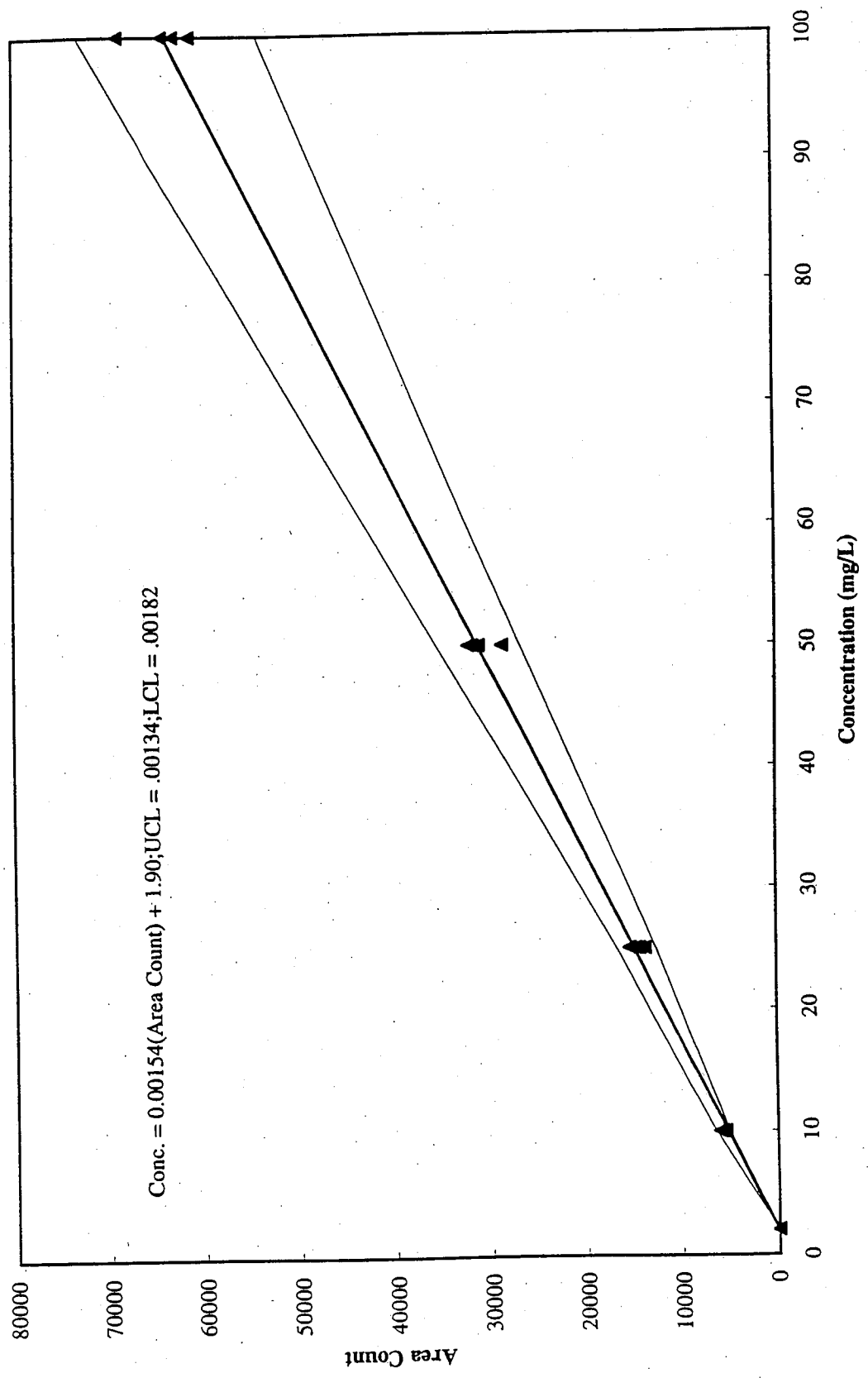
Figure A.1 MC standard curve

Conc. = 0.001643(Area Coumt) + 2.96; UCL = 0.00129; LCL = 0.00233
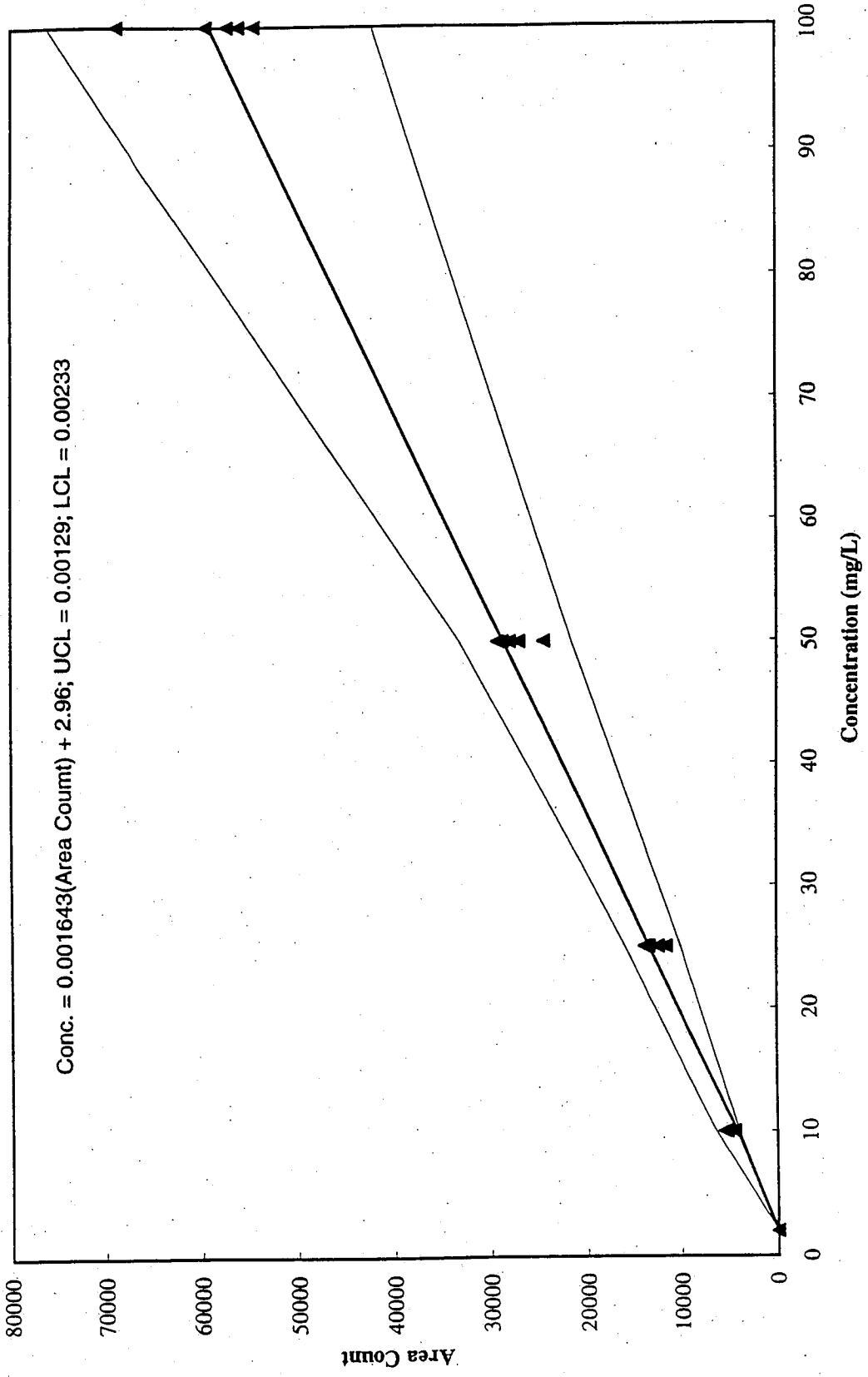
Figure A.2 TCE standard curve

Conc. = 0.000217(Area Count) + 1.36; UCL = 0.000183; LCL = 0.000287
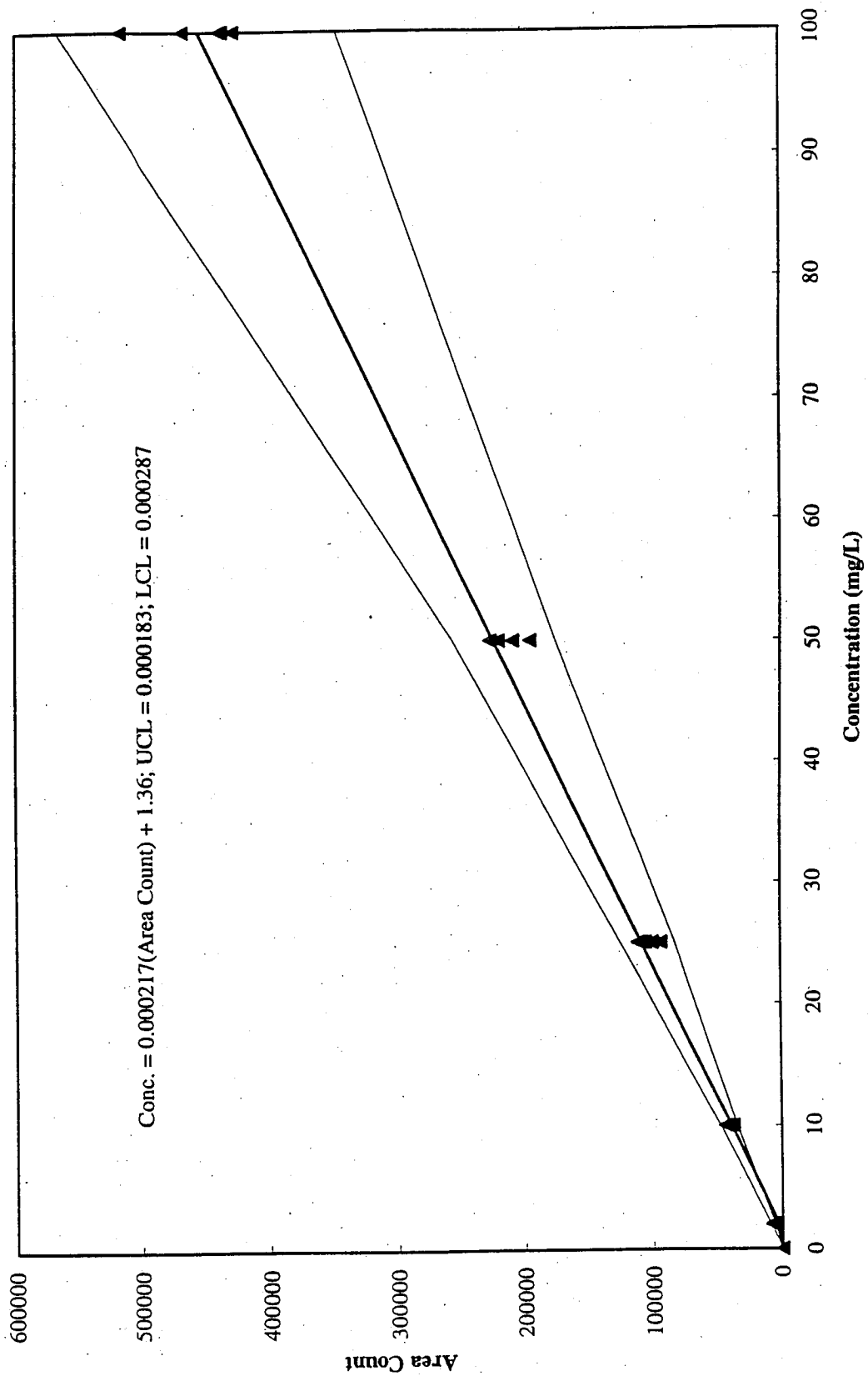
Figure A.3 TOL standard curve

Conc. = 0.00253(Area Count) + 1.93; UCL = 0.000214; LCL = 0.000358
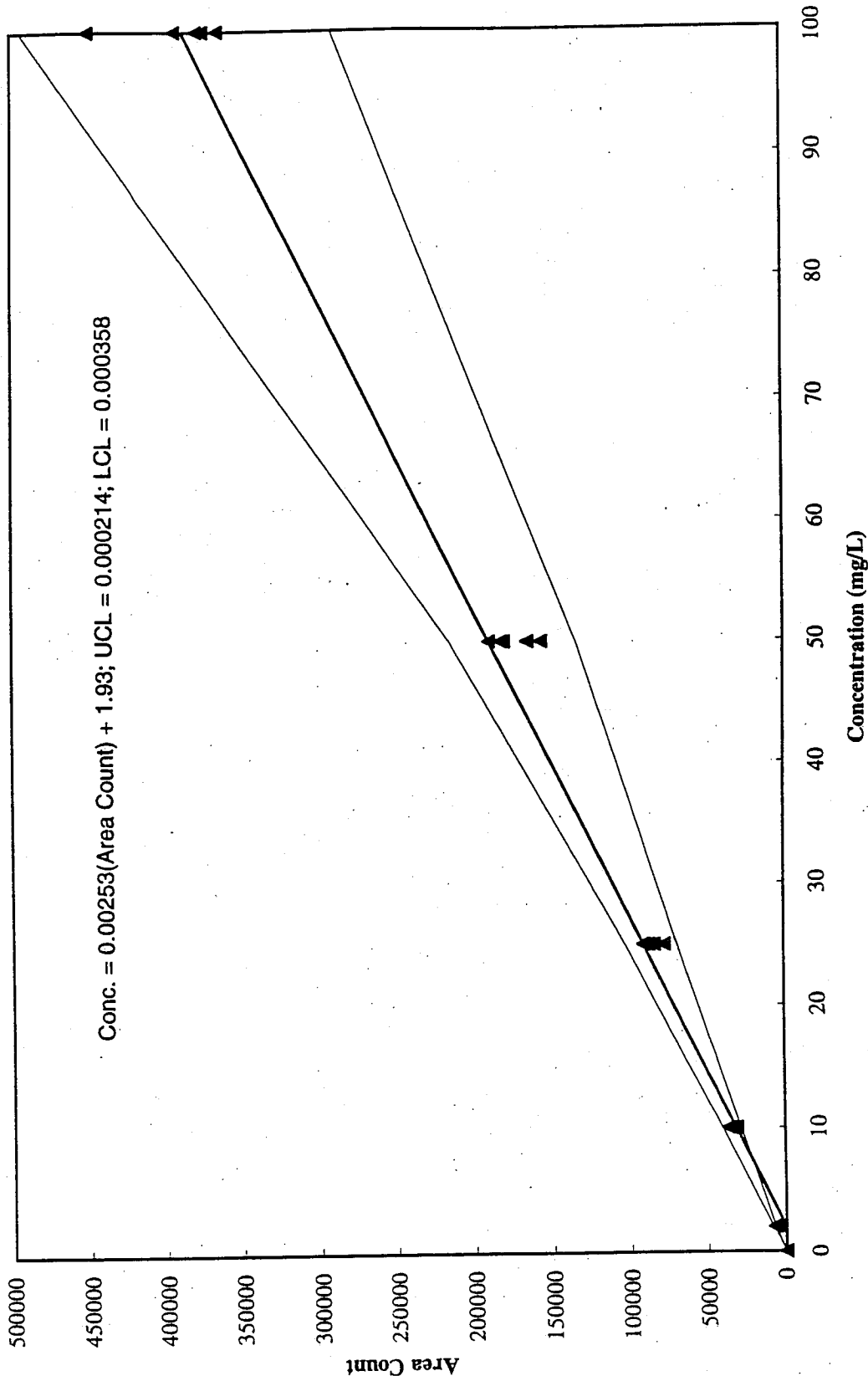
Figure A.4 MX standard curve

APPENDIX B

SOIL ANALYSIS REPORT

Samples Analyzed By:

SOIL & PLANT ANALYSIS LAB
1711 MINERAL POINT ROAD
MADISON, WI 53705

SOIL TEST REPORT

LAB NO. 0- 415

State	County	Account No.
DANE	900	

Date Rec'd	Date Processed
10/17/91	23-Oct-91

JAMES IMBRIE
342 KENT LANE #301
MADISON, WI. 53713

This Report is for:

JAMES IMBRIE

- IDENTIFICATION -

Field	SAND
Acres	
Soil Name (or subsoil group)	GROUP E
Plow Depth	6.5

LABORATORY ANALYSIS

Sam. No.	Test. code	Est. CEC	Soil pH	O.M. %	P ppm	K ppm	Ca ppm	Mg ppm	B ppm	Mn ppm	Zn ppm	SO₄-S ppm	S Avail. Index	Other Tests	Sample Density g/cm³	Buffer Code
1	1	0	6.3	.2	50	25	100	10							1.57	7.4

OPTION 1: RECOMMENDATIONS

Cropping year	Crop to be Grown	Crop Yield Goal	Soil Test Interpretation 1/ P	K	Nutrient Needs N	P₂O₅	K₂O	Fertilizer Replacement Credit 2/ N	P₂O₅	K₂O	Nutrients to Apply N	P₂O₅	K₂O
1	Miscellaneous												
2													
3													

Lime required for this rotation to reach pH   is   T/a of 60-69 lime or   T/a of 80-89 lime.

THE OPTIMUM PH FOR A CROP IN THIS ROTATION IS NOT ESTABLISHED.

