Effect of multiple contaminant migration on diffusion and adsorption of some domestic waste contaminants in a natural clayey soil

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This paper describes laboratory model tests involving the placement of domestic landfill leachate on top of a layer of saturated undisturbed clayey soil and allowing chemical constituents to migrate into the soil by diffusion only. During the testing period (15 days), samples from the overlying leachate were regularly collected and analyzed for the chemical constituents of interest (i.e., Cl^-, Na^+, K^+, Mg^{++}, and Ca^{++}). At the end of the test, the soil layer was sectioned to determine the pore-water and adsorbed concentration variations with depth for each species. Mathematical model POLLUTE was then used to back-figure both the diffusion coefficient (D) and the adsorption term (ρK). The measured diffusion coefficients at a temperature of 10°C were determined to be $D_{Cl^-} = 7.5 \times 10^{-6}$ cm²/s, $D_{Na^+} = 4.6 \times 10^{-6}$ cm²/s, and $D_{K^+} = 6.0 \times 10^{-6}$ cm²/s. The corresponding adsorption terms were $\rho K_{Cl^-} = 0$, $\rho K_{Na^+} = 0.25$, and $\rho K_{K^+} = 1.7$.

Ca^{++} and Mg^{++}, originally predominant on the clay exchange sites, were heavily desorbed to accommodate the adsorption of migrating Na^+, K^+, and possibly NH_4^+, causing hardness halo effects that the model could not fit. This behaviour corresponds to that commonly observed at domestic waste sites in southern Ontario.

The importance of multiple contaminant migration on diffusion rates was assessed by comparing the leachate models with similar models using a variety of single salts dissolved in distilled water as the source solutions. For the single-salt models, all species considered, including Ca^{++} and Mg^{++}, behaved in a way that could be described by conventional Fickian theory. A comparison of the diffusion and adsorption parameters obtained from the two types of models indicated that for both Na^+ and K^+, the measured D and ρK from the leachate models were 20 and 60% lower, respectively, than the values obtained from the single-salt models. For Cl^-, the diffusion coefficient obtained from the leachate models was 25% higher than that obtained from the single-salt models.

For the Sarnia grey soil used, both D and ρK are significantly influenced by the types and amounts of co-diffusing species present in the initial source solutions. Laboratory tests conducted to determine diffusion parameters for use in design should be run with soils and source solutions chemically identical to those expected in the field.

Key words: domestic waste leachate, multiple contaminant migration, clayey soil, diffusion, adsorption, laboratory study.

Cet article décrit des essais en laboratoire impliquant le dépôt d'un lixiviant d'enfouissement sanitaire sur une couche de sol argileux saturé non remanié et permettant la migration des constituants chimiques à travers le sol par diffusion seulement. Durant la période d'essais (15 jours), des échantillons du lixiviant ont été prélevés régulièrement et analysés pour déterminer les constituants chimiques d'intérêt (c.-à-d., Cl^-, Na^+, K^+, Mg^{++} et Ca^{++}). À la fin de l'essai, la couche de sol a été sectionnée pour déterminer les variations de l'eau interstitielle et de la concentration adsorbée en fonction de la profondeur de chaque élément. Le modèle mathématique POLLUTE a alors été utilisé pour déterminer à rebours le coefficient de diffusion (D) et le terme d'adsorption (ρK). Les coefficients de diffusion mesurés à la température de 10°C ont été établis à $D_{Cl^-} = 7,5 \times 10^{-6}$ cm²/s, $D_{Na^+} = 4,6 \times 10^{-6}$ cm²/s et $D_{K^+} = 6,0 \times 10^{-6}$ cm²/s. Les termes correspondants d'adsorption étaient $\rho K_{cl^-} = 0$, $\rho K_{Na^+} = 0,25$ et $\rho K_{k^+} = 1,7$.

Ca^{++} et Mg^{++}, qui sont prédominants originellement dans les cations échangeables de l'argile, ont été fortement désadsorbés pour permettre l'adsorption des cations en migration Na^+, K^+ et possiblement NH_4^+ produisant des effets de halo de dureté que le modèle ne pouvait pas représenter. Ce comportement correspond à celui qui est communément observé dans les sites d'enfouissement sanitaires du sud de l'Ontario.

L'importance de migration de contaminants multiples sur la vitesse de diffusion a été évaluée en comparant les modèles de lixiviants avec des modèles similaires qui utilisent une variété de mélanges d'eau distillée avec un seul sel comme solution à la source. Pour les modèles de sel unique, tous les éléments considérés, incluant Ca^{++} et Mg^{++}, ont eu un comportement qui pourrait être décrit par la théorie conventionnelle Fickienne. Une comparaison des paramètres de diffusion et d'adsorption obtenus de ces deux types de modèles indique que pour les deux cations Na^+ et K^+, les valeurs de D et ρK mesurées au moyen des modèles de lixiviants étaient respectivement 20 et 60% plus faibles que celles obtenues en partant des modèles de sel unique, alors que pour Cl^- le coefficient de diffusion obtenu des modèles de lixiviants était de 25% plus élevé que celui donné par les modèles de sel unique. Pour le sol gris de Sarnia utilisé dans les essais, les valeurs de D et ρK sont influencés de façon significative par les types et les quantités d'éléments co-diffusants présents dans les solutions initiales. Les essais de laboratoire réalisés pour déterminer les paramètres de diffusion en vue de leur utilisation dans le calcul devrait être fait sur des sols et avec des solutions sources qui sont chimiquement identiques à ceux que l'on peut s'attendre de trouver sur le site à l'étude.

Mots clés : lixiviant sanitaire, migration de contaminants multiples, sol argileux, diffusion, adsorption, étude en laboratoire.

[Traduit par la revue]

Introduction

Clay-rich geological materials are often used as barriers to the migration of potential contaminants from waste disposal sites. Since it is impossible to practically provide complete containment of leachate derived from waste, the design of a suitable clayey barrier (either as a primary barrier for municipal waste sites or as a backup barrier for hazardous waste) requires an estimation of the potential rate of contaminant transport and the impact on the surrounding groundwater system. However, prior to any quantification of contaminant transport, one must first establish values for the controlling parameters.

For situations where the clayey barrier has a very low hydraulic conductivity and (or) negligible hydraulic gradient, contaminant transport will be very slow and controlled by diffusion through the clay pore fluid. For these conditions, the controlling parameters become the diffusion coefficient (D) and the adsorption term (ρK), which represents adsorption interactions between the solute and the solid phase. As will be demonstrated in this paper, these parameters depend not only on the clay and contaminant species of interest but also on the chemical composition of the source leachate and possibly on biological factors not easy to measure.

