

## Laboratory Determination of Multicomponent Effective Diffusion Coefficients for Heavy Metals in a Compacted Clay

M. ZEKİ ÇAMUR & HASAN YAZICIGİL

Middle East Technical University, Department of Geological Engineering, TR06531 Ankara, Turkey  
(e-mail: mzeki@metu.edu.tr)

**Abstract:** Diffusion and sorption of heavy-metal ions (Cd, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn) through an Ankara clay liner were studied experimentally. The Ankara clay consists of calcite, quartz, smectite and illite, and is a highly plastic inorganic clay with optimum weight water content of 32% and corresponding dry density of 1.413 g/cm<sup>3</sup>. Under optimum compaction conditions, effective porosity (volumetric water content) and hydraulic conductivity in the material were determined as 0.45 and 1.3 to 2.6x10<sup>-9</sup> cm/s, respectively. The Ankara clay adsorbed Cd, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn metals, but desorbed Ca, Mg and Na metals for the solution concentration range used. Sorption isotherms of these ions were experimentally established. Effective diffusion coefficients of Cd, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn metals, determined through column experiments are, respectively, 2.5, 9.5, 2.2, 2.9, 2.2, 7.9, 3.1, 1.6, 3.2 and 2.5 (x10<sup>-6</sup>) cm<sup>2</sup>/s. The tortuosity factor of non-reactive chloride is approximately 0.47. The factor changes between 0.34 and 0.45 for the other ions. The results show that diffusion is the dominant mass transport mechanism in an Ankara clay liner. Due to sorption processes, transported heavy metals studied in this research will be significantly attenuated in the liner. Because diffusion and sorption processes depend on solution composition, mass transport determinations in clay liners require case studies using multicomponent systems similar to those presented in this study.

**Key Words:** contaminant transport, diffusion coefficients, heavy metals, clay liner, Ankara clay

### Sıkıştırılmış Kil İçerisindeki Ağır Metallerin Çok Bileşikli Etkin Difüzyon Katsayılarının Laboratuvarında Belirlenmesi

**Özet:** TAğır metal iyonların (Cd, Cr, Cu, Fe, K, Mn, Ni, Pb ve Zn) Ankara kili taban malzemesindeki yayılma (difüzyon) ve iyon değişimi (sorptionu) deneysel olarak çalışılmıştır. Ankara kili kalsit, kuvars, smektit ve illit minerallerinden oluşmaktadır. Ankara kili yüksek plastiziteli inorganik kil olup %32 optimum su ağırlık içeriği ve buna karşılık gelen 1.413 g/cm<sup>3</sup> kuru yoğunluğa sahiptir. Optimum sıkıştırma koşullarında malzemenin etkin porozitesi (hacimsel su içeriği) ve hidrolik iletkenliği sırasıyla 0.45 ve 1.3 – 2.6x10<sup>-9</sup> cm/s olarak belirlenmiştir. Ankara kili kullanılan çözelti konsantrasyonu aralığında Cd, Cr, Cu, Fe, K, Mn, Ni, Pb ve Zn metallerini çözeltilerden bünyelerine alırken (adsorbsiyon) Ca, Mg ve Na metallerini bünyelerinden çözeltiliye aktarmışlardır (desorbsiyon). Çalışmada metal iyonların değişim (sorption) izotermeleri deneysel olarak belirlenmiştir. Kolon deneyleri yapılarak Cd, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb ve Zn metallerinin etkin yayılma (difüzyon) katsayıları sırasıyla 2.5, 9.5, 2.2, 2.9, 2.2, 7.9, 3.1, 1.6, 3.2 and 2.5 (x10<sup>-6</sup>) cm<sup>2</sup>/s olarak tesbit edilmiştir. Malzeme ile reaksiyona girmeyen klorürün tortuositi faktörü yaklaşık olarak 0.47 dir. Diğer iyonların faktörü 0.34 ile 0.45 arasında değişmektedir. Sonuçlar Ankara kili taban malzemesinde hakim kütle taşınımı mekanizmasının yayılma (difüzyon) olduğunu göstermektedir. İyon değişiminden dolayı çözelti içindeki metal konsantrasyonların önemli miktarı Ankara kili tarafından tutulmaktadır. Yayılma ve iyon değişimi işlemleri çözelti bileşimine bağlı olduğu için, herhangi bir kil taban malzemesine yönelik kütle taşınımı belirlemeleri, çok bileşik sistemli o malzeme ve ilgili çözeltiliye has çalışmalar gerektirmektedir.

**Anahtar Sözcükler:** kirlenici taşınımı, yayılma (difüzyon) katsayıları, ağır metaller, kil taban malzemesi, Ankara kili

### Introduction

Extra care in waste-disposal site designs should be given to the base liner to ensure protection of groundwater resources. A variety of natural and industrial materials have been developed and used for the base liner of

landfills. Investigations have proven that clays are important natural resources for such applications (e.g., Emcon Associates 1983; Mundell & Bailey 1985; Quigley & Rowe 1986). However, to properly use these materials as a base liner, more theoretical and experimental

research is necessary to delineate material-leachate interactions and mass-transport processes. The suitability of a clay liner has been conventionally evaluated on the basis of hydraulic conductivity to control advective contaminant transport. Previous works, however, indicate that chemical diffusion is an important transport process in liner systems with low hydraulic conductivities and must be taken into consideration (Quigley & Rowe 1986; Quigley *et al.* 1987a; Rowe 1988, 1994; Rowe *et al.* 1988; Barone *et al.* 1989).

Most of the available data related to diffusive transport in clay liners were acquired from column experiments performed using solutions with a limited number of species (binary or ternary systems) (e.g., Quigley *et al.* 1987a; Rowe *et al.* 1988). In addition, heavy-metal related diffusion data applicable to the transport processes in liners are limited and cover few metals (e.g., Barone *et al.* 1989). Moreover, some available data were collected using intact soils (e.g., Quigley *et al.* 1987a; Rowe 1988, 1994; Rowe *et al.* 1988; Barone *et al.* 1989).

