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Diffusive Contaminant Transport in Natural Clay: A Field Example and Implications for Clay-Lined Waste Disposal Sites

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■ Vertical core samples were obtained from an impervious, unweathered, water-saturated clay deposit beneath a 5-year-old hazardous waste landfill at a site in southwestern Ontario. Sections of the cores were analyzed for chloride and volatile organic compounds. Waste-derived chloride was detected in the clay to a maximum depth of 83 cm below the bottom of the landfill. The most mobile organic compounds were found only to a depth of ~15 cm. The downward transport of these chemical species into the clay was the result of simple Fickian diffusion. This study has implications for low-permeability clay liners used at waste disposal sites. For liners of typical thickness (~1 m), simple diffusion can cause breakthrough of mobile contaminants in approximately 5 years; the diffusive flux of contaminants out of such liners can be large.

Introduction

Clay liners are frequently employed at waste disposal sites as a means of minimizing the potential for groundwater contamination. It is commonly thought that if the hydraulic conductivity (K) of the clay is low and if there are no structural defects, then the liner will provide an adequate barrier between the waste and the underlying hydrogeologic domain. Guidelines for the properties of clay liners commonly specify that they should have a K less than 10^{-7} cm/s in order that the rate of advective transport will be small. However, even when advection is minimal, contaminants can migrate through clay by simple Fickian diffusion at rates that can be significant.

Goodall and Quigley (1) and Crooks and Quigley (2) have evaluated the transport of inorganic ions by simple diffusion in a low- K , clayey till. They determined vertical profiles of several leachate-derived constituents by analyzing core samples taken from weathered clay in shallow pits beneath a municipal landfill in southwestern Ontario. Their data suggested diffusion as the dominant cause of profile development. However, due in part to advective

transport in fractures in the weathered zone, their success in fitting a diffusion model to their data was limited.

Using several study locations near those of Quigley and co-workers, Desaulniers (3) and Desaulniers et al. (4, 5) studied the permeability of the local clay and the flow rates and age of the accompanying groundwater. Those investigators concluded that (1) below ~5 m from ground surface, the clay is unweathered and has an average K less than 5×10^{-8} cm/s, (2) groundwater flow is downward at an average linear velocity of less than a few millimeters per year, (3) isotopic dating results indicate that groundwater in the unweathered clay is generally many thousands of years old, (4) natural solutes in the groundwater (e.g., Cl^- and ^{18}O) have developed upward-directed concentration profiles, the source of the solutes being the underlying bedrock, and (5) the character of the upward profiles has been determined largely by simple diffusion since the retreat of the Pleistocene glaciers. Desaulniers et al. (4) successfully simulated the vertical concentration profiles by means of one-dimensional diffusion models and diffusion times of 12 000–16 000 years.

Myrand et al. (6) has conducted laboratory diffusion experiments for organics using clays from another site in southwestern Ontario. On the basis of measurements of effective diffusion coefficients for several organics, those workers concluded that sorption of the organic compounds onto organic matter in the clays is important in retarding transport through the clays. They also determined that the extent to which the organics partition to the solids is strongly dependent on the concentrations of the organics, i.e., that sorption of their study compounds on the clays is nonlinear.

Prudic (7) examined the migration patterns of a variety of radionuclides in a glacial till in New York State. He concluded that tritium had moved up to 3 m during a 7–11-year time period as the result of simple diffusion. He also concluded that other radionuclides moved at slower rates, which could be predicted by the extent of partitioning of the radionuclides onto the till.

Gray and Weber (8) used the data of Goodall and Quigley (1), Crooks and Quigley (2), and Desaulniers et al.

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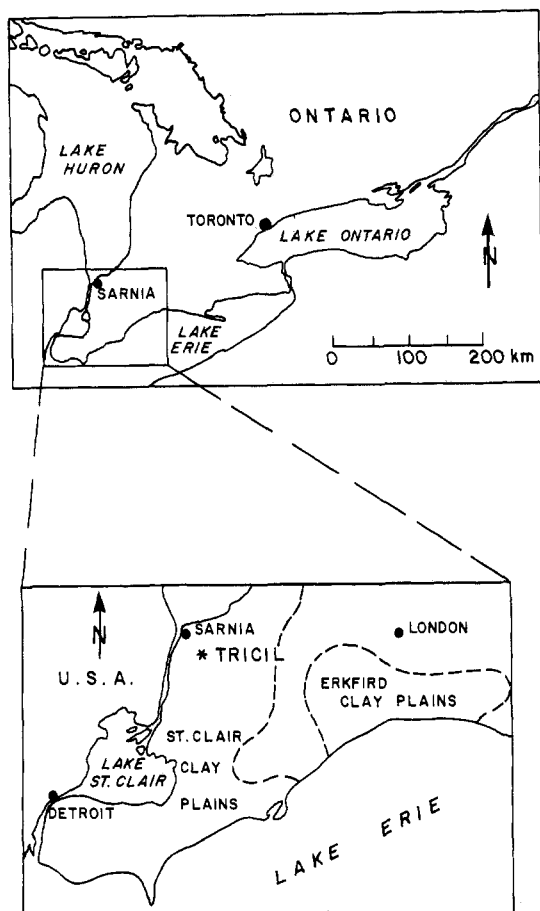


Figure 1. Upper: Regional map showing the location of the site on the St. Clair clay plain. Lower: Sarnia area map.

(4) to examine the potential importance of simple diffusion in low-permeability clay liner systems. The conclusion of Gray and Weber (8) was that all available theoretical and experimental data support the conclusion that simple diffusion can play an important role in carrying contaminants across low-permeability clay liner barriers used to "seal" hazardous waste disposal sites.

The purpose of this work was to investigate the nature of diffusive transport through clay beneath an *actual* hazardous waste disposal site. This paper therefore describes a field investigation of vertical contaminant profiles in pore water extracted from core samples of natural clay underlying such a site. The work of Myrand et al. (6) described above was conducted with clay from the same site and was carried out in conjunction with this work. The goals of this investigation were to (1) determine the rates at which inorganic and organic compounds from the waste are migrating downward through the clay, (2) assess the applicability of simple diffusion models for predicting those rates, and (3) evaluate the importance of simple diffusion in transporting contaminants across clay liners. The current investigation is similar in some respects to the work of Quigley and co-workers, but differs significantly in that it examines clay at a depth where it is not weathered and also considers organic contaminants.

Site Description

The study site selected is a waste disposal facility operated by Tricil Limited located 15 km southwest of Sarnia, Ontario (Figure 1). Individual landfills are located at the site in pits excavated in the natural clay of that region. The site was selected because the natural clay deposit is 40-m thick, and therefore vertical boreholes

through the waste could be drilled 1–2 m into the clay beneath the pits without significantly decreasing the ability of the overall deposit to contain the waste. The site possesses additional favorable logistical attributes, such as waste material that offers no obstructions to drilling, accurate information on the locations and depths of the landfills, and hydrogeological conditions that have been determined in detail in previous investigations. The particular waste disposal landfill selected for this investigation was excavated in 1979 and received its final load of waste in 1980. The waste mass consisted of fly ash from a nearby coal-fired electrical generating station to which the liquid hazardous wastes were mixed prior to disposal. The waste is ~15-m deep and is covered with compacted clay that is 2-m thick.