The diffusion coefficient D and the adsorption term ρK are generally determined by laboratory model studies in which a source solution containing a single salt (e.g., NaCl) dissolved in distilled water is placed in contact with a layer of soil and the source constituents (Na$^+$, Cl$^-$) allowed to migrate into the soil predominantly by diffusion. The resulting diffusion profiles are then fitted using conventional Fickian diffusion theory (e.g., Crooks and Quigley 1984; Rowe et al. 1988). However, because these experiments have involved the use of a source solution of distilled water containing a single salt, the reported values of D and ρK do not incorporate the effect of co-diffusing species that would exist in a real leachate – clay barrier system.

This paper describes the results of laboratory model tests utilizing an actual domestic landfill leachate as the source solution. The specific objectives of the study were (1) to deduce both D and ρK for sodium (Na$^+$), potassium (K$^+$), magnesium (Mg^{++}), calcium (Ca^{++}), and chloride (Cl$^-$) when migration is from a real leachate solution into an undisturbed clayey soil and (2) to compare these parameters with those obtained from similar tests using a single salt dissolved in distilled water as the source solution.

Theoretical development

The conventional equation used to predict diffusive transport of a single reactive solute in a saturated porous medium can be written in one-dimensional form as (Freeze and Cherry 1979)

$$[1] \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - \frac{\rho K}{n} \frac{\partial c}{\partial t}$$

where c is the solute concentration in the solution phase [m/L^3], t is time [T], z is the distance from the contaminant source [L^2/T], K is the adsorption (distribution) coefficient of the solute [L^3/m], ρ is the dry density of the soil [m/L^3], and n is the soil porosity or volumetric water content (dimensionless).

In this investigation, a laboratory model was designed to simulate one-dimensional contaminant migration through a clay liner by diffusion only. A volume of leachate was

placed on top of a layer of saturated undisturbed clayey soil, and the chemical constituents in the leachate allowed to migrate into the soil layer by diffusion for a period of 15 days. Assuming that the concentration of dissolved constituents in the source leachate remains uniform throughout the reservoir, it can be shown (Rowe and Booker 1985) that the concentration in the reservoir, c_T, at any time t is a function of the initial concentration c_0 (at time zero), the reservoir volume, the cross-sectional area of the soil sample, and the mass flux $f_T(t)$ across the boundary between the reservoir and the sample. This boundary condition is given by the equation

$$[2] \quad c_T(t) = c_0 - \frac{1}{H_f} \int_0^t f_T(t) \, dt$$

where H_f is the height of leachate in the reservoir calculated as the volume of leachate divided by the cross-sectional area of the soil sample, perpendicular to the direction of diffusion. The mass flux $f_T(t)$ can be further related to the concentration gradient across the top of the soil sample $(\partial c(t)/\partial z)_T$ by Fick's first law, which says

$$[3] \quad f_T(t) = -nD \left(\frac{\partial c(t)}{\partial z} \right)_T$$

where n is the material porosity, which for 100% saturation is taken as the ratio of pore-water volume to total volume in accordance with usual geotechnical practice.

The base of the sample was sealed with an impermeable Plexiglas plate, so as to create a zero-flux base boundary condition, that is,

$$[4] \quad f_B(t) = -nD \left(\frac{\partial c(t)}{\partial z} \right)_B = 0$$

Diffusion of dissolved chemical constituents through the soil layer is thus described by [1]–[4]. A solution to these equations has been given by Rowe and Booker (1985) and has been implemented in the computer program POLLUTE (Rowe et al. 1983). The program POLLUTE permits very accurate calculation of concentration in only a few seconds on a microcomputer and hence is well suited for use in interpretation of the experimental results by mathematically considering each contaminant species separately.

Using POLLUTE, the solution to the equations outlined above was fitted to (1) the observed concentration variation with time in the source reservoir, (2) the pore-water concentration at various depths in the soil, and (3) the adsorbed concentration variation with depth in the soil layer. The fitting process involved varying both the diffusion coefficient (D) and adsorption term (ρK) while keeping other geometrical and material parameters constant. The diffusion coefficient and adsorption term giving the best fit to the observed data were chosen as the experimental values.

Materials and methods

The soil used for the models consisted of an undisturbed, unweathered grey clayey till from a site southeast of Sarnia, Ontario. The soil was waxed and had been maintained in a controlled environmental chamber at a constant temperature of 10°C prior to use. The geotechnical index characteristics, mineralogy, and pore-water chemistry of this soil are summarized in Table 1.

Leachate used for the source solution was obtained from the leachate collection system at a domestic landfill site

TABLE 1. Soil description

Specific gravity	2.73
Moisture content (%)	23
Saturation (%)	100
Porosity (%)	39
Dry density (g/cm)	1.68
Clay content* (%)	~45
Mineralogy* (<74 µm) (%)	
Calcite and dolomite	34
Quartz and feldspars	15
Illite	25
Chlorite	24
Smectite	2
Calcite/dolomite ratio (<74 µm)	0.42
Cation exchange capacity	9.66–10.93†
(meq/100 g dry wt.)	
Dissolved species (mg/L)	
Cl^-	50–55†
Na^+	150–155
K^+	10
Ca^{++}	85–232
Mg^{++}	66–120
Exchangeable cations	
(meq/100 g dry wt.)	
Na^+	0.48–0.90†
K^+	0.38–0.43
Ca^{++}	5.60–6.90
Mg^{++}	2.65–2.90

*Obtained from Quigley et al. (1987b).
†Range of analyses.

TABLE 2. Chemical characteristics of the domestic waste leachate used

1. Data obtained on leachate centrifuged at 10 000 rpm for 30 min

Na	955 mg/L*
K	400
Ca	250
Mg	291
NH_4	1 260
Cl	1 000
SO_4	<0.01
pH	7.0

2. Supplementary data provided by the City of London for leachate filtered through a Whatman #4 paper filter

Cd	0.05†
Cr	<0.06
Cu	0.10
Fe	161
Ni	0.48
Zn	4.1
Pb	0.3
Mn	2.4
Ag	<0.03
Conductivity	11 600 µmhos/cm
Biological oxygen demand	3 876
Total Kjeldahl nitrogen	946

*All units in mg/L except pH and conductivity.
†Analysis for metals involved acidifying the leachate prior to filtration.

located in London, Ontario. The leachate was transported to the laboratory in completely full, tightly sealed plastic bottles wrapped with duct tape to prevent exposure to light. On arrival in the laboratory, the leachate was immediately centrifuged at 10 000 rpm for 30 min to remove most suspended solids. The centrifuged leachate was then placed in polyethylene bottles, tightly sealed, and maintained at 10°C for 2 days prior to use. Some chemical properties as well as the concentration of various inorganic constituents of the leachate are summarized in Table 2.