The purpose of this study is to estimate experimentally the effective diffusion coefficients for metals (Cd, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn) in a multicomponent system using Ankara clay material

compacted under optimum conditions. Reddish-brown mudstone layers in the Upper Pliocene sediments around the Ankara plain in Turkey are called “Ankara clay” (Birand 1963; Ordemir *et al.* 1965). Mineralogical, chemical and geotechnical characteristics of the clay are given in Table 1.

**Advective-Diffusive Mass Transport**

Contaminant transport through porous media can be modelled using the one dimensional advection-dispersion equation including linear sorption isotherm of Freeze & Cherry (1979):

$$(1 + (\rho_b K_d / n_e)) (\partial c / \partial t) = D_h (\partial^2 c / \partial z^2) - v_s (\partial c / \partial z)$$

where

- c : ion concentration at a given depth z and time t,
- D<sub>h</sub> : hydrodynamic dispersion coefficient,
- v<sub>s</sub> : seepage velocity (= v<sub>a</sub> / n<sub>e</sub>),
- v<sub>a</sub> : advective (Darcy) velocity,
- ρ<sub>b</sub> : dry density of the soil,
- K<sub>d</sub> : distribution or partitioning coefficient,
- n<sub>e</sub> : effective porosity.

Table 1. Description of the Ankara clay.

Specific gravity	2.71	Exchangeable cations (meq/100 gr dry wt.)	
Bulk porosity (%)	48	Ca	5.4411
Optimum compaction parameters		Cd	0.0001
dry density (g/cm <sup>3</sup> )	1.413	Cr	0.0334
weight water content (%)	32	Cu	0.0022
degree of saturation (%)	94	Fe	2.5615
hydraulic conductivity (cm/s)	0.13 x 10 <sup>-8</sup>	K	0.7239
Particle size distribution (%)		Mg	2.5962
clay	50	Mn	0.0383
silt	34	Na	0.064
sand	11	Ni	0.0046
gravel	5	Pb	0.001
Mineralogy (%)		Zn	0.0065
calcite	37		
quartz	32		
smectite	12		
illite	11		
feldspar	6		
chlorite+kaolinite	2		
Cation exchange capacity (meq/100gr dry wt.)	11.5		

If the values of  $\rho_b$ ,  $K_d$ ,  $n_e$ ,  $v_s$ , and  $D_h$  are known, the concentration distribution of a single ion at any time  $t$  and space  $z$  can be calculated using the above equation for a given porous material and boundary conditions. The equation can also be used to estimate the hydrodynamic dispersion coefficient for an ion if the ion's concentration, effective porosity, seepage velocity, dry density and distribution coefficient are known at a given time and space (as in the case of experiments explained in the following sections) (e.g., Rowe *et al.* 1988; Domenico & Schwartz 1999).

The hydrodynamic dispersion coefficient,  $D_h$  is often expressed as sum of the effective diffusion coefficient,  $D_e$ , and mechanical dispersion coefficient,  $D_m$ , or  $D_h = D_e + D_m$ . Previous studies indicate that the hydrodynamic dispersion coefficient can be regarded as the effective diffusion coefficient under very low seepage velocity conditions, as is typically observed in clay liners (Gillham & Cherry 1982; Rowe 1988, 1993; Barone *et al.* 1989; Shackelford 1993). In other words, diffusion can be the dominant mass transport process in clay liners. In order to estimate effective diffusion coefficients from fundamental principles, several relationships between diffusion coefficients in pure water and various parameters (e.g., tortuosity, viscosity factor, volumetric water content) have been defined by previous workers (Porter *et al.* 1960; Kemper *et al.* 1964; Olsen & Kemper 1968; Berner 1971; Li & Gregory 1974; Nye 1979; Gillham *et al.* 1984; Drever 1997). However, it is difficult to calculate the diffusion coefficient from fundamental

principles. Instead, a simpler "engineering approach" is commonly adopted (e.g., van Genuchten 1978; Rowe *et al.* 1988; Barone *et al.* 1989), in which the effective diffusion coefficient is estimated from the mass-transport equation given above using data collected from geotechnical, sorption (batch) and column experiments.

### Sorption Experiments

The distribution coefficient ( $K_d$ ) of an ion is one of the variables that should be known to solve the mass-transport equation for the estimation of the effective diffusion coefficient. Multicomponent batch-equilibrium experiments were performed at room temperature to determine the sorption isotherms for Cd, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn parameters. The experiments were carried out using five different initial solutions having the concentration ranges of interest. A stock solution (A) containing average waste-leachate concentrations of Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn was prepared in the laboratory using chemicals (Cd in dilute HCl, Cr in dilute NaOH, Cu, Ni in dilute HNO<sub>3</sub>, Pb in dilute HNO<sub>3</sub>, ZnSO<sub>4</sub>·7H<sub>2</sub>O, MgSO<sub>4</sub>·7H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O, MnCl<sub>2</sub>·2H<sub>2</sub>O, KCl, NaCl, CaCl<sub>2</sub>). The pH of the solution was adjusted to about 6.7 using NaOH solution. By diluting the stock solution to about 80%, 60%, 40%, and 20%, the other four initial solutions (B, C, D, E, respectively) were prepared for batch experiments. The atomic adsorption spectrometric (AAS) analysis of the initial solutions used in the sorption experiments is given in Table 2.

**Table 2.** Initial and equilibrium concentrations (mg/l) of cations in sorption experiments. Measured pH range is 6.86–7.35.