OPTION 2: RECOMMENDATIONS

Cropping year	Crop to be Grown	Crop Yield Goal	Soil Test Interpretation 1/ P	K	Nutrient Needs N	P₂O₅	K₂O	Fertilizer Replacement Credit 2/ N	P₂O₅	K₂O	Nutrients to Apply N	P₂O₅	K₂O
1	Miscellaneous												
2													
3													

Lime required for this rotation to reach pH   is   T/a of 60-69 lime or   T/a of 80-89 lime.

THE OPTIMUM PH FOR A CROP IN THIS ROTATION IS NOT ESTABLISHED.

1/ Soil Test Interpretation Codes: VL (very low), L (low), Opt (optimum), H (high), VH (very high), EH (excessively high)

2/ These credits are determined from information provided relative to legume-sod plowdown and manure application.

Note: if spring nitrogen availability test has been run, subtract the nitrogen credit from crop nitrogen needs.

COMMENTS SECTION

Crop	INTERPRETATIONS & COMMENTS For Option 1 Crops							Crop	INTERPRETATIONS & COMMENTS For Option 2 Crops					
Year	Ca- VL	Mg- VL	B -	Mn-	Zn-	SAI-		Year	Ca- VL	Mg- VL	B -	Mn-	Zn-	SAI-
1	Ca7	Mg7					\ SEE INDICATED /	1	Ca7	Mg7				
2							- COMMENTS ON -	2						
3							/ ENCLOSED SHEET \	3						

BECAUSE OF THE LOW POTASSIUM BUFFERING CAPACITY OF THIS SOIL THIS FIELD SHOULD BE RETESTED EVERY TWO YEARS.
THE NITROGEN RECOMMENDATION SHOULD BE APPLIED IN SIDEDRESSED OR SPLIT APPLICATION ON SANDY SOILS.
SOIL NAME FOR THIS FIELD WAS NOT SPECIFIED. MORE SPECIFIC RECOMMENDATIONS ARE POSSIBLE IF THE SOIL NAME IS PROVIDED.

SOIL TEST REPORT

Samples Analyzed by:

SOIL & PLANT ANALYSIS LAB

COOPERATIVE EXTENSION
University of Wisconsin-Extension
University of Wisconsin-Madison
Soils Department, Madison WI

LAB NO. G- 415			JAMES IMORIE	This Report is for:

State	County	Account No.
DANE		999

Date Rec'd	Date Processed
10/17/91	23-Oct-91

JAMES IMORIE

IDENTIFICATION

Field	CLAY
Acres	
Soil Name (or subsoil group)	GROUP C
Plow Depth	6.5

LABORATORY ANALYSIS

Sam. No.	Test code	Est. CEC	Soil pH	O.M. %	P ppm	K ppm	Ca ppm	Mg ppm	S ppm	Mn ppm	Zn ppm	SO₄-S ppm	S Avail. Index	Other Tests	Sample Density g/cm³	Buffer Code
2	4	26	7.2	.6	3	90	4200	660							1.21	N.R.

OPTION-1 / RECOMMENDATIONS

Cropping year	Crop to be Grown	Crop Yield Goal	Soil Test Interpretation 1/ P	K	Nutrient Needs N	P₂O₅ lbs/a	K₂O	Fertilizer Replacement Credit 2/ N	P₂O₅ lbs/a	K₂O	Nutrients to Apply N	P₂O₅ lbs/a	K₂O
1	Miscellaneous												
2													
3													

Lime required for this rotation to reach pH   is   T/a of 60–69 lime or   T/a of 80–89 lime.

THE OPTIMUM PH FOR A CROP IN THIS ROTATION IS NOT ESTABLISHED.

OPTION-2 / RECOMMENDATIONS

Cropping year	Crop to be Grown	Crop Yield Goal	Soil Test Interpretation 1/ P	K	Nutrient Needs N	P₂O₅ lbs/a	K₂O	Fertilizer Replacement Credit 2/ N	P₂O₅ lbs/a	K₂O	Nutrients to Apply N	P₂O₅ lbs/a	K₂O
1	Miscellaneous												
2													
3													

Lime required for this rotation to reach pH   is   T/a of 60–69 lime or   T/a of 80–89 lime.

THE OPTIMUM PH FOR A CROP IN THIS ROTATION IS NOT ESTABLISHED.

1/ Soil Test Interpretation Codes: VL (very low), L (low), Opt (optimum), H (high), VH (very high), EH (excessively high)

2/ These credits are determined from information provided relative to legume-sod plowdown and manure application.

Note: if spring nitrogen availability test has been run, subtract the nitrogen credit from crop nitrogen needs.

COMMENTS SECTION

Crop	INTERPRETATIONS & COMMENTS For Option 1 Crops							Crop	INTERPRETATIONS & COMMENTS For Option 2 Crops					
Year	Ca- H	Mg- H	B -	Mn-	Zn-	SAI-		Year	Ca- H	Mg- H	B -	Mn-	Zn-	SAI-
1	Ca3	Mg4					\ SEE INDICATED /	1	Ca3	Mg4				
2							- COMMENTS ON -	2						
3							/ ENCLOSED SHEET \	3						

N.R. = NOT REQUIRED FOR CALCULATION OF LIME REQUIREMENT WHEN THE SOIL PH IS 6.6 OR HIGHER.

SOIL NAME FOR THIS FIELD WAS NOT SPECIFIED. MORE SPECIFIC RECOMMENDATIONS ARE POSSIBLE IF THE SOIL NAME IS PROVIDED.

Dealer's Copy

Samples Analyzed By:

SOIL TEST REPORT

LAB NO. 5- 415		JAMES IMBRIE

State	County	Account No.
DANE		900

Date Rec'd	Date Processed
10/17/91	23-Oct-91

This Report is for:

JAMES IMBRIE

IDENTIFICATION

Field	TOP
Acres	
Soil Name (or subsoil group)	GROUP B
Plow Depth	6.5

LABORATORY ANALYSIS

Sam. No.	Text. code	Est. CEC	Soil pH	O.M. %	P ppm	K ppm	Ca ppm	Mg ppm	B ppm	Mn ppm	Zn ppm	SO4-S ppm	S Avail. Index	Other Tests	Sample Density g/cm³	Buffer Code
3	3	37	7.2	7.6	21	95	4250	1540							1.03	N.R.
4																

OPTION 1

RECOMMENDATIONS

Cropping year	Crop to be Grown	Crop Yield Goal	Soil Test Interpretation 1/ P	K	Nutrient Needs N	P2O5 lbs/a	K2O	Fertilizer Replacement Credit 2/ N	P2O5 lbs/a	K2O	Nutrients to Apply N	P2O5 lbs/a	K2O
1	Miscellaneous												
2													
3													

Lime required for this rotation to reach pH _____ is _____ T/a of 60-69 lime or _____ T/a of 80-89 lime.

THE OPTIMUM PH FOR A CROP IN THIS ROTATION IS NOT ESTABLISHED.

OPTION 2

RECOMMENDATIONS

Cropping year	Crop to be Grown	Crop Yield Goal	Soil Test Interpretation 1/ P	K	Nutrient Needs N	P2O5 lbs/a	K2O	Fertilizer Replacement Credit 2/ N	P2O5 lbs/a	K2O	Nutrients to Apply N	P2O5 lbs/a	K2O
1	Miscellaneous												
2													
3													

Lime required for this rotation to reach pH _____ is _____ T/a of 60-69 lime or _____ T/a of 80-89 lime.

THE OPTIMUM PH FOR A CROP IN THIS ROTATION IS NOT ESTABLISHED.

1/ Soil Test Interpretation Codes: VL (very low), L (low), Opt (optimum), H (high), VH (very high), EH (excessively high)

2/ These credits are determined from information provided relative to legume-sod plowdown and manure application.

Note: if spring nitrogen availability test has been run, subtract the nitrogen credit from crop nitrogen needs.

COMMENTS SECTION

Crop Year	INTERPRETATIONS & COMMENTS For Option 1 Crops							Crop Year	INTERPRETATIONS & COMMENTS For Option 2 Crops				
	Ca- H	Mg- H	B -	Mn-	Zn-	SAI-			Ca- H	Mg- H	B -	Mn-	Zn-	SAI-
1	Ca3	Mg4					\ SEE INDICATED /	1	Ca3	Mg4				
2							I- COMMENTS ON -I	2						
3							/ ENCLOSED SHEET \	3						

N.R. = NOT REQUIRED FOR CALCULATION OF LIME REQUIREMENT WHEN THE SOIL PH IS 6.8 OR HIGHER.

SOIL NAME FOR THIS FIELD WAS NOT SPECIFIED. MORE SPECIFIC RECOMMENDATIONS ARE POSSIBLE IF THE SOIL NAME IS PROVIDED.

SOIL & PLANT ANALYSIS LABORATORY   James Imbrie   LAB # TRA?
5711 MINERAL POINT ROAD   346 Kent Lane, #301   ACCT # 90?
MADISON, WI 53705   Madison, WI 53713   Civil Engr.
                                                 2-133-R839A19 1500 4

SOIL TEXTURE REPORT

SAMPLE ID	% SAND	% SILT	% CLAY	SOIL TEXTURE
16 SAND 1	99	1	0	SAND (A)
17 CLAY 2	34	42	24	LOAM (D)
18 TOP 3	51	37	12	LOAM (D)

APPENDIX C

TRACER STUDY BREAKTHROUGH CURVES
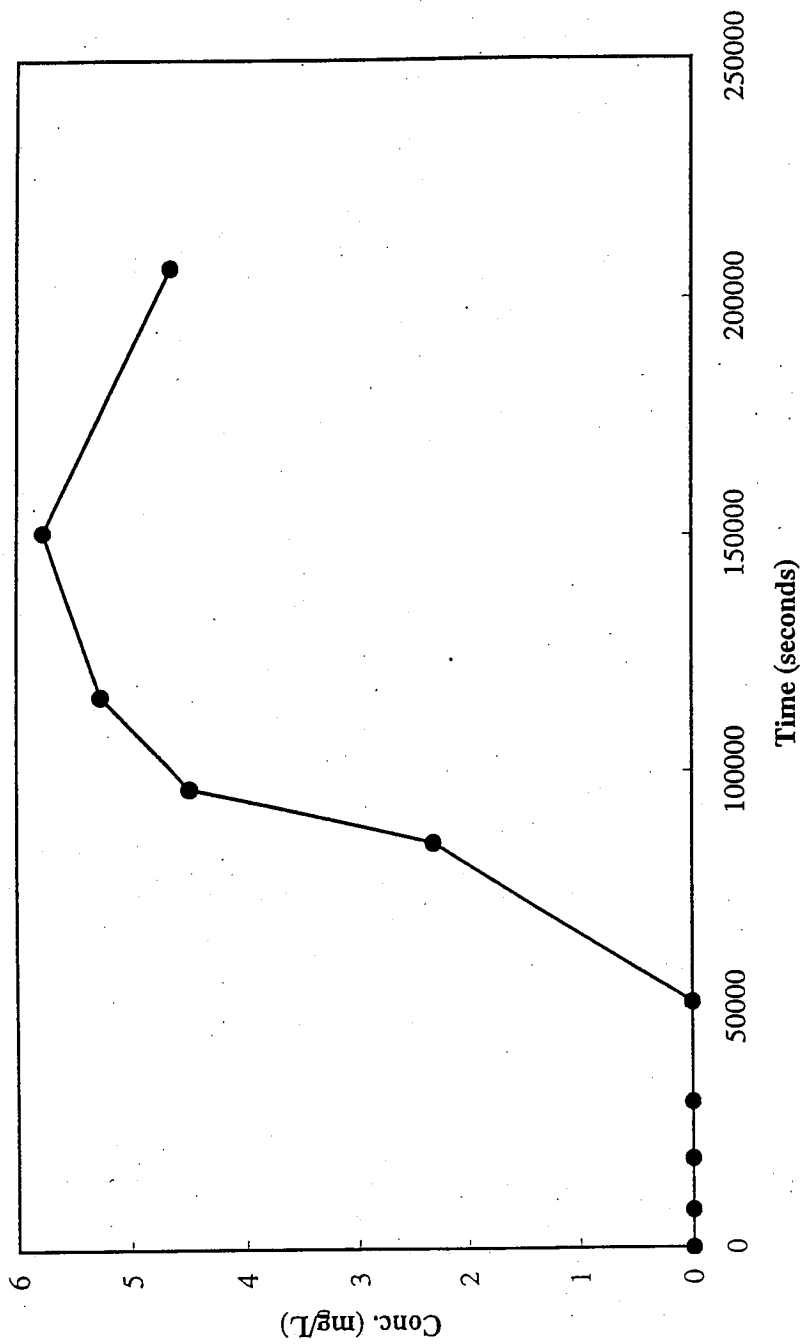
Figure C.1 Bromide Breakthrough Curve for Column T4.1
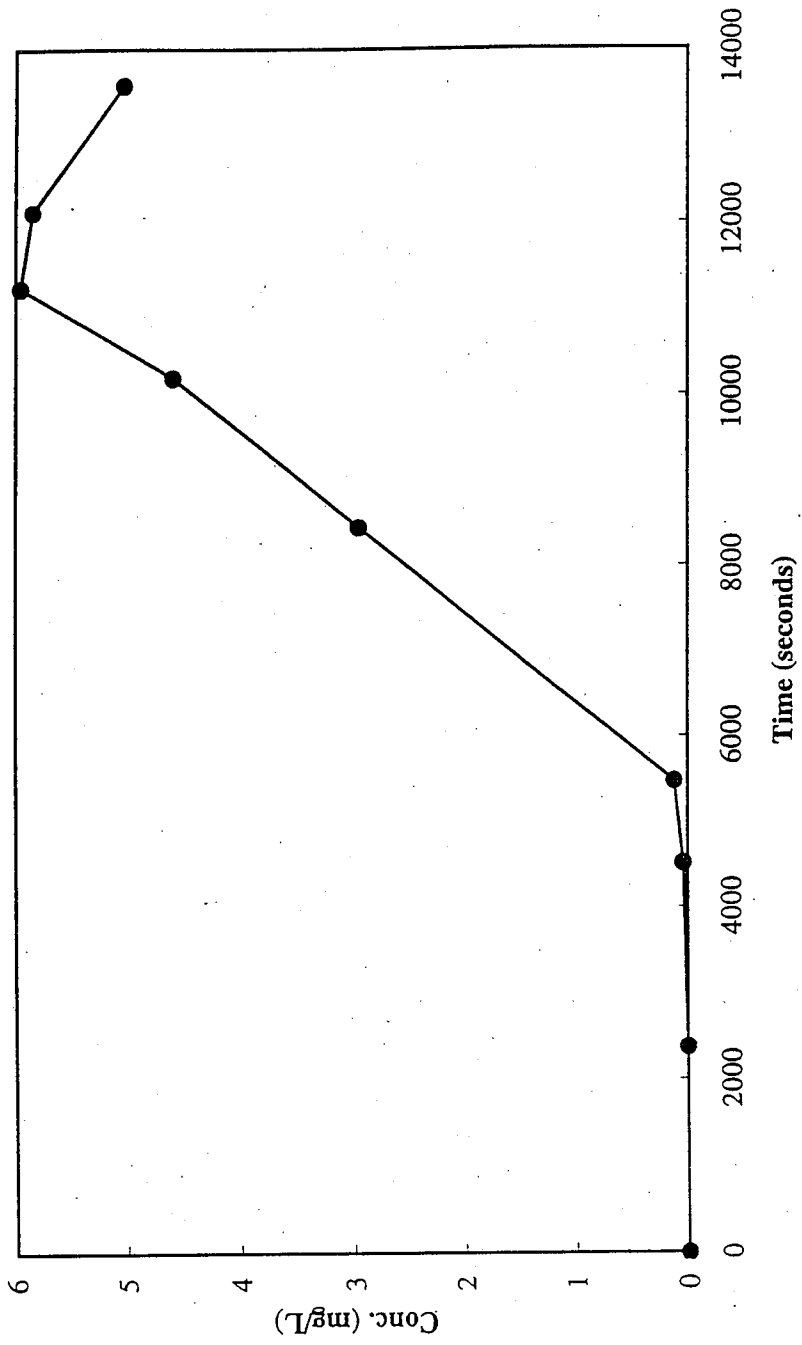
Figure C.2 Bromide Breakthrough Curve for Column C5.1
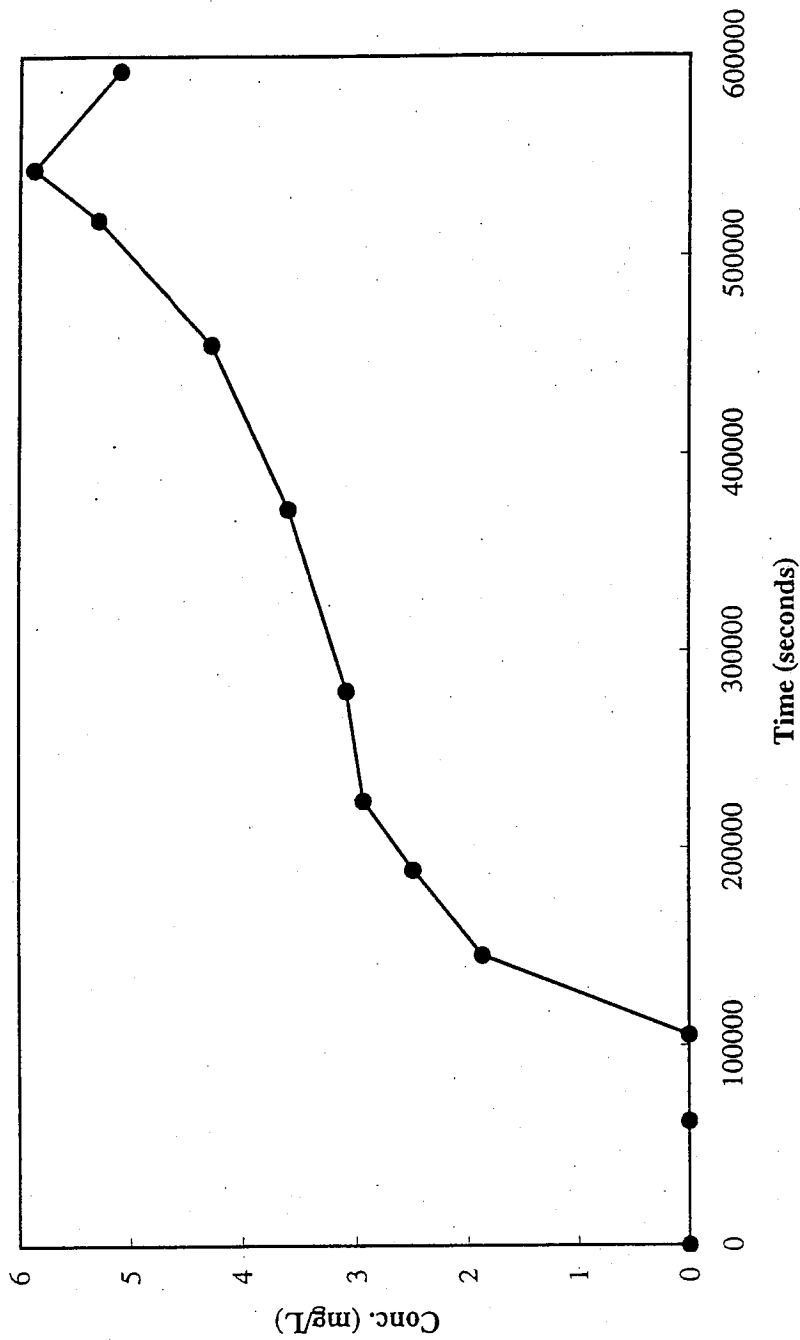
Figure C.3 Bromide Breakthrough Curve for Column C6.1