The experimental models consisted of a hollow Plexiglas cylinder with an inside diameter of 6.74 cm and a length of 11 cm. A brass cutting ring with an inside diameter of 6.80 cm was fitted to the end of the Plexiglas cylinder and an undisturbed 7.00 cm diameter sample of 4.5 cm length was pressed into the Plexiglas cylinder with a triaxial compression machine. Once the soil sample was in place, an impermeable Plexiglas plate was placed at the base of the cylinder (directly below the soil layer) using a silicone seal bond. A 6 cm height of source solution (either leachate or distilled water containing a single salt) was then placed above the soil layer. The source solution was continuously mixed so as to maintain a uniform concentration throughout the source reservoir. Continuous mixing was provided by a Teflon stirring paddle connected to a 6 rpm motor. Once assembled, the models were maintained in a controlled environmental chamber at a constant temperature of 10°C. A schematic representation of an assembled diffusion model is given in Fig. 1.

During the testing period, 0.1 mL specimens of the source solutions were taken from the models at about 2 day intervals for solute concentration monitoring. The source solution specimens were taken by pipette through the sampling port
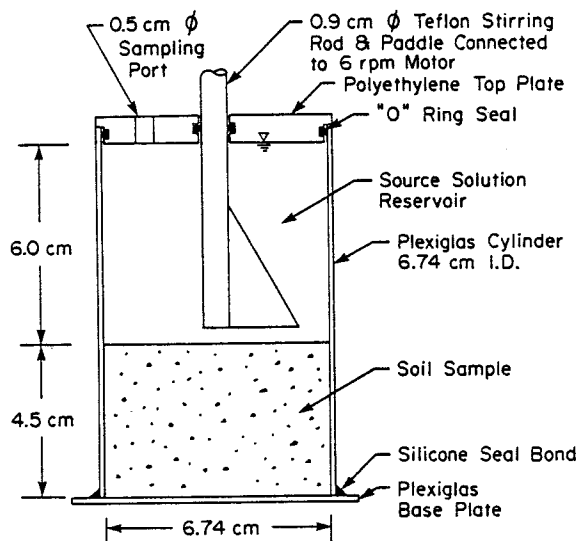

FIG. 1. Schematic diagram of the diffusion model.

shown in Fig. 1. After a specified period of time had elapsed for migration to take place (15 days), the models were taken apart and the soil layer sectioned to determine the vertical distribution of the selected chemical constituents. Pore fluid from each subsection was obtained using a pneumatic pore-water squeeze apparatus at a pressure of 25 MPa for approximately 3 h. For the soil and chemical constituents considered herein, it was determined that removal of pore water using a squeeze pressure up to 25 MPa would not result in incorrect measurements of "free pore-water" concentrations due to the removal of double-layer water. The entire sectioning and squeezing process was conducted at laboratory temperature (22 ± 1°C). Cation concentrations were measured using an atomic absorption spectrometer. Chloride

TABLE 3. Model test details

Test detail	Leachate models		Single-salt models*			
	Leachate	Leachate	NaCl	KCl	CaCl$_2$	MgCl$_2$
Initial concn. of source solution species (mg/L)						
Cl$^-$	1000	1000	1480	364	450	856
Na$^+$	955	955	955	—	—	—
K$^+$	400	400	—	400	—	—
Ca^{++}	250	250	—	—	250	—
Mg^{++}	291	291	—	—	—	291
Background pore-water concn. (mg/L)						
Cl$^-$	53	53	55	52	53	55
Na$^+$	150	150	150	155	150	150
K$^+$	10	10	10	10	10	10
Ca^{++}	85	85	120	232	85	230
Mg^{++}	120	120	66	115	66	120
Background adsorbed concn. (meq/100 g)						
Na$^+$	0.90	0.90	0.90	0.64	0.70	0.48
K$^+$	0.38	0.38	0.43	0.40	0.38	0.38
Ca^{++}	6.90	6.90	5.60	6.31	6.95	6.15
Mg^{++}	2.65	2.65	2.90	2.89	2.90	2.65
Soil porosity (%)	39	39	39	39	39	39
Height† of source soln. (cm)	6.0	6.0	6.0	6.0	6.0	6.0
Thickness of soil layer (cm)	4.5	4.5	4.5	4.5	4.5	4.5
Testing period (days)	15	15	15	15	15	15

*Salt was dissolved in distilled water.
†Calculated as the volume of source solution divided by the cross-sectional area of the soil specimen perpendicular to the direction of diffusion.

ion concentrations were determined using a specific-ion electrode attached to a multipurpose meter. Dilutions were required to bring the concentrations into range.

A mass balance for the selected species was performed for each test to check for any losses (due to, e.g., precipitation within the leachate reservoir, fixation, and (or) sorption onto the experimental apparatus). To perform mass balance calculations, it was required to know the mass of solute in the source solution and soil layer before and after the test. The mass of solute in the source reservoir was calculated from the solute concentration and the volume of source solution. Except for chloride, the total mass of solute (dissolved + adsorbed) in the soil layer required careful extraction. For each subsection, sodium and potassium were extracted by a single wash of 10 g of wet soil in 100 mL of silver thiourea solution for about 24 h in 250 mL plastic centrifuge bottles. The mixture was then centrifuged and the supernatant analyzed. With this technique, any adsorbed sodium or potassium on the clay exchange sites is effectively replaced by the silver ion from the wash solution. For calcium and magnesium, use of silver thiourea resulted in incorrect (high) concentrations in the supernatant because of dissolution of calcite and dolomite. To overcome this problem, a wash solution containing 2 g/L KCl in distilled water was found by the authors to provide complete exchange of Ca^{++} and Mg^{++} with K$^+$ without dissolving any carbonates.

Tests conducted

A total of six tests were conducted as previously described. Two identical tests were performed using a domestic landfill leachate as the source solution. The other four tests involved a source solution consisting of a single salt (i.e.,

sodium chloride, potassium chloride, calcium chloride, or magnesium chloride) dissolved in distilled water. For each single-salt model, the initial concentration of the source cation was made the same as that for the leachate models.

The details for each model test are summarized in Table 3. It should be noted that all tests involve similar soil, cell geometry, volume of source solution, temperature, and time period. Thus, any differences in migration observed between the leachate models and the corresponding single-salt model (e.g., NaCl model) for a species (i.e., Na$^+$) would be due primarily to variations in the many chemical interactions that influence diffusion (Quigley et al. 1987a).