	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
Initial (E)	376	0.0468	0.198	0.03	3.78	115.5	65	4.95	591	0.14	1.19	5.19
Equilibrium	1258	0.039	0.099	0.03	2.181	47	276	0.283	1932	0.053	0.35	2.0
Initial (D)	752	0.094	0.396	0.06	7.55	236.2	130	9.91	1182	0.27	1.41	10.37
Equilibrium	1380	0.049	0.144	0.034	3.721	134.8	298	1.34	2122	0.08	0.412	2.80
Initial (C)	1127	0.14	0.595	0.09	11.33	388.9	196	14.86	1773	0.41	1.46	15.56
Equilibrium	1545	0.065	0.192	0.042	5.71	234	327	3.359	2385	0.092	0.428	4.50
Initial (B)	1503	0.187	0.793	0.12	15.1	496.3	261	19.82	2364	0.55	1.68	20.74
Equilibrium	1835	0.08	0.204	0.053	6.382	296	362	5.264	2601	0.141	0.458	6.30
Initial (A)	1879	0.234	0.991	0.15	18.88	618.2	326	24.77	2955	0.68	1.82	25.93
Equilibrium	2149	0.096	0.252	0.061	7.798	404.4	410	7.296	2956	0.183	0.468	10.60

Ankara clay, dried at room temperature, was mixed with the solutions (A, B, C, D, E) at a mass ratio of 1:10 (2.5 g/25 ml) in 50 ml centrifuge tubes to obtain saturation conditions. Four different sets of these slurries were prepared and shaken at a rate of 250 strokes per minute for 8 h, 16 h, 24 h, and 36 h, respectively, to obtain the equilibrium condition at a room temperature of 22 °C. After shaking, the slurries were centrifuged at 3500 rpm for 30 minutes and the clear supernatants were analyzed using the AAS. An equilibrium condition was reached for Mg in all sets, for K, Mn, Na, Ni, Zn at 16 h, 24 h and 36 h, and for Ca, Cd, Cr, Cu, Fe, Pb in the 24 h and 36 h sets. The determined equilibrium concentrations for each ion in the 24 h test are listed in Table 2. The sorption isotherm for each ion of interest was fit to a power equation, expressed as the Freundlich isotherm, and were used in the mass-transport equation for  $K_d$  determination (Figure 1). The best fit equations, together with the correlation coefficients, are listed in Table 3. The Ankara clay adsorbed Cd, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn, and desorbed Ca, Mg and Na in the experimental concentration ranges.

### Column Experiments

A schematic diagram of the column apparatus made of plexiglass and used in this experiment is given Figure 2. Ankara clay was compacted under optimum conditions, using the standard Proctor method, into the lower part of the column (diameter: 11 cm, length: 11.7 cm) after a 1-mm-thick polyethylene plate (bulk porosity = 0.38) was placed at the bottom of the sample. The porous polyethylene plate at the bottom of the sample was later used to set the bottom boundary condition. Background pore-water concentrations of the metals in the clay are given in Table 4.

The lower part of the column was placed onto the plexiglass base plate with a 5 mm hole in the middle. The boundary between the base plate and the lower part of the column was sealed on the outside using commercial transparent silicon. A plastic tube was mounted to the base plate through which the effluent (if present) could be drained into the collection bottle (into which the other end of the tube was inserted through a tightly closed cap). Once the clay sample was in the lower part of the column, a perforated plexiglass disk having 0.38 bulk porosity and 10 mm thickness was placed onto the clay-

sample surface by applying effective pressure via a threaded rod to ensure that the solution entered the clay sample surface evenly and provided uniform concentration. The boundary between the plexiglass disk and the column was also sealed.

The upper part of the column (solution reservoir with a length of 25 cm) was then placed onto the lower part and the boundary between was sealed from outside. A solution approximating the waste-leachate composition of the İstanbul (European side) waste-disposal site was prepared in the laboratory using the chemicals described above. The pH of the solution was adjusted to about 6.7 using NaOH solution. Concentrations of the metals in the solution are listed in Table 4. The upper part of the column was filled with the solution (representing waste leachate) to a final height of 22 cm. Finally, the upper part was closed using a plexiglass lid to prevent evaporation. The lid has a hole in it into which may be inserted either a mixer or a sampling pipette. The solution was mixed periodically with a polyethylene mixer to maintain a relatively uniform concentration distribution throughout the reservoir depth during the experiment.

Subsequently, a 6-ml sample of solution was collected from the source reservoir through the sampling port for monitoring solute concentrations. To prevent a drop in height of solution in the reservoir, the volume of distilled water equal to the volume of reservoir solution and effluent (if present) collected was added after each monitoring period. The dilution resulting from the addition of distilled water was taken into consideration during data evaluation. Total fluid flow through the sample into the collection bottle, if present, was also monitored. After 321 days, the experimental set up was taken apart. During the experiment, the lowest and the highest laboratory temperatures recorded were 23 °C and 29 °C, respectively. The compacted Ankara clay sample was sectioned to determine the vertical distribution of the selected chemical constituents in pore water extracted from the sections using a pneumatic pore-water squeeze apparatus at a pressure of 25 MPa for 3 hr.