APPENDIX D

BATCH ISOTHERMS
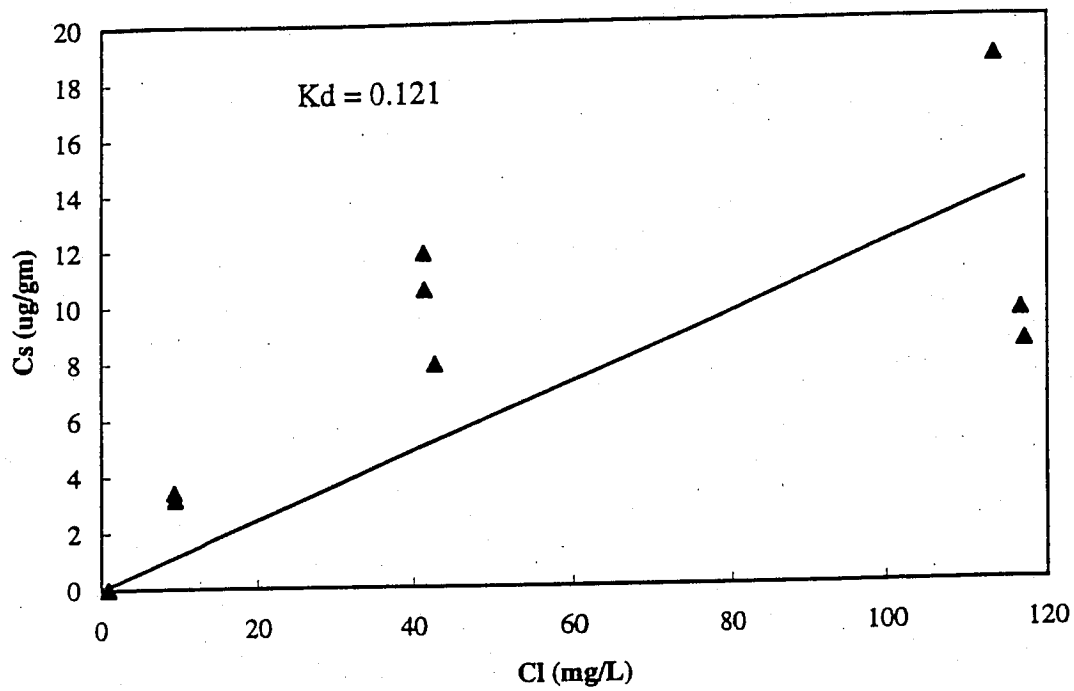
Figure D.1 Batch isotherm MC and sand
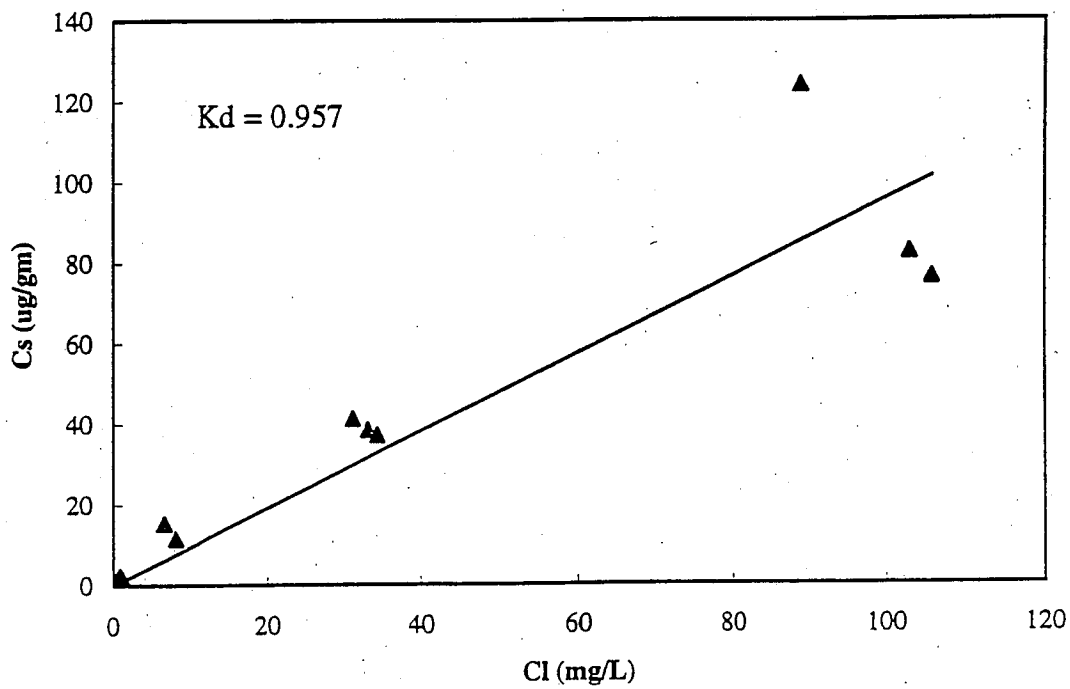
Figure D.2 Batch isotherm TCE and sand
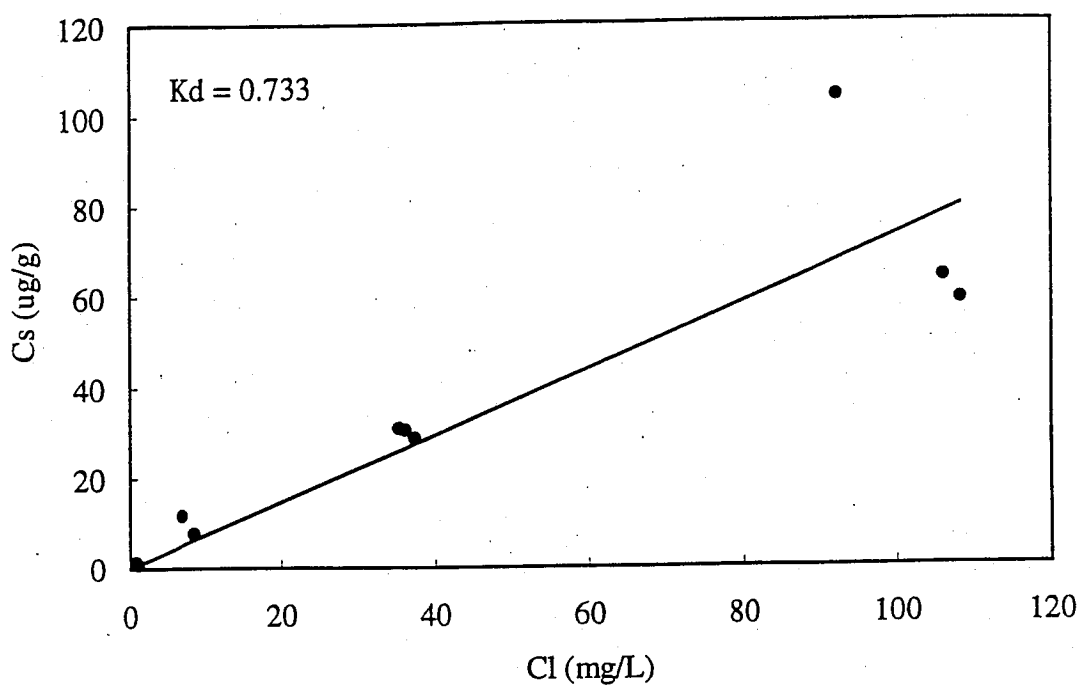
Figure D.3-Batch isotherm TOL and sand
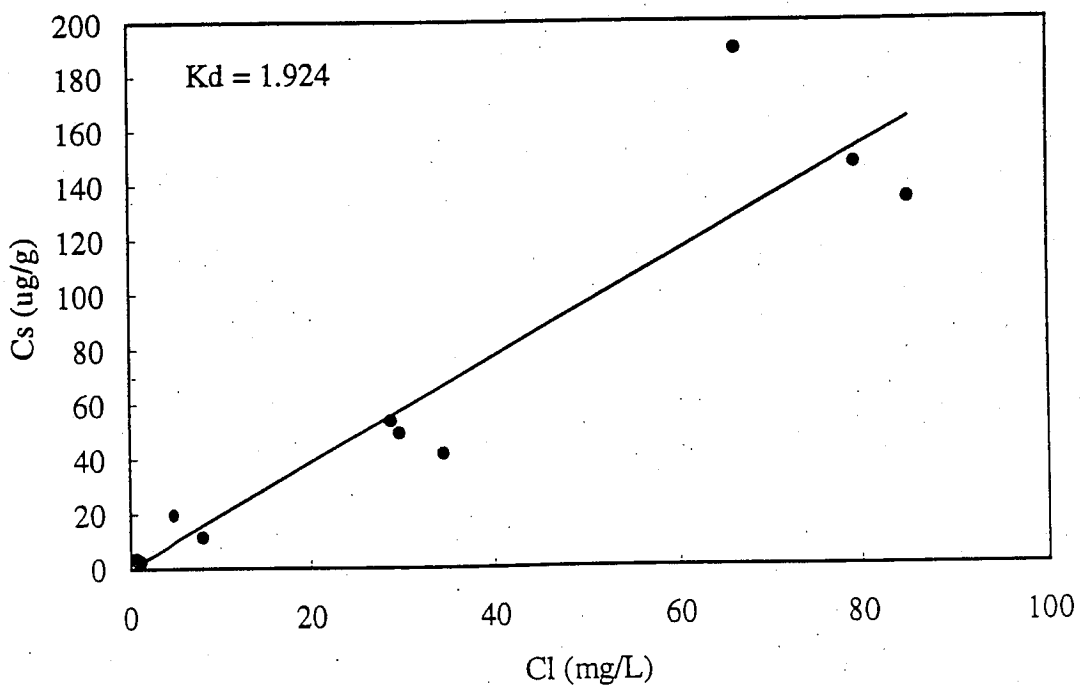
Figure D.4-Batch isotherm MX and sand
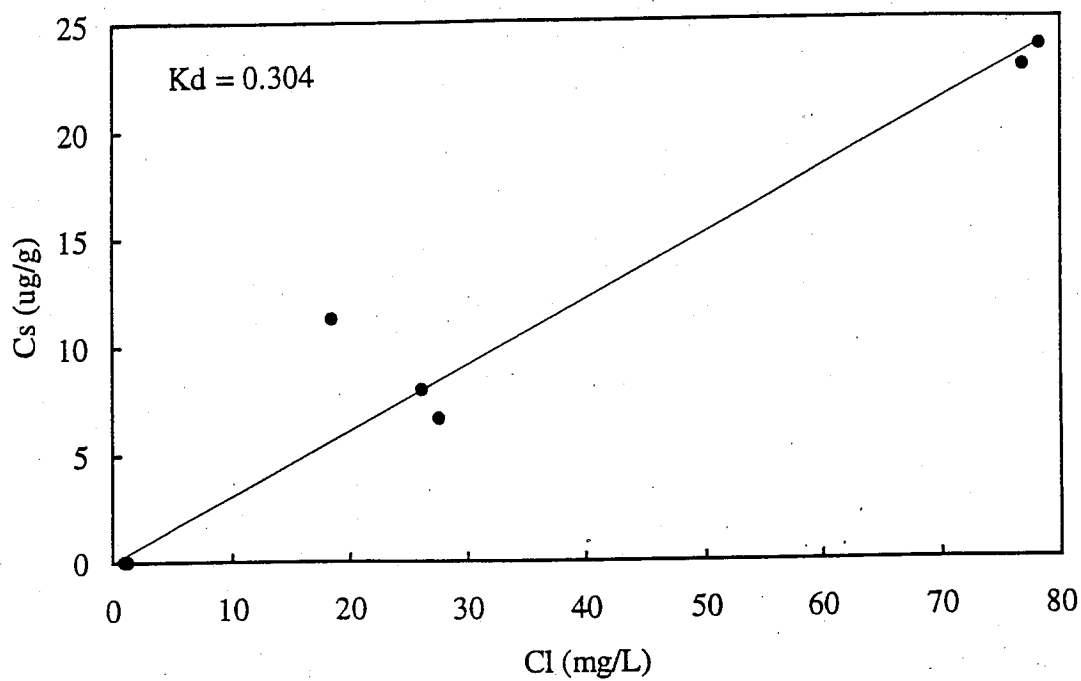
Figure D.5-Batch isotherm MC and clay
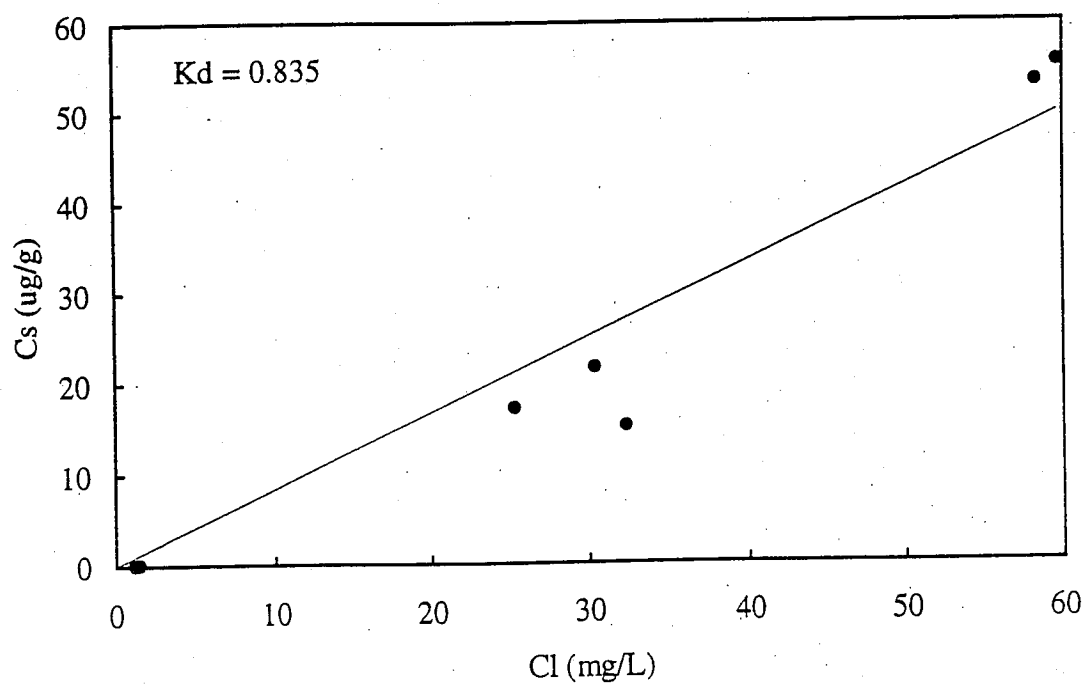
Figure D.6-Batch isotherm TCE and clay
