Batch and Column Experiments to Support Heavy Metals (Cu, Zn, and Mn) Transport Modeling in Alluvial Sediments Between the Mogan Lake and the Eymir Lake, Gölbaşı, Ankara

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Batch and Column Experiments to Support Heavy Metals (Cu, Zn, and Mn) Transport Modeling in Alluvial Sediments Between the Mogan Lake and the Eymir Lake, Gölbaşı, Ankara

by E. Dişli

Abstract

This article describes laboratory batch sorption and column transport experiments that were conducted using heterogeneous alluvial sediments with a wide physical characteristic from wells, located between Lake Mogan and Lake Eymir, Gölbaşı, Ankara. The batch sorption experiment was conducted in two separate systems, that is, single and multicomponents. Single batch experiment was performed to determine equilibrium condition between the heavy metal ions and the soil adsorption sites. The sorption isotherms data from multibatch experiments were used to calculate the sorption parameters. Single batch experiment indicated that equilibrium was attained within 9 days from the start of the sorption test. As a result of multicomponents batch experiments, for Zn and Mn, the sorption process was well described by the Freundlich or Langmuir isotherm model, whereas sorption of Cu was better described by the linear isotherm model. The K_d of Cu were found to be highest in soil 1 (32550.350 L kg^{-1}) and lowest in soil 5 (18170.76 L kg^{-1}). The maximum and minimum sorption capacity values for Zn were found to be in soil 1 (10985.148 mg kg^{-1}) and in soil 2 (8597.14 mg kg^{-1}) units, respectively. [Correction added after online publication 15 July, 2010: In the preceding sentence, the words "minimum" and "maximum" were initially switched.] Similarly, soil 1 (7587.391 mg kg^{-1}) and soil 5 (4908.695 mg kg^{-1}) units provided the maximum and minimum values for Mn. In the column experiments, flow and tracer transport was studied under saturated conditions using conservative tracer to determine the transport parameters. Transport parameter values were obtained by curve-fitting using the nonlinear least-squares optimization code CXTFIT. Results of the column experiments indicated that the dispersivity values obtained for soil samples were in the range of 0.024 to 1.13 cm.

Introduction

Water and soil pollutions with inorganic and organic contaminants are caused by human activities such as metal mining and smelting, industrial and energy production, land application, waste disposal practices, or by accident. The movement of these contaminants through soil or surface water to groundwater is affected by many variables, including properties of the contaminant itself, soil conditions, interaction between water sources, and climatic factors. Especially, heavy metal pollution has raised serious environmental concerns worldwide because bio-accumulation of these elements beyond the tolerance thresholds of living organisms poses long term risk to the earth's ecosystem and human health (Voegelin et al. 2003; Han et al. 2001). Protection of human health and ecosystems rely on the ability to predict the transport and distribution of contaminants in ground and groundwater system. A sound and reasonable prediction of the transport of contaminants of concern in groundwater or geological environments depends deeply on reliable and valid transport-related parameters. To reach this end, either batch or column methods are frequently conducted in the laboratory to estimate transport-related parameter such as sorption and desorption rates and dispersivity.

The column and batch experiments are conventionally used to estimate model parameters describing the sorption-desorption and transport behavior of contaminants in soils, sediments, and aquifer materials. Batch experiments are carried out by adding certain amount of solid into solution containing specific concentration of contaminants with a specific