### Data Evaluation

Two column experiments were carried out simultaneously under similar conditions to test the reliability of the results. In Column I, the solution started to flow into the

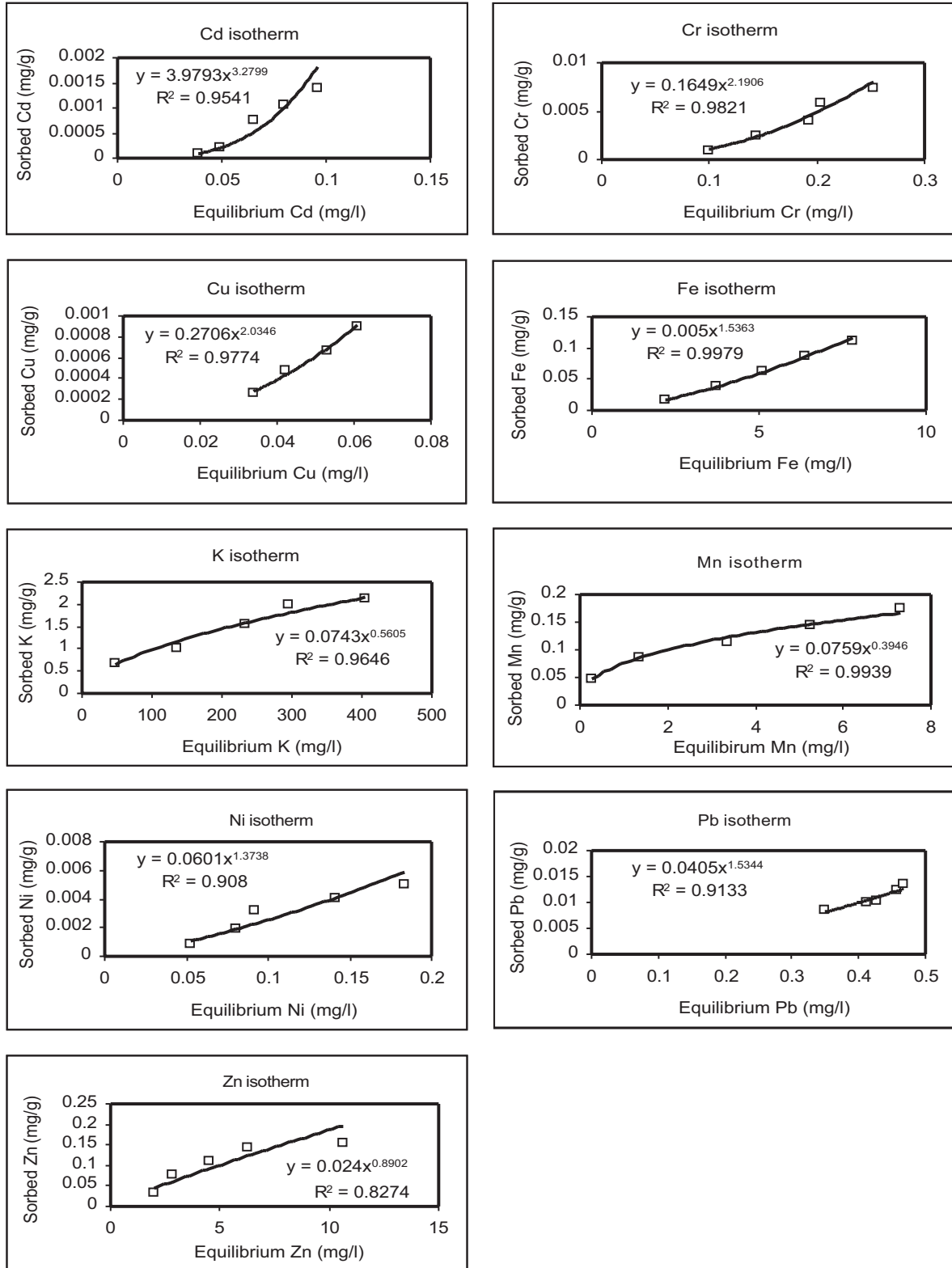


Figure 1. Freundlich sorption isotherms.

**Table 3.** Best fit equations of sorption isotherms and related correlation coefficients.  $S = K_d \cdot c^n$ . S: sorbed amount.  $K_d$ : distribution coefficient. c: equilibrium concentration. n: constant.

Parameter	$K_d$	n	$R^2$
Cd	3.9793	3.2799	0.95
Cr	0.1649	2.1906	0.98
Cu	0.2706	2.0346	0.98
Fe	0.005	1.5363	0.99
K	0.0743	0.5605	0.97
Mn	0.0759	0.3946	0.99
Ni	0.0601	1.3738	0.91
Pb	0.0405	1.5344	0.91
Zn	0.024	0.8902	0.83

**Table 4.** Initial concentrations (mg/l) in source solution and pore water.

mg/l	Initial source solution	Initial pore water	
Cl	4640	Cd	0.0001
Ca	1235	Cr	0.0029
Cd	0.23	Cu	0.0007
Cr	1.75	Fe	0.7123
Cu	0.18	K	0.2489
Fe	6.97	Mn	0.0029
K	618.2	Ni	0.0009
Mg	187.7	Pb	0.001
Mn	16.77	Zn	0.002
Na	1930		
Ni	0.58		
Pb	1.28		
Zn	21.5		
pH	6.70		

collection bottle after 80 days. A total volume of 103 ml of effluent was collected. Based on the collected data, the advective velocity, hydraulic conductivity and volumetric water content were estimated as  $4.03 \times 10^{-8}$  cm/s,  $1.35 \times 10^{-8}$  cm/s, and 0.45, respectively. In Column II, the

solution began to flow into the collection bottle after 168 days. A total volume of 20 ml of effluent was collected. The advective velocity, hydraulic conductivity and volumetric water content were estimated as  $0.78 \times 10^{-8}$  cm/s,  $0.26 \times 10^{-8}$  cm/s, and 0.45, respectively. The