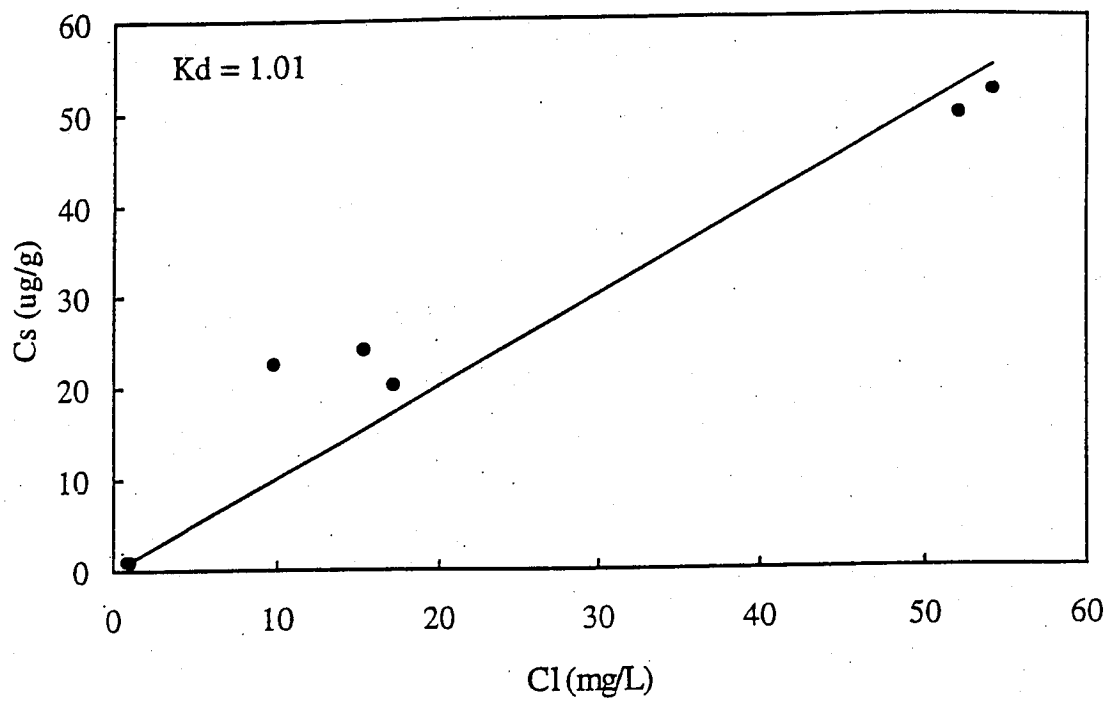
Figure D.7-Batch isotherm TOL and clay
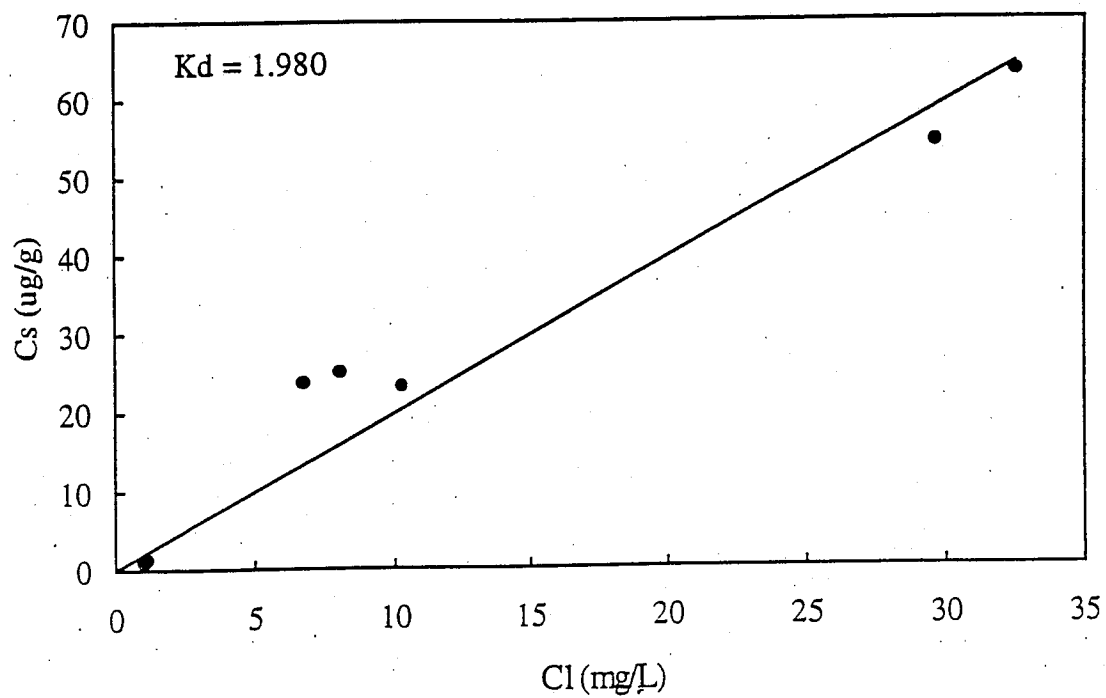
Figure D.8-Batch isotherm MX and clay
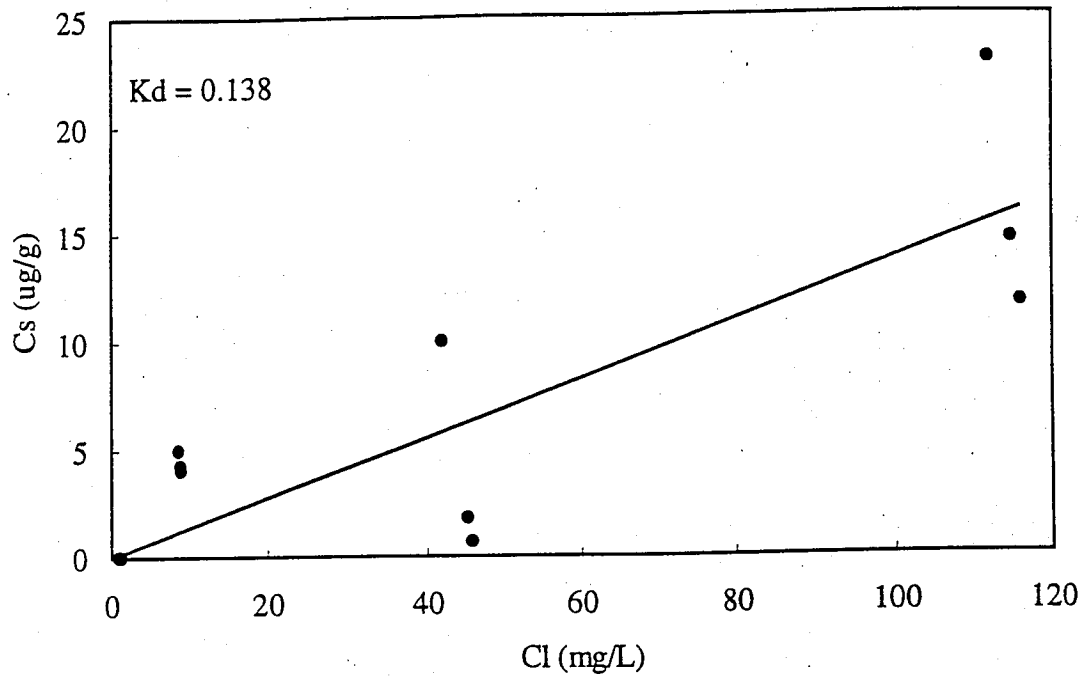
Figure D.9-Batch isotherm MC and topsoil
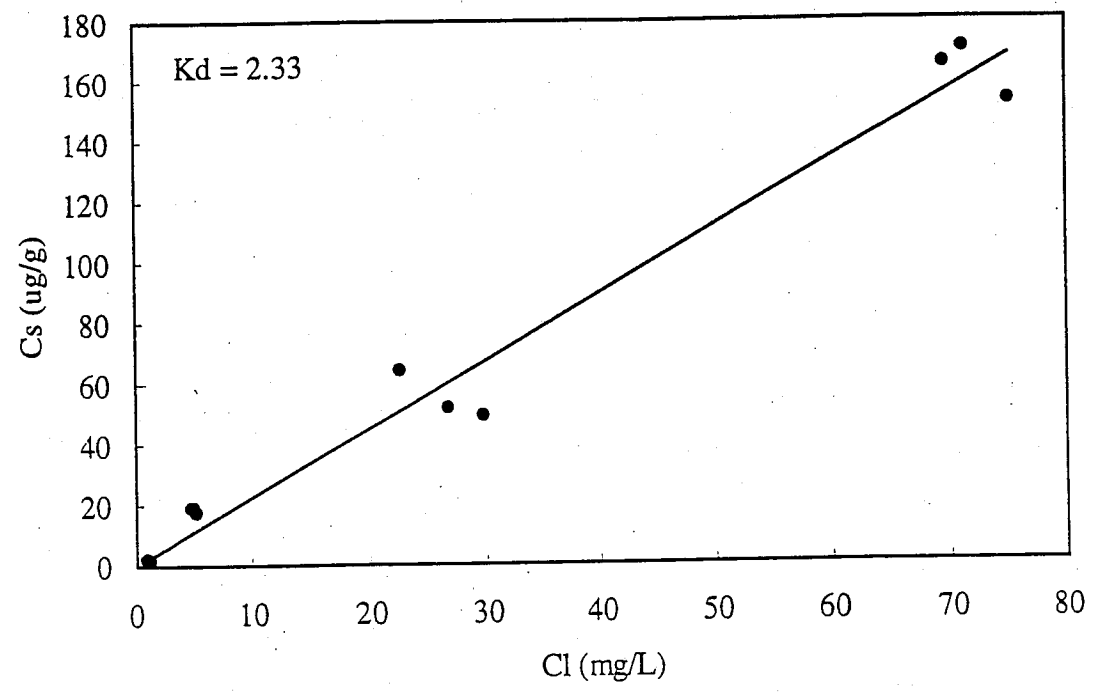
Figure D.10-Batch isotherm TCE and topsoil
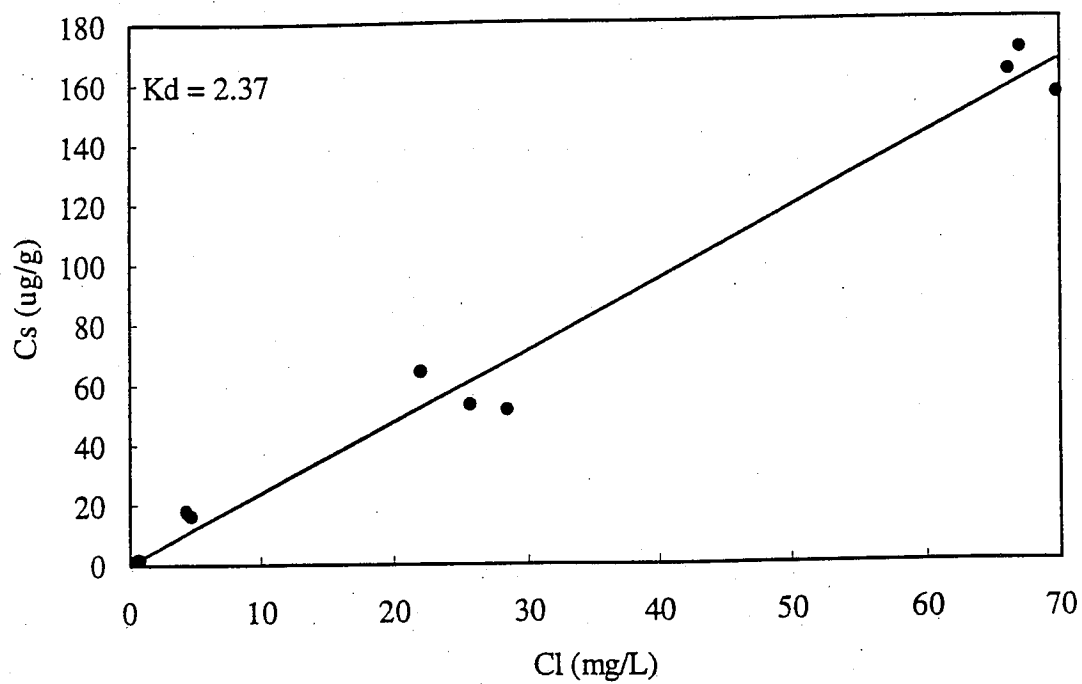
Figure D.11-Batch isotherm TOL and topsoil
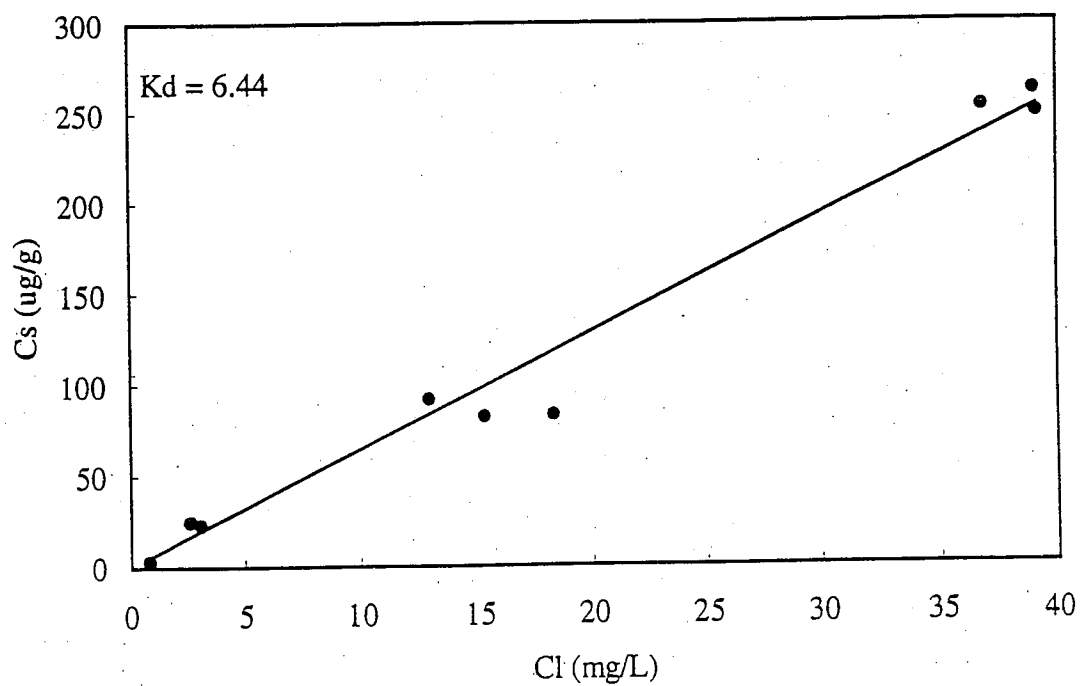
Figure D.12-Batch isotherm MX and topsoil