Experimental results and interpretation

For direct comparison, the profiles illustrating cation migration for both the leachate and single-salt models are presented as Figs. 2–5 inclusive. The corresponding chloride ion concentration profiles are presented in Figs. 6 and 9. For convenience of presentation, the leachate models are discussed first, then the single-salt models.

Leachate models

For the case involving the use of domestic waste leachate as the source solution, the data points in Figs. 2–6 represent the average of two identical tests. The results obtained from the two appeared to be in good agreement, indicating the repeatability for this type of test; nevertheless, the range of values for the dissolved and adsorbed concentration data is indicated on the figures (where no range is shown, the difference in results was negligible).

Mass balance calculations at the end of the tests showed a recovery for Cl$^-$, Na$^+$, K$^+$, and Mg^{++} of no less than
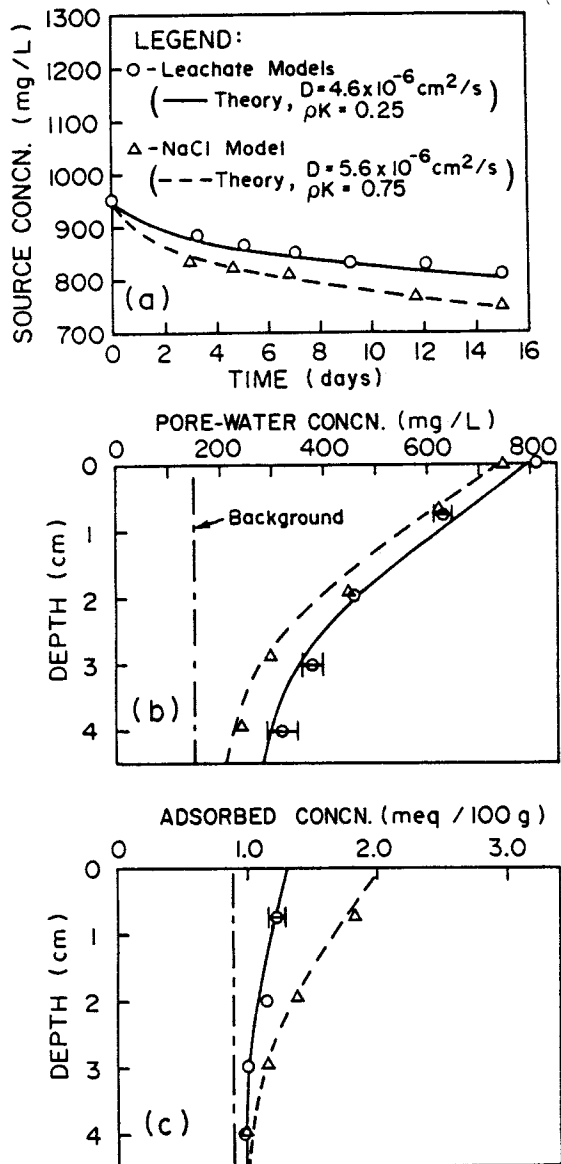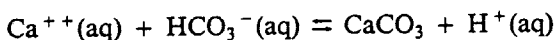
FIG. 2. Sodium: (a) source concentration vs. time; (b) pore-water concentration vs. depth; (c) adsorbed concentration vs. depth (t = 15 days).
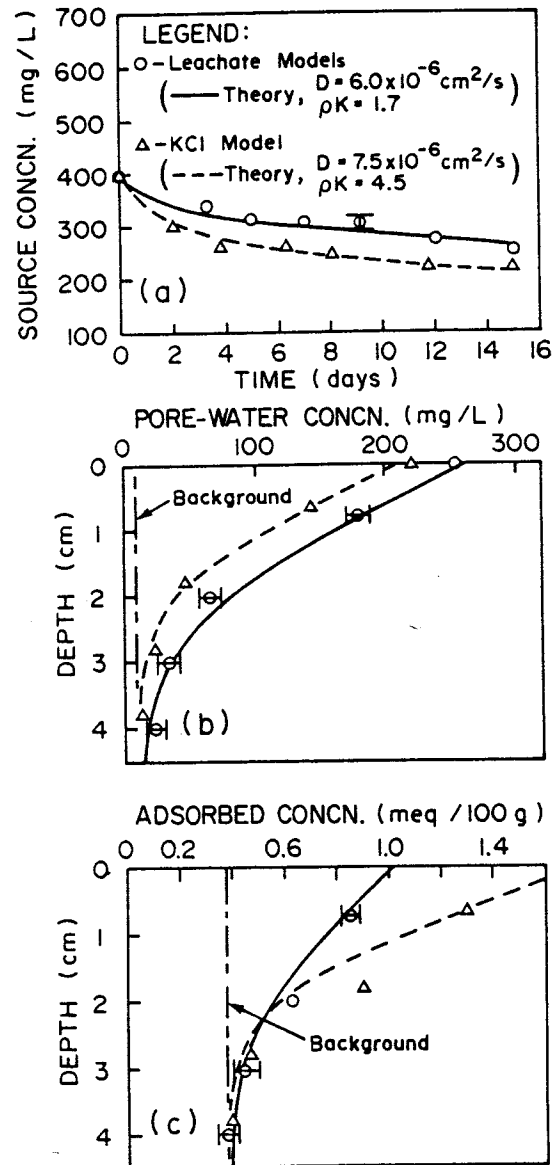

FIG. 3. Potassium: (a) source concentration vs. time; (b) pore-water concentration vs. depth; (c) adsorbed concentration vs. depth (t = 15 days)

97% of their original mass, suggesting that losses due to precipitation within the leachate reservoir, K^+ fixation, and (or) adsorption onto the experimental apparatus were insignificant. For Ca^{++}, however, only 71% of the original mass was recovered, at best. Loss of Ca^{++} is believed to be associated with the formation of precipitates within the leachate reservoir, in the form of fine-grained calcite ($CaCO_3$). The chemical reaction for the formation of these precipitates is thought to be as follows:

$$Ca^{++}(aq) + HCO_3^-(aq) = CaCO_3 + H^+(aq)$$

In the above equation, the bicarbonate ion, HCO_3^-, results from the production of CO_2 during microbial degradation of organic matter within the leachate (Baedecker and Back 1979). To provide evidence of calcite formation within the leachate, a sample of centrifuged leachate was placed in a tightly sealed glass jar and maintained at 10°C. Within 2 weeks, a white precipitate was observed on the bottom of the jar and identified by X-ray powder diffraction

as calcite. The fact that these white precipitates were not directly observed on the soil–leachate interface suggests that they were probably dispersed throughout the leachate reservoir by the stirring mechanism, which was in continuous use.