solid/liquid ratio. The results of batch experiments showed that the factors controlling exchange between heavy metal in the solution and the soil particles were: soil type, metal speciation, metal concentration, soil pH, solid:solution mass ratio, multiple ions in the solution (interacting ions), and contact time. Among them soil pH has the greatest effect of any single factor on the solubility or retention of metals, with a greater retention and lower solubility of metal cations which occurs at high soil pH (Martinez et al. 2000). The mobility of most heavy metals in the soil and subsoil depends on the physico-chemical properties of the solid and liquid phases (Fic et al. 1989). In the presence of multiple ions, competition between the metallic ions for adsorption sites occurs (Phadungchewit 1990), affects sorption in soil and consequently, gives rise to difficulties in assessing the process (Murali and Aylmore 1983). The preferred soil adsorption of one heavy metal over another species is called selective adsorption, and it is dominantly influenced by the ionic size of heavy metals (Elliott et al. 1989). Ionic size and ionic charge, as well as hydrolysis properties of the selected heavy metals are known to influence the sorption of metals to soil surfaces (Adriano 2001). Gomes et al. (2001) have shown that heavy metal selectivity sequences varied among soils but the most common sequence was Cr > Pb > Cu > Cd > Zn > Ni, with Cr and Zn exchanging places with Pb and Cd, respectively, for some soils. Basta and Tabatabai (1992), who obtained competitive sorption isotherms of Cd, Cu, Ni, Pb, and Zn as a function of pH for two soils, found that competition was enhanced as the initial metal concentration increased. In general, metal affinity for both soils was: Pb > Cu > Ni ≥ Cd ≈ Zn. The migration rates of heavy metals through landfill liners vary according to their cation hydrated radius, mobility pattern and interactions, their ability to form inorganic and organic complexes, and their retention mechanisms (Yong et al. 1992). Specific sorption involves the exchange of heavy metal cations with surface ligands to form partly covalent bonds with lattice ions and has been used to explain why soil colloids can sorb heavy metals in concentrations greater than their cation exchange capacity (Alloway 1995). The proportion of heavy metals involved in specific (and nonspecific) interactions increases with increasing pH (Naidu et al. 1994). McDonald and Evangelou (1997) indicated that the solid-to-solution is a critical experimental parameter for estimating K_d in the solid-liquid system. Heavy metal adsorption to soils is often described by the Freundlich approach (Hooda and Alloway 1998). Selim et al. (1996) have stated that the term "retention" or the commonly used term "sorption" should be used when the mechanism of solute removal from solution is unknown, and the term "adsorption" should be used only to describe the formation of solute-surface site complexes.

The dependence of dispersivity on the travel distance or lengths of porous media have been reported by Wierenga and Van Genuchten (1989), Pickens and Grisak (1981), and Gelhar et al. (1992). Theis (1963) realizes that the variations in dispersivity values under field conditions could be due to the wide variations in hydraulic conductivity and flow velocity through aquifers. Fired et al. (1972) obtained equal values for dispersivity under laboratory and field conditions and concluded that travel distance has no effect on dispersivity of porous media. Sudicky and Cherry (1979) from field studies found that dispersivity for chloride increased with mean travel distance in the groundwater flow zone. Wierenga and Van Genuchten (1989) arranged 30 and 60 cm long columns filled with sandy loam soils and found the average dispersivity values for tritium and chloride in the shorter column equal to 0.80 and 0.87, respectively. Gelhar et al. (1992) investigated 104 dispersivity values obtained from 59 different locations and found dispersivity values in the range of 10^{-2} to 10^{-4} m for scale in the range of 10^{-1} to 10^{5} m.

The aim of this study is to identify and describe relevant mechanisms determining the transport of reactive carriers and contaminants in the heterogeneous alluvial deposits aged Quaternary between Mogan Lake and Eymir Lake. The study is based on two types of experiments: batch and column experiments performed in laboratory conditions. These experiments were conducted to investigate the relationships between measured soil physical parameters and transport parameters (distribution coefficient, dispersivity) that most interfere in the fate of three heavy metals (Cu, Mn, and Zn). Batch experiments were performed to study the chemical equilibrium state of the soil/solution system under static conditions. Lastly, flow and tracer transport was studied under saturated conditions using conservative tracer (Dişli 2007, 2008).