APPENDIX E

LEACH RATE CURVE FITS AND PARAMETERS
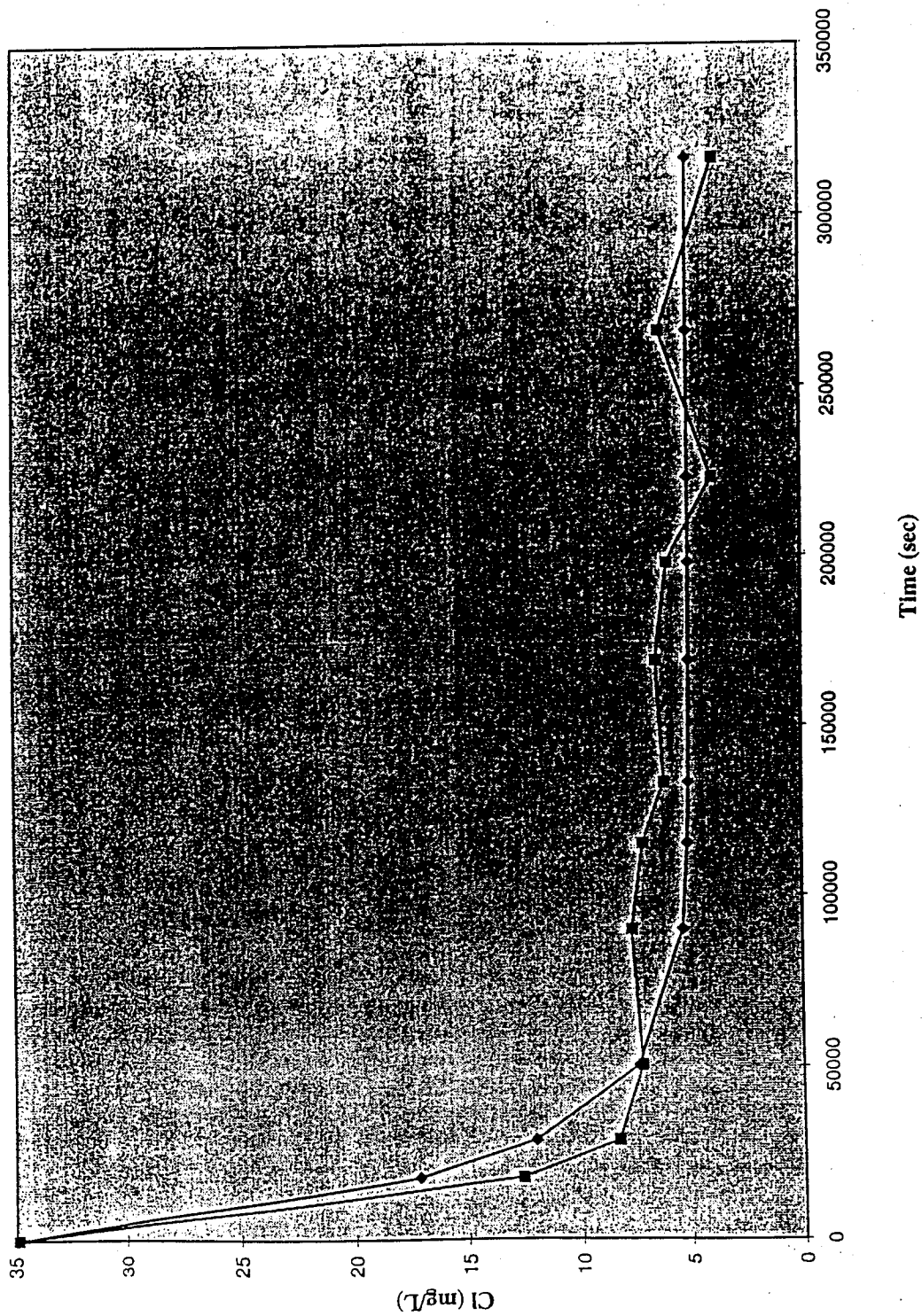
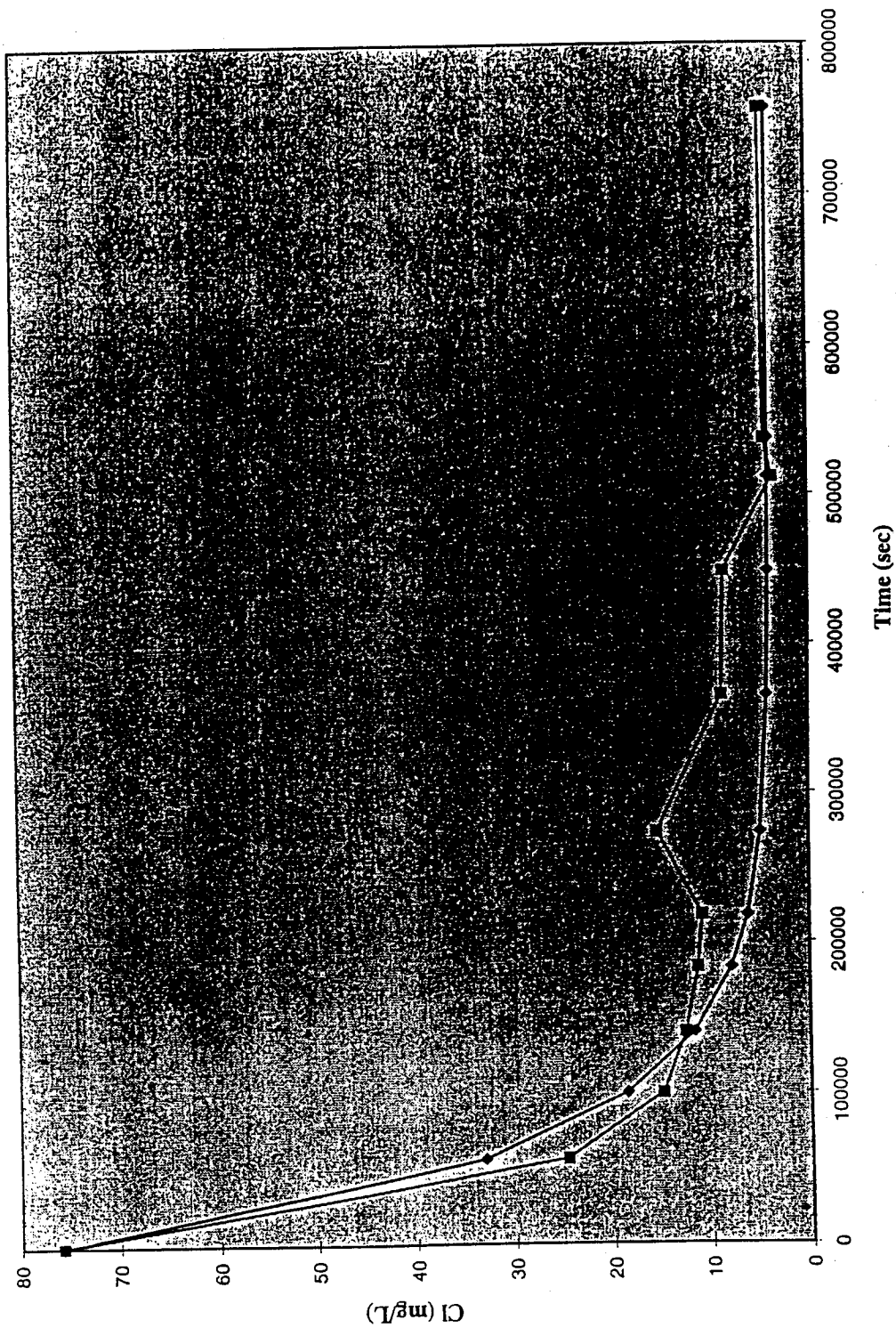Figure E.1 Leach Rate Curve Fit Column C3-1 and MC
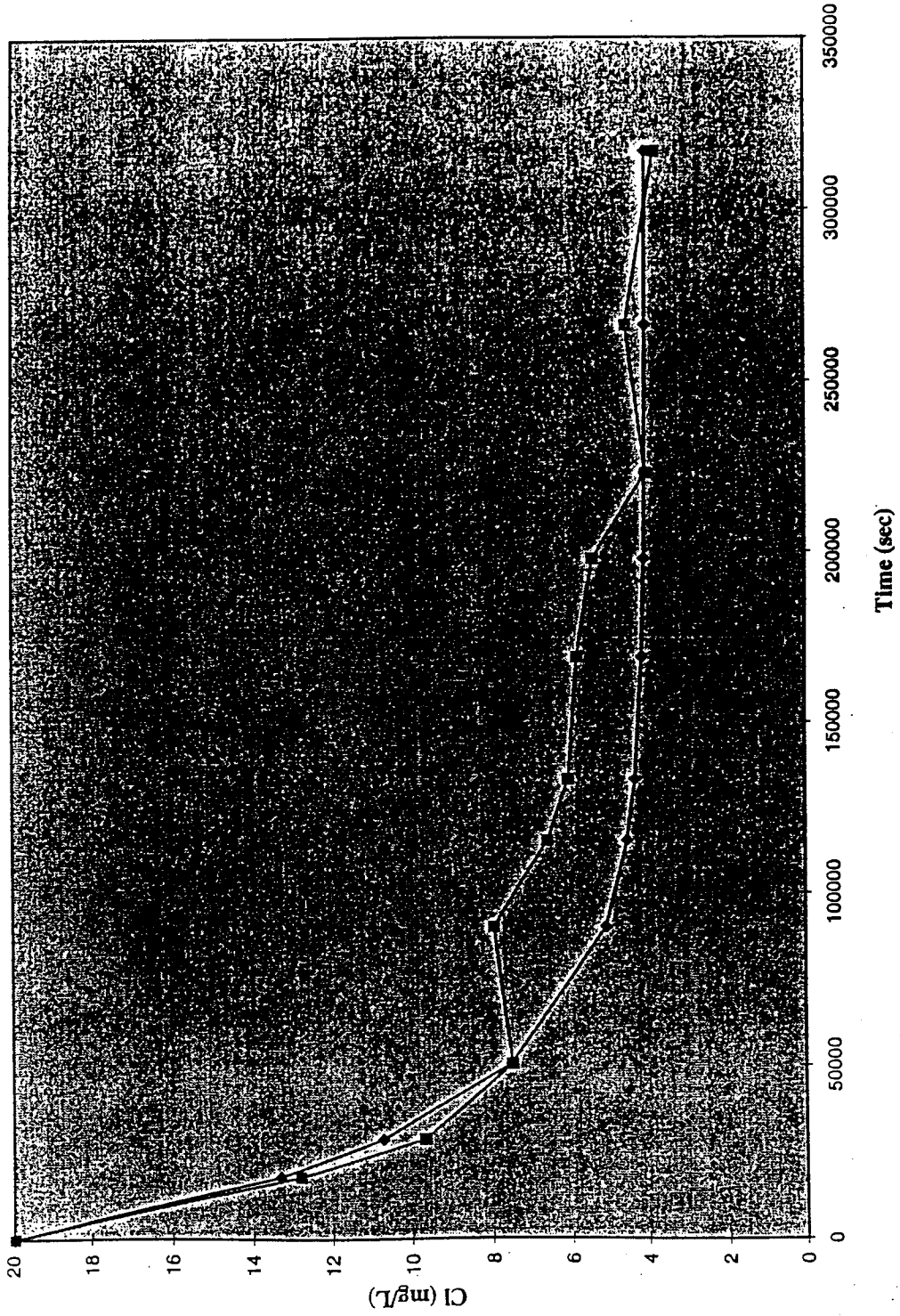
Figure E.2 Leach Rate Curve Fit Column C3-1 and TCE
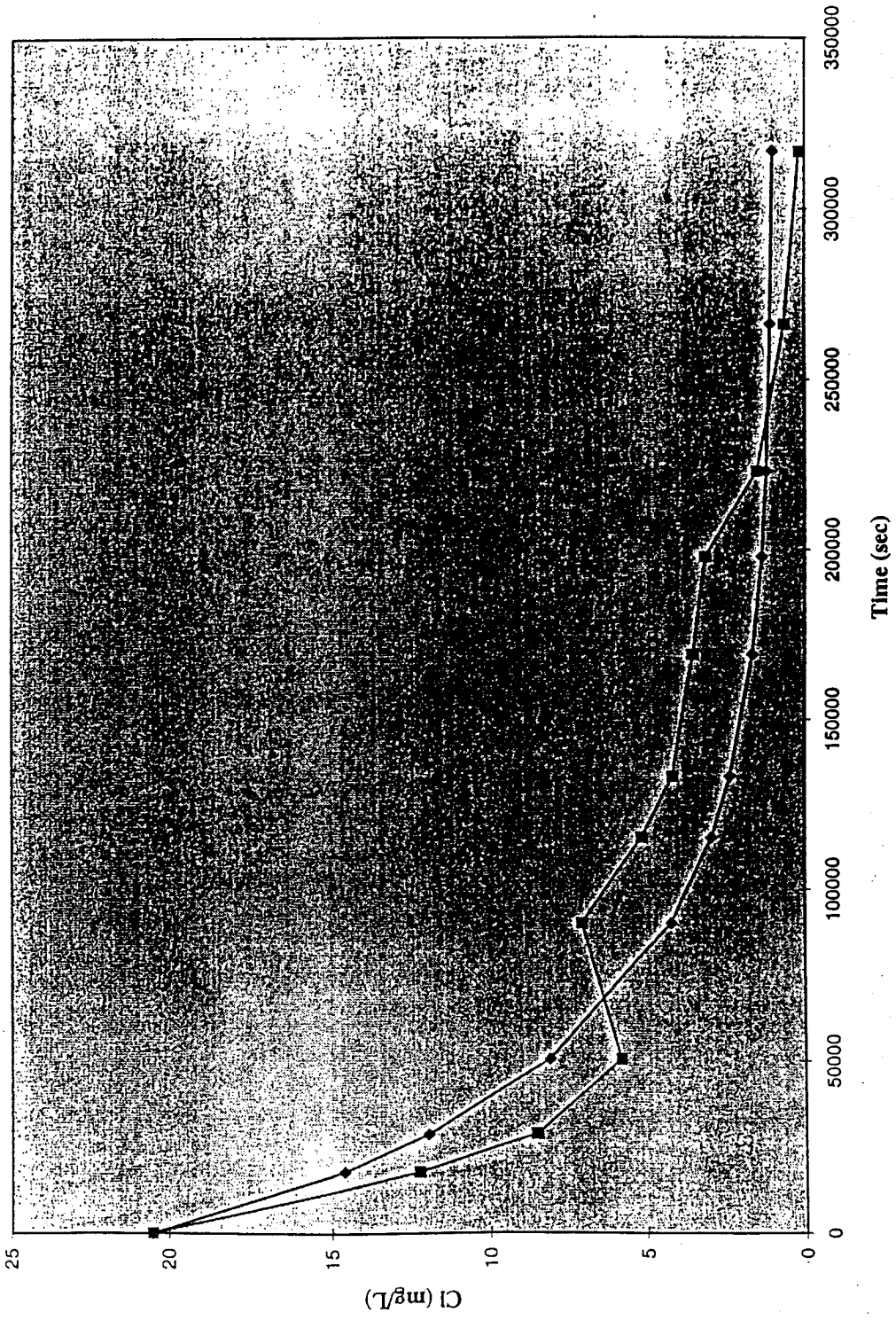
Figure E.3 Leach Rate Curve Fit Column C3-1 and TOL
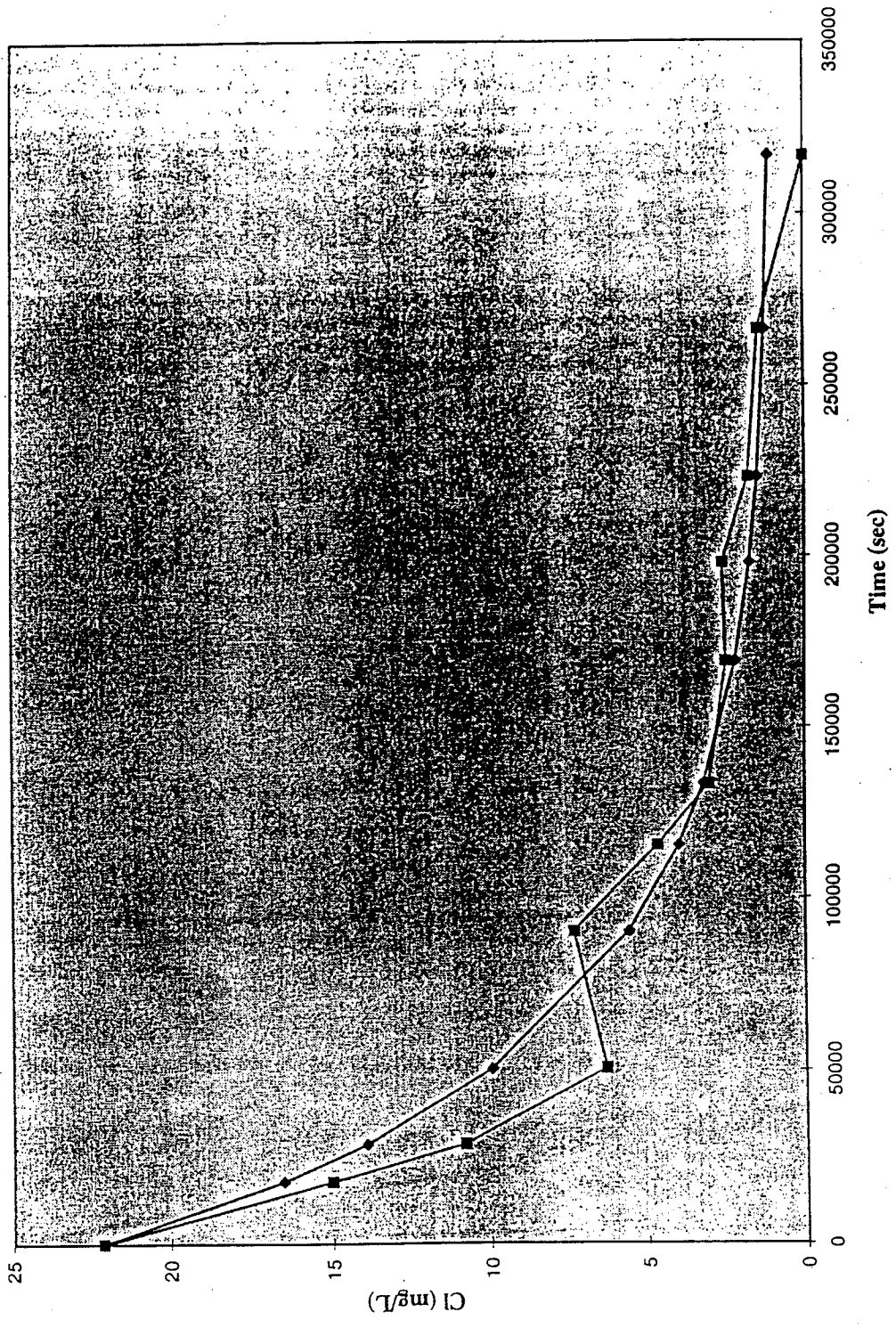
Figure E.4 Leach Rate Curve Fit Column C3-1 and MX
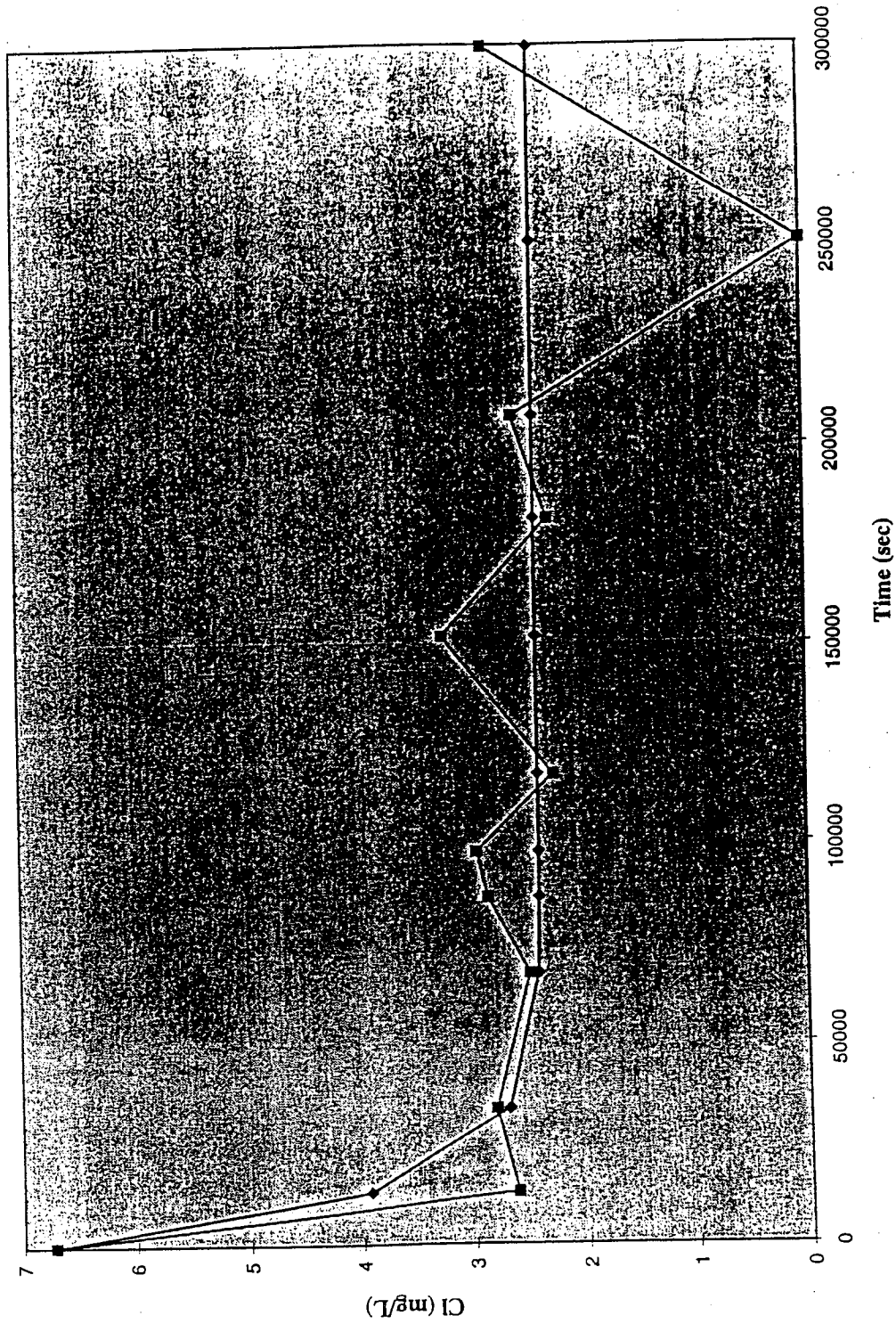