As shown in Figs. 2 and 3, both Na^+ and K^+ appear to have migrated by diffusion from the source leachate into the soil layer where their mass was distributed between the pore water and cation exchange sites. This is shown by the decrease in Na^+ and K^+ concentration with time in the source leachate accompanied by development of pore-water and adsorbed concentration profiles at or above soil background levels.

The adsorbed concentration profile for Mg^{++} (Fig. 4c) shows that Mg^{++}, originally abundant on the clay exchange sites at 2.7 meq/100 g, has been desorbed to accommodate the adsorption of Na^+, K^+, and likely other cations (e.g., NH_4^+) present in the leachate. The desorption of Mg^{++} was most dominant near the soil–leachate interface where Na^+ and K^+ adsorption was greatest. Elevated Mg^{++}
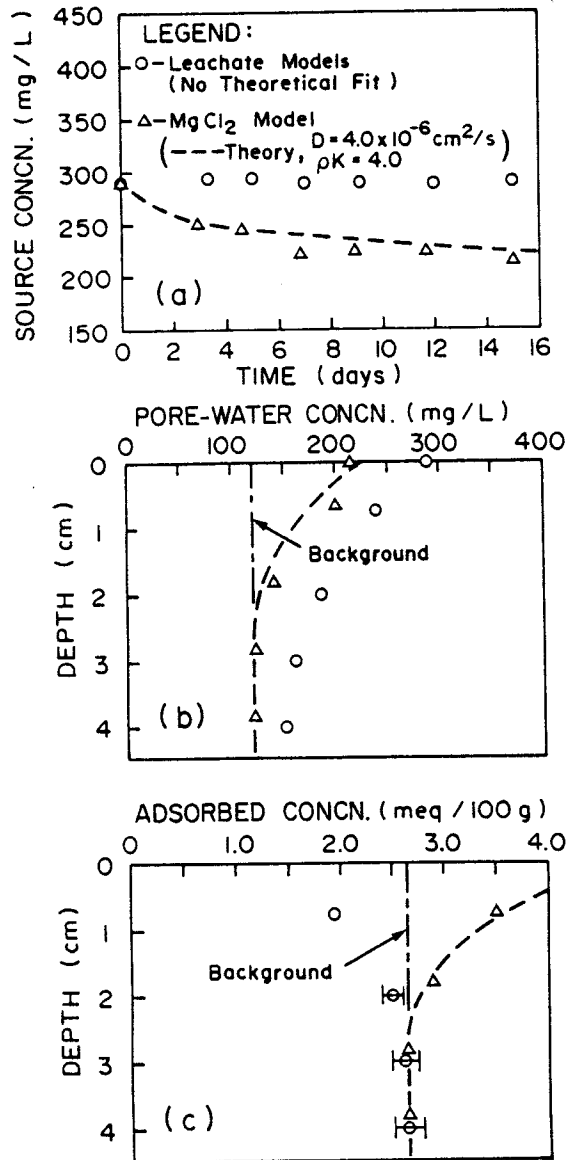
FIG. 4. Magnesium: (a) source concentration vs. time; (b) pore-water concentration vs. depth; (c) adsorbed concentration vs. depth ($t = 15$ days)

pore-water concentrations due to desorption induced both upward and downward diffusion, as indicated by a slight increase in Mg^{++} concentration in the source leachate (Fig. 4a) and an above-background pore-water concentration near the base of the soil layer (Fig. 4b) where Mg^{++} desorption was not observed.

The significant decrease of Ca^{++} concentration in the leachate reservoir (Fig. 5a) is primarily the result of calcite precipitation, as previously mentioned, rather than mass transfer into the soil by diffusion. Ca^{++} was also significantly desorbed (like Mg^{++}), particularly near the soil–leachate interface (Fig. 5c). Elevated Ca^{++} pore-water concentrations in the lower two-thirds of the soil (Fig. 5b) suggest that the desorbed Ca^{++} moves downwards as a halo probably to provide charge balance for Cl^- (Fig. 6), which generally migrates the fastest. This front of calcium is known as a "hardness halo" and is commonly observed in the vicinity of landfill sites underlain by clayey soils having a high adsorbed Ca^{++} concentration (Cartwright et al. 1977).
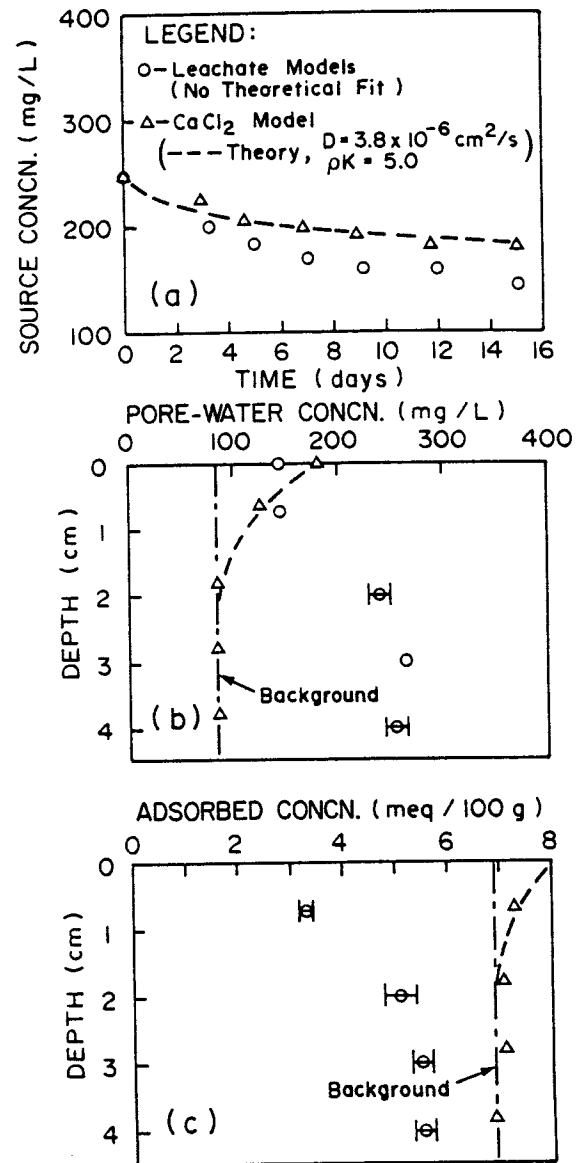
FIG. 5. Calcium: (a) source concentration vs. time; (b) pore-water concentration vs. depth; (c) adsorbed concentration vs. depth ($t = 15$ days)

Figure 7 illustrates the variation in Σ (Na^+, K^+, Mg^{++}, Ca^{++}) adsorbed concentration with depth at the end of the leachate diffusion experiments. The decrease in this sum near the interface, compared with a background value of 10.8 meq/100 g, suggests that other cations present in the leachate diffused into the soil layer and were adsorbed at the expense of original Ca^{++} and Mg^{++}. NH_4^+ is the most likely species, since leachate analysis (Table 2) indicates concentrations as high as 1260 mg/L.