Materials and Methods

Soil Samples and Analytical Methods

This study was conducted in Gölbaşı province, about 20 km from Ankara, Turkey. The site of this study area lies between longitudes 32°46′30″ and 32°49′30″E and latidudes 39°44′40″ and 39°47′45″N (Figure 1). The studies were carried out using the soil samples which were collected at 10 sites in different locations from alluvial deposition aged Quaternary between soil surface and about 950 m above MSL (mean sea level) and analyzed for grain size distribution, organic material (OM), specific surface area (SSA), and other hydraulic parameters. All these parameters of soils were determined following the guidelines provided by ASTM (1997). The soil particle size distribution was determined by hydrometer and sieve analyses. Silt and clay sized fractions were determined by hydrometer. Total porosity was calculated using the bulk density of undisturbed samples and the average particle density as $n = 1 - (\rho_b/G_s)$ where ρ_b is the bulk density and G_s is the sediment density. Soil pH was measured in 1 : 5 (v/v) ratio of soil and water suspension after the soil suspension had been equilibrated at room temperature (24 ± 1 °C) for 10 min by hand. In the laboratory, the saturated hydraulic conductivity K was determined by the constant head method.

Specific Surface Area of Soil

The specific surface area of a soil sample is the total surface area contained in a unit mass of soil. Soils with high specific surface areas have high water holding capacities, more adsorption of contaminants, and greater swell potentials.

In this study, soil surface area (SSA) was calculated using the following formula prescribed by TSE (1985):
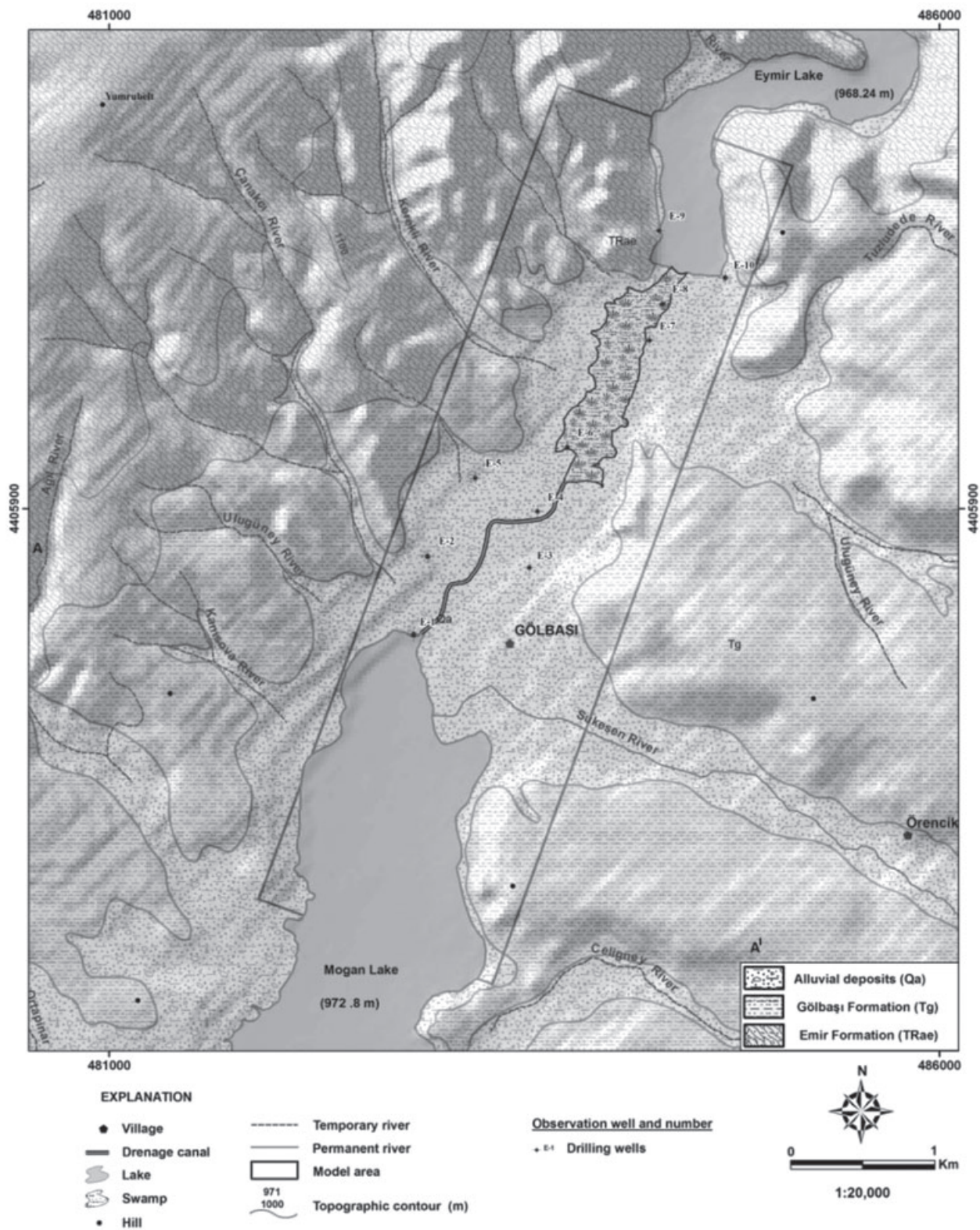
Figure 1. Sampling locations between the Mogan Lake and the Eymir Lake in Gölbaşı County (Ankara, Turkey).