Figure E.5 Leach Rate Curve Fit Column C5-1 and MC
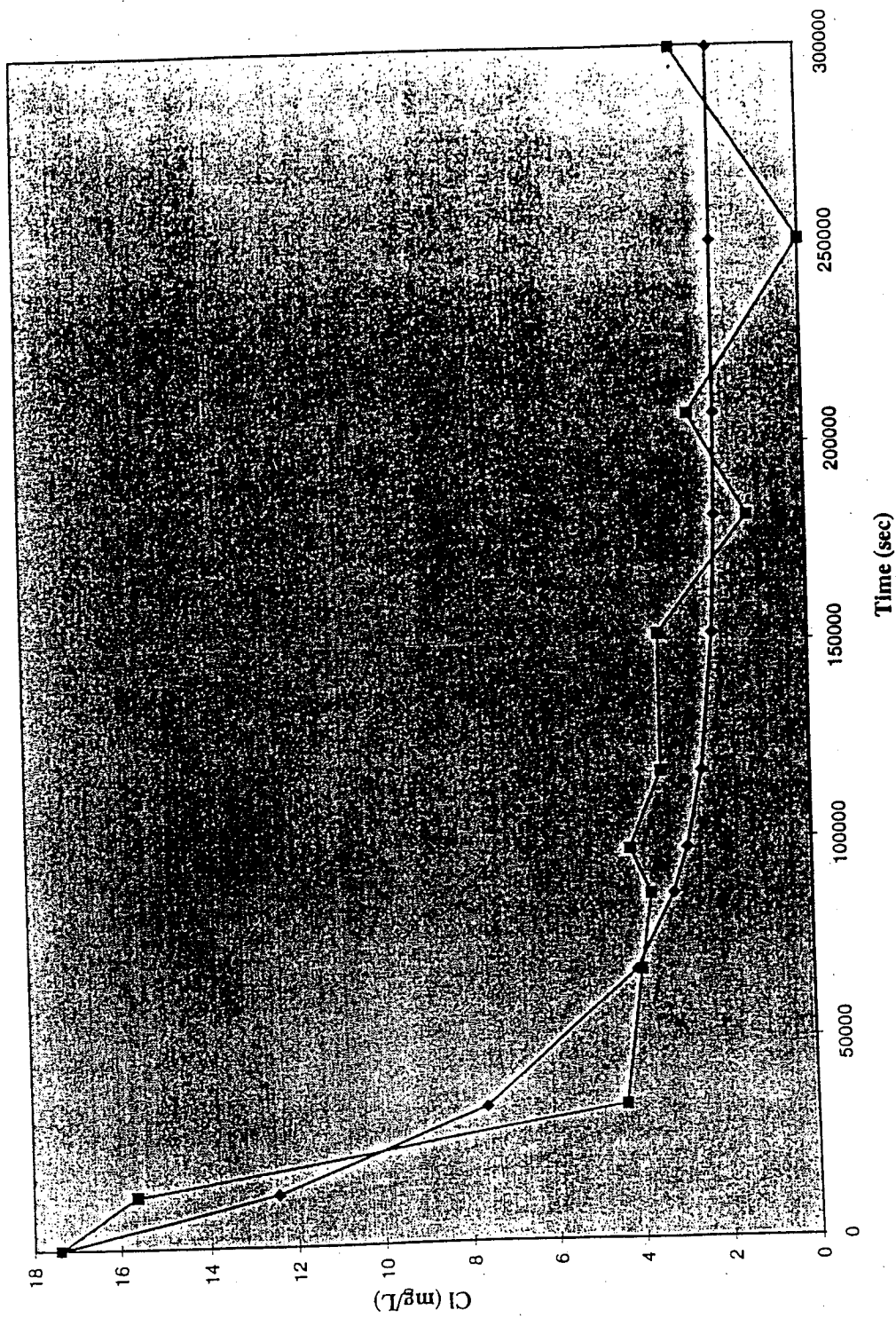
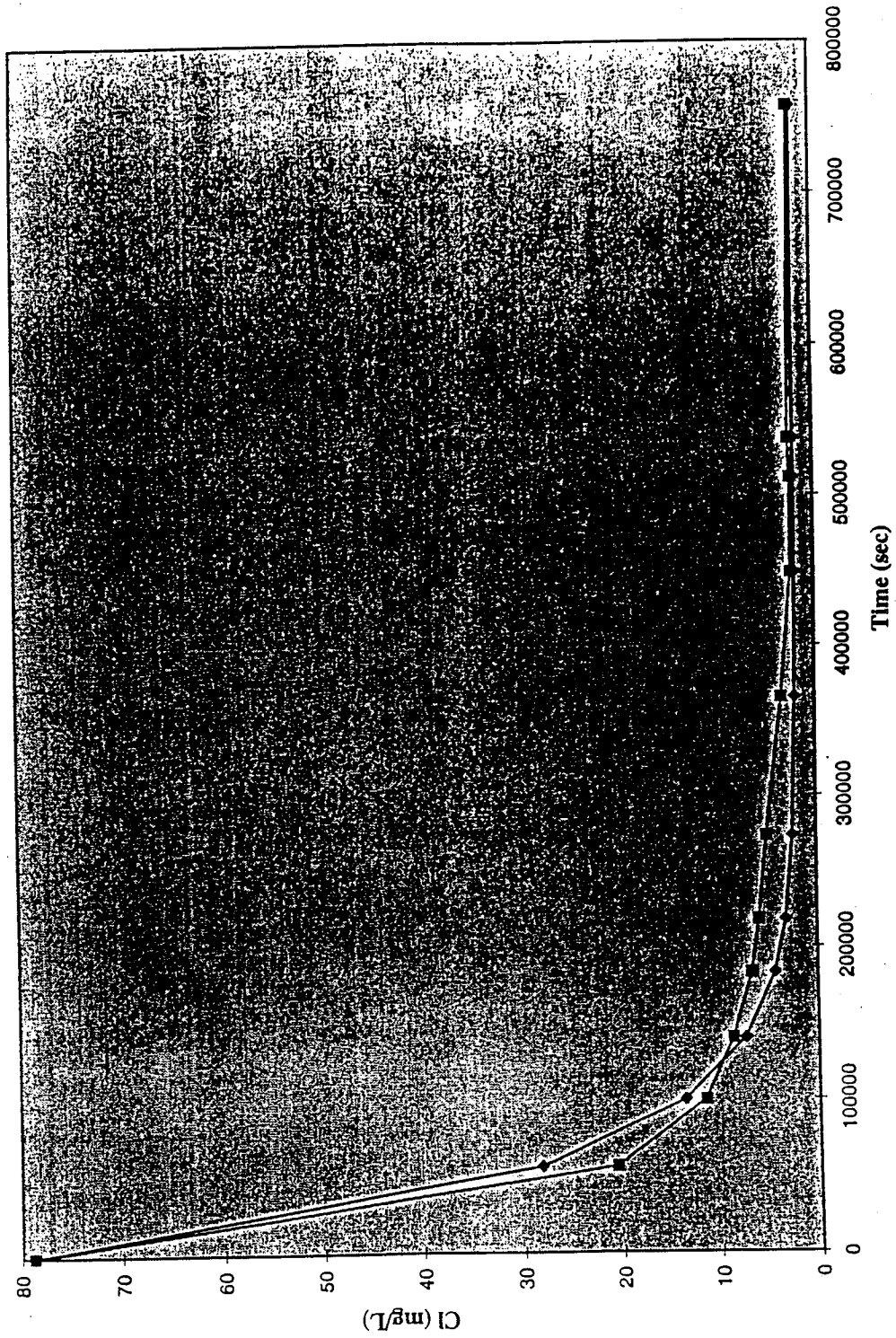**Figure E.6 Leach Rate Curve Fit Column C5-1 and TCE**
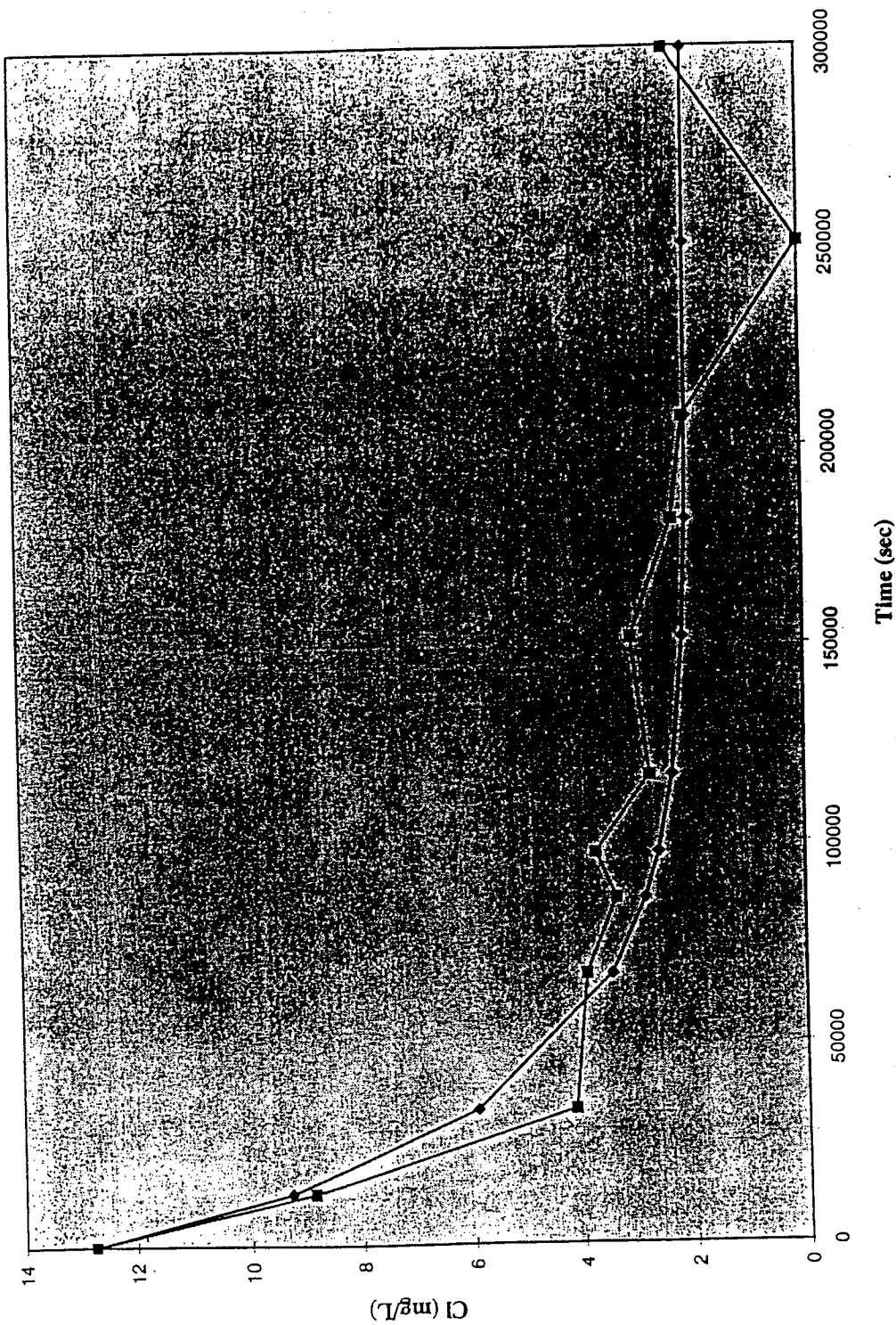
Figure E.7 Leach Rate Curve Fit Column C5-1 and TOL
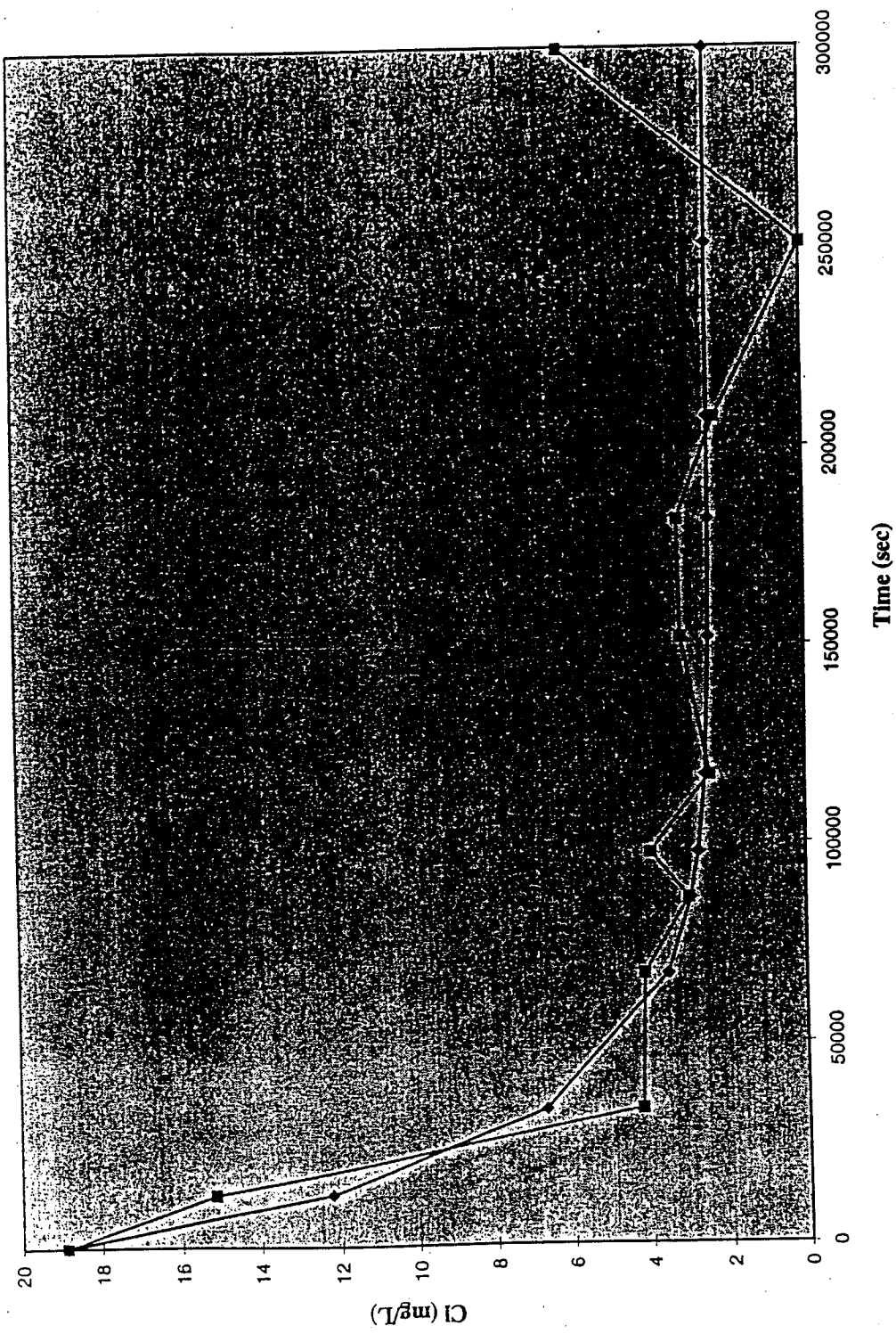
Figure E.8 Leach Rate Curve Fit Column C5-1 and MX
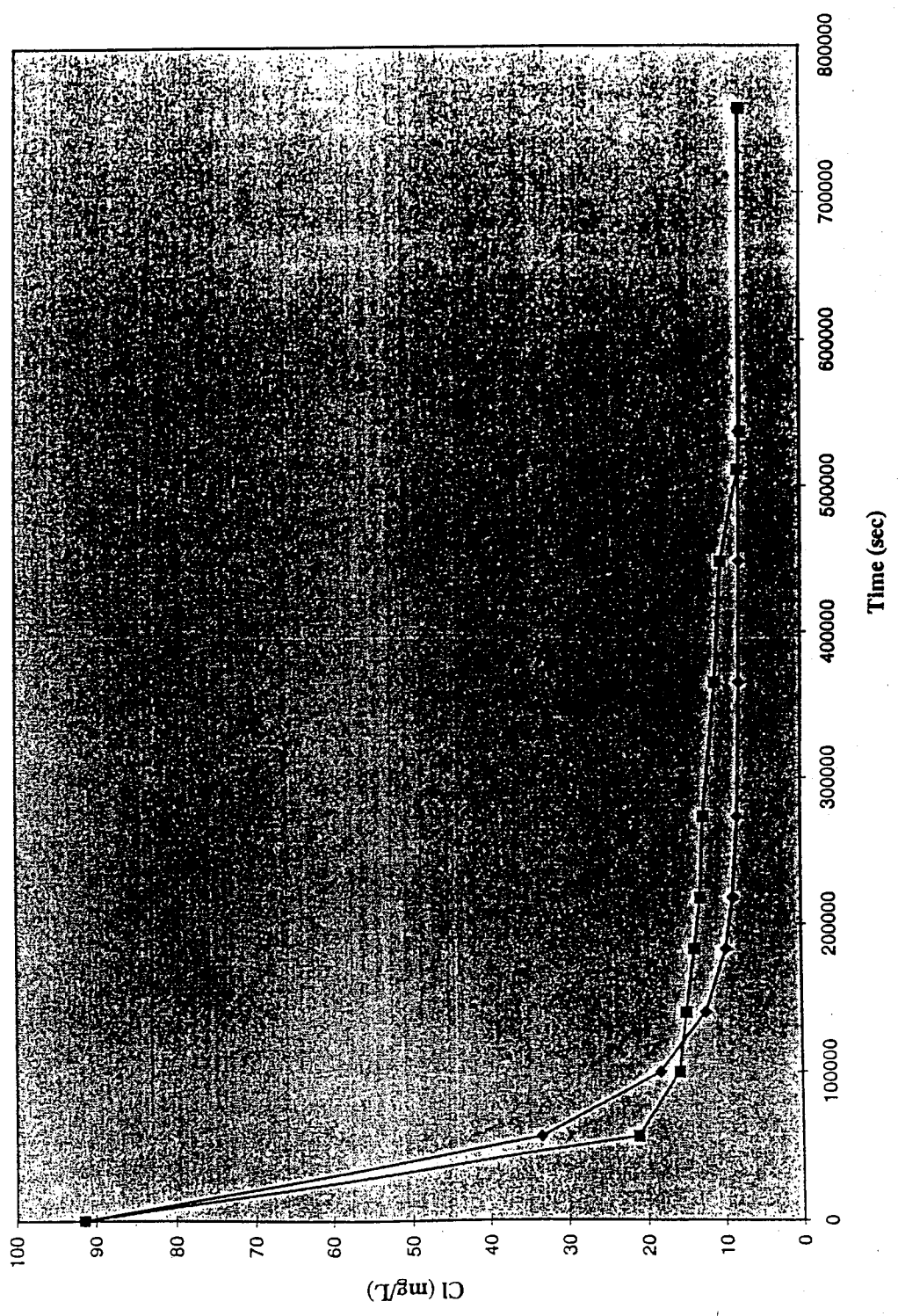
Figure E.9 Leach Rate Curve Fit Column C6-1 and MC