The Tricil site is situated in the St. Clair clay plain, which extends more than 20 km in all directions from the site (Figure 1). The clay deposit, which is late Quaternary in age, was formed by glaciers that protruded into a large glacial lake. The deposit contains numerous granules of shale bedrock indicative of the glacial till origin of the deposit. About 40% of this till is clay-sized particles, which are primarily illite and chlorite (9). The remainder consists of silt and sand-sized material and includes a small percent of pebbles. The clay is unweathered, uniform, and has a very low K ($<5 \times 10^{-8}$ cm/s). It thus has all of the features normally desired of a clay liner.

Experimental Section

Sample Collection and Preparation. Samples from three boreholes located approximately 5 m apart were collected from the 5-year-old landfill with a Central Mine Equipment (CME Model 75) drill rig with continuous flight, 1.6-m- (5-ft) long hollow-stem augers. After reaching ~0.5 m above the bottom of the landfill, cores were taken with a 1.6-m (5-ft) split-spoon tube sampler. In this manner, each borehole sample collected was continuous from the bottom of the waste, through the waste/clay interface, and to a depth of ~2 m below that interface. As the samples were brought to the surface, they were removed from the split-spoon sampler and lightly washed with water to remove most of the external contamination. Samples of the semiliquid waste material were retained to estimate concentrations at the interface.

Immediately after sampling, the cores were taken to an on-site laboratory and placed in a fume hood for further sample preparation. The interface between the waste and clay was easily located because of its abruptness. Moving from the interface, the core was cut into either 3.8- or 7.6-cm (1.5- or 3-in.) sections with a sharp knife. Whatever contamination remained on the exterior of each section was then carefully trimmed away with two frequently cleaned knives. Each section was wrapped in aluminum foil, placed in a 500-mL amber jar, and sealed with a cap lined with aluminum foil. (Both the jar and the foil had been pre-cleaned by heating at 450 °C for 1 h.) The samples were then stored at 4 °C.

Pore water was removed from the core sections by compressing the sections in nine identical, specially designed consolidometers (Figure 2). The design of these devices was similar to that described by Patterson et al. (10) and included a capped cylinder surrounding a moveable piston. Pressure was exerted on a sample by the piston, which was driven by compressed nitrogen gas. Samples were typically pressurized to 600 psi (42 kg/cm²). Since the piston area was 44 cm², a total force of approximately 2000 kg was exerted on each sample. Two glass-fiber filters (Gelman Inc., Ann Arbor, MI) followed by a 100-mesh stainless steel screen helped to retain the clay

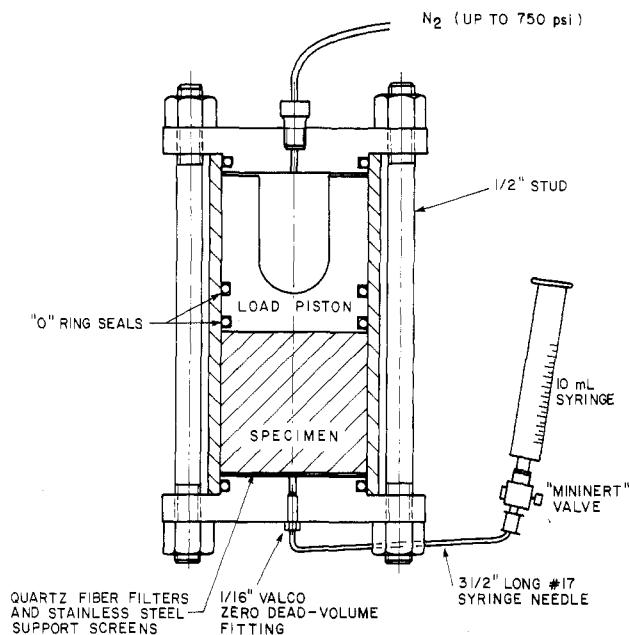


Figure 2. Cross-sectional view of one of the consolidometers.

particles in the bottom of each consolidometer. A $1/16$ in. o.d. tube carried the filtered pore water to a 10-mL syringe, which was fitted with a small Teflon valve (Mininert, Pierce Chemical, Rockford, IL). The valve permitted the leak-free removal of the syringe from the consolidometer. The samples were only exposed to stainless steel, glass, and Teflon during the pore water extractions. All extractions were carried out at 10 °C to ensure that concentrations in the extracted pore water (i.e., the pore water/clay distributions) were the same as in the undisturbed clay.

Upon completion of the squeezing, the valve on the syringe was closed, the syringe removed, and the liquid transferred to two sample bottles. The first bottle (1.5 mL, precleaned amber glass) was carefully filled to minimize volatilization; no significant headspace remained. This bottle was capped with a Teflon-lined septum and stored for organics analysis. The remainder of the sample was then placed in a 25-mL amber glass bottle and saved for inorganics analysis. Both sample bottles were stored at 4 °C until analyzed. Between uses the consolidometers were disassembled, washed with soap and water and acetone, and baked for at least 6 h at 250 °C.

Chloride Determinations. Chloride determinations were by ion chromatography. In addition to the regular analyses, approximately 15% of the samples were resubmitted as blind duplicates. Synthetic, spiked, and serially diluted samples were also submitted for quality assurance. Accuracy and precision were excellent on all samples. Extracts from one core (No. 1) were also analyzed for major ions and trace metals and those results will be reported elsewhere.

Organics and Total Organic Carbon (TOC) Determinations. Volatile organic compound determinations were by purge and trap with whole-column cryotrapping (P&T/WCC) on a gas chromatograph/mass spectrometer/data system (GC/MS/DS) as described by Pankow and Rosen (11). Briefly, an aliquot of a sample was first diluted with organic-free water to 5.0 mL in the purge vessel of the P&T unit. The volume of the aliquot varied between 0.030 and 1.0 mL and depended on the expected concentration. The aliquot size was 1.0 mL for pore water samples relatively far away from the waste and was decreased as the interface was approached. After dilution, 10 μ L of a P&T internal standard (IS) solution in methanol was added to the purge vessel. The IS solution contained

7.7 ng/ μ L each of bromochloromethane, 1-chloro-2-bromopropane, and 1,4-dichlorobutane. Each sample was then analyzed by P&T/WCC with a Chrompack CP-Si18 CB, 1- μ m film thickness capillary column (Chrompack, Inc., Raritan, NJ). Quantitation was based on the responses of the characteristic ions of the target analyte compounds and the IS compounds. TOC analyses were performed on one core's (No. 1) pore water samples by oxidation with ultraviolet light and with infrared detection using a Dohrmann DC-80 analyzer (Envirotech, Corp. Mountain View, CA).

Fraction Organic Carbon Content. The fractional organic carbon contents ($0 \leq f_{oc} \leq 1$) were determined for each section of core that contained a significant amount of the target organic compounds. A combustion method was used [Johnson (12); Johnson et al. (13)]. All samples were analyzed at least in duplicate and the results averaged. Steps in the analysis procedure were as follows: (1) samples were dried at 80 °C to constant weight; (2) samples were acidified with 5% SnCl_2 in 3 N HCl to remove inorganic carbon and dried at 80 °C; (3) a known mass of sample was placed in a precleaned copper combustion boat; (4) a batch of 12 samples and standards was placed in a sample carousel; (5) each sample was dropped into a combustion oven at 700 °C; (6) carrier gas (90% $\text{He}/10\% \text{O}_2$) swept the CO_2 evolved from the sample into a methanator where it was quantitatively converted to methane; and (7) methane was detected with a flame-ionization detector.

