Effects of volatile organic compounds on clay landfill liner performance. [DNR-061] 1988

Edil, Tuncer B. et al.
Madison, Wisconsin: Wisconsin Department of Natural Resources, 1988

Effects of Volatile Organic Compounds on CLay Landfill Liner Performance

EFFECTS OF VOLATILE ORGANIC COMPOUNDS ON CLAY LANDFILL LINER PERFORMANCE

T. B. Edil
P. M. Berthouex
J. K. Park
L. Stanstrom
and
S. Zelmanowitz

Department of Civil and Environmental Engineering
University of Wisconsin, Madison

May 11, 1988

1. INTRODUCTION

This is the second interim report of the research concerning the effects of volatile organic chemicals (VOC) on clay landfill liner performance. The report gives a summary of the procedures used and the results obtained to date from the tests performed on the clay liner material proposed for the Eau Claire County municipal sanitary landfill.

2. OBJECTIVES

In 1987 very low levels of VOCs were observed in clay borrow materials intended for use in the liner system of the expansion of the Sevenmile Sanitary Landfill, Eau Claire County, Wisconsin. These VOCs were suspected to have originated from a nearby Superfund site where similar organic chemicals had been found in soil and groundwater.

Because of these contaminants, questions were raised by the Wisconsin Department of Natural Resources (DNR) regarding the potential effects of the organic chemicals on the performance of the clay materials as a landfill liner. Particular issues include potential effects on liner permeability and interactions of the organic chemicals with typical municipal landfill leachate. These issues were directed to the concern of whether the pre-contamination of the clay may cause leachate to pass through the liner system at an accelerated rate and thereby result in potential groundwater contamination.

The objectives of this research are:

(1) To investigate the effects of organic chemicals on physical properties of the clay;
(2) To examine the performance of the clay in transmitting and releasing organic chemicals, employing compacted clay specimens in flexible wall permeameters using clean and pre-contaminated clay materials; and
(3) To evaluate the sorption capacity of clay borrow materials intended for use in the liner system using batch isotherm experiments.

3. MATERIALS AND METHODS

3.1. Test Materials

The clay borrow material tested was intended for use in the liner system of the expansion of the Sevenmile Sanitary Landfill, Eau Claire County, Wisconsin. Some of clay borrow materials were contaminated by very low levels of VOCs, especially acetone, toluene, xylenes, and ethyl benzene. The highest concentration documented in any field sample was approximately 3.0 ppm, although the typical concentrations are much lower or below detection limits (Friedman, 1988). The clay that had not been contaminated by any organic chemicals was used for this study.

Organic chemicals selected for the tests were: acetone, *m*-xylene, methylene chloride, toluene, and trichloroethylene. The first two organic chemicals were used to precontaminate the clay and the next three organic chemicals were used as a permeant solution. The physical properties of these organic chemicals are summarized in Table 1.

Table 1. Physical properties of organic chemicals tested.

Organic chemical	Molecular weight[a], g/mol	Vapor pressure[a], mm Hg	Aqueous solubility[a], mg/L	*log* K_{ow}[a]	Henry's constant[b,c], dimensionless
Acetone	58.08	270	∞	-0.24	1.49×10^{-3}
m-Xylene	106.17	6	200	3.20	0.257
Toluene	92.13	22.4	515	2.69	0.275
Trichloroethylene	131.29	60	1100	2.53	0.479
Methylene chloride	84.94	349.0	16700	1.25	0.093

[a] Dostal (1988).
[b] Nirmalakhandan and Speece (1988).
[c] Thibodeaux (1979).

3.2. Organic Chemical Analysis

Analysis of influent and effluent samples from the permeameters and of adsorption samples were conducted by headspace analysis with a capillary column and flame ionization detector on a Model 3700 Varian Gas Chromatograph. Samples and standards contained 10 mL headspace and 10 mL of liquid. In order to achieve detection limits of 0.01 ppm for methylene chloride, trichloroethylene, toluene, and *m*-xylene, 3 g of salt were added to each vial. The vials were heated to 80°C to increase the proportion of contaminant in the headspace as compared to the amount in the liquid phase, thus increasing sensitivity. The column temperature was maintained at 55°C, which was determined as optimum for separation of the various peaks generated. Peak integrations and

Analysis of soil sample extracts used to determine soil contamination concentrations was accomplished by direct injection of 0.5 μL iso-octane onto the capillary column. Samples were kept at room temperature for analysis. The column was maintained at 55°C and the software package mentioned above was used to integrate the peaks and compared them with standard peaks. Standards were rerun periodically to assure consistency and accuracy of the analyses.

3.3. Experimental Procedures

3.3.1. Static Compaction Procedure

All of the test specimens were produced by static compaction using a hydraulic compression machine and a 4-in. diameter, 4.5-in. high, standard Proctor mold. The static compaction procedure consisted of:

(1) Mix water or solution containing organic chemicals with the soil until a uniform consistency is observed.
(2) Hand tamp three equal layers of wet soil into the Proctor mold.
(3) Apply the desired load for 30 seconds.
(4) Trim, weigh, and remove the specimen from the mold using a hydraulic jack.

3.3.2. Atterberg Limit Test Procedure

Each test was performed in duplicate using single point liquid limit test following ASTM D 4318 Method D except using water and organic chemicals.

3.3.3. Sedimentation Test Procedure

There is no standardized method. Sedimentation tests consisted of settling the soil suspensions prepared at a soil mass to solution ratio of 1:20 in sealed glass cylinders of 500 mL and monitoring sediment, suspension, and supernatant solution volumes by time for a week.

3.3.4. Precontamination of Soil Specimens

The soil samples were intentionally contaminated with acetone and *m*-xylene to simulate the soil contamination in the field. The contaminated specimens were prepared in the laboratory under controlled conditions by contaminating a portion of the natural soil to two levels of target contamination: high (9 ppm acetone, 1 ppm *m*-xylene) and low (1 ppm acetone, 0.1 ppm *m*-xylene).

Contamination was achieved by mixing soil and contaminant solutions spiked to twice the desired level (in order to take into account volatilization during mixing). To achieve 20% moisture content, 45 mL of solution was added to 250 g of soil (residual moisture estimated at 2%) and mixed thoroughly and methodically in a blender. Several batches were prepared, combined and stored in sealed glass containers.

Samples were taken to measure actual contaminant levels in the soil before and after compaction of the soils to make permeameter cores. 40 mL of iso-octane were added to each centrifuge tube with 25 g of soil and extracted by mixing for 24 hours. The supernatant iso-octane was collected for GC analysis. The tests performed on the contaminated soil specimens indicate an acetone concentration of little above 6 ppm and a *m*-xylene concentration of about 0.1 to 0.2 ppm for high concentration. The samples to have low level of contamination were prepared by mixing soil and contaminant solutions at concentrations about 1/10 of the ones used in preparing the high concentration samples. The final verification tests on the low concentration soils are not available at this time.

3.3.5. Permeation Test Procedure

The permeability tests were conducted using twelve specially constructed permeameters for approximately four months. Figure 1 gives a schematic diagram of the UW permeameter system. The flexible-wall permeameter was preferred over a rigid-wall permeameter because of the more stringent control of side flow required in a chemical transport study.

The permeameter components were constructed from materials that do not react with the intended permeants. All influent/effluent reservoirs (mariotte bottles) and burettes were glass, flow lines were Teflon, valves and fittings were brass, the specimen base and cap were brass, and the porous filters were singed brass.

Compacted specimens were sealed on their lateral surfaces by first wrapping them with Teflon tape (1 in. wide), coating the Teflon tape with silicone caulk, and then covering them with two latex membranes separated by another coat of silicon caulk. In order to distribute it evenly on the specimens, the confining pressure was applied immediately within a half hour of coating the specimen with the silicon caulk. The two latex membranes were then sealed to the base and the

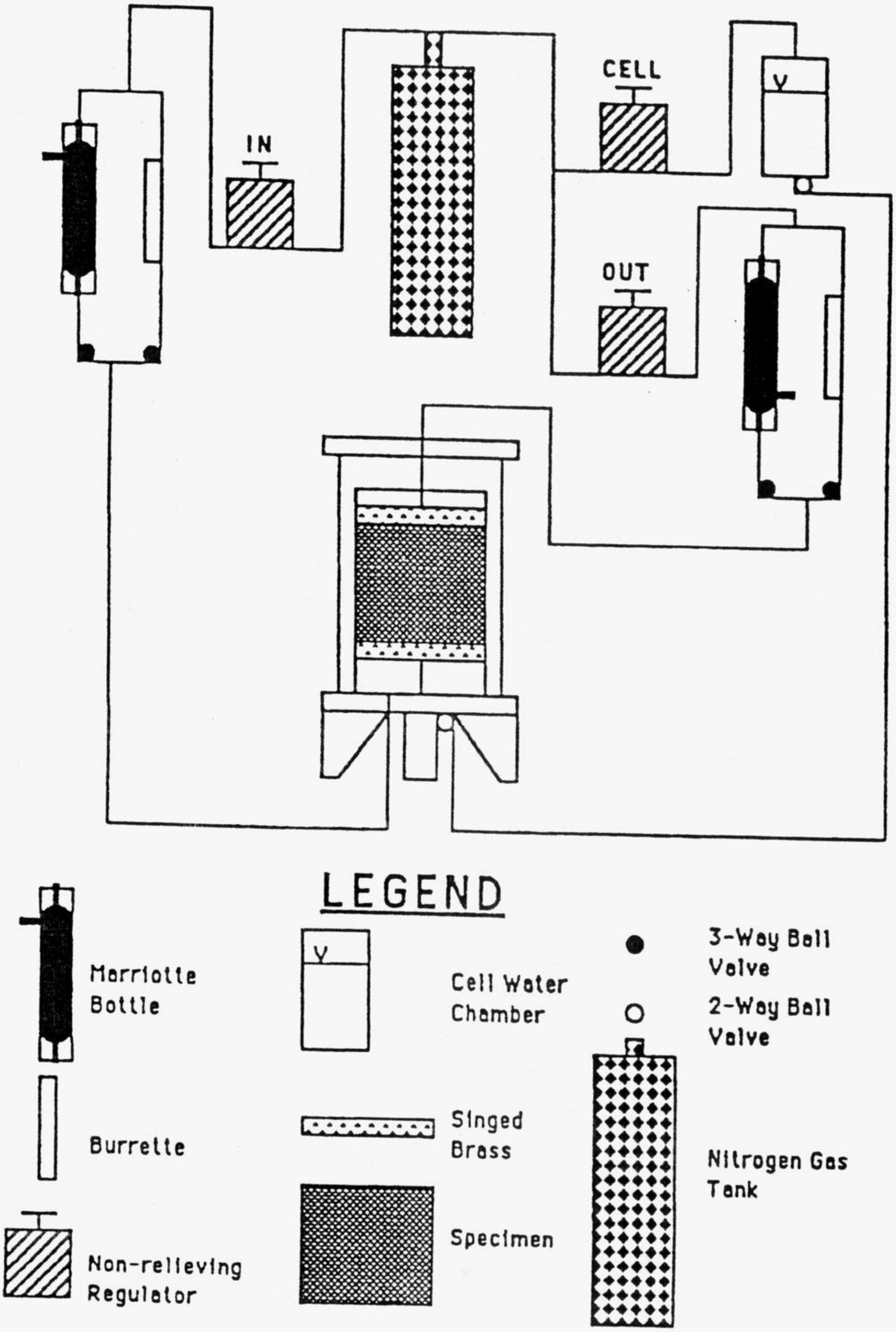


Figure 1. Schematic diagram of the flexible wall permeameter setup.

cap by double O-rings, one placed over the Teflon tape overlapping the base and the cap, and the other on the bare portion of the base and the cap. O-rings did not always provide a good seal when placed directly over the Teflon tape.