The moisture content distribution with depth after the diffusion experiment (Fig. 8) indicates only a slight increase compared with the initial value of 23.1. This slight increase may be the result of clay double-layer expansion due to replacement of adsorbed divalent cations (Ca^{++}, Mg^{++}) with monovalent cations (Na^+, K^+) (Quigley et al. 1987b).

Single-salt models

Mass balance calculations performed for each of the single chloride salt models revealed not less than 96% recovery of Cl^-, Na^+, K^+, Mg^{++}, and Ca^{++}. Unlike the leachate

models, a good Ca^{++} balance indicates that there was no precipitation of calcite in the reservoir. For each model, analysis for the source cation (Figs. 2–5) shows decreasing concentration with time in the source reservoir, as well as pore-water and adsorbed concentration profiles at or above background. The single-salt chloride profiles are presented in Figs. 9a–9d and in normalized form relative to initial source concentration and background pore-water concentration in Fig. 10. The actual chloride profiles all yield similar diffusion coefficients, and the normalized curves are nearly identical. This would suggest that for the single-salt tests, the Cl^- migration characteristics are not significantly affected by the nature of the associated source cation at the concentration levels employed for these test soils.

In the single-salt models, diffusion from the soil into the source solution takes place for species not present in the source solution. This is illustrated for the KCl model in Fig. 11. In Fig. 11a, pore-water cations (Na^+, Ca^{++}, and Mg^{++}) are seen to be migrating upwards, from high background pore-water concentration to low reservoir concentration. This trend occurs despite desorption of the same cations from the clay by K^+ adsorption illustrated in Fig. 11b. Slight increases in pore-water concentration (above background) near the base of the sample (Fig. 9a) probably reflect increases to provide charge balance for Cl^-, which migrates faster than the source K^+.

Discussion

Comparing the results obtained from the two types of models, it is apparent that migration has progressed further in the leachate models. For example, as shown in Fig. 2b, the Na^+ concentration at the base of the soil layer after 15 days is approximately 300 mg/L for the leachate models compared with 200 mg/L for the NaCl model. K^+ shows a similar trend (Fig. 3b). The apparently faster advance of Ca^{++} and Mg^{++} for the leachate models (Figs. 4b and 5b) is not however associated directly with diffusion from the reservoir, but rather is the result of desorption associated primarily with adsorption of Na^+, K^+, and probably NH_4^+.

Mathematical fitting of the migration profiles for both the leachate and single-salt diffusion models after 15 days of the migration was performed using the computer program POLLUTE. The geometrical and material parameters used for the theoretical analysis are as indicated in Table 3. By adjusting the diffusion coefficient, D, and the adsorption term, ρK, while keeping all material and geometrical parameters constant, the resulting theoretical curves were fitted to the observed source, pore-water, and adsorbed concentration profiles. The theoretical best fits to the experimental data are shown on all relevant figures and the relevant D and ρK values are presented in Table 4.

For the leachate models, the values for the adsorption term, ρK, giving the best fit for the Na^+ and K^+ data were 0.25 and 1.7 respectively, compared with 0.75 and 4.5 deduced from the NaCl and KCl models. The fact that the ρK values are about 60% lower for the leachate models reflects the higher degree of competition for exchange sites when dissolved cations migrate simultaneously.

The diffusion coefficients for Na^+ and K^+ as obtained from the leachate models were 4.6×10^{-6} and 6.0×10^{-6} cm^2/s respectively. These values are approximately 20% lower than those derived from the single-salt
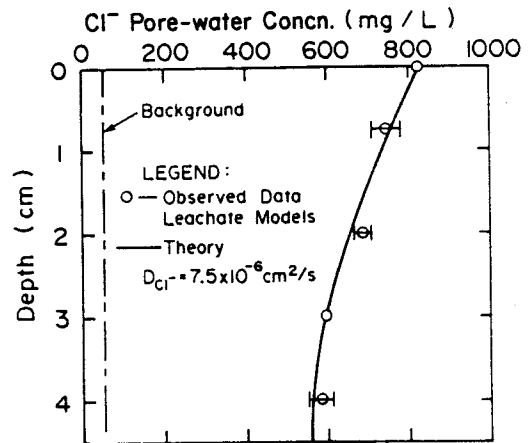
FIG. 6. Chloride pore-water concentration variation vs. depth for the leachate models ($t = 15$ days).
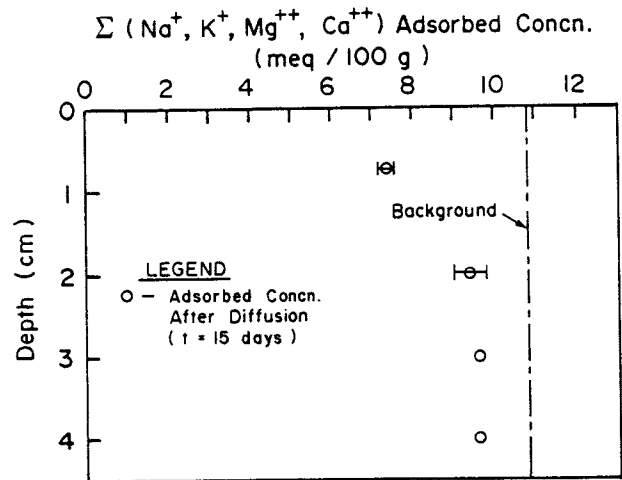
FIG. 7. Variation in Σ (Na^+, K^+, Mg^{++}, Ca^{++}) adsorbed concentration with depth for the leachate models.