Two methods of calibration were used: combustion of known volumes of standard solutions of organic compounds (e.g., sugars) and analysis of "standard soils". The standard soils spanned a range of f_{oc} values (0.0011–0.04) and had been analyzed previously by several laboratories [Hassett (14)]. These soils were prepared and analyzed in the same manner as the samples. Excellent agreement between the two types of calibration was obtained.

Batch Sorption Experiments. Sorption experiments were conducted using uncontaminated clay from the site. The clay was dried to constant weight at 80 °C. Quantities of clay of 10 g each were placed in 40-mL vials, to which 25 mL of water containing the compounds of interest was added. The vials were equilibrated for 24 h by tumbling end-over-end at 30 rpm. Equilibrated water concentrations were analyzed by headspace GC, calibrated with standard solutions.

Water Content, Bulk Density, and Total Porosity. The water content, bulk density, and total porosity of sections of core 3 were estimated by drying and weighing portions of the core by the methods of Blake (15) and Vomocil (16). A core section of known mass and volume was placed into a pretared vial and dried at 105 °C for 12 h. The vial and clay were reweighed, and the weight loss was attributed to water loss. The water content of each core was estimated as the mass of water lost divided by the total mass of the water and clay. Bulk density was estimated as the dry weight of the clay divided by its volume. The total porosity was estimated by using the calculated bulk density and an assumed particle density of 2.7 g/ cm^3 .

Results and Discussion

Chloride concentrations for three cores are presented in Table I. The concentrations in the waste from just above the clay interface in each core were taken as the concentrations at the interface. Concentrations normalized to the interface values are also presented. In each of the cores, the Cl^- content was high in the waste and decreased downward into the clay. The maximum distances from the interface that waste-derived Cl^- could be distinguished

Table I. Cl^- Concentration Data

core 1		core 2		core 3		porosity
depth ^a	Cl^- concn, ^b	depth	Cl^- concn	depth	Cl^- concn	
-15.2 to -7.6	1409 (1.1465)	-7.6 to 0.0	2167 (1.0000)	-7.6 to -3.8	2100 (1.1444)	0.52
-7.6 to 0.0	1229 (1.0000)	0.0-7.6	1467 (0.6770)	-3.8 to 0.0	1835 (1.0000)	0.51
0.0-7.6	1084 (0.8820)	7.6-15.2	579 (0.2672)	3.8-7.6	1545 (0.8420)	0.32
7.6-15.2	769 (0.6257)	15.2-22.9	542 (0.2501)	7.6-11.4	1315 (0.7166)	0.36
15.2-22.9	779 (0.6338)	22.9-30.5	715 (0.3299)	11.4-15.2	297 (0.1619)	0.35
22.9-30.5	664 (0.5403)	30.5-38.1	741 (0.3419)	15.2-19.1	128 (0.0698)	0.37
30.5-38.1	459 (0.3735)	38.1-45.7	390 (0.1800)	19.1-22.9	58 (0.0316)	0.38
38.1-45.7	379 (0.3084)	45.7-53.3	252 (0.1163)	22.9-26.7	36 (0.0196)	0.37
45.7-53.3	253 (0.2059)	53.3-61.0	205 (0.0946)	26.7-30.5	40 (0.0218)	0.39
53.3-61.0	167 (0.1359)	61.0-68.6	85 (0.0392)	30.5-38.1	24 (0.0131)	0.39
61.0-68.6	105 (0.0854)	68.6-76.2	32 (0.0148)	38.1-45.7	14 (0.0076)	0.37
68.6-76.2	74 (0.0602)					
76.2-83.8	55 (0.0448)					
background ^c	121 \pm 8	background	213 \pm 31	background	125 \pm 10	

^a Centimeters below the waste/clay interface. ^b Background-subtracted concentrations (in mg/L) and normalized concentrations in parentheses. ^c Background data not background-subtracted.

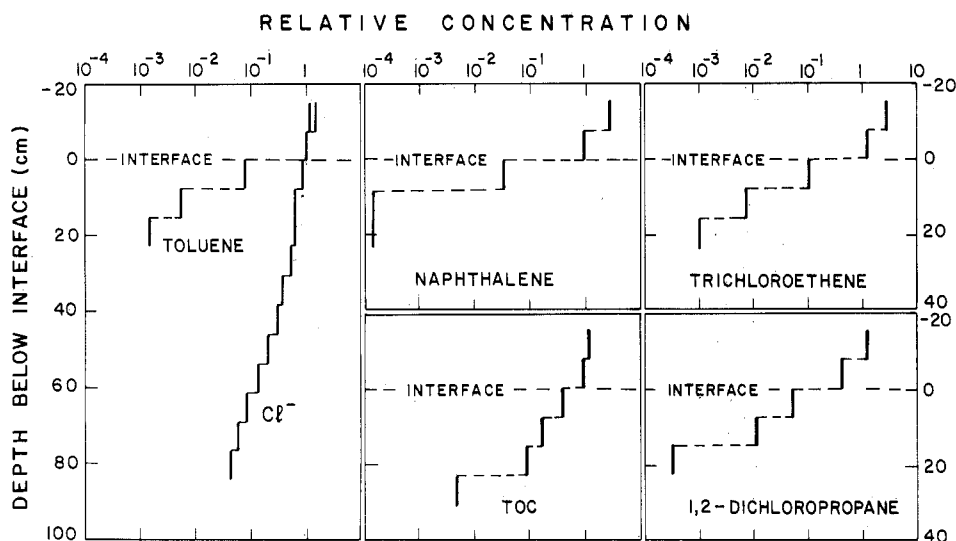


Figure 3. Semi-log plots of chloride and several organics for core 1.

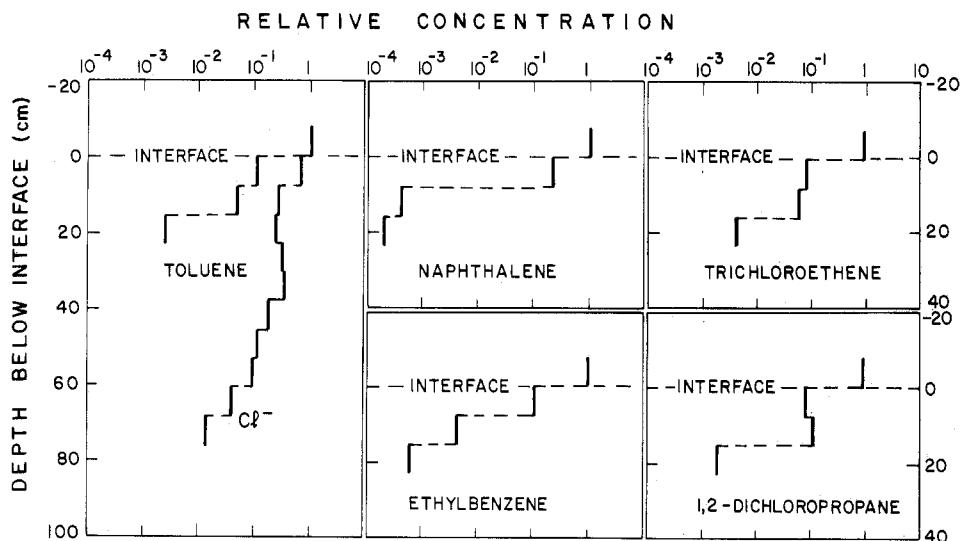


Figure 4. Semi-log plots of chloride and several organics for core 2.

from background were 83 cm in core 1, 75 cm in core 2, and 46 cm in core 3. Background Cl^- values in the clay were approximately a factor of 10 lower than the waste values and were calculated from the average Cl^- concentrations in the core sections at depths greater than the penetration depths of the waste-derived Cl^- . Background Cl^- in the clay originated in the bedrock shale beneath the

clay (4). The profiles with depth for the cores are presented in semi-log format in Figures 3-5.