$$S = Kx \frac{e^{3/z} x t^{1/z}}{dx (1-e) x \eta^{1/z}} \qquad (1)$$

where SSA is the specific surface are of the soil (L^2M^{-1}); K, is the constant of the device (20.436); e is porosity (L^3L^{-3}), t is the measured time of flow (T); η is the viscosity of air

(poise) at the experiment temperature and d is the density of the cement sample (ML^{-3}).

Determination of the Cation Exchange Capacity

The cation exchange capacity (CEC) of a soil is simply a measure of the quantity of sites on soil surfaces that

can retain positively charged ions (cations) by electrostatic forces. CEC is an important soil property that is required in soil databases (Manrique et al. 1991). CEC is used as an input data in soil and environmental models (Keller et al. 2001). There are numerous methods for determining CEC and many will give quite different results. Although CEC can be measured directly, its measurement is difficult, expensive, and time-consuming, and pedotransfer functions can provide an alternative by estimating it from more readily available soil data (Amini et al. 2005). So far many of the pedotransfer functions have been developed to predict various soil properties. MacDonald (1998) developed two pedotransfer functions to predict soil CEC based on soil organic carbon (OC) and clay (CL) as CEC = 2.0 OC + 0.5 CL and CEC = 3.8 OC + 0.5 CL for Quebec and Alberta soil state in Canada, respectively.

In this study, two different methods were used to calculate CEC capacity of the soil samples, that is, the method of ammonium acetate and pedotransfer function. The method of ammonium acetate used for determination of the CEC capacity of soils was carried out as described by Dohrmann (1997). The sample is first ammonium exchanged, then the ammonium ions in the supernatant are deprotonated into ammonia with sodium hydroxide solution and determined by distillation into a known amount of acid and which is backtitrated (Kjeldahl-method). In the second method, pedotransfer function, which was developed by Fooladmand (2008), was used to predict soil CEC based on soil OC, CL and sand (S) as CEC = 8.501 + 0.078 × CL − 0.073 × S + 1.693 × OM, where CEC is the cation exchange capacity (cmol kg^{-1}), C is clay content (%), S is sand content (%), and OM is soil organic matter content (%).

Batch Sorption and Column Experiments

The batch sorption experiments were generally conducted to determine the relationship between adsorbent and adsorbate by varying the amounts of adsorbate, both at equilibrium and as a function of time. In this study, the sorption parameters (distribution coefficient, K_d; Freundlich [K_F] and Langmuir [K_L] coefficient) of Cu, Zn