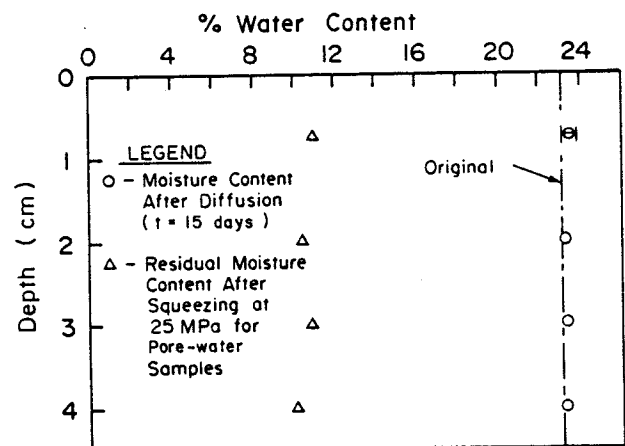FIG. 8. Variation in moisture content with depth for the leachate models.

models, 5.6×10^{-6} and 7.5×10^{-6} cm^2/s. A difference also exists between the Cl^- diffusion coefficient obtained from the two types of models. The Cl^- diffusion coefficient corresponding to the best fit for the two leachate models (7.5×10^{-6} cm^2/s) is about 25% higher than the average D value of 5.9×10^{-6} cm^2/s obtained from the

TABLE 4. Summary of diffusion coefficients, adsorption terms, and retardation factors

| | D (cm^2/s) | | ρK, R_F† | |
Species	Leachate models	Single-salt models	Leachate models	Single-salt models
Cl$^-$	7.5×10^{-6}	5.9×10^{-6}*	0, 0	0, 0
Na$^+$	4.6×10^{-6}	5.6×10^{-6}	0.25, 1.6	0.75, 2.9
K$^+$	6.0×10^{-6}	7.5×10^{-6}	1.7, 5.4	4.5, 12.5
Ca^{++}	No theoretical fit	3.8×10^{-6}	No theoretical fit	5.0, 13.8
Mg^{++}	No theoretical fit	4.0×10^{-6}	No theoretical fit	4.0, 11.3

*Average Cl$^-$ diffusion coefficient of four single-salt models.
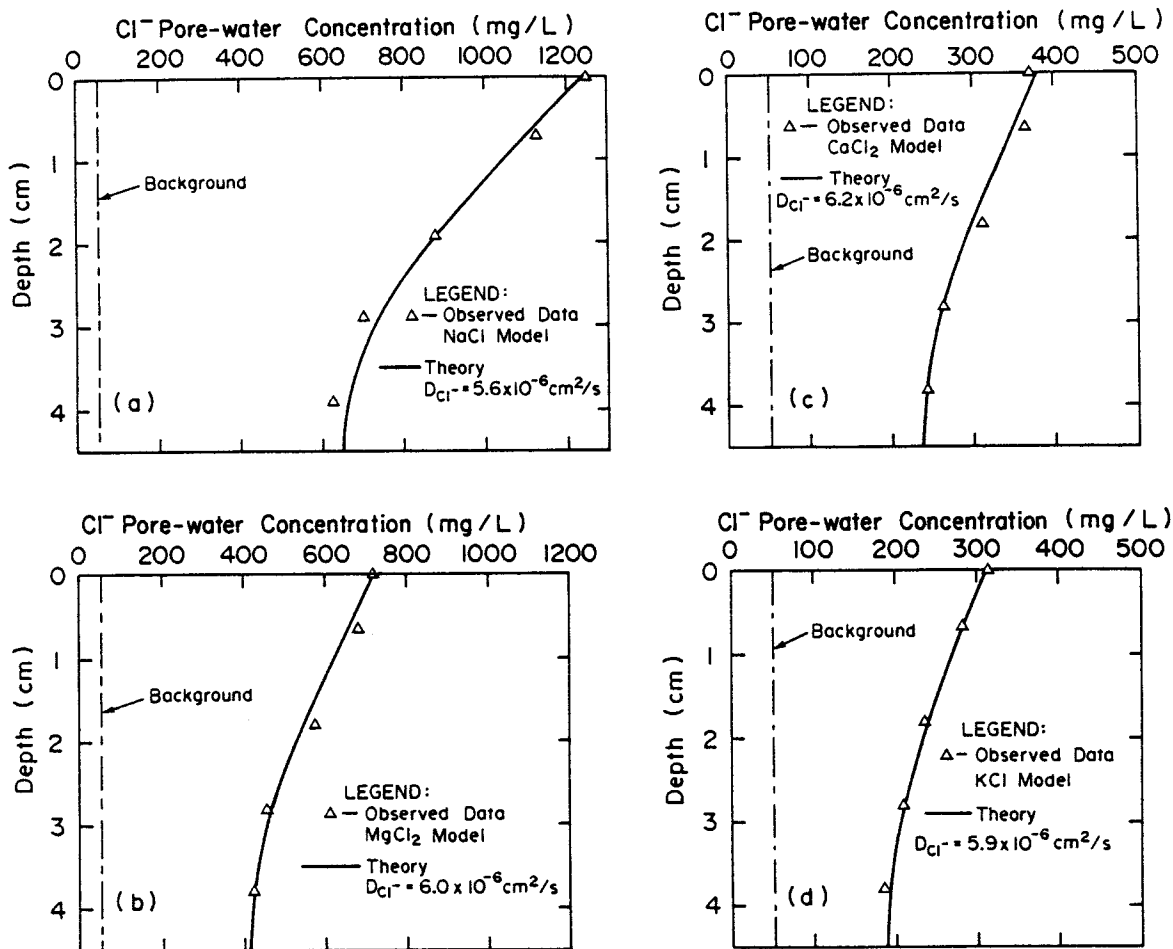†Retardation factor $R_F = 1 + \rho K/n$ where $n = 0.39$.

FIG. 9. Chloride pore-water concentration variation with depth: (a) NaCl model; (b) MgCl$_2$ model; (c) CaCl$_2$ model; (d) KCl model (t = 15 days).

single-salt models. This finding indicates that the diffusion coefficient of chloride, a conservative species, is also dependent on the nature of the source solution above our test soil (i.e., leachate vs. single-salt solution).