Subsequent to setting up the compacted specimen, the permeameter cell was assembled and connected to the mariotte bottles. The permeameter chamber was filled with water, and the system was pressurized and allowed to reach equilibrium under an effective confining pressure of 10 psi (chamber pressure of 50 psi and back pressure of 40 psi) for a period of 1 to 3 days under zero driving head.

After the consolidation/equilibrium period, the permeameter cells were installed to the permeability test system and the permeation was initiated by raising the inflow pressure by 5 psi. Nitrogen gas was used over the inflow, outflow, and chamber fluids to generate the fluid pressures. The specimens were 4-in. in diameter and 2-in. in height. They were prepared by static compaction by compressing a sample of the soil (already equilibrated to a moisture content of about 20%) to an equivalent dry unit weight of 110 lb/ft^3 in a Proctor mold. This required application of about 9,000 lbs of force for a period of 30 seconds.

In setting up the permeability tests, the organic leachate was placed in the inflow reservoir and applied to the base of the specimen, and Madison tap water was placed in the outflow reservoir and applied to the top of the specimen right from the beginning. Madison tap water was also used in generating the confining cell pressure. Provisions were made for periodic sampling of the inflow, outflow, and chamber fluids.

4. SOIL CHARACTERIZATION TESTS

The soil characterization tests were conducted to determine the basic properties of the clay sample supplied to us for this project. Four pans of this clay were delivered to us by Ayres Associates as a representative "clean" sample of the proposed liner material.

The results of the Atterberg limits, specific gravity of solids, grain size distribution, and compaction tests, performed in general accordance with the ASTM standards, are summarized in Table 2. Listed also in Table 2 are the results of similar tests performed by Ayres Associates (Eau Claire office) on two samples of the same batch of clay. The index properties reported by us and Ayres Associates agree within the expected range of variability for such soils and tests.

Table 2. Properties of Eau Claire County liner soil sample.

Parameter	Pan 1	Pan 2	Pan 3	Pan 4	Avg.	Sample 1	Sample 2	Avg.
Liquid limit	34.0	35.0	34.5	35.0	34.6	33.2	37.2	35.2
Plastic limit	21.5	18.5	21.5	20.5	21.5	18.5	18.1	18.3
Plasticity index	12.5	16.5	13.0	14.5	14.1	14.7	19.1	16.9
Specific gravity	2.74				2.74			2.69
% gravel						0.0	0.0	
% sand						19.7	3.8	
% silt						49.5	58.2	
% clay						30.8	38.0	
Modified proctor maximum dry density	111.7 111.9					118.8	112.6	
Optimum moisture	18.2 18.0					13.5	16.6	
Organic carbon[a], %	0.53	0.47	0.47	0.47	0.49			
pH	7.6	7.7	7.7	7.7	7.7			
Conductivity, 10^{-5}mhoms/cm	40	35	35	30	35			
Cation exchange capacity, meq/100 g	13.4	12.0	10.9	11.0	11.8			

[a] Organic matter was determined for test soils and converted to organic carbon by dividing by 1.7.

The average liquid limit and the plasticity index obtained for this sample are shown in Figure 2 which was developed by Ayres Associates for the best fit relationship between these quantities as part of the clay borrow site investigations. The clay used in this research appears to fall in the middle of the range of textural characteristics for the borrow material. Thus, it was concluded that the clay sample supplied to us is texturally representative of the proposed liner material.

Table 2 also shows the results of the chemical characterization tests. The organic carbon content was determined to be less than 0.5%. Previous tests by Ayres Associates indicated a range of 0.5 to 2.0% organic contents. Four soil samples taken from each pan were extracted with iso-octane and the extractants were analyzed using a gas chromatography (GC). There were no discernable peaks to identify during the GC analyses. Therefore, it was concluded that the clay was not contaminated with any organic chemicals.

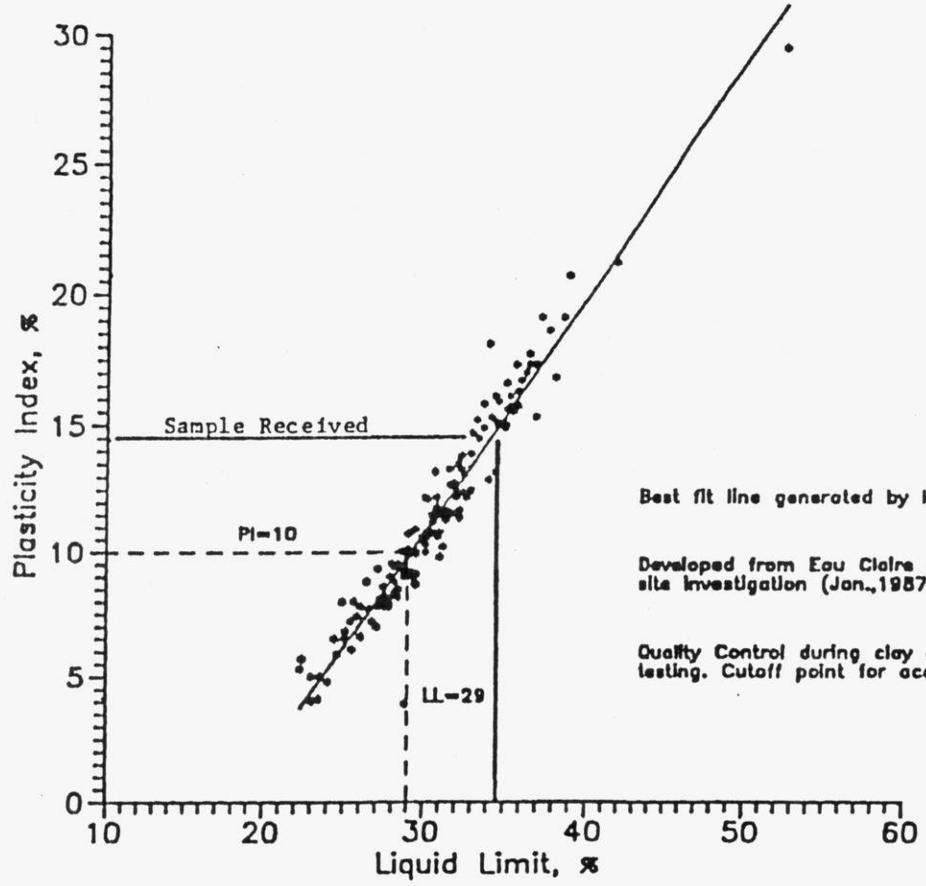
5. CLAY-ORGANIC CHEMICAL INTERACTION INDEX TESTS

5.1. Atterberg Tests

Atterberg limit tests were conducted to provide additional information about the interaction of VOCs with the clay liner material. The experimental conditions are summarized in Table 3.

Liquid limit and plastic limit are index properties of clay soils that are controlled by the interparticle electrochemical forces. As such, they are affected by the mineralogy of clays and the nature of the pore fluid and index the resulting forces of interaction at the moisture contents they correspond. Because of these considerations, Atterberg limits can be used to disclose significant alterations of the interparticle force system and potential impact clay fabric arising from the change of pore fluid chemistry. There are certain limitations to the use of Atterberg limits in this manner; however, it does provide a first step in identifying significant interactions. A review of the Atterberg limits given in Table 3 indicates that the VOCs at the concentrations and combinations used do not impact clay-pore fluid interaction except pure acetone. Most of the liquids used were dilute solutions of VOCs.

Atterberg Limits, Eau Claire County
Feasibility Study



Best fit line generated by Method of Least Squares.

Developed from Eau Claire County Feasibility Study, clay borrow site investigation (Jan.,1987).

Quality Control during clay excavation performed by liquid limit testing. Cutoff point for acceptance of clay is LL=29.

Figure 2. Atterberg limits of the sample tested.

Table 3. Experimental conditions and atterberg limit test results.

Run	Liquid used	Concentration, ppm	Liquid limit, %		Plastic limit, %
1	Water	-	30.6	30.6	18.9
2-A	Acetone & *m*-xylene mixture (9:1)	1	29.6	29.6	19.4
B		6	29.8	29.6	19.4
C		10	30.5	29.9	19.1
D		100	30.4	30.0	18.5
3-A	Methylene chloride, toluene & TCE[a] mixture (1:1:1)	1	29.7	29.8	19.3
B		10	29.5	29.9	19.3
C		50	28.1	30.2	18.4
D		100	29.2	29.5	18.7
4	2-B & 3-C mixture (1:1)	-	30.1	30.0	18.9
5-A	Acetone & water	50%	28.9	29.1	19.4
B		100%	25.6	24.5	27.7

[a] TCE: trichloroethylene.

Acetone in a 50% solution in water also did not show any impact; however, pure acetone drastically impacted clay behavior. This conforms with the reported impact of organic solutions on clay fabric observed with aqueous solutions with a concentration of 80% or higher (Mitchell and Madsen, 1987). The numerical values of Atterberg limits corresponding to 100% acetone solution, while indicating the impact of pure acetone on clay, should not be viewed in a quantitative sense. When mixed with acetone, clay behaves like silt losing most of its plasticity. The detailed data and test notes are given in Appendix A.

5.2. Sedimentation Test

Sedimentation tests were conducted to investigate the effect of organic chemicals on the physiochemical properties of the clay. The experimental conditions of the sedimentation tests are given in Table 4 and the test results are shown in Figures 3 and 4. Clay particles in suspensions of clay-water systems form particle associations in a number of modes (van Olpher, 1964) during their Brownian motions and settle under the action of gravity. The rate of settlement (formation of the supernatant solution) and the volume of the sediment arising from the same amount of clay particles can be viewed as indexes of clay-liquid interaction. If flocculation is dominant, this results in more rapid settlement of particle flocs (due to their larger size) and a larger volume of sediment than a dispersed system where a repulsive interparticle force system operates. The rate of settlement was quite comparable for most solutions tested except acetone/*m*-xylene solution of 80% and 100% (see Figure 3). Again, the impact of acetone at 80% or higher concentration was observed in conformity with previous reports of similar behavior.

Table 4. Experimental conditions of the sedimentation tests.

Run No.	Liquid
1	Distilled water
2	Acetone and *m*-xylene mixture at a ratio of 9 to 1 in water
2-A	20% acetone and *m*-xylene mixture and 80% water
2-B	40% acetone and *m*-xylene mixture and 60% water
2-C	60% acetone and *m*-xylene mixture and 40% water
2-D	80% acetone and *m*-xylene mixture and 20% water
2-E	100% acetone and *m*-xylene mixture and no water
3	Methylene chloride, trichloroethylene (TCE), and toluene mixture at the ratio of 1:1:1 in water
3-A	20% methylene chloride, TCE, and toluene mixture and 80% water
3-B	40% methylene chloride, TCE, and toluene mixture and 60% water
3-C	60% methylene chloride, TCE, and toluene mixture and 40% water
3-D	80% methylene chloride, TCE, and toluene mixture and 20% water
3-E	100% methylene chloride, TCE, and toluene mixture and no water

Figure 4 shows that the smallest sediment volume was generated by the distilled deionized water suspension. This was expected because water having no cations results in a dispersed system with more repulsive interparticle force systems. The rate of settlement was slow, as shown in Figure 3, and the volume of sediment consisted of more efficiently packed face-to-face oriented particles. Addition of organic chemicals tended to cause more flocculation of the suspension.

Figure 5 shows the variation of sediment volume with concentration of acetone/m-xylene. Maximum flocculation occured at 40% concentration. More flocculation with organic chemicals relative to deionized water appears to be partly due to the lower dielectric constant of organic chemcials (e.g., acetone: 20.7; m-xylene: 2.4) compared to water (80). Suspensions of the other organic chemicals (methylene chloride, trichloroethylene, and toluene) had a maximum concentration of only 100 ppm of an equal mixture of these chemicals. At this relatively low concentration, their impact on sediment volume and rate of settlement was insignificant.