The Cl^- concentrations for core 1 exhibit a classic diffusion profile (Figure 6). The Cl^- profile from core 2 shows a reversal in concentration gradient in the middle of the profile, but follows the diffusion shape in the lower portion. Core 3 follows the expected diffusion profile in the sections

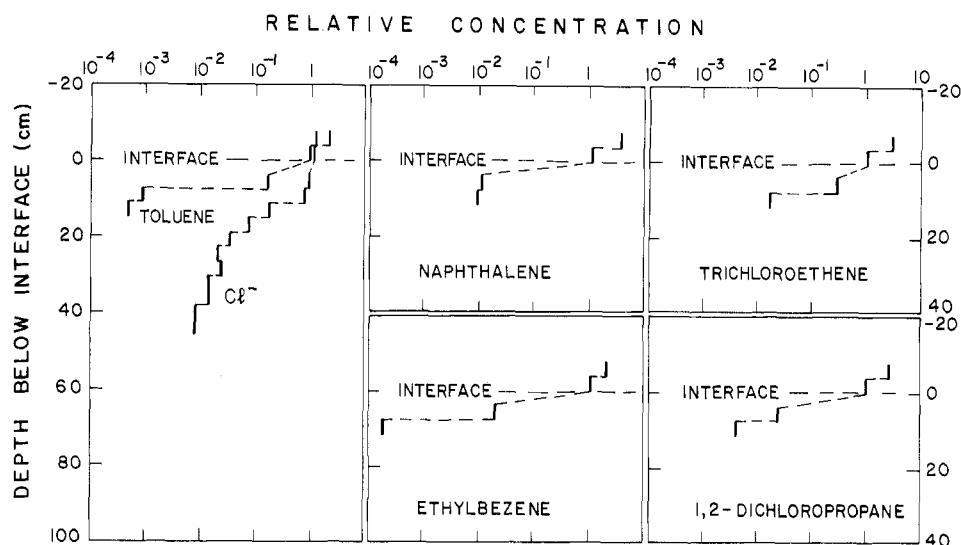


Figure 5. Semi-log plots of chloride and several organics for core 3.

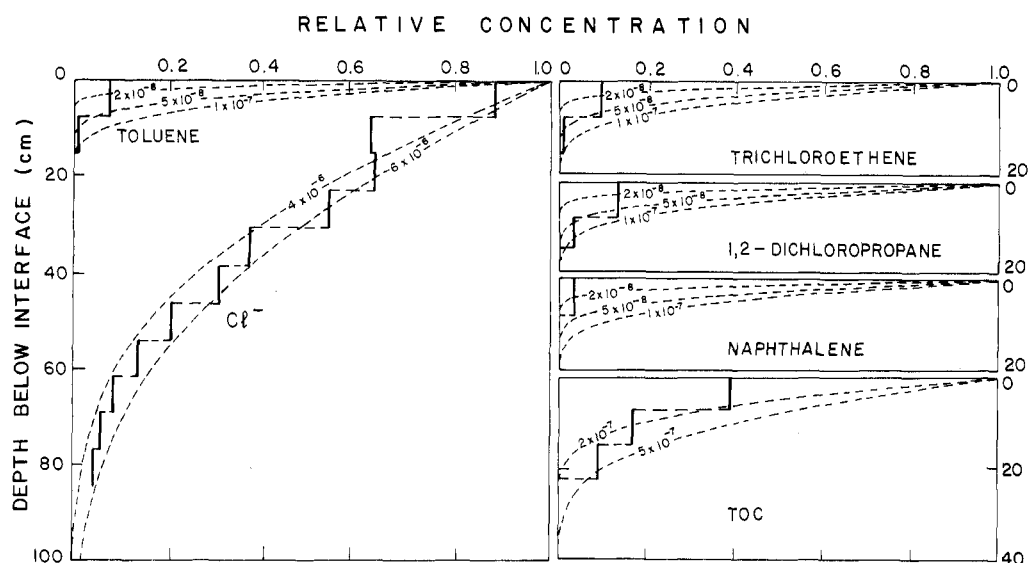


Figure 6. Linear plots of chloride and several organics in core 1, along with simulation data. Time = 1800 days. Diffusion coefficient values are indicated (cm^2/s).

just below the interface, but then drops sharply to lower values. The reversal in core 2 and the differences in depth of penetration of Cl^- in the three cores suggest that the Cl^- concentrations in the waste at the interface may have varied in time. However, even when temporal Cl^- variations in the waste at the bottom of the pit are considered possible, the reversal in core 2 is difficult to explain because its position in the core would require a change in the concentration at the waste/clay interface more than 1 year after the landfill was capped.

The shallow Cl^- profile observed in core 3 may have resulted from a depth-dependent effective diffusion coefficient due to heterogeneities in the clay. To evaluate this hypothesis, the porosities of the core 3 sections were estimated from the water content data (Table I). They are similar to the values (35–40%) reported for the clay by Hydrology Consultants Limited (17). The porosity of the section nearest the interface (i.e., the 0.0–3.8-cm section) was somewhat lower than those farther into the clay. In fact, no pore water was recoverable by compression from this section. This may have been the result of compaction or dehydration during the excavation of the landfill. The restriction to movement caused by the lower porosity of the clay nearest the interface in core 3 may account in some degree for the fact that Cl^- migrated a smaller dis-

tance in this core. Comparisons with the other cores in this context cannot be made because the water contents of the other cores were not determined.

Organics analysis data for the three cores are given in Table II. As with the Cl^- data, the core concentrations were also normalized to the concentrations in the waste just above the interface. Normalized data for the organics are plotted versus depth in Figures 3–6. The organic compounds were detected at a maximum distance of 15 cm below the interface. In the waste at the interface, the dominant organic compounds, such as benzene, toluene, and ethylbenzene, were present at concentrations of many hundreds to several thousand micrograms per liter. The limits of detection for these compounds in the clay were on the order of $1 \mu\text{g}/\text{L}$ or less. The fact that they were not found (even at very low concentrations) at distances greater than ~ 15 cm indicates that there was a relatively abrupt migration front. Comparison of the maximum migration distance of Cl^- (83 cm) with the maximum distances for the organic compounds indicates that the organics were retarded relative to Cl^- . As discussed below, batch sorption and f_{∞} values indicate that sorption played an important role in causing this retardation.