Figure E.10 Leach Rate Curve Fit Column C6-1 and TCE

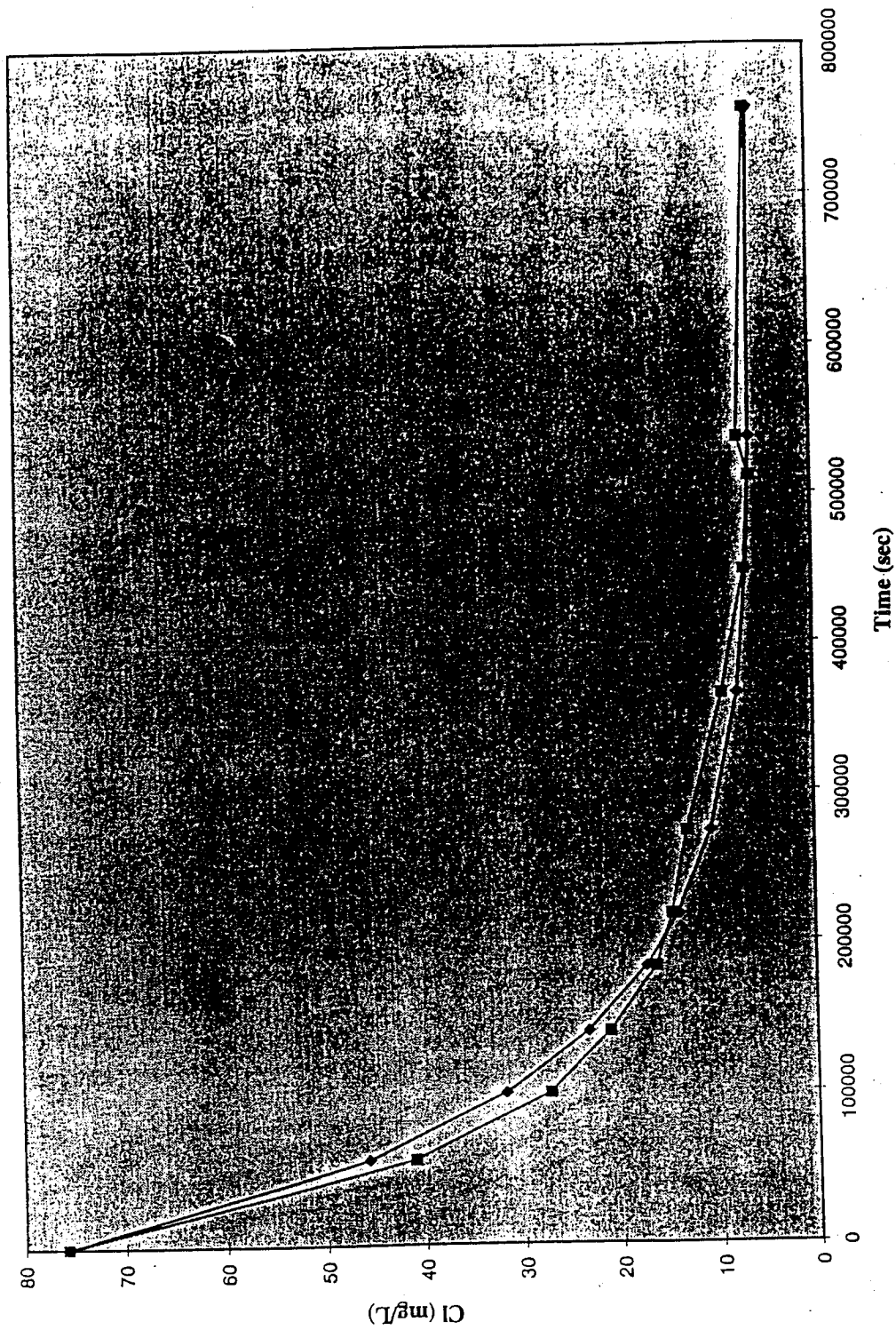Figure E.11 Leach Rate Curve Fit Column C6-1 and TOL

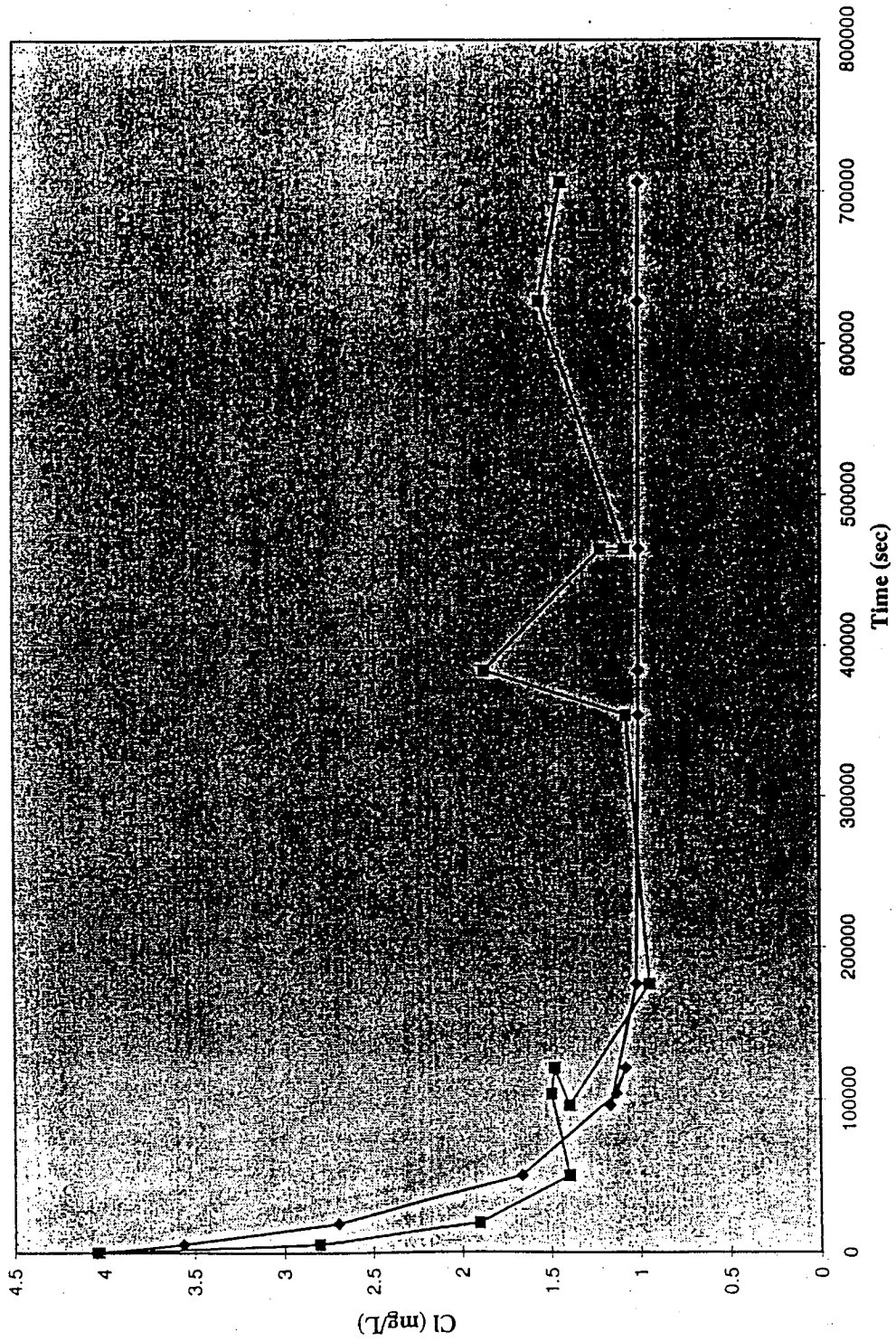Figure E.12 Leach Rate Curve Fit Column C6-1 and MX

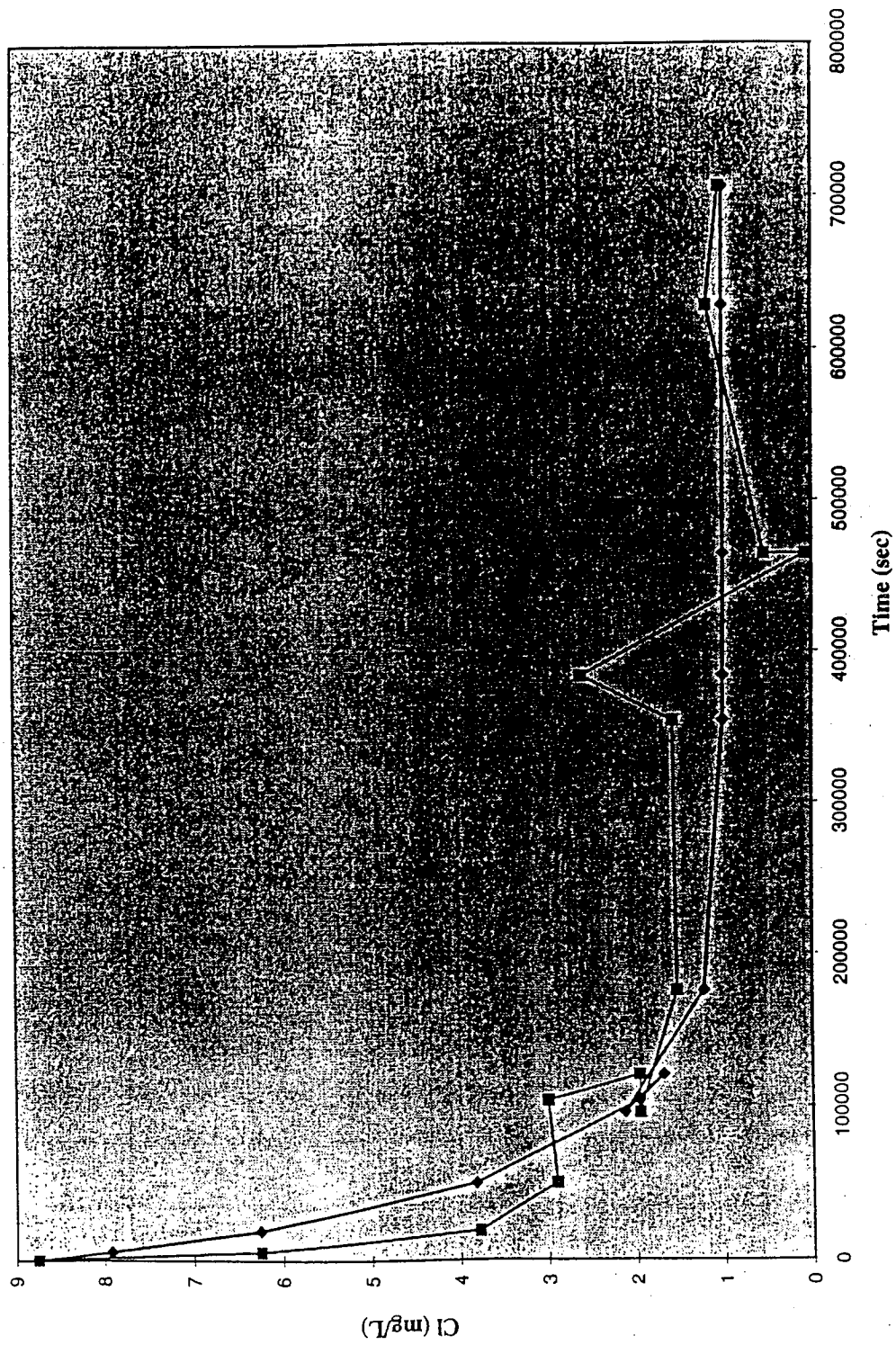Figure E.13 Leach Rate Curve Fit Column S1-2 and TCE