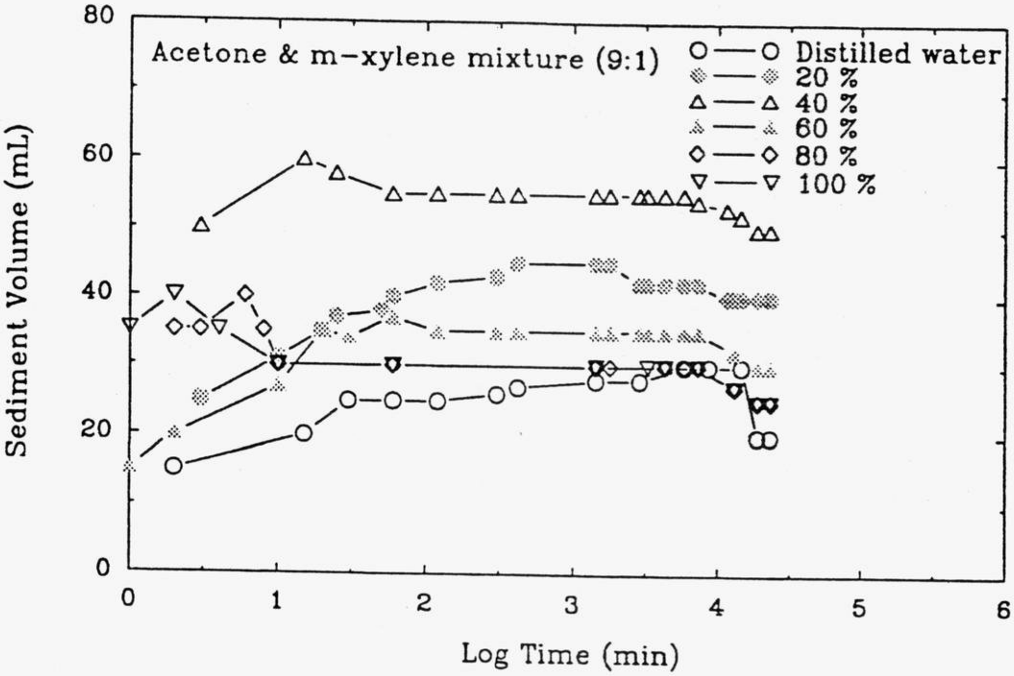


Figure 3. Sedimentation test results with acetone/*m*-xylene mixture (9:1).

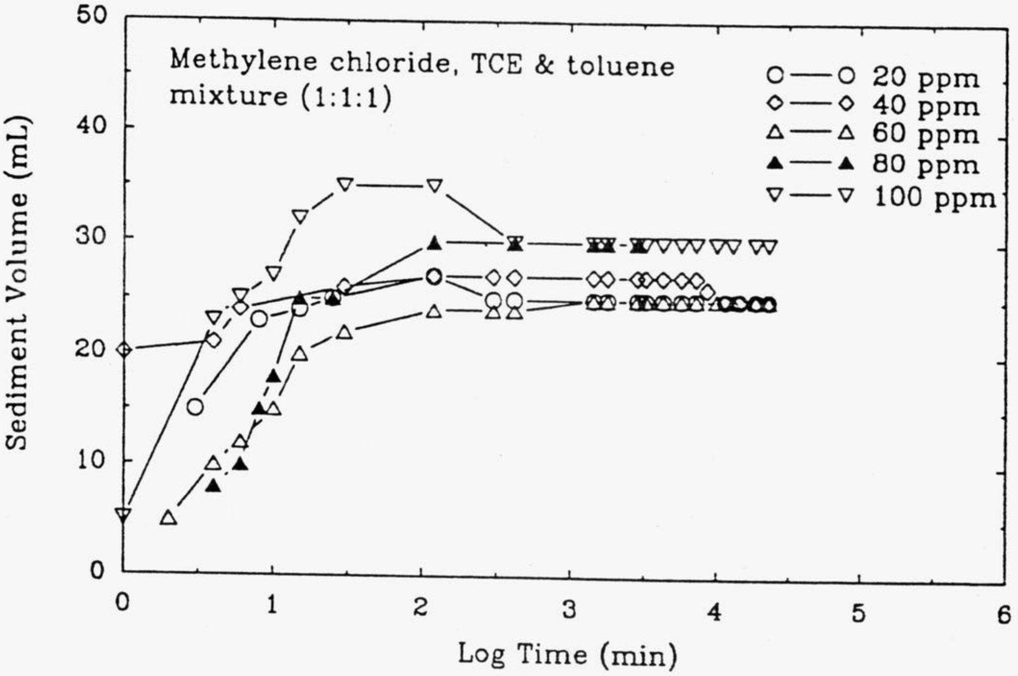


Figure 4. Sedimentation test results with methylene chloride, trichloroethylene, and toluene mixture (1:1:1).

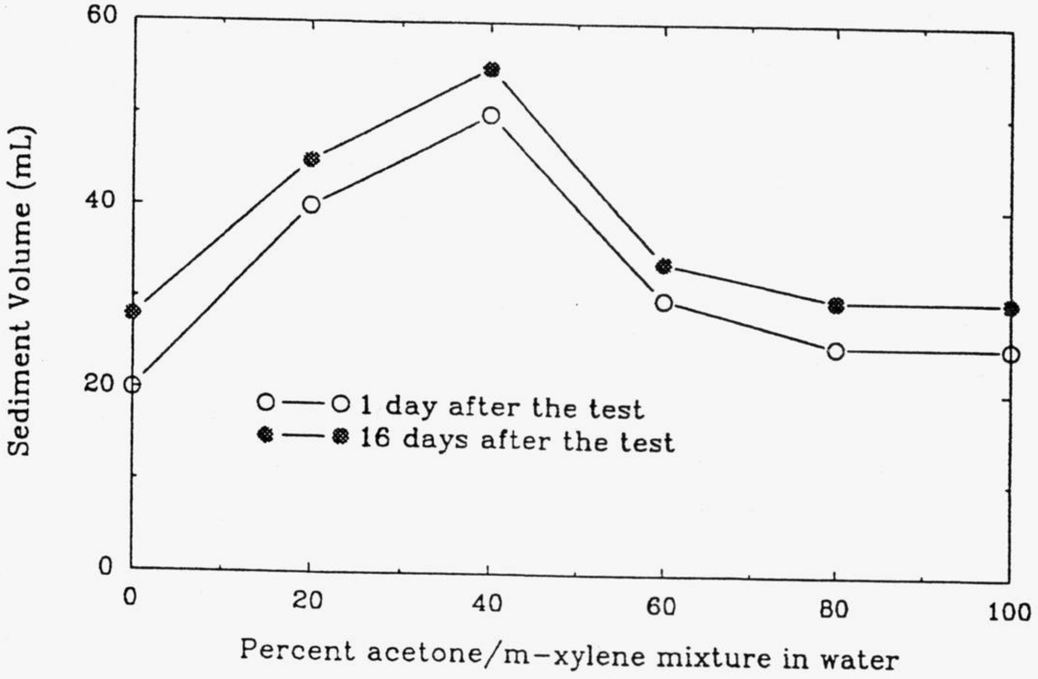


Figure 5. Variation of sediment volume with respect to percent acetone/*m*-xylene mixture (9:1) in water.

Figure 6 is a photograph of the sediment cylinders taken a day after starting the test. Detailed data from the sedimentation test is given in Appendix B.

6. PERMEATION TESTS ON COMPACTED SPECIMENS

6.1. Results

Permeability tests were conducted with six specimens in replicate representing three levels of soil contamination permeated with clean water and organic chemical leachate.

Table 5 summarizes the experimental conditions of the permeability test specimens. Figure 7 shows the variation of hydraulic conductivity (coefficient of permeability) as a function of pore volume of flow. The pore volume of the specimens were about 150 cc depending on the unit weight achieved. The final permeabilities of the specimens are given in Table 5. Even though the same procedure was followed in preparing the specimens, there was some variation in their densities and moisture contents, and thus in their permeabilities.

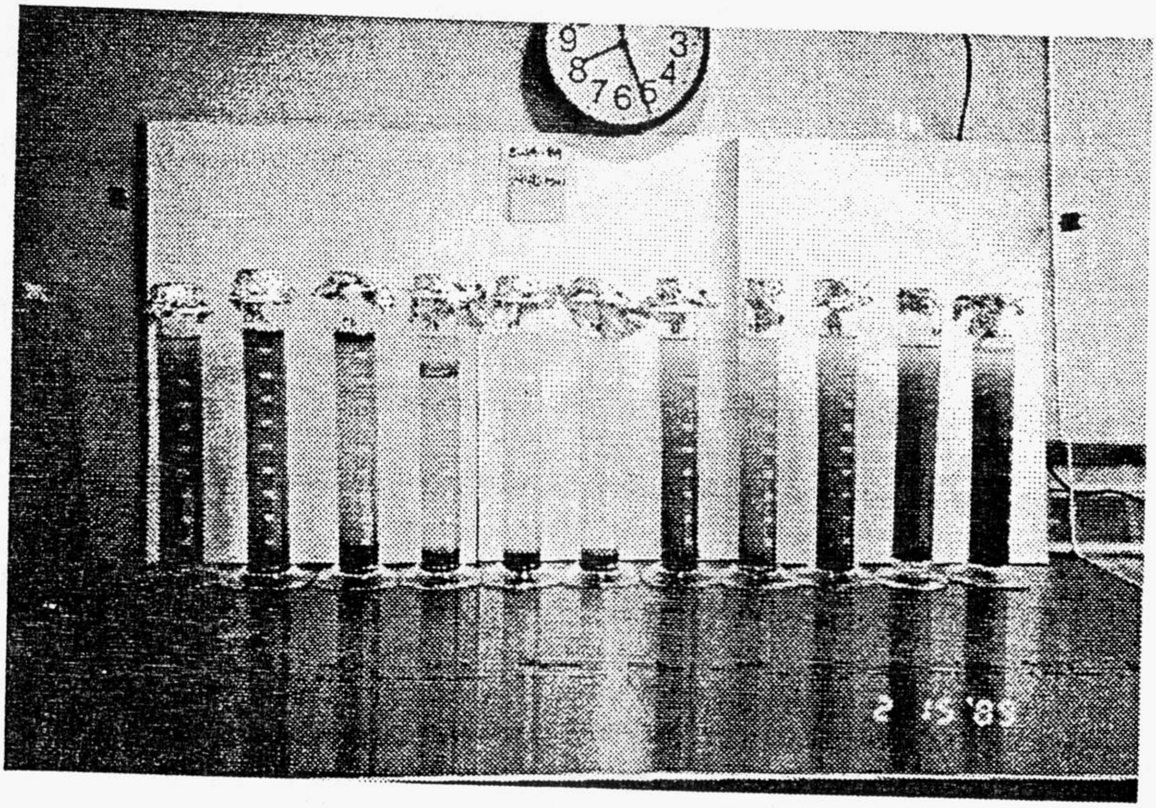


Figure 6. Photograph of the sediment cylinders one day after the test.