The profile for TOC in the core 1 pore water extends significantly deeper than any of the organic compounds

Table II. Organics Concentration Data [Absolute ($\mu\text{g/L}$) and Normalized (in Parentheses)]

depth interval	benzene	tri-chloroethene	toluene	ethylbenzene	naphthalene	1,2-dichloropropane	f_{oc} g/g of soil	TOC, mg/L
(a) Core 1								
-15.2 to -7.6	7920 (2.3432)	844.0 (2.3123)	9520 (1.5208)	3320.0 (1.5660)	2352.0 (3.0231)	821.0 (2.7276)	NA ^c	1112.0 (1.2008)
-7.6 to 0.0	3380 (1.0000)	365.0 (1.0000)	6260 (1.0000)	2120.0 (1.0000)	778.0 (1.0000)	301.0 (1.0000)	NA	926.0 (1.0000)
0.0-7.6	283 (0.0837)	32.7 (0.0896)	470 (0.0751)	72.9 (0.0344)	23.9 (0.0307)	39.2 (0.1302)	0.010	353.0 (0.3812)
7.6-15.2	167 (0.0494)	2.5 (0.0068)	37 (0.0052)	1.3 (0.0006)	0.1 (0.0001) ^b	9.0 (0.0299)	0.013	149.0 (0.1609)
15.2-22.8	4 (0.0012) ^b	0.4 (0.0011) ^b	9 (0.0014) ^b	0.8 (0.0004) ^b	0.1 (0.0001)	0.3 (0.0010) ^b	0.012	79.0 (0.0853)
22.8-30.5	4 (0.0012)	0.4 (0.0011)	9 (0.0014)	0.8 (0.0004)	0.1 (0.0001)	0.3 (0.0010)	0.013	4.0 (0.0043)
(b) Core 2								
-7.6 to 0.0	801 (1.0000)	83.0 (1.0000)	3628 (1.0000)	1503.0 (1.0000)	516.0 (1.0000)	120.0 (1.0000)	NA	
0.0-7.6	63 (0.0787)	7.3 (0.0880)	393 (0.1083)	168.0 (0.1118)	109.0 (0.2112)	11.5 (0.0958)	0.010	
7.6-15.2	300 (0.3745)	5.8 (0.0699)	175 (0.0482)	6.6 (0.0044)	0.2 (0.0004)	16.5 (0.1375)	0.013	
15.2-22.8	4 (0.0054) ^b	0.4 (0.0048) ^b	9 (0.0025) ^b	0.8 (0.0006) ^b	0.1 (0.0002) ^b	0.3 (0.0025) ^b	0.009	
(c) Core 3								
-7.6 to -3.8	620 (3.7126)	67.0 (2.9386)	2230.0 (1.8740)	755.0 (1.9162)	76.0 (3.2759)	198.0 (2.6757)	NA	
-3.8 to 0.0	167 (1.0000)	22.8 (1.0000)	1190.0 (1.0000)	394.0 (1.0000)	23.2 (1.0000)	74.0 (1.0000)	NA	
3.8-7.6	122 (0.7305)	6.5 (0.2851)	166.0 (0.1395)	7.6 (0.0193)	0.2 (0.0086) ^b	1.9 (0.025)	0.007	
7.6-11.4	36 (0.2156)	0.4 (0.0175) ^b	0.9 (0.0008)	0.1 (0.0002) ^b	0.2 (0.0086)	0.3 (0.0041) ^b	0.010	
11.4-15.2	3 (0.0192) ^b	0.4 (0.0175)	0.5 (0.0004) ^b	0.1 (0.0002)	0.2 (0.0086)	0.3 (0.0041)	0.013	

^a Distance below the interface (cm). ^b Minimum depth at which the concentration was at or below the minimum detectable level. ^c Not analyzed.

quantitated by the P&T analysis procedure (Figure 6). It is interesting to note in this context that the sum of the concentrations of the compounds in Table II represents less than 1% of the observed TOC concentrations. The bulk of the TOC was probably made up of water-miscible solvent compounds. Indeed, although they were not quantitated, acetone, methyl ethyl ketone, and methyl isobutyl ketone were identified in the GC/MS analyses; their presence in the waste at the site has been confirmed by Nesbitt (18). These compounds sorb minimally to the soil organic carbon and would, therefore, be expected to migrate 3–20 times faster than the compounds in Table II.

The f_{oc} determinations indicate that the carbon content of the clay is 0.007–0.013 by weight as carbon, with an average of 0.011 (Table II). The average f_{oc} may be combined with the literature values for the compound-dependent organic carbon/water partition coefficient (K_{oc} , Table III) to calculate predicted estimates of the clay/water partition coefficients, i.e.,

$$K_{d, \text{calcd}} = K_{oc} f_{oc} \quad (1)$$

However, as presented in Table III, at equilibrium aqueous concentrations of ~ 1 mg/L, the actual measured partition coefficient (K_d) values of trichloroethene, benzene, toluene, and ethylbenzene were found to be significantly higher than the corresponding $K_{d, \text{calcd}}$ values. These results are consistent with those of Myrand et al. (6). Those workers found even stronger sorption at lower aqueous concentrations, although at concentrations significantly higher than 1 mg/L, their measured K_d values begin to approach the $K_{d, \text{calcd}}$ values. The "excess sorption" at low concentration may be due to interactions between the organics and the clay minerals (19). This possibility, and its effect on diffusion, are currently being investigated and will be reported on elsewhere.

Modeling

The hydraulic conductivity of the clay has been measured by Hydrology Consultants Limited (17) using piezometer tests in the field and permeameter tests of core samples in the laboratory. Values of K were in the range of 10^{-8} – 10^{-9} cm/s, with a geometric mean value of 6×10^{-9} cm/s. The water table in the waste was found to be close

to the level of the original ground surface, but was below the cap. The average level of the potentiometric surface in the bedrock just below the clay was ~ 7 m below ground surface. A 7-m average difference in hydraulic head therefore acted across the 25-m thickness of clay beneath the pit. By use of Darcy's law with a porosity (n) = 0.37, a downward velocity of 0.15 cm/year is predicted. Even if the downward hydraulic gradient across the clay existed from the date of burial of the wastes (~ 5 years prior to the acquisition of the cores), and if the only process causing downward migration was advection, then the Cl^- penetration distance would have been only 0.75 cm. The observed penetration distances for Cl^- in the three cores (83, 75, and 46 cm) indicate that this advection distance is insignificant in comparison to the expected and observed diffusion distances. It is concluded, therefore, that advective flow does not provide a major influence on Cl^- migration at the site. Desaulniers et al. (4) reached a similar conclusion in their investigation of bedrock-derived Cl^- and isotopes in the clay in the Sarnia area. Since retardation due to sorption affects advective and diffusive transport in the same way, the same conclusion may also be reached for the organics found at the Tricil site.

The minor role of advection and the relatively homogeneous nature of the clay at the Tricil site make it appropriate to simulate the downward migration of contaminants at the site by means of diffusion models based on Fick's second law:

$$\partial C / \partial t = D_{e,c} (\partial^2 C / \partial z^2) \quad (2)$$

where z is the vertical direction (measured positively downwards) and $D_{e,c}$ is the effective solute diffusion coefficient in the clay.