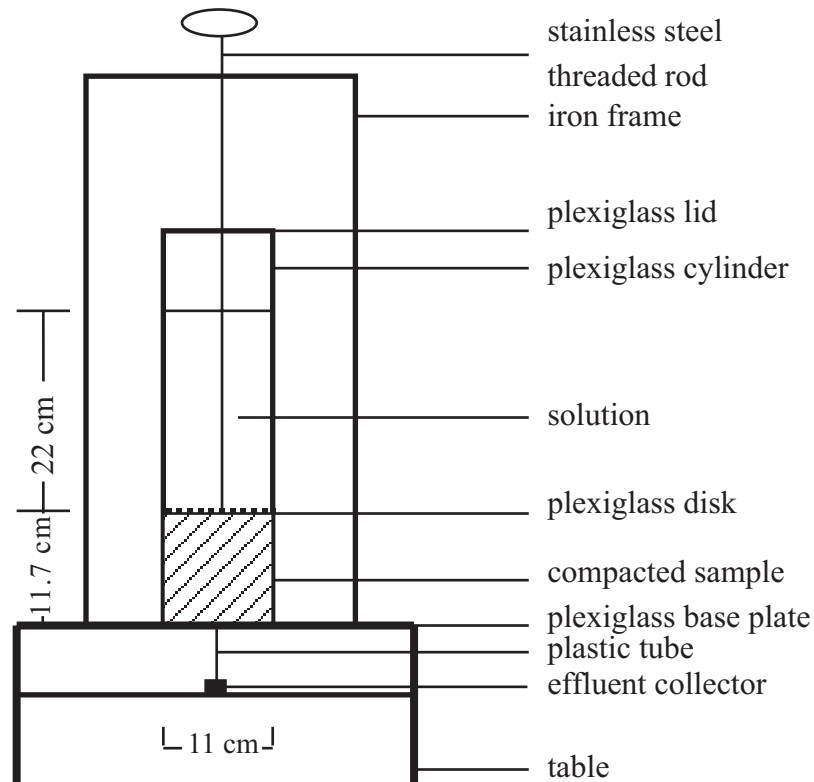


Figure 2. Schematic diagram of the column apparatus.



estimated values of hydraulic conductivity, especially from the Column II experiment, are close to the values determined from triaxial hydraulic conductivity tests ( $0.13 \times 10^{-8}$  cm/s), taking into account particle-size heterogeneities in the material and differences in the applied measurement techniques. This suggests that there was no significant channelling of flow along the sample-plexiglass interface in the case of Column II. Moreover, the results suggest that 94% saturation in the initial stage was maintained during experiments:

$$S = \theta / n_b \quad (= 0.45/0.48) = 0.94$$

where S is decimal degree of saturation,  $\theta$  is volumetric water content, and  $n_b$  is bulk porosity. Therefore, measured volumetric water content could be assumed to represent effective porosity in the experimental clay material.

Mass-balance calculations at the end of the experiments indicate that a recovery of Cd, Cr, Cu, K, Mn, Ni, Pb, and Zn was greater than 97% of their original mass, suggesting that precipitation and/or adsorption losses within the leachate reservoir were insignificant. In Fe mass calculations, 77% of the original mass was recovered, suggesting Fe precipitation within the reservoir. Inferred precipitation was observed as yellow precipitates in the reservoir.

The mass-transfer equation was solved for different values of  $D_h (=D_e)$  for each ion until the match was obtained between observed and theoretical concentrations in the source solution as a function of time using known parameters  $\rho_b$ ,  $v_s$ ,  $n_e$ ,  $K_d$ , and source-solution concentrations. Freundlich nonlinear sorption isotherms were used to calculate equivalent linear distribution coefficients by an iterative technique (Rowe *et al.* 1994). The mass-transfer equation was solved using the POLLUTE software of Rowe *et al.* (1994). A finite-mass top boundary condition was used in the calculations. The source concentration in the reservoir,  $c_R(t)$ , 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 compacted sample, and the mass flux across the boundary between the reservoir and the compacted sample. This boundary condition is expressed by Rowe *et al.* (1994) as

$$c_R(t) = c_0 - 1/(H) \int_0^t f_R(t) dt$$

where H is the height of solution (representing leachate) in the reservoir calculated as the volume of solution divided by the cross-sectional area of the compacted sample, perpendicular to the direction of diffusion.  $f_R(t)$  is the mass flux into the compacted sample at time t. A zero flux bottom boundary condition was adapted for cases where there was no effluent flow into the collection bottle. In the case of advective flow conditions, the bottom boundary was specified as fixed outflow (Rowe *et al.* 1994). Concentration in the collector  $c_B(t)$  at any time t can be expressed as

$$c_B(t) = \int_0^t (f_B(t) dt) / (n_b h) - \int_0^t (v_a c_B(t)) / (n_b h) dt$$

where  $f_B$  is the flux into the collector plate at time t,  $n_b$  is the porosity of the polyethylene collector plate, h is the thickness of the polyethylene collector plate, and  $v_a$  is the advective (Darcy) velocity of flow through the sample.

Similar effective diffusion coefficients were estimated from the data of the Column I and Column II experiments. The determined coefficients for Cl, Cd, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn were ( $\text{cm}^2/\text{year}$ ): 300, 80, 70, 90, 70, 250, 97, 50, 100, 80, respectively. Theoretical concentrations (triangle) calculated in the reservoir using these effective diffusion coefficients are compared with the experimental concentrations (square) in Figure 3 where a line was drawn using theoretical simulation values. Correlation coefficients between experimental and theoretical values range from 0.95 to 0.99. Since similar effective diffusion coefficients were determined, only Column II results are presented in the figure (except for chloride) to illustrate the similarity. The variation in the effluent concentrations (circle) with time is also plotted in Figure 3.

Because averaging of concentration occurred in the collection bottle during the periods between sampling, the observed effluent concentration does not represent the true outflow concentration from the clay. Therefore, the effluent-concentration data were not analyzed quantitatively, only considered during mass-balance calculations. Nevertheless, the last measured effluent concentrations are qualitatively consistent with base pore-water concentrations.