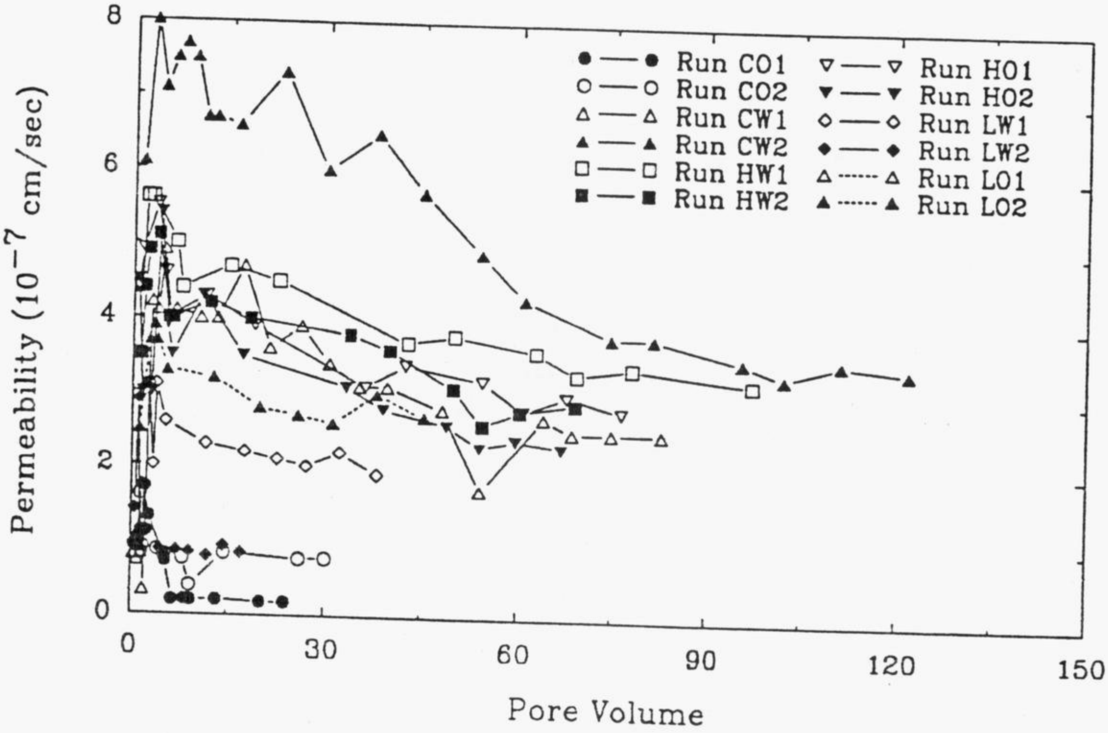


Figure 7. Variation of permeabilities of 12 specimens tested with respect to pore volume.

Table 5. Experimental conditions of permeability test specimens.

Run number[a]	Type of influent	Degree of soil contamination	Dry unit weight, lb/ft^3	Moisture content, %	Consolidation period, days	Stabilized permeability, 10^{-7} cm/sec	Porosity	Pore volume, L	Weight of specimen, kg
CW1	Tap water	Clean	110.9	20	1	0.2	0.35	0.135	0.685
CW2			109.7	20	1	0.8	0.36	0.138	0.676
CO1	Leachate	Clean	106.2	20	3	3.0	0.38	0.160	0.717
CO2			109.2	18	2	3.8	0.36	0.153	0.739
HW1	Tap water	High con.[b]	105.7	18.5	3	3.7	0.38	0.166	0.739
HW2			109.2	18.5	1	3.0	0.36	0.152	0.735
HO1	Leachate	High con.[b]	108.7	18.5	3	3.8	0.36	0.152	0.735
HO2			109.8	18.5	1	3.4	0.36	0.151	0.744
LW1	Tap water	Low con.[c]	108.4	21	1	0.8	0.37	0.146	0.694
LW2			106.0	21	1	3.2	0.38	0.164	0.730
LO1	Leachate	Low con.[c]	107.4	21	1	2.5	0.37	0.158	0.730
LO2			110.2	21	1	1.0	0.36	0.142	0.703

[a] Numbering system: C = clean soil, L = low contamination soil, H = high contamination soil, W = Madison tap water, O = organic chemical leachate (mixture of methylene chloride, toluene and trichloroethylene), and 1 & 2 = replicate specimens.

[b] High level of contamination: Acetone 6 mg/L and *m*-xylene 0.1 mg/L.

[c] Low level of contamination: Acetone 3 mg/L and *m*-xylene 0.1 mg/L.

As a control, the replicate runs (Runs CW1 & CW2) used specimens made of clean soil and were permeated with clean Madison tap water. As expected, no organic chemical's were detected by gas chromatograph analyses.

The influent and effluent concentrations of methylene chloride, toluene, and trichloroethylene for Runs CO1 & CO2 are shown in Figures 8 and 9. The soil specimens were made of clean soil and the "leachate" consisting of three organic chemicals was used as a permeant solution.

Figures 10 and 11 shows the influent and effluent concentrations for Runs HO1 & HO2 in which the soil specimens were intentionally contaminated with approximately 6 ppm of acetone and 0.1 ppm of *m*-xylene. Figures 12 and 13 shows the influent and effluent concentrations for Runs LO1 & LO2 which are supposed to have lower level of soil contamination. Organic chemical leachate effluent concentrations for acetone and *m*-xylene contaminated soil specimens (Runs HW1, HW2, LW1 & LW2) did not significantly differ from those for clean soil specimens (Runs CW1 & CW2). Therefore, it can be said that contamination of soil with 6 ppm acetone and 0.1 ppm *m*-xylene did not enhance the breakthrough times of other organic chemicals neither the performance of soil liners.

Figure 14 shows the effluent concentrations of acetone for permeameters which have contaminated soil specimens (Runs HO1, HO2, HW1, HW2, LO1, LO2, LW1, & LW2). From Figure 14, it can be seen that virtually all of the acetone originally present in the soils was flushed out within three pore volumes. For example, the amount of acetone originally present in the soil used in Run HO2 is 6 ppm (mg/kg) × 0.744 kg (weight of specimen) = 4.46 mg and the amount of acetone in three pore volumes of effluents is approximately 4.3 mg. This demonstrates a reasonable mass balance of acetone.

Runs HO1 & HO2 and Runs HW1 & HW2 were replicates except for the different consolidation periods that were used, i.e., three days for Runs HO1 & HW1 and one day for Runs HO2 & HW2. During the consolidation period, acetone diffused from the specimen to the influent and effluent reservoir to a significant degree. This was confirmed from the fact that acetone was detected in the reservoirs which originally contained a clean tap water.

From Figure 14, the breakthrough curves for Runs HO1 & HW1 and Runs HO2 & HW2 are almost identical, implying that acetone was flushed out at the same degree regardless of whether the influent contained organic chemicals or not.

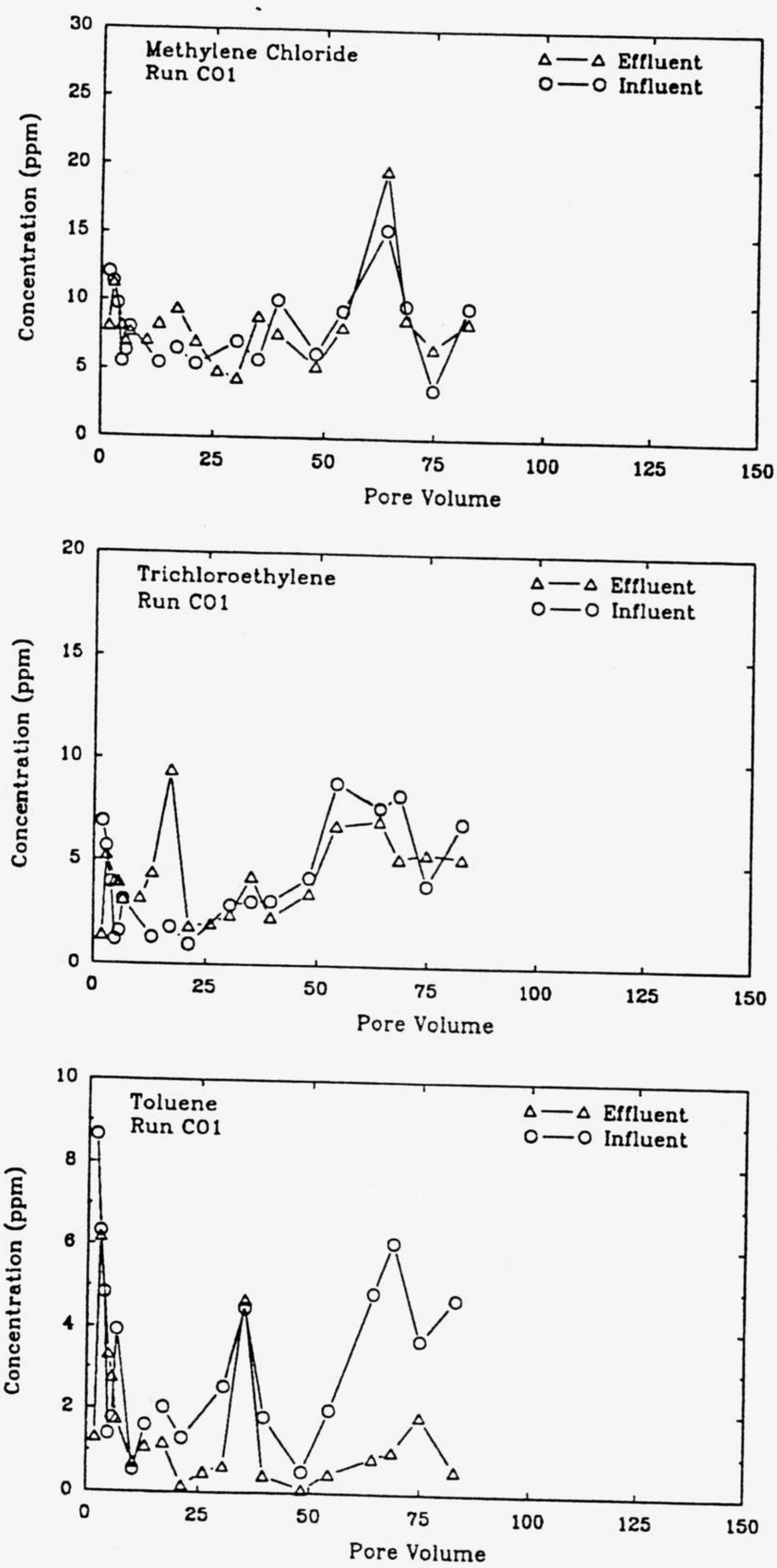


Figure 8. Breakthrough curves of organic chemical leachates for Run CO1.