Materials diffusing into the clay must first diffuse through the waste to the interface. Assuming that the contaminant concentrations in the waste are initially uniform with depth, and that the initial concentrations of the contaminants in the clay are zero, a concentration gradient will form in the waste near the interface. However, as discussed by Crank (20), the concentration at the interface will stabilize at a value determined by the initial concentration in the waste and the values of the diffusion coefficients in the waste and clay. Furthermore, if $D_{e,w} > D_{e,c}$, when normalized to the concentration at the interface,

Table III. Sorption and Diffusion Coefficient Values at 10 °C

compound	free-soln diff coeff D , cm ² /s	org C partitn const K_{oc}	calcd partitn coeff ^f $K_{d,calcd}$	org C retardatn factor ^g R_{oc}	calcd diff coeff ^h D'_{calcd} , cm ² /s	obsd partitn coeff K_d	retardation factor ⁱ R	calcd diff coeff ^h D'_{calcd} , cm ² /s	obsd diff coeff ^f $D'_{e,c}$, cm ² /s
chloride	2×10^{-5a}	0.0	0.0	1.0	5×10^{-6}	0.0	1.0	5×10^{-6}	5×10^{-6}
benzene	7×10^{-6b}	65 ^d	0.65	3.9	4×10^{-7}	10	44	4×10^{-8}	2×10^{-7}
trichloroethene	7×10^{-6c}	126 ^d	1.26	6.5	3×10^{-7}	15	65	3×10^{-8}	5×10^{-8}
toluene	6×10^{-6b}	300 ^d	3.00	14.2	1×10^{-7}	19	82	2×10^{-8}	5×10^{-8}
1,2-dichloropropane	8×10^{-6c}	48 ^d	0.48	3.1	6×10^{-7}	ND ^m	ND	ND	1×10^{-7}
ethylbenzene	6×10^{-6b}	870 ^d	8.70	39	4×10^{-8}	62	269	6×10^{-9}	2×10^{-8}
naphthalene	6×10^{-6c}	940 ^d	9.40	42	4×10^{-8}	ND	ND	ND	2×10^{-8}

^aFrom Li and Gregory (22). ^bFrom Binoli and Witherspoon (23). ^cCalculated by using eq 5 and $D = 7 \times 10^{-6}$. ^dFrom Mabey et al. (26). ^eBy use of $\log K_{oc} = \log K_{ow} - 0.21$ [Karickhoff (27)] and $\log K_{ow} = 3.15$. ^f $K_{d,calcd} = f_{oc}K_{oc} = 0.01 K_{oc}$. ^g $R_{oc} = 1 + (1.6K_{oc}/n)$. ^h $D'_{calcd} = D \times 0.25/R_{oc}$. ⁱFrom the batch sorption experiments at $\sim 1000 \mu\text{g/L}$. ^j $R = 1 + (1.6K_d)/n$. ^k $D'_{calcd} = D \times 0.25/R$. ^lMeasured in core 1. ^mND, not determined.

the concentration profiles in the clay will depend only on $D_{e,c}$ and will be independent of $D_{e,w}$. Because the waste is much less compact and cohesive than the clay, $D_{e,w}$ is almost certainly greater than $D_{e,c}$. If the concentrations at the bottom of the clay are near zero, then the solution to eq 2 is (20)

$$\frac{C}{C_0} = 1 - \frac{z}{L} - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left(\frac{n\pi z}{L} \right) \exp \left(\frac{-D_{e,c} n^2 \pi^2 t}{L^2} \right) \quad (3)$$

where C_0 is the concentration at the interface, and L is the thickness of the clay.

The observed profile for Cl^- in core 1 and simulated diffusion profiles based on eq 3 are shown in Figure 6. The solid line represents the measured concentrations in the core sections. The dashed lines are model profiles using a burial time of 5 years (1825 days) and $D_{e,c}$ values as indicated. There is a close match between the observed Cl^- concentrations and the simulated profile when $D_{e,c}$ takes on values in the range $(4 - 6) \times 10^{-6} \text{ cm}^2/\text{s}$. This range is quite similar to values observed by Desaulniers (3) and Crooks and Quigley (2). For core 2, $D_{e,c} = 4 \times 10^{-6} \text{ cm}^2/\text{s}$ produces a good match for the lower portions of the observed Cl^- profile. In the portion of core 2 closest to the interface, however, the Cl^- concentrations are much lower than simulated, and the profile is fit best with $D_{e,c} = 8 \times 10^{-7} \text{ cm}^2/\text{s}$. For core 3, the penetration distance for Cl^- is smaller than for the other two cores, and the profile again cannot be fitted closely by a single simulation. The portion of the profile closest to the interface is best fit by $D_{e,c} = 2 \times 10^{-6} \text{ cm}^2/\text{s}$. The lower portion of the core is best simulated by $D_{e,c} = 3 \times 10^{-7} \text{ cm}^2/\text{s}$. The latter value is much smaller than those determined in the laboratory studies. This suggests that the initial concentration distribution of Cl^- in the waste may have changed with time. The possible effects of a nonconstant interface concentration on the diffusion profiles were evaluated. An attempt was made to duplicate the observed profiles in cores 2 and 3 by using a constant $D_{e,c} = 4 \times 10^{-6} \text{ cm}^2/\text{s}$, but varying the concentration at the interface in time. This was not successful, and the reasons for the variations from ideal diffusion behavior in cores 2 and 3 remain unclear.

The value of $D_{e,c}$ will be less than the free-solution diffusion coefficient (D) at the corresponding temperature due to the tortuous path that the diffusing species must follow through the porous medium. In this case,

$$D_{e,c} = D\tau \quad (4)$$

where τ is a factor ($0.0 < \tau < 1.0$) that accounts for tortuosity effects (21). Values of τ for the clay can be estimated based on best fit $D_{e,c}$ values for Cl^- and the literature value of D at the in situ clay temperature (10 °C). For $D = 1.5 \times 10^{-5} \text{ cm}^2/\text{s}$ (22), and $D_{e,c} = 4 - 6 \times 10^{-6} \text{ cm}^2/\text{s}$, τ is in the range 0.20–0.33.

The diffusion model can also be used to simulate profiles of the organic compounds in the clay (Figure 6). In this case, in addition to tortuosity, the effects of molecular size and sorption must be taken into account. The effect of molecular size on the diffusion coefficient can be estimated for the Table II compounds by using literature data. For example, D values have been measured for a variety of organics in dilute aqueous solution by Bonoli and Witherspoon (23). They suggest that values of D in the range $(5 - 9) \times 10^{-6} \text{ cm}^2/\text{s}$ are appropriate for benzene, toluene, and several cycloalkanes at 25 °C. D values for other compounds can be extrapolated from their data by using an approximation equation for the diffusion coefficient that takes into account the effect of molecular size (24):

$$\frac{D_1}{D_2} = \left(\frac{MW_2 \rho_1}{MW_1 \rho_2} \right)^{0.6} \quad (5)$$

where D_1 and D_2 are the free-solution diffusion coefficients of a pair of organic compounds of interest at the temperature of interest, MW_1 and MW_2 are their molecular weights, and ρ_1 and ρ_2 are the densities of the compounds at their boiling points. The latter are generally not known. Substitution of densities at a standard temperature generally provides relative diffusion coefficients within 10% of experimental values.