Theoretical concentrations (triangle) calculated in the pore water using the estimated effective diffusion coefficients are also compared with experimental pore-water concentrations (filled square) in Figure 4 where the

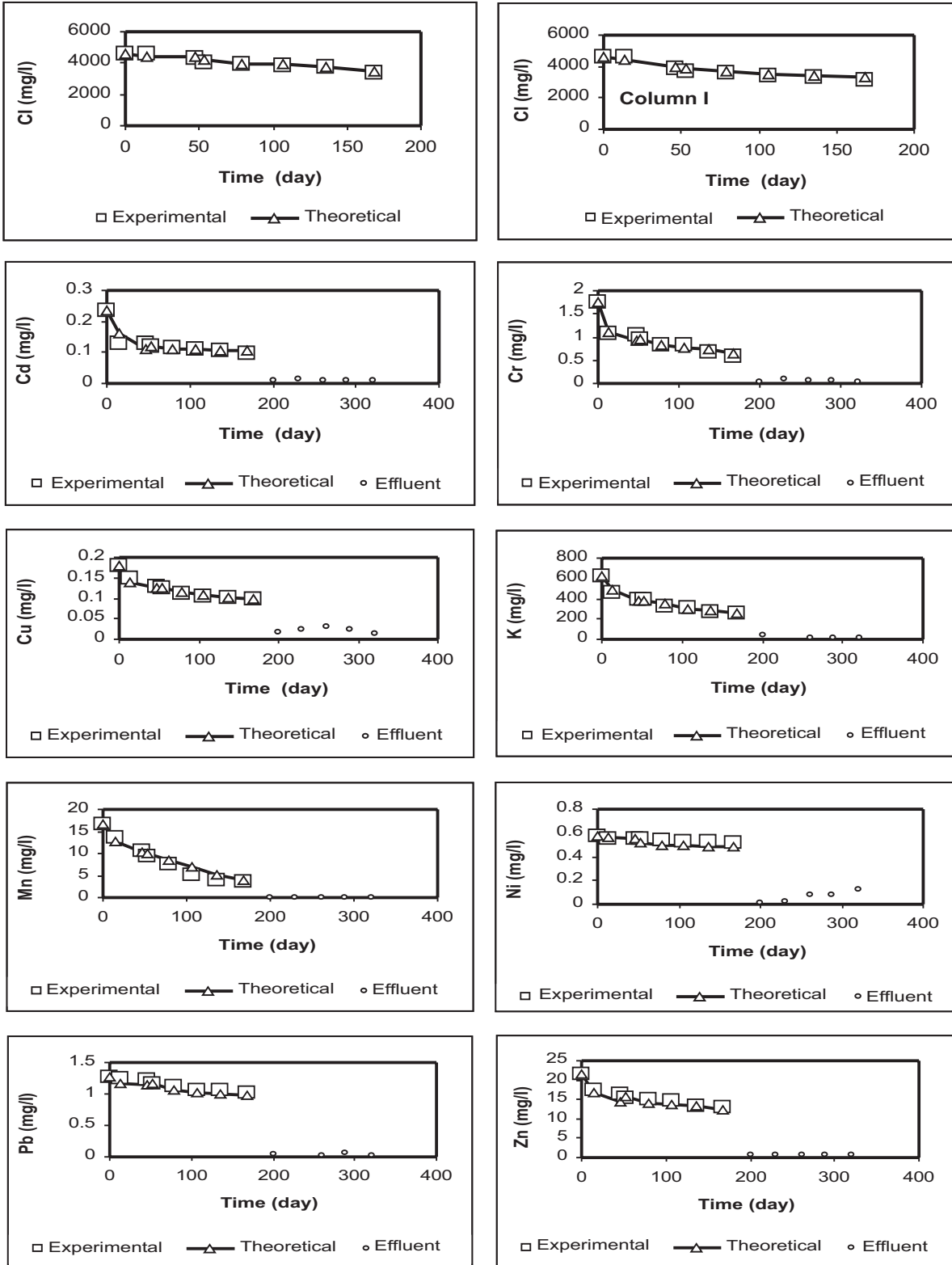


Figure 3. Comparison of experimental (square) and theoretical (triangle, line) concentrations in the reservoir. Circle: Effluent concentration.