LEACHATE - CLEAN CLAY

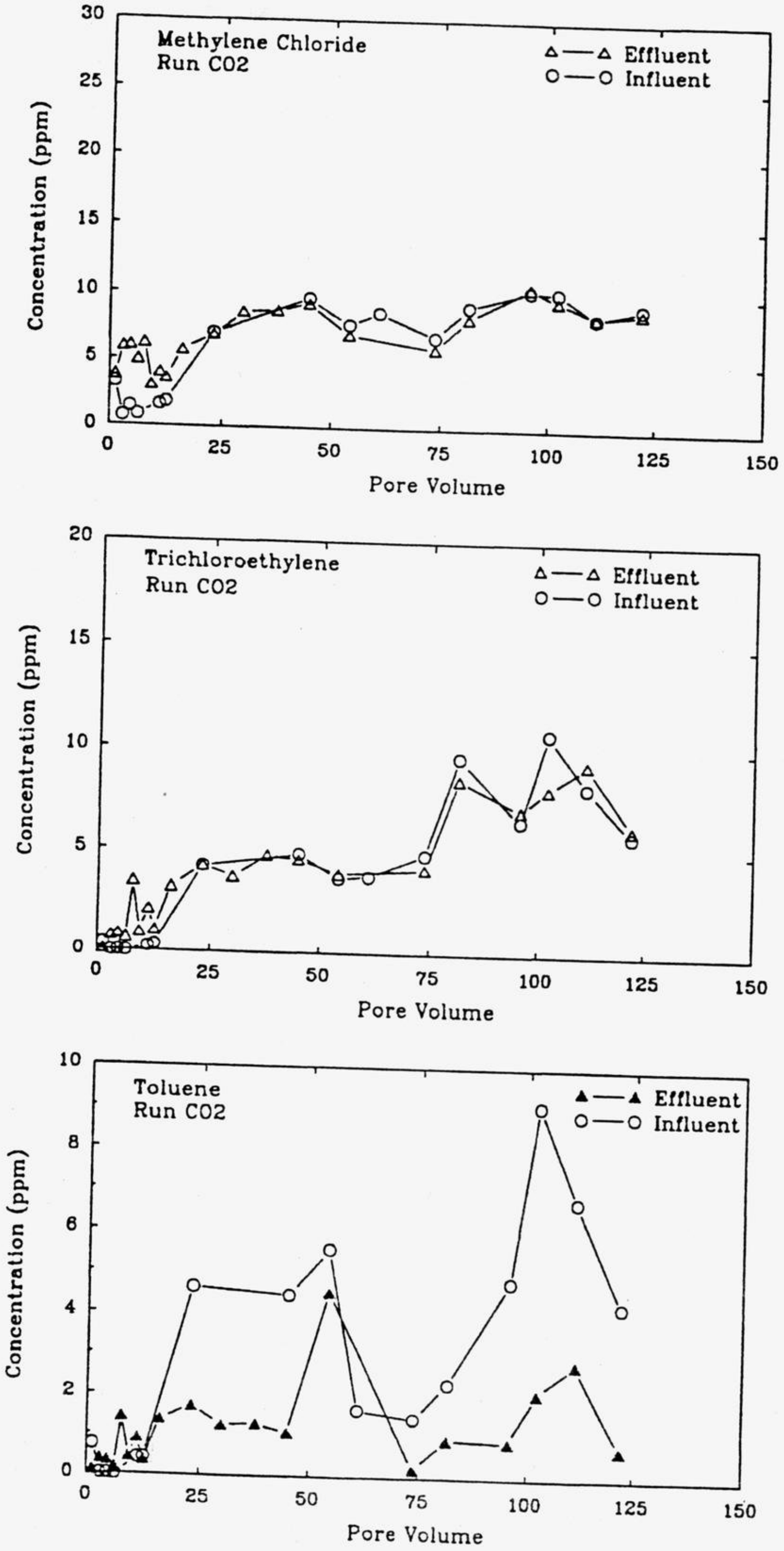


Figure 9. Breakthrough curves of organic chemical leachates for Run CO2.

LEACHATE - CLEAN CLAY

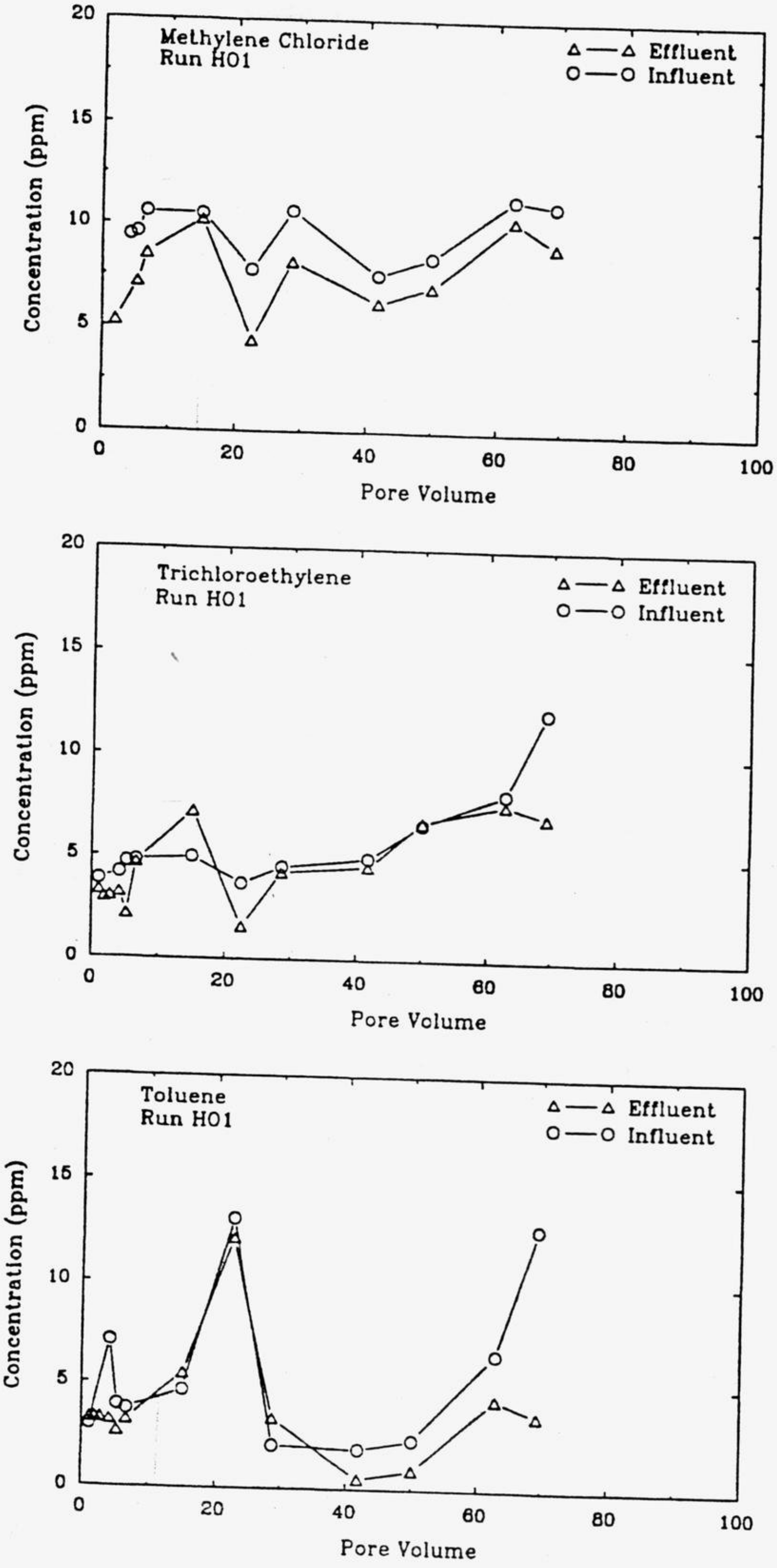


Figure 10. Breakthrough curves of organic chemical leachates for Run HO1.

LEACHATE - H. CONTAM. CLAY

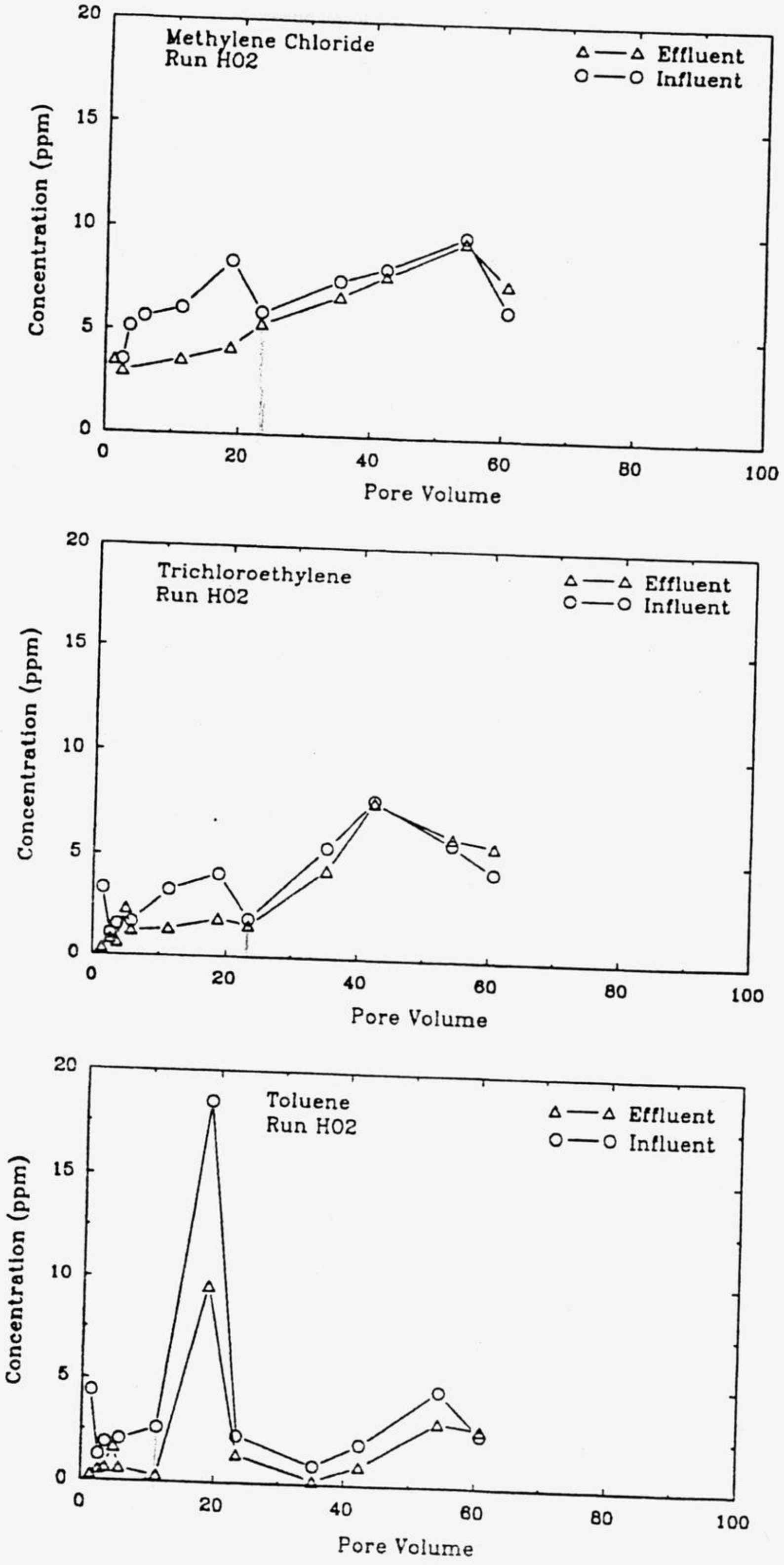


Figure 11. Breakthrough curves of organic chemical leachates for Run HO2.