Diffusion coefficients (observed and calculated) for the organics are found in Table III. The values observed for the organics in the field cores are much smaller than would be predicted from the product of D and tortuosity. The primary reason for the differences in diffusion coefficient values of Cl^- and the organics is undoubtedly the sorption of the organics to the clay.

The effect of sorption on diffusion profiles can be modeled by substituting $D'_{e,c} = D_{e,c}/R$ for $D_{e,c}$ in eq 2 and 3 where R is the retardation factor

$$R = 1 + \rho_b K_d / n \quad (6)$$

and ρ_b is the clay bulk density (g/cm^3) and n is the total clay porosity. K_d may be determined in laboratory tests or estimated based on eq 1. Both approaches have been employed here, and the results are tabulated in Table III. The combination of sorption and molecular weight effects leads to estimated total reduction factors in diffusion coefficient values relative to Cl^- of from 1/5 to 1/50.

Future Downward Movement of the Contaminants at the Site

Equation 3 was used to predict the future diffusion of the contaminants at the Tricil site. For Cl^- , a $D_{e,c}$ of $4 \times 10^{-6} \text{ cm}^2/\text{s}$ was used to simulate migration of Cl^- for periods of up to 10000 years through the 25-m-thick deposit of clay beneath the landfill (Figure 7a). These simulations suggest that waste-derived Cl^- will begin to arrive in the bedrock at detectable levels ($C/C_0 = 0.01$) in ~3000 years. A steady-state flux of Cl^- to the aquifer will be achieved in ~10000 years.

These predictions, and those that follow, assume that the contaminant concentrations beneath the clay are maintained at near-zero values as the result of groundwater flow. They also assume that the mass contaminants in the waste is not significantly depleted during the simulation. Because the clay is 25-m thick while the waste is 15-m thick, and because there are no solid inorganic chlorides in the waste, it is expected that depletion will in fact affect the development of the Cl^- profiles in the clay after a few thousand years. This will result in shallower than predicted profiles. Nevertheless, the model will provide order of magnitude estimates of breakthrough times.

Predicted diffusion profiles for organic compounds using $D'_{e,c}$ values of 2×10^{-7} and $2 \times 10^{-8} \text{ cm}^2/\text{s}$ are given in Figure 7a. The largest value represents the rapidly migrating organics (e.g., benzene) in core 1. The smaller value represents the more retarded organic compounds identified in the waste. Breakthrough of organics should be defined on the basis of a lower C/C_0 than for Cl^- because the organics are often of concern at very low concentrations. If breakthrough is defined as the arrival of $C/C_0 = 0.001$, periods of 5000–15000 years are required for breakthrough to occur. For compounds that resist degradation, the subsequent attainment of steady-state diffusion profiles will only be reached in many tens of thousands of years. In addition to ensuring a long breakthrough time, the thickness of the deposit results in a concentration gradient

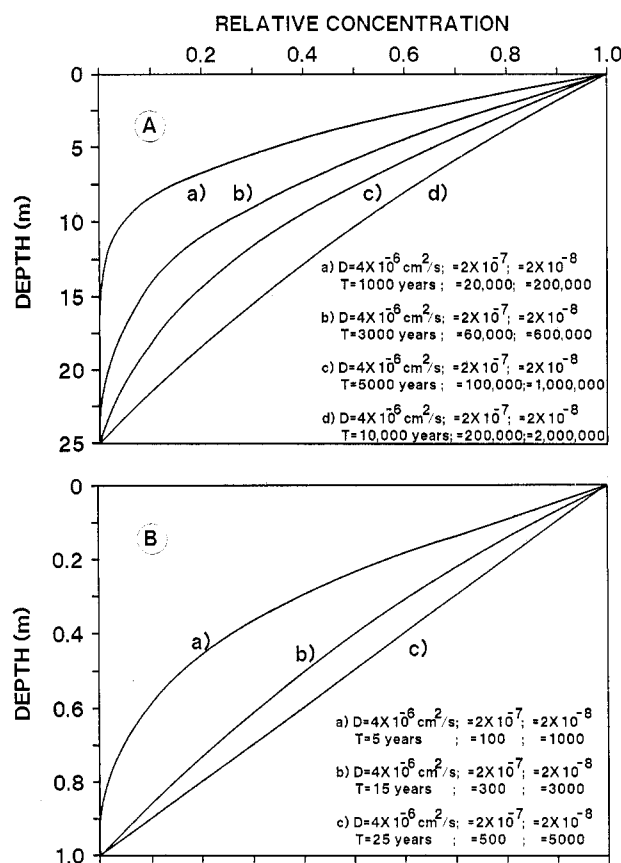


Figure 7. Simulations for (A) 25-m- and (B) 1-m-thick clay liners using the indicated diffusion coefficients (cm^2/s) and times (years).

within the clay that is comparatively shallow. This means that, even after breakthrough occurs, the diffusive fluxes out of the clay will remain small.

Implications for Hazardous Waste Disposal at Sites with Clay Liners

Hazardous waste landfills are commonly lined with compacted clay of ~1-m thickness as a means of isolating the waste from the underlying hydrogeologic domain. Although the clay deposit beneath the Tricil site is exceptionally thick in a waste disposal context, the field results obtained there can be used to develop predictions regarding diffusive contaminant migration through comparatively thin man-made clay liners.

Figure 7b, which was produced by using the diffusion model described above and assuming a 1-m-thick liner, indicates that Cl^- will reach a breakthrough concentration of $C/C_0 = 0.01$ in approximately 5 years ($D_{e,c} = 4 \times 10^{-6} \text{ cm}^2/\text{s}$). The diffusive mass flux out of the liner will attain 10% of the eventual steady-state value in less than 10 years and will reach steady state in approximately 40 years. Organic compounds such as benzene will be retarded relative to chloride. However, it is again appropriate to calculate breakthrough times for such organics based on C/C_0 values of 0.001. When the effective diffusion coefficient for benzene obtained in this study ($2 \times 10^{-7} \text{ cm}^2/\text{s}$ at 10°C) is used to calculate a breakthrough time for a 1-m-thick liner, 70 years is obtained. There are many other organic compounds as mobile as benzene, and some that are more mobile (e.g., acetone and dichloromethane). Thus, diffusion-controlled breakthrough of the marginally retarded organic compounds may occur in a few decades or less, and steady-state conditions will be approached in a few hundred years. For a 1-m-thick liner, the concentrations in the waste may be only slightly depleted, and

steady-state fluxes will remain substantial.