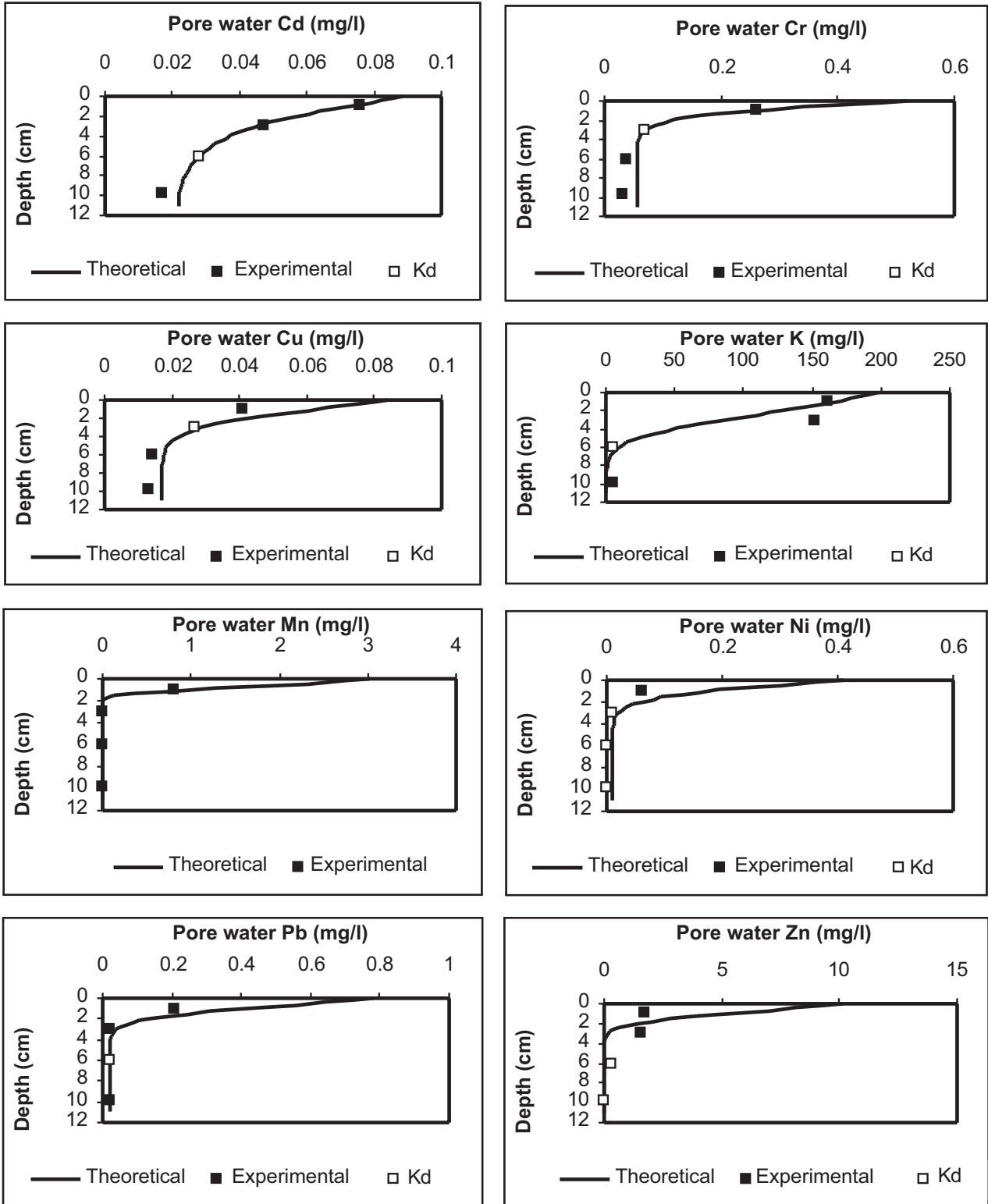


Figure 4. Comparison of experimental (square) and theoretical (line) concentrations in the pore water (at 320.74 day).

line was drawn using theoretical simulation values. Because the amount of extracted pore water from each compacted clay section was quite small, it was not possible to obtain concentration values for all ions. As a result, some pore-water concentrations (open square) shown in Figure 4 were calculated using  $K_d$  equations from the known sorbed amount. Note that although some pore-water concentrations appear to be zero in the figure due to scale, they are not zero, as shown in Table 5. Concentrations determined from the clay are given in Figure 5.

## Discussion

Mass transfer of different ions in soils is affected by ionic radius, ionic charge, presence of other ions, etc. All these factors are incorporated into the determined effective diffusion coefficients and should be manifested in tortuosity (ratio of effective diffusion coefficient to free solution diffusion coefficient). The tortuosity factor of non-reactive Cl is about 0.47 based on the free solution diffusion data of Li & Gregory (1974). This factor varies between 0.34 and 0.45 for the other ions.

During data evaluation, it was assumed that the porosity determined from volumetric water content was available for ion transfer, representing the effective porosity. Actual effective porosity would be lower if some pore water was not involved in the flow regime. To test this possibility, we calibrated effective diffusion coefficients from experimental data at lower porosity values (e.g., 0.32, 0.15). The calibrated values were close to those determined using a porosity of 0.45. These tests suggest that the differences between the actual effective porosity and volumetric water content porosity do not significantly affect the results of the method and materials used in this work for the determination of effective diffusion coefficients.

Because similar effective diffusion coefficients were obtained from both the Column I and II experiments, the effect of advective velocity or dispersion seems to be negligible under compaction conditions applied to the experimental material. Note that Column II represents zero flux conditions from compacted clay to the collection bottle (similar to pure diffusion experiments), but Column I represents partially fixed outflow velocity conditions (advective-dispersive experiment). As a result, the estimated hydrodynamic dispersion coefficients can be accepted as effective diffusion coefficients.

Previous workers have shown that diffusion coefficients depend on the properties of both material (pore size, cation exchange capacity etc.) and solution (binary, multiple, composition etc.). For example, effective diffusion coefficients for chloride from single salt solutions using intact clay soils as reported in the literature range from 180  $\text{cm}^2/\text{year}$  to 200  $\text{cm}^2/\text{year}$  – lower than the 300  $\text{cm}^2/\text{year}$  value determined in this study. However, Barone *et al.* (1989) reported that in multiple solutions, the Cl diffusion coefficient is about 25% higher than that of binary solutions. They also reported that diffusion coefficients of Na (changing from 176  $\text{cm}^2/\text{year}$  to 145  $\text{cm}^2/\text{year}$ ) and K (changing from 237  $\text{cm}^2/\text{year}$  to 190  $\text{cm}^2/\text{year}$ ) are about 20% lower in multiple solutions. These results suggest that the diffusion coefficient of ions – even that of a conservative chloride ion – depends on the nature of the source solution. Therefore, reported effective diffusion coefficients in the literature are not directly comparable to the coefficients obtained in this study.

To check the dominant mass-transport process in the experimental liner, 20 years of mass-transport theoretical simulations were carried out using a 1000 mg/l constant Cl source concentration on top of a one-meter-thick liner (made of the experimental clay material). The simulations

Table 5. Concentrations (mg/l) in pore water.