Leachate [illegible] Contam, Chem

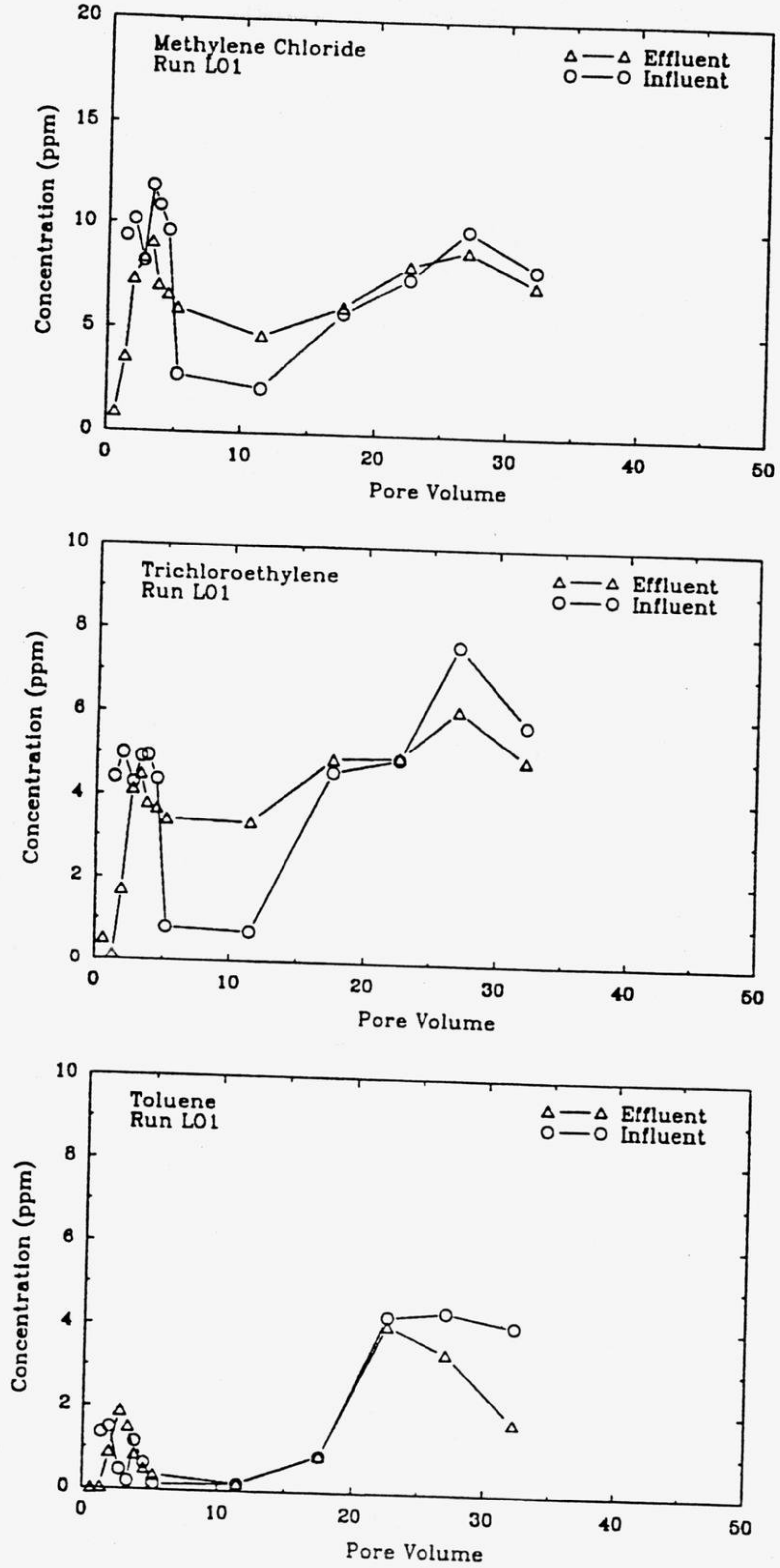


Figure 12. Breakthrough curves of organic chemical leachates for Run LO1.

LEACHATE - LOW. CONC. CLAM

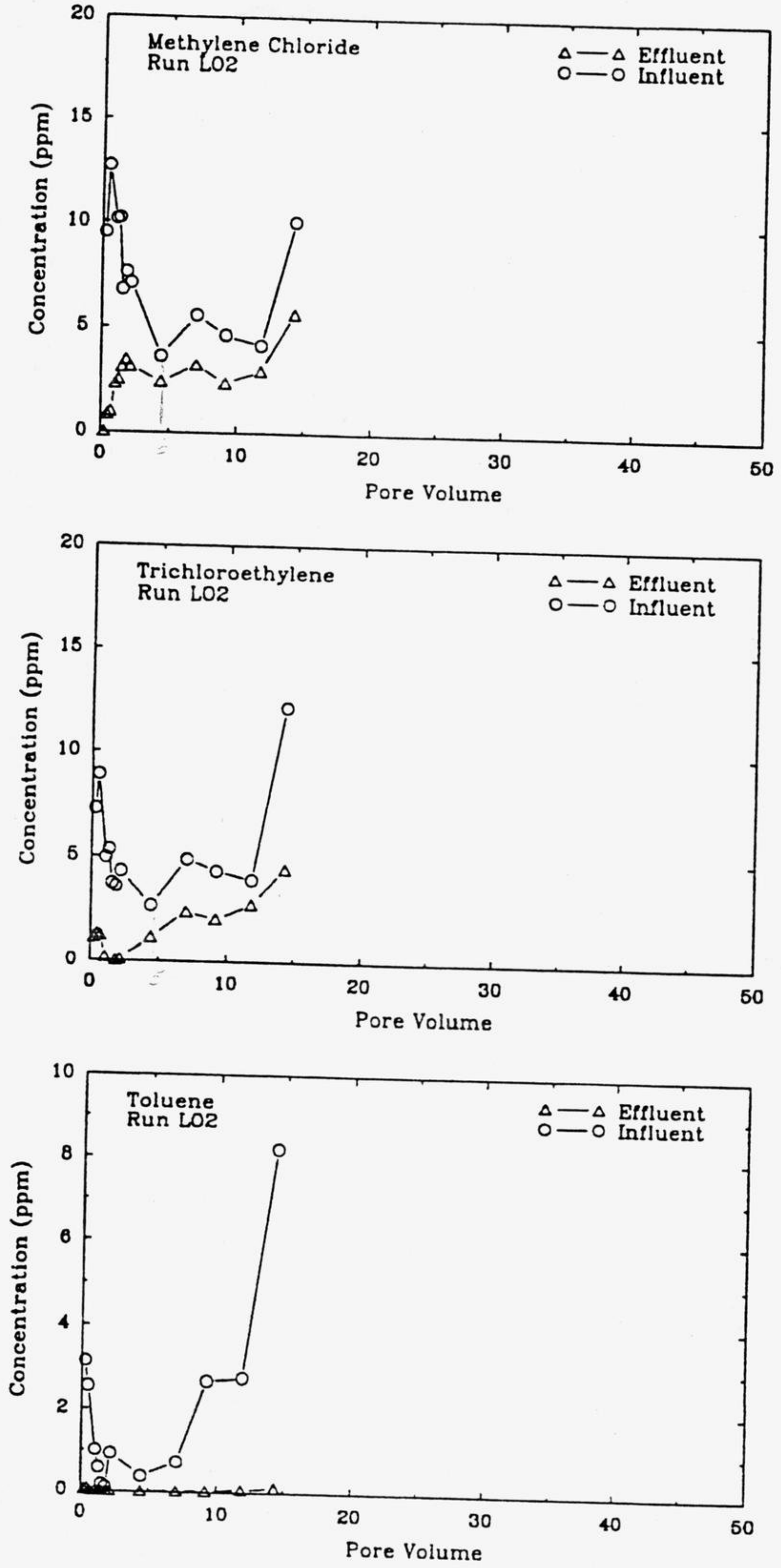
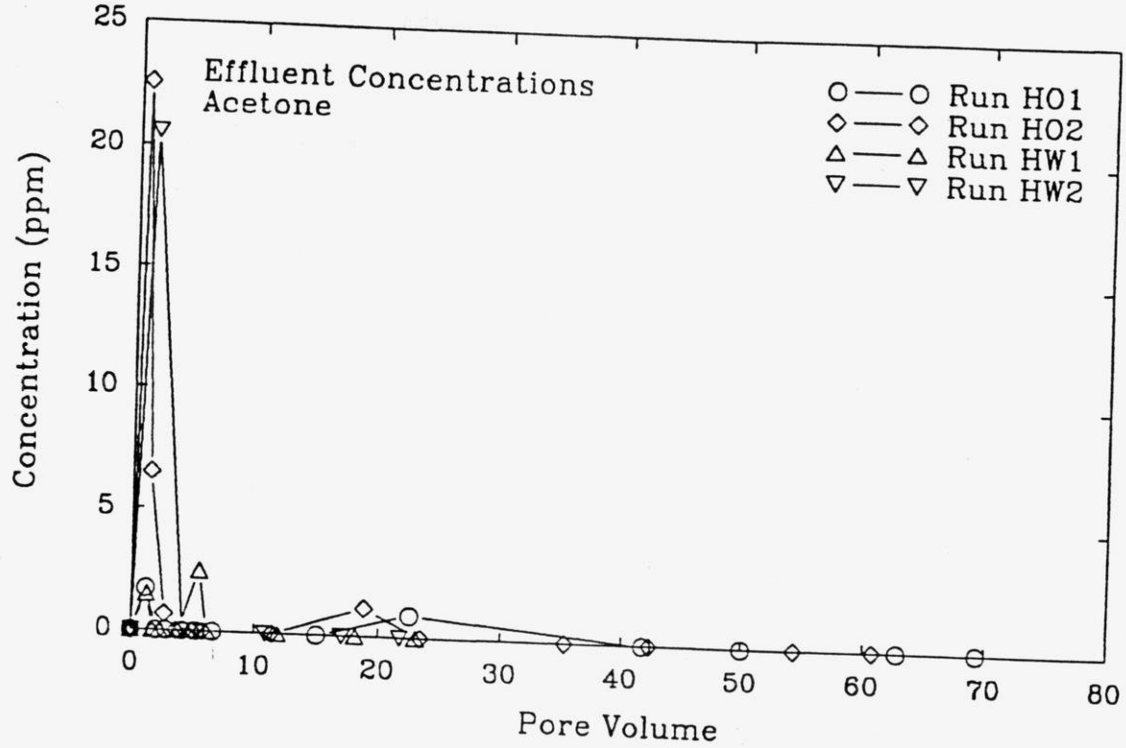


Figure 13. Breakthrough curves of organic chemical leachates for Run LO2.

[illegible]



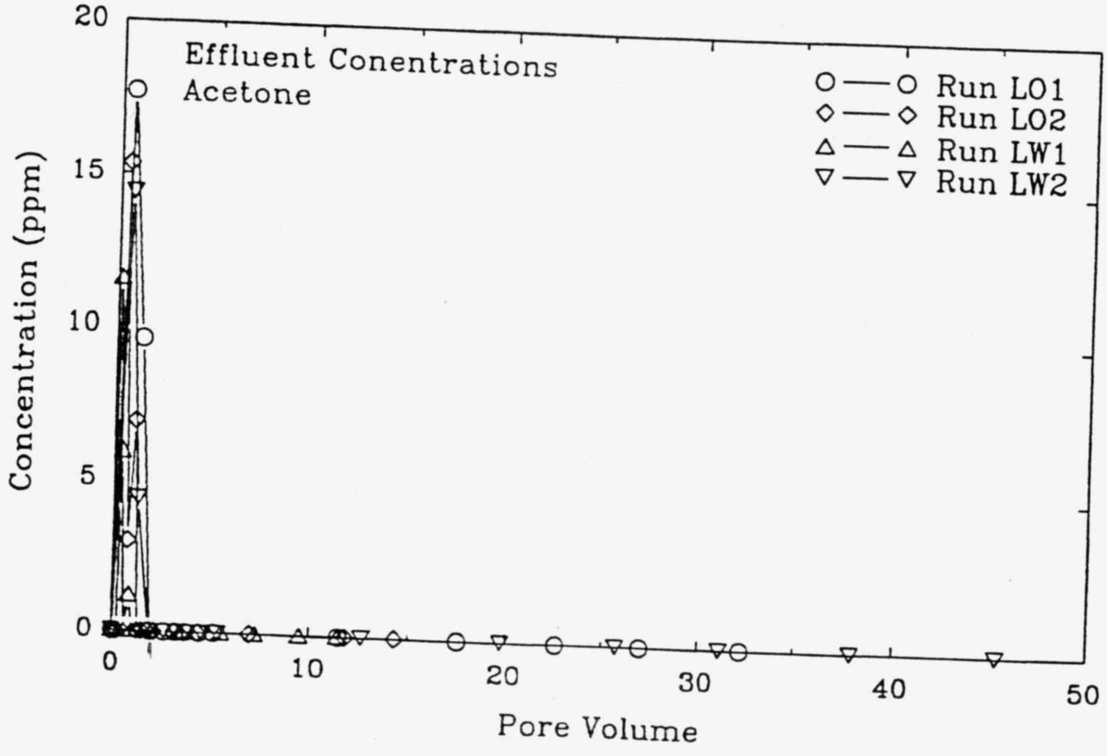


Figure 14. Effluent concentrations of acetone leached from precontaminated specimens.

6.2. Discussion

The influent organic chemical concentrations varied significantly due to volatilization in the influent reservoirs. In a confined vessel, the organic chemical concentrations in the vapor and liquid phases can be estimated using Henry's law and a mass balance equation. Figure 15 shows the theoretical variation of three organic chemical leachate concentrations. Because of the high volatilization rate (high Henry's law constant), the trichloroethylene concentration decrease up to approximately 20% when 10% of the influent bottle is leachate and 90% is gas. Methylene chloride concentrations are expected to vary approximately 30 to 40% during the influent refill cycle. The concentrations measured just before adding a new influent solution into the reservoir were used as influent concentrations in all the figures shown in this report.