As shown by Husted and Low (1954), to maintain electroneutrality, the diffusion of anions is coupled to that of cations. Recognizing the need for electroneutrality in the present tests, the lower diffusion coefficient for Cl$^-$ and the higher diffusion coefficient for cations observed for migration from a single-salt source solution may be explained as follows. As the Cl$^-$ ions move ahead of the retarded source cation species, they seem to seek charge balance from other in situ cations that have been desorbed from the clay exchange sites. Because the concentration of these cations

in the initial source solution is zero, they experience an upward diffusive driving force that tends to reduce their ability to migrate downward with the Cl$^-$ ions. This in turn reduces the rate of downward diffusive transport for Cl$^-$ in comparison with the leachate models where the upward movement of desorbed cations is less significant owing to the lower concentration gradient near the source–leachate interface. The reduced downward mobility of the desorbed cations in the single-salt models induces a concurrent demand on the source cation to help maintain charge balance for the Cl$^-$ anion. This would explain the higher diffusion coefficient for the source cations Na$^+$ and K$^+$ when diffusion is from a single-salt source solution.
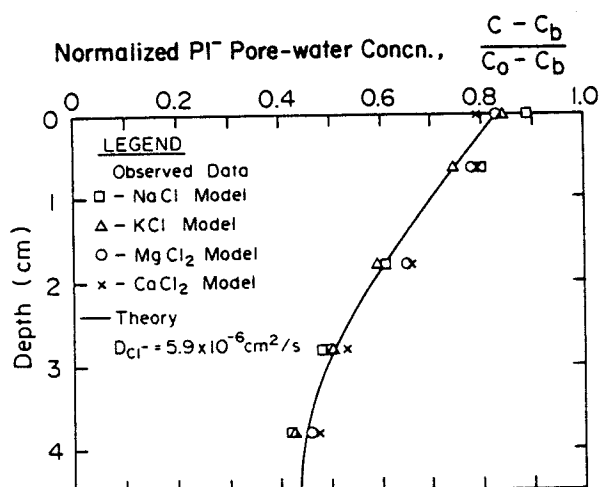
The mathematical model used to fit the experimentally

Normalized Pl⁻ Pore-water Concn., $\dfrac{C - C_b}{C_0 - C_b}$

FIG. 10. Normalized Cl^- pore-water concentration vs. depth for the single-salt models ($t = 15$ days). C_0 = initial Cl^- concentration in the source solution (Table 3); C_b = initial Cl^- concentration in the soil pore water (Table 3).

FIG. 11. KCl model: (a) pore-water concentration vs. depth; (b) adsorbed concentration vs. depth for Na^+, Mg^{++}, and Ca^{++} ($t = 15$ days).

observed migration profiles considers only the migration of a single species and does not explicitly consider interactions between chemical species. When leachate is used as the source solution, chemical interactions between species in the system become very important, causing some species to behave in a manner not compatible with the mathematical model. For example, concentration profiles obtained for Ca^{++} and Mg^{++} from the leachate models could not be fitted, since the migration of these species was significantly influenced by replacement of Ca^{++} and Mg^{++} originally present on the soil exchange sites by other ions in the leachate. The migration of Ca^{++} was further complicated by its precipitation as $CaCO_3$. Consequently, parameters for these species are not reported. When the initial source solution consists of a single salt, however, the mathematical model can be used to back-figure the diffusion coefficient and adsorption term even for Mg^{++} and Ca^{++}. Parameters determined for tests conducted using $MgCl_2$ and $CaCl_2$ as the source solution yielded diffusion coefficients for Mg^{++} and Ca^{++} of 4.0×10^{-6} and 3.8×10^{-6} cm^2/s respectively. The values of ρK were $\rho K_{Mg^{++}} = 4.0$ and $\rho K_{Ca^{++}} = 5.0$.

Finally, it should be pointed out that the research results reported herein apply only to the soil, the leachate, and the low-concentration single-salt models studied.

Conclusions

(1) Laboratory-measured diffusion and adsorption parameters may be highly dependent on the composition of the source solution (i.e., leachate vs. single-salt solutions). Thus, diffusion experiments should be carried out using test soils and source solutions as similar as possible to those expected in the field situation.

(2) For both the leachate and single-salt solutions, the migration of Na^+, K^+, and Cl^- could be modeled using a mathematical model for a single contaminant with the effect of chemical interactions being reflected in the magnitude of the parameters.

(3) For Na^+ and K^+, the diffusion coefficient (D) obtained using a real leachate was about 20% lower than that obtained using a source solution containing only a single salt. However, for Cl^-, the diffusion coefficient determined
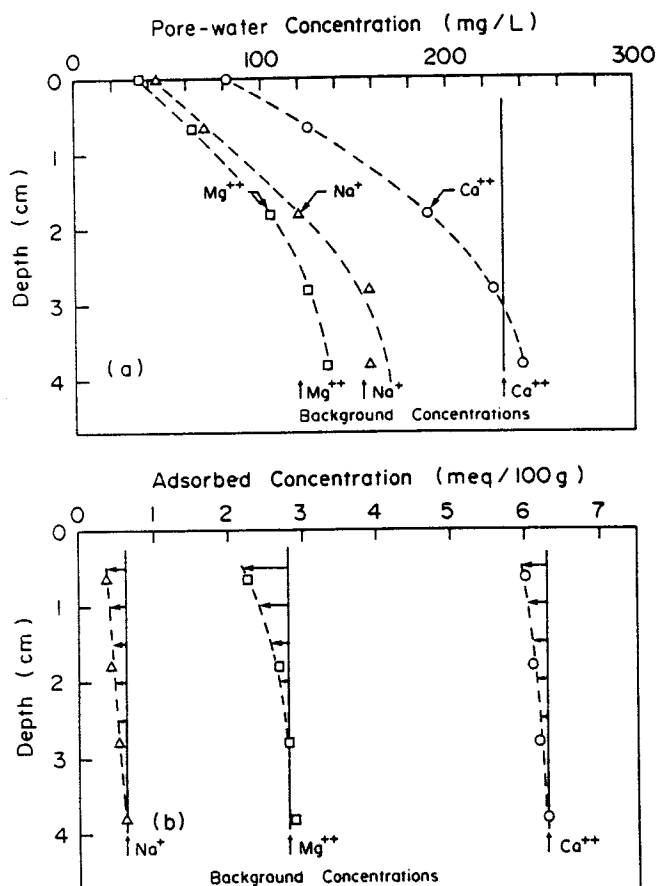
using a real leachate was about 25% higher. The difference in D values obtained for the two source solutions is believed to be associated to the nature of electrochemical interactions between dissolved species as discussed in the text.

(4) The adsorption term (ρK) for Na^+ and K^+ as determined using a real leachate was about 60% lower than that deduced for a single-salt source solution. This finding reflects the higher degree of competition for the clay exchange sites experienced by cations migrating simultaneously.

(5) For the leachate models, both Ca^{++} and Mg^{++}, originally dominant on the clay exchange sites, were heavily desorbed to accommodate the adsorption of Na^+, K^+, and most likely NH_4^+. The resulting dissolved and adsorbed cation concentration profiles could not be fitted using the mathematical model for a single contaminant, since the model does not account for exchange of in situ Ca^{++} and Mg^{++} by other cations present in the leachate. However, profiles obtained from tests using aqueous solutions of $CaCl_2$ or $MgCl_2$ as the source solution were adequately modeled.

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