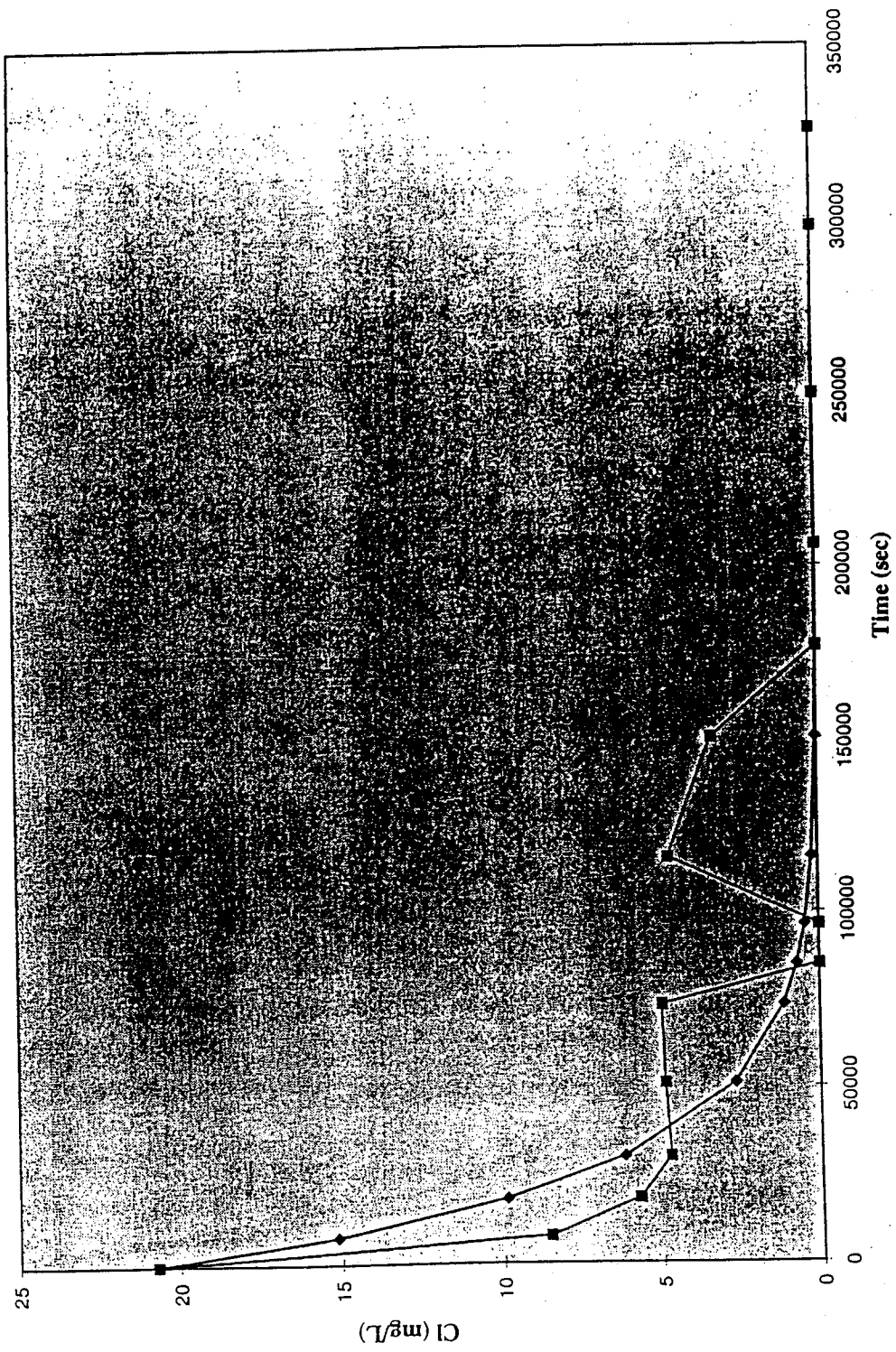**Figure E.14 Leach Rate Curve Fit Column S1-2 and TOL**

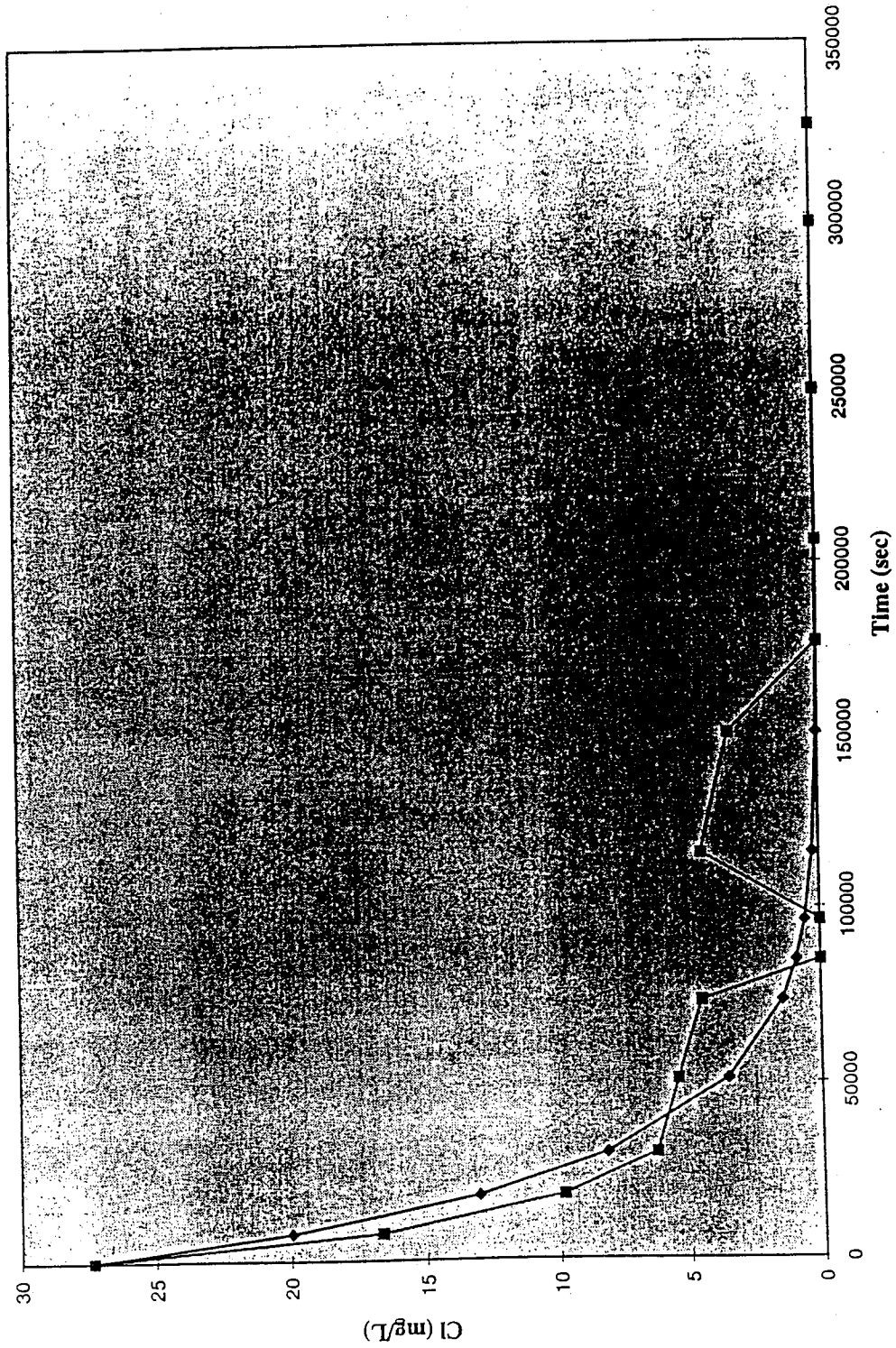Figure E.15 Leach Rate Curve Fit Column T4-1 and MC

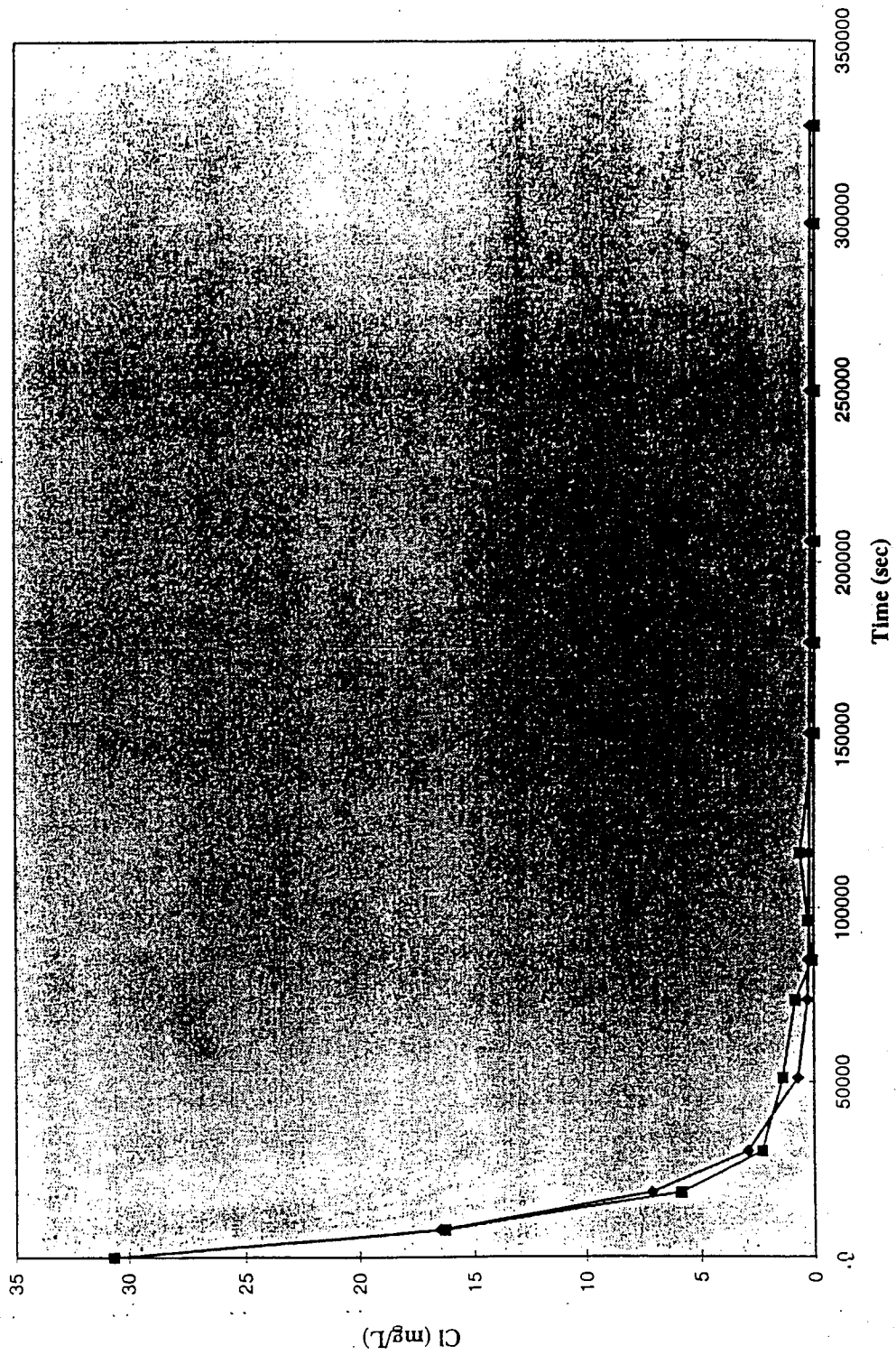Figure E.16 Leach Rate Curve Fit Column T4-1 and TCE

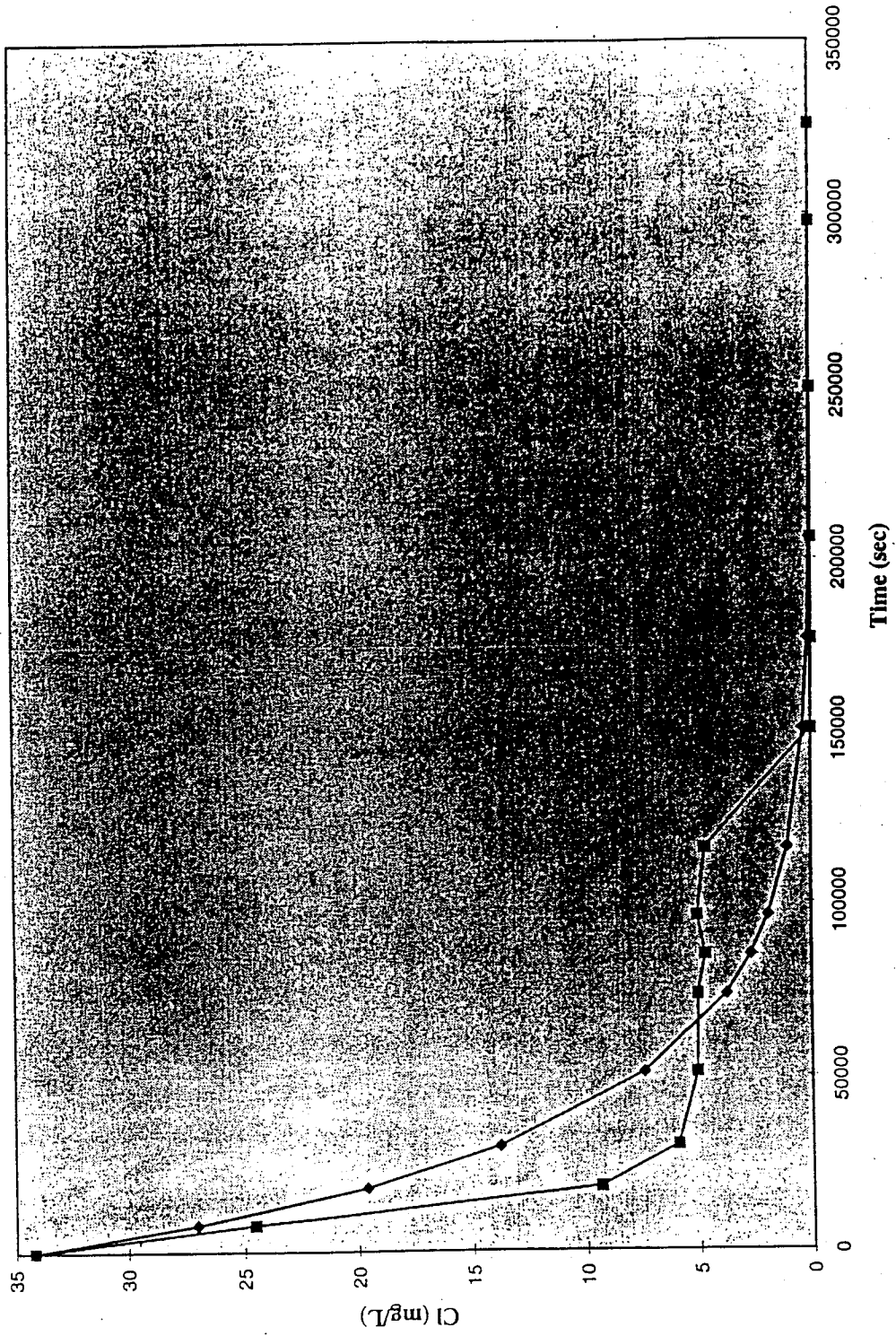Figure E.17 Leach Rate Curve Fit Column T4-1 and TOL

Figure E.18 Leach Rate Curve Fit Column T4-1 and MX

Table E.1 Leach Rate and Leach Rate Parameter Summary

Soil Column	VOC	EXP Leach Rate (1/sec)	C_o (mg/L)	C_t (mg/L)	Corr. Coeff r	Piwoni Pred. Kd (L/kg)	Batch Exp. Kd (L/kg)	Hydraulic Conductivity K (cm/sec)	Dry Unit Weight (gm/cc)	Water Content	h (m)	Equation Leach Rate (1/sec)
C3.1	MC	5.00E-05	31.00	5.00	0.98	0.042	0.304	6.435E-05	1.72	0.44009	0.051	0.002473
C3.1	TCE	3.00E-05	20.00	4.00	0.97	0.326	0.835	6.435E-05	1.72	0.44009	0.051	0.001266
C3.1	TOL	2.00E-05	20.50	1.00	0.95	0.421	1.01	6.435E-05	1.72	0.44009	0.051	0.001088
C3.1	MX	1.70E-05	22.50	1.00	0.96	0.628	1.98	6.435E-05	1.72	0.44009	0.051	0.000833
C5.1	MC	8.00E-05	6.80	2.40	0.80	0.042	0.304	0.0002837	1.48	0.38717	0.051	0.012429
C5.1	TCE	3.00E-05	17.40	2.00	0.95	0.326	0.835	0.0002837	1.48	0.38717	0.051	0.006422
C5.1	TOL	3.00E-05	12.70	2.00	0.96	0.421	1.01	0.0002837	1.48	0.38717	0.051	0.005528
C5.1	MX	4.00E-05	18.90	2.40	0.95	0.628	1.98	0.0002837	1.48	0.38717	0.051	0.004242
C6.1	MC	2.10E-05	91.00	8.00	0.98	0.042	0.304	4.914E-06	1.79	0.23129	0.051	0.000316
C6.1	TCE	1.60E-05	75.80	4.00	0.98	0.326	0.835	4.914E-06	1.79	0.23129	0.051	0.000119
C6.1	TOL	1.90E-05	78.80	2.00	0.99	0.421	1.01	4.914E-06	1.79	0.23129	0.051	9.82E-05
C6.1	MX	1.00E-05	75.90	6.00	1.00	0.628	1.98	4.914E-06	1.79	0.23129	0.051	7.14E-05
S1.2	TCE	3.00E-05	4.04	1.00	0.91	0.113	1.17	0.0001411	1.36	0.70274	0.051	0.003243
S1.2	TOL	2.00E-05	8.80	1.00	0.92	0.144	0.886	0.0001411	1.36	0.70274	0.051	0.003091
T4.1	MC	4.00E-05	20.70	0.00	0.89	0.51	0.138	0.0005921	0.923	0.56813	0.051	0.011219
T4.1	TCE	4.00E-05	27.30	0.00	0.97	4	2.23	0.0005921	0.923	0.56813	0.051	0.002736
T4.1	TOL	8.00E-05	30.70	0.20	1.00	5.1	2.37	0.0005921	0.923	0.56813	0.051	0.002209
T4.1	MX	3.00E-05	34.20	0.00	0.94	8.27	6.5	0.0005921	0.923	0.56813	0.051	0.001421