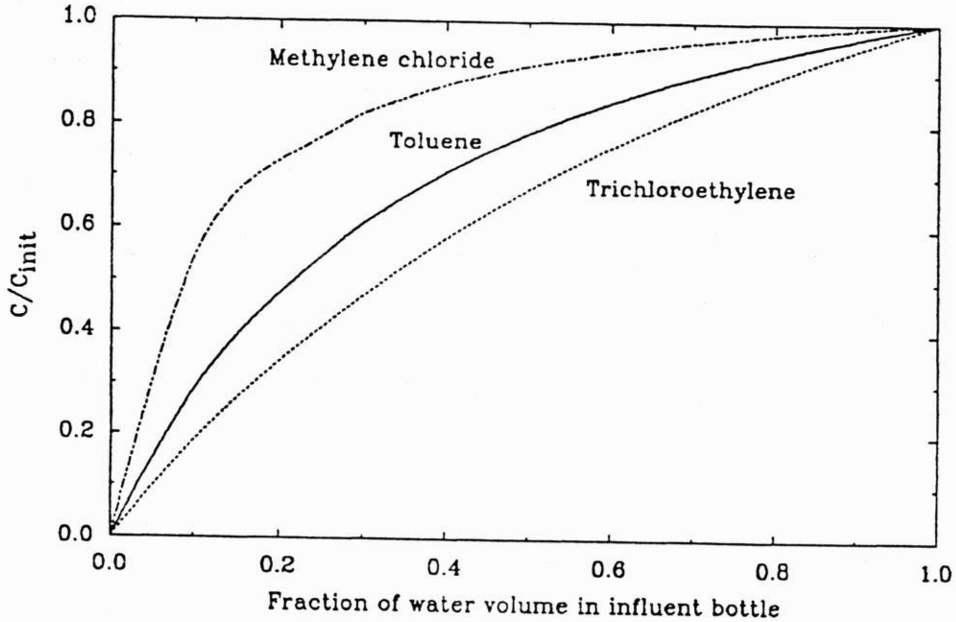


Figure 15. Theoretical variation of influent leachate concentrations with respect to leachate volume in the reservoir if gas-liquid phase equilibrium is assumed.

In general, the soils exhausted their organic chemical sorption capacity within 1 to 10 pore volumes and the effluent concentrations were closely mirrored by the fluctuation of the influent leachate concentrations. The fluctuation of the influent leachate concentrations may result partly from the adsorption and desorption mechanisms but random measurement error is also evident.

7. BATCH ISOTHERM EXPERIMENTS

Batch isotherm tests are being conducted to develop adsorption equations for methylene chloride, trichloroethylene, and toluene on the soil used for the permeameter experiments. Five levels of contaminant concentrations will be used to develop isotherm curves. Single and multiple contaminant solutions will be tested in order to account for the effects of multiple compound leachates on adsorption.

Specifically, the following treatments will be included in the batch isotherm study:

1. Contaminant Combinations: 7 levels
    a. Methylene chloride only
    b. Trichloroethylene only
    c. Toluene only
    d. All three
    e. Toluene and Methylene Chloride
    f. Toluene and trichloroethylene
    g. Methylene Chloride and trichloroethylene
2. Contaminant Concentrations in Water: 5 levels
    1, 10, 30, 50, and 70 ppm
3. Three controls.

Soil and contaminant solutions will be added to centrifuge tubes in a ratio of 1:2 (this ratio may be modified if deemed necessary in the course of the experiment). The soil solution will be mixed by tumbling end over end for 24 hours and then centrifuged for 20 minutes at 10,000 rpm to separate the solid and liquid phases. Liquid supernatant will be extracted for headspace analysis as described in the GC methods section.

Both soil and liquid phases will be tested for several samples to estimate overall recovery of the compounds. Soil will be extracted with iso-octane as described in the section on soil contamination procedures. Contaminant solutions without soil will be subjected to the mixing and centrifuging regimes to estimate losses of compounds via volatilization during the experimental procedure.

8. SORPTION CAPACITY OF CLAY LINERS

The "breakthrough" curves observed in the permeation experiments cannot be estimated precisely but the observation are generally consistent with theoretical estiamtes given in this section. The theory has not been confirmed for the clay and organic chemicals being studied, but some work toward this is needed.

The amount of organic chemical sorbed onto soil can be estimated using the following Freundlich sorption isotherm:

$$\frac{X}{M} = K_f \cdot C_e^{1/n} \tag{1}$$

where: X = mass of organic chemical sorbed, mg;
M = mass of sorbent, kg;
K_f = adsorption coefficient in the Freundlich sorption isotherm;
C_e = equilibrium concentration, mg/L; and
n = constant.

When $1/n = 1$, linear isotherms are produced and K_f reduces to a partition coefficient and has units of L solution/kg soil. K_f is commonly expressed in terms of the soil's organic carbon fraction instead of total soil weight. This gives an organic chemical-organic carbon partition coefficient, K_{oc}, defined as:

$$K_{oc} = \frac{K_f \times 100}{\%\ \text{organic carbon}} \tag{2}$$

Among the equations proposed to predict K_{oc} values, Park *et al.* (1989) found that the following equations of Hassatt *et al.* (1983), which were derived from the extensive experimental data of other workers, gave the best predictions on sorption capacity of various types of soils (sand, clay loam, fine sandy loam):

$$\log K_{oc} = 3.95 - 0.62 \log S \tag{3}$$

$$\log K_{oc} = 0.088 + 0.909 \log K_{ow} \tag{4}$$

where: S = aqueous solubility, mg/L; and
K_{ow} = octanol-water partition coefficient.

The sorption capacities of liner soil for the three organic chemicals used in this study were estimated using Eq. 4 and Eqs. 1 and 2 and the results are summarized in Table 6. The pore volume and the weight of specimens used in the permeability test are 0.16 L and 0.730 kg. The pore volumes of leachate required to exhaust the sorption capacity were estimated assuming that all the organic chemical entering the soil specimen will be rapidly sorbed onto the soil and that a local equilibrium always exists. Methylene chloride appeared in the effluent very quickly. Toluene and trichloroethylene appear to have exhausted in 10 or less pore volumes.

Table 6. The summary of clay sorption capacities for five organic chemicals.

Organic chemical	*log* K_{ow}[a]	K_{oc}[b]	K_f[c], L/kg	$K_f \cdot M$[d], L	Number of pore volumes required[e]
Acetone	-0.24	0.74	0.004	0.003	0.02
m-Xylene	3.20	993	4.9	3.6	22.2
Toluene	2.69	341	1.7	1.2	7.6
Trichloroethylene	2.53	244	1.2	0.9	5.5
Methylene chloride	1.25	17	0.1	0.07	0.4

[a] Dostal (1988).
[b] Obtained from Eq. 4.
[c] Calculated from Eq. 2 with 0.49% organic carbon content
[d] Specimen mass, $M = 0.73$ kg.
[e] Calculated by dividing $K_f \cdot M$ by the pore volume of 0.16 L.

According to the theory, acetone and methylene chloride are extremely soluble and thus within one pore volume the soil sorption capacities (0.02 and 0.4 respectively) were exhaused. Since *m*-xylene has the lowest solubility and the greatest K_{oc} values, the soil sorption capacity was the greatest (22.2), followed by toluene (7.6) and trichloroethylene (5.5).

The Utah Water Research Laboratory (1983) adopted a system based on K_{oc}, the soil-organic carbon partition coefficient. Polar organic chemicals such as alcohols and ketones are classified as "*very high mobility*" in a water-saturated soil environment. This is because their K_{oc} value is very low so they are less sorbable. They also are very soluble, thus tending to stay in the water phase. At the other extreme, organic chemical such as DDT and dioxin having very high K_{oc} values are classified as "*very low mobility*." Table 7 shows the relative mobility of some organic chemicals.

Table 7. Mobility classification of some organic chemicals based on their soil-water partition coefficient (K_{oc}) (Park *et al.*, 1989).

Organic chemical	K_{oc}	Mobility class
Methanol, Acetone, 2-Butanone, Ethyl acetate, *o*-Cresol, *p*-Cresol, Methylene chloride, *o*-Chlorophenol		Very high mobility
m-Cresol, Dichlorofluoromethane (F-21), Nitrobenzene, Benzene, 1,2-Dichloropropane	below	Highly mobility
Trichloroethylene, 1,1,1-Trichloroethane	100	Medium mobility
Carbon tetrachloride Toluene	200	
Dichlorodifluoromethane (F-12)		
Tetrachloroethylene Chlorobenzene	300	
o-Xylene 1,1,2-Trichloro-1,2,2-trifluoroethane (F-113) 1,3-Dichlorobenzene 1,2-Dichlorobenzene		
	400	
1,2-Dichlorotetrfluoroethane (F-114) 1,1,2,2-Tetrachloro-1,2-difluoroethane (F-112) Trichlorofluoromethane (F-11)		
1,1,1,2-Tetrachloro-2,2-difluoroethane (F-112a)	500	Low mobility
p-Xylene		
m-Xylene	600	
Ethyl benzene		
	700	
Chloropentafluoroethane (FC-115)		
	800	
o-Dichlorobenzene	900	
Nonane, Hexane Lindane, DDT, Dioxin	over 1000	Very low mobility

9. CONCLUSIONS

From the soil-organic chemical index tests, the following conclusions can be drawn:

(1) From Atterberg tests, acetone, *m*-xylene, methylene chloride, trichloroethylene, and toluene at the concentrations used did not impact clay-pore fluid interaction except pure acetone.
(2) From sedimentation tests, addition of acetone, *m*-xylene, methylene chloride, trichloroethylene, and toluene tended to cause more flocculation of the suspension than distilled water. For acetone/*m*-xylene mixture, maximum flocculation occurred at 40% concentration.
(3) From sedimentation tests, the impact of methylene chloride, trichloroethylene, and toluene on sediment volume and rate of settlement was insignificant up to their each concentration level of 100 ppm.

From the permeability test results, the following conclusions can be drawn:

(1) Precontaminated clay with acetone and *m*-xylene at the levels studied did not appear to impact organic chemical leachate transport/adsorption adversely, when compared to clean clay.
(2) Acetone was mostly flushed out within three pore volumes. *m*-Xylene was probably released at very low concentrations (below detection limit of 10 µg/L).
(3) In general, methylene chloride, trichloroethylene, and toluene broke through within a few pore volumes. After breakthrough, effluent concentrations were closely mirrored fluctuations in influent concentrations.

10. REFERENCES

Dostal, K. A. (1988). *WERL Treatability Database* (Computer Program), Risk Reduction Engineering Laboratory, U.S. EPA, Cincinnati, OH.

Friedman, M. A. (1988). *Volatile Organic Compounds in Groundwater and Leachate at Wisconsin Landfills*, Wisconsin Department of Natural Resources, PUBL-WR-192.

Hassett, J. J., Banwart, W. L., and Griffin, R. A. (1983). Correlation of Compound Properties with Sorption Characteristics of Nonpolar Compounds by Soils and Sediments: Concepts and Limitations, In "*Environment and Solid Wastes*," Edited by Francis, C. W. and Auerbach, S. I., An Ann Arbor Science Book, 161-178.

Mitchell, J. K. and F. T. Madsen. (1987). Chemical effects on clay hydraulic conductivity, *Proc. of ASCE Conference on Geotechnical Practice for Waste Disposal '87*, pp. 87-116.

Nirmalakhandan, N. N. and Speece, R. E. (1988). QSAR Model for Predicting Henry's Constant, *Environ. Sci. Technol.*, 22, 11, 1349-1357.

Park, J. K., Holsen, T. M., Bontoux, L., Jenkins, D., and Selleck, R. E. (1989). *Permeation of Plastic Pipe by Organic Chemicals*, University of California, Berkeley, Sanitary Engineering and Environmental Health Research Laboratory, Report No. 89-1, Jan. 1989, 391 p.