To obtain an indication of the rates at which contaminants may diffuse through a liner at steady state, consider a 1-m-thick liner with an area of 10^4 m^2 . Once steady state has been achieved, flux out of the liner will be described by Fick's first law:

$$\text{flux} = -nD_{e,c} \frac{dc}{dz} \quad (7)$$

$D_{e,c}$ is used in eq 7 rather than $D'_{e,c}$ because at steady state there is no longer any net retardation. If the contaminant has a concentration of 1 g/L in the waste at the top of the liner, $D_{e,c} = 1.5 \times 10^{-6} \text{ cm}^2/\text{s}$, and $n = 0.4$, and if the groundwater flow maintains the concentration beneath the liner at a small fraction (e.g., 0.01) of the concentration in the waste, then the steady-state mass transport rate through the liner will be approximately 19 kg/year ($1.9 \text{ g m}^{-2} \text{ year}^{-1}$). For some compounds, an annual release of this magnitude would cause a major adverse impact on groundwater quality. For example, 19 kg of benzene has the potential to contaminate 3.8 billion liters of water at the EPA drinking water limit of 0.005 mg/L.

Recent designs for liners at hazardous waste disposal sites specify that double liners be used and that a sand or gravel drainage blanket be placed between the two liners. The drainage blanket drains to sumps or other leachate extraction facilities and serves as an interception zone for free leachate that flows through the upper liner. The primary objective behind this design is to minimize advection through the lower liner. If the liners are constructed of a porous material such as clay, simple diffusion will cause contaminants to migrate through the upper liner into the drainage blanket. If the sand or gravel is not dry, downward diffusive migration will continue in the drainage blanket and into the bottom liner. Passage of contaminants through the bottom clay liner by diffusion will be unavoidable and may occur even when the drainage blanket yields no leachate to the collection system. In a diffusion context, this situation is nearly equivalent to the case of a single-liner system, albeit with a greater overall thickness. Thus, even when a drainage blanket is performing its designed function properly, one will not be able to assume that contaminants are not migrating through the bottom liner. The point here is not to argue that properly constructed double liners with drainage blankets cannot provide a useful degree of additional environmental protection, but rather to emphasize that simple diffusion is a mechanism of contaminant movement that cannot be ignored.

In the foregoing consideration of the implications of diffusion on contaminant migration through clay liners, diffusion coefficient values similar to those found for the cores from this study were used. Many clay liners at waste disposal sites are formed of compacted local clay, or of local unconsolidated geologic materials mixed with bentonitic clay. The compaction of neither local clay nor bentonite mixtures are expected to produce a material with Cl^- diffusion coefficients more than half an order of magnitude lower than the Tricil clay. In addition, many natural clays and bentonite mixtures contain less solid-phase organic matter and may retard organic compounds less than the Tricil clay. It is expected, therefore, that simple diffusion through clay barriers will be of general relevance in many clay liner applications.

Above of the breakthrough times and the fluxes discussed above are based on the assumption that advection through the liner is insignificant. In many situations, however, hydraulic gradient across liners are large (i.e., >1). In such cases, the average linear velocities across the liners may

in fact provide significant advective transport. For conditions in which the average linear velocity is greater than a few centimeters per year, breakthrough times and mass transfer rates should be calculated by use of models that include both advection and diffusion, such as those described by Desaulniers et al. (3), Rowe and Booker (25), and Gray and Weber (8). The diffusion analysis presented above thus represents a best case analysis in that it provides maximum breakthrough times and minimum fluxes.

Summary

The field data presented here demonstrate that simple Fickian diffusion can be an important mechanism for transport of contaminants in low-permeability systems. In the first core sample obtained at the Tricil site, Cl^- was found to have traveled nearly 1 m in the 5-year period since the wastes were buried. The concentration profile matched the results of the diffusion model using a laboratory-measured diffusion coefficient very closely. For the second and third cores, the matches between field data and the model were good for some parts of the cores, while the model overestimated the concentrations for other parts. The influence of advection was found to be negligible and diffusion modeling based on laboratory-determined coefficients was found to provide maximum chloride migration rates. The fact that the organic compounds migrated a distance of less than 20 cm during 5 years was consistent with model results using effective diffusion coefficients that were adjusted for the effects of molecular size and adsorption.

The clay deposit at the study site is thick. Therefore, more than 1000 years will pass before contaminants from the waste will arrive at the aquifer beneath it. When the diffusion model was applied to a 1-m clay liner, however, breakthrough times for many compounds were found to be less than 10 years, and steady-state diffusion fluxes were found to be large. This study suggests that clay liners possessing low permeability will not prevent nonsorbing contaminants from rapidly entering the hydrogeologic domains beneath the liners. Adsorption of organic contaminants may extend the time before breakthrough, but for some of the common priority pollutants, the breakthrough times will still be a few decades or less.

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Registry No. Benzene, 71-43-2; trichloroethene, 79-01-6; toluene, 108-88-3; ethylbenzene, 100-41-4; naphthalene, 91-20-3; 1,2-dichloropropane, 78-87-5.

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Aluminum Complexation by Catechol as Determined by Ultraviolet Spectrophotometry

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■ Methods of ultraviolet (UV) spectrophotometry were used to determine the stoichiometry and association constant for the Al-catechol complex from pH 3.8 to 4.6. Job's method of continuous variation indicated the Al-catechol complex had a 1:1 stoichiometry in the pH range studied. Aluminum titrations of catechol and pH titrations of catechol plus Al resulted in a shift in the UV spectra due to the formation of an Al-catechol complex absorbing UV radiation uniquely different than that of free catechol. General equations were developed for the determination of association constants assuming an organic and Al-organic complex absorb UV radiation. Aluminum titrations with constant catechol concentration yielded a $\log K_{0.1}^c$ of 16.22 for a 1:1 Al-catechol complex. Calculated absorbance as a function of pH agreed well with experimental pH titrations of solutions containing catechol plus Al. The fact that Al can be complexed by catechol at low pH indicates the *o*-hydroxy group provides a potential source for Al complexation in soil and surface waters.

Introduction

With the advent of increased Al mobility in the environment due to acid precipitation, interest in Al chemistry of soils and surface waters has developed. Adverse effects of soluble Al include potential toxicity to fish (1), trees (2), and agricultural crops (3). The toxicity of Al, however, is

not related to total Al concentration. Aluminum can form complexes with organic compounds, reducing the activity and subsequent toxicity of Al^{3+} in solution (1, 4, 5). Equilibrium constants for Al complexation is therefore important for predicting levels of available Al^{3+} in the environment. The *o*-hydroxy groups of polyphenols are of particular interest because of the production of polyphenols during the biodegradation of lignin (6).

Ultraviolet (UV) spectrophotometry can provide valuable information on the composition and stability constant of a metal-ligand complex. Although the UV method for determining composition and association constants is not valid for mixed-ligand systems and humic substances with multifunctional groups (7, 8), the method can be used to define a single metal-ligand complex (9-11). The determination of composition and association constants is based on the fact that an ultraviolet or visible spectrum of the metal or ligand alone is different from the spectrum of the complex. Association constants of Al^{3+} complexes with Tiron, 2,3-pyridinediol, 5-sulfosalicylic acid, and salicylic acid have been determined by using information provided by UV spectral shifts (12-14). In flavonoid chemistry, bathochromic shifts upon $AlCl_3$ addition are used to indicate the presence of *o*-hydroxy or *o*-hydroxycarbonyl chelating groups (15).

Objectives of the present study were to develop equations for the determination of association constants of Al-ligand complexes by UV spectrophotometry and to use the equations in conjunction with Job's method of continuous variation to determine the composition and asso-

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