Depth	1–2 cm	2–4 cm	4–8 cm	8–11.7 cm
Cd	0.076	0.047	0.028	0.017
Cr	0.260	0.070	0.037	0.032
Cu	0.041	0.027	0.014	0.013
K	160.7	151.4	6.000	4.960
Mn	0.800	0.007	0.004	0.003
Ni	0.060	0.01	0.001	0.001
Pb	0.205	0.022	0.020	0.019
Zn	1.700	1.600	0.300	0.010

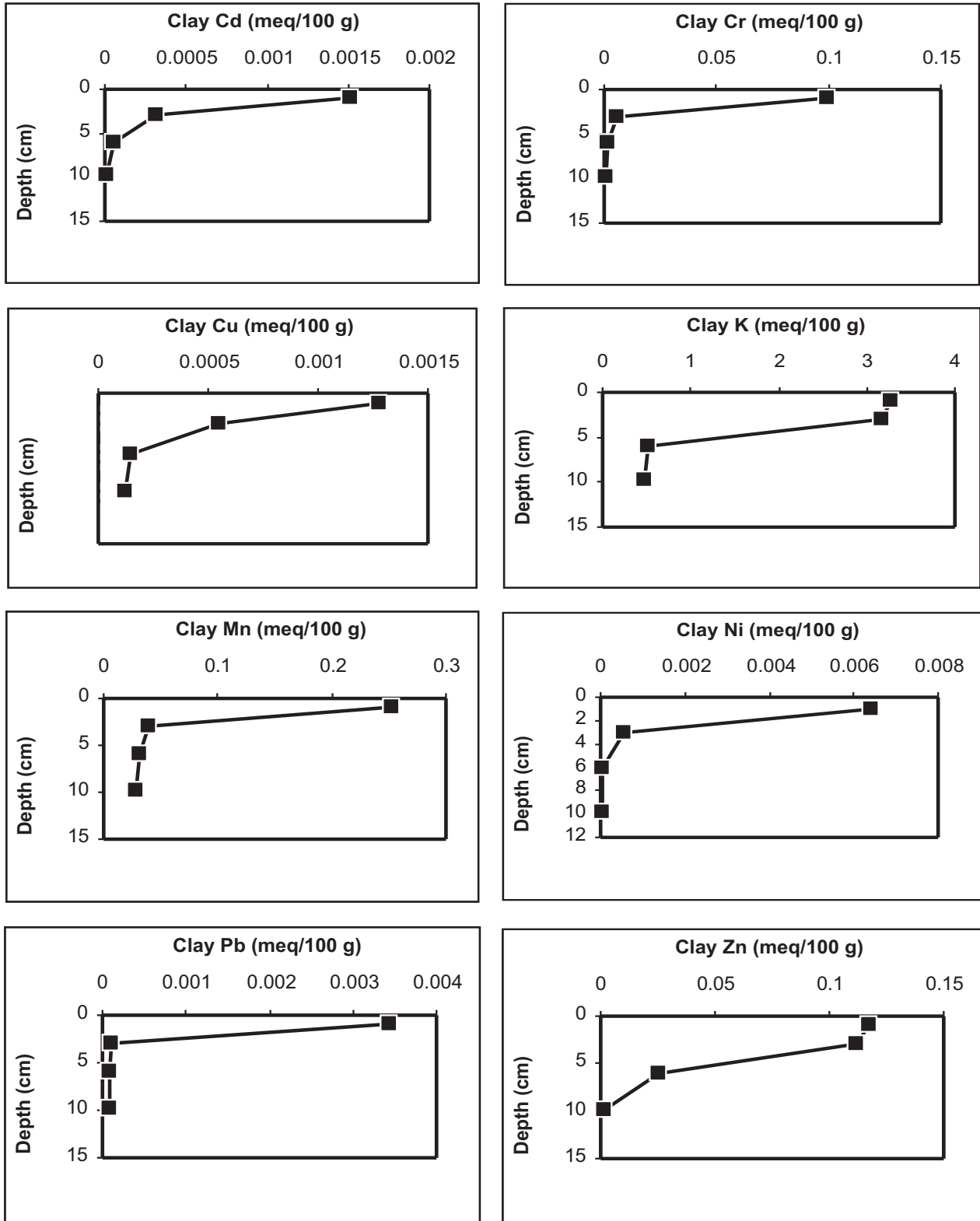


Figure 5. Distribution of concentrations in the clay (at 320.74 day).

were performed for two cases: (1) advective transport only ( $V_a = 0.78 \times 10^{-8}$  cm/s,  $D_h = 0$  cm<sup>2</sup>/s); and (2) diffusive transport only ( $V_a = 0$ ,  $D_h = 9.51 \times 10^{-6}$  cm<sup>2</sup>/s). Results of the advective simulation indicated that even after 20 years, non-reactive Cl concentration would be zero mg/l below about 0.25 m of liner. On the other hand, the diffusion simulation indicated that Cl concentration would be about 70 mg/l at a depth of one meter after only five years. These results indicate that chemical diffusion is the dominant transport process in the Ankara clay liner and should be taken into consideration.

Similar simulations which were performed for heavy-metal ions, assuming a constant 100 mg/l source concentration, suggested that migration of these ions is restricted to the upper sections (0–0.2 m) of the clay liner even after 20 years. Similar results were observed in studies of copper, lead, zinc and iron migration in an *in situ* natural clay barrier below a domestic landfill (Quigley *et al.* 1987b). They determined that these ions are restricted to the upper 0.1–0.2 m of the clay after a 16-year period. Heavy-metal cations are apparently retarded by chemical reactions (cation exchange) with clay. These

simulation results suggest that diffusive transport of heavy-metal ions in the liner consisting of Ankara clay would be quite limited.

In conclusion, the diffusion coefficients estimated in this study incorporate extremely complex processes. Our results show that diffusion is the dominant mass-transport mechanism in the Ankara clay liner. Due to sorption processes, heavy metals would have much lower concentrations than those present in a source, and their distribution will be limited to short distances in clay liners. Because diffusion and sorption processes depend on solution composition, mass-transport determinations in clay liners require case-related studies using multicomponent systems similar to those presented herein.

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