Thibodeaux, L. J. (1979) *Chemodynamics: Environmental Movement of Chemicals in Air, Water, and Soil*, John Wiley & Sons, New York, p. 46.

Utah Water Research Laboratory. (1983). *In-situ Treatment Techniques Applicable to Large Quantities of Hazardous Waste Contaminated Soils*, Edited by Sims, R. E., Draft Document Prepared for the U.S. EPA, Cincinnati, OH.

van Olpen, H. (1963). *An Introduction to Clay Colloid Chemistry*, Wiley Interscience, New York, 301 p.

APPENDIX A.

ATTERBERG TEST RAW DATA

SUMMARY OF ATTERBERG LIMITS TEST RESULTS
UNIVERSITY OF WISCONSIN--MADISON
EAU CLAIRE COUNTY LANDFILL LINER CLAY

SAMPLE	LIQUID USED	CONCENTRATION	(1) LIQUID LIMIT RUN 1 MOISTURE CONTENT (%)	(1) LIQUID LIMIT RUN 1 NUMBER OF BLOWS	(1) LIQUID LIMIT RUN 2 MOISTURE CONTENT (%)	(1) LIQUID LIMIT RUN 2 NUMBER OF BLOWS	(2) CORRECTED LIQUID LIMIT RUN 1 (%)	(2) CORRECTED LIQUID LIMIT RUN 2 (%)	PLASTIC LIMIT (%)	COMMENTS
1	DI H20	--	31.4	20	31.3	21	30.6	30.6	18.9	(3)
2.1	ACETONE	1 ppm	30.1	22	29.9	23	29.6	29.6	19.4	(3)
2.2	&	6 ppm	30.3	22	29.9	23	29.8	29.6	19.4	(3)
2.3	m-XYLENE	10 ppm	30.5	25	30.1	24	30.5	29.9	19.1	(3)
2.4	SOLUTION	100 ppm	30.6	24	30.2	24	30.4	30.0	18.5	(3)
3.1	MeCl2,	1 ppm	30.0	23	30.1	23	29.7	29.8	19.3	(3)
3.2	TCE &	10 ppm	29.1	28	29.4	29	29.5	29.9	19.3	(3)
3.3	TOLUENE	50 ppm	27.8	27	30.0	26	28.1	30.2	18.4	(3)
3.4	SOLUTION	100 ppm	29.6	22	29.8	23	29.2	29.5	18.7	(3)
4	MIX OF SOLUTIONS 2.2 & 3.3		30.4	23	30.3	23	30.1	30.0	18.9	(3)
5.1	ACETONE	50%	28.9	25	29.1	25	28.9	29.1	19.4	(3)
5.2		100%	25.8	23	24.8	23	25.6	24.5	27.7	(3),(4)

NOTES:

(1) Moisture content of soil during test, not corrected for liquid limit at 25 blows

(2) Liquid limits were corrected for 25 blows using ASTM D4318
formula: LL = K * Wn
Wn = water content
K = correction factor from Table 1 of ASTM D4318

(3) Started with air dry P40 soil (moisture content=0.4%)
Tests were performed on air dry P40 soil
Moistened to approximately the liquid limit &
Sealed in glass jar with taped lid for 24 hours.
Casagrande grooving tool was used
Liquid limit test was performed twice
Plastic limit test start moisture content was near the liquid limit
Test time:
Run 1--Liquid limit: 2 min
Run 2--Liquid limit: 2 min
Plastic limit: 4-5 min

(4) Plastic limit was determined for an approximately 1/4 in. diameter soil thread due to relatively low cohesion of soil mixed with 100% acetone

SUMMARY OF ATTERBERG LIMITS TEST RESULTS
UNIVERSITY OF WISCONSIN--MADISON
EAU CLAIRE COUNTY LANDFILL LINER CLAY

SAMPLE	LIQUID	CONCENTRATION	MOISTURE CONTENT DURING LIQUID LIMIT TEST (9)				PLASTIC LIMIT			COMMENTS
			RUN 1 (%)	RUN 2 (%)	RUN 3 (%)	RUN 4 (%)	RUN 1 (%)	RUN 2 (%)	RUN 3 (%)	
5.1	ACETONE	50% (7)	30.0	28.9	28.1	27.0	18.1	18.9	20.5	(1)
	NUMBER OF BLOWS		27	37	70	(3)	--	--	--	
	TESTING TIME (min)		0.5 (4)	5 (4)	10 (4)	15 (4)	4 (5)	3 (6)	3 (6)	
5.2	ACETONE	100% (8)	28.9	25.8	22.4	21.1	30.0	27.3	26.2	(2)
	NUMBER OF BLOWS		5	6	12	(3)	--	--	--	
	TESTING TIME (min)		0.5 (4)	5 (4)	10 (4)	15 (4)	0.5 (5)	1 (5)	2 (5)	

NOTES:

(1) Started with air dry P40 soil (moisture content=0.4%)
LIQUID LIMIT
Start moisture content after mixing was about 30%
ASTM grooving tool used
Increased blow counts indicate moisture change or hydration
Soil acts sticky, not smooth as a clay (CL) soil should
No correction factor applied
PLASTIC LIMIT
Worked soil until it reached plastic limit (1/8 in. diameter soil thread)

(2) Started with air dry P40 soil (moisture content=0.4%)
LIQUID LIMIT
Start moisture content after mixing was about 30%
ASTM grooving tool used
Evaporation of liquid taking place very quickly during test
Soil acts like a silt (ML)
No correction factor applied
PLASTIC LIMIT
Plastic limit was determined for an approximately 1/4 in. diameter soil thread due to relatively low cohesion of soil mixed with 100% acetone

(3) Non-workable, unable to groove

(4) Time from start of mixing to start of liquid limit test

(5) Time from start of mixing to end of rolling, start moisture content was about 30%

(6) Time from start of mixing to end of rolling, start moisture content was about 21%

(7) Soil was a hard lump, difficult to crush, after oven drying at end of test

(8) Soil was very friable, easily crushed, after oven drying at end of test

(9) Moisture content of soil during test, not corrected for liquid limit at 25 blows

APPENDIX B.

SEDIMENTATION TEST RAW DATA

Notes:

The soil consisted of P40 air-dried soil.
The air-dried moisture content was 0.4 %.

25 grams of soil was poured into each 500 ml graduated cylinder and mixed with the test liquid by shaking in the graduated cylinder for 1 minute.

(1) Level in ml of top of suspended solids in 500 ml graduated cylinder.

(2) Level in ml of top of sediment in 500 ml graduated cylinder.

(3) Graduated cylinder broke (applies only to Table 4).

(4) Bottom level in ml of concentrated Meta-Xylene floating at top in 500 ml graduated cylinder (applies only to Table 3).

* After approximately 3 days (or 6 days in the case of deionized water), settlement of solids had slowed to the point that the top level of the suspended solids zone was no longer dropping. To estimate further particle settlement, a relative clearness scale was devised to describe the zone still containing the suspended solids; 1 is very cloudy and 10 is very clear.

SUMMARY OF LABORATORY SEDIMENTATION TEST RESULTS
UNIVERSITY OF WISCONSIN-MADISON
EAU CLAIRE COUNTY LANDFILL LINER CLAY

STOCK SOLUTION: Acetone & Meta-Xylene, 9 to 1 mixture.

SAMPLE	1		2.1		2.2		2.3		2.4		2.5	
CONCENTRATION	DI WATER		20%		40%		60%		80%		100%	
START CLOCK TIME February 14, 1989	0810		0816		0822		0828		0834		0841	
CHANGE IN TIME	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
0 min	500	0	500	0	500	0	500	0	500	0	500	0
1min	---		---		---		450(4)	15	---		215	35
2 min	495	15	---		---		420(4)	20	300	35	40	40
3 min	---		500	25	495(4)	50	---		150	35	---	
4 min	---		---		---		---		---		35	35
6 min	---		---		---		---		40	40	---	
8 min	---		---		---		---		---		---	
10 min	---		500	31	---		415(4)	27	35	35	30	30
15 min	495	20	---		490(4)	60	---		30	30	---	
20 min	---		495(4)	35	---		415(4)	35	---		---	
25 min	---		495(4)	37	490(4)	58	---		---		---	
30 min	495	25	---		---		415(4)	34	---		---	
50 min	---		495(4)	38	---		---		---		---	
60 min	495	25	495(4)	40	490(4)	55	415(4)	37	30	30	30	30
120 min	490	25	495(4)	42	485(4)	55	415(4)	35	---		---	
300 min	490	26	495(4)	43	480(4)	55	415(4)	35	---		---	
420 min	490	27	495(4)	45	480(4)	55	415(4)	35	---		---	
24 hr	480	28	495(4)	45	480(4)	55	415(4)	35	30	30	30	30
30 hr	---		495(4)	45	480(4)	55	415(4)	35	30	30	---	
48 hr	450	28	495(4)	42	480(4)	55	415(4)	35	---		---	
55 hr	---		495(4)	42	480(4)	55	415(4)	35	---		30	30
72 hr	---		6*	42	7*	55	8*	35	9*	30	10*	30
97.5 hr	400	30	7*	42	8*	55	9*	35	10*	30	---	
122 hr	---		8*	42	9*	54	10*	35	10*	30	10*	30
144 hr	9*	30	---		---		---		---		---	
169 hr	---		---		---		---		---		---	
193 hr	---		8.5*	40	9.5*	53	---		---		---	
216 hr	---		9*	40	---		10*	32	10*	27	10*	27
240 hr	9.5*	30	9.5*	40	10*	52	---		---		---	
[illegible]2 hr(13 days)	10*	20	10*	40	10*	50	10*	30	10*	25	10*	25
384 hr(16 days)	10*	20	10*	40	10*	50	10*	30	10*	25	10*	25

SUMMARY OF LABORATORY SEDIMENTATION TEST RESULTS
UNIVERSITY OF WISCONSIN--MADISON
EAU CLAIRE COUNTY LANDFILL LINER CLAY

STOCK SOLUTION: 100 ppm of MeCL2, TCE, Toluene

SAMPLE	3.1		3.2		3.3		3.4		3.5	
CONCENTRATION	20%		40%		60%		80%		100%	
START CLOCK TIME FEBRUARY 14, 1989	0848		0851		0854		0858		0902	
CHANGE IN TIME	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
0 min	500	0	500	0	500	0	500	0	500	0
1 min	---		500	20	---		---		500	5
2 min	---		---		500	5	---		---	
3 min	500	15	---		---		---		---	
4 min	---		500	21	500	10	500	8	500	23
6 min	---		500	24	500	12	500	10	500	25
8 min	500	23	---		---		500	15	---	
10 min	---		---		500	15	500	18	500	27
15 min	490	24	---		480	20	500	25	500	32
25 min	480	25	---		---		495	25	---	
30 min	---		475	26	480	22	---		495	35
120 min	475	27	480	27	480	24	490	30	480	35
300 min	475	25	475	27	475	24	---		---	
420 min	475	25	475	27	475	24	490	30	480	30
24 hr	450	25	450	27	450	25	480	30	475	30
30 hr	450	25	425	27	450	25	475	30	450	30
48 hr	400	25	375	27	400	25	425	30	450	30
55 hr	400	25	350	27	400	25	(3)		400	30
72 hr	7*	25	8*	27	6*	25	---		2*	30
96.5 hr	8*	25	8*	27	7*	25	---		3*	30
122 hr	8*	25	8*	27	7*	25	---		6*	30
144 hr	---		9*	26	---		---		---	
169 hr	---		---		8*	25	---		7*	30
193 hr	9*	25	10*	25	---		---		---	
216 hr	---		---		9.5*	25	---		8*	30
240 hr	10*	25	10*	25	---		---		---	
312 hr(13 days)	10*	25	10*	25	10*	25	---		9.5*	30
384 hr(16 days)	10*	25	10*	25	10*	25	---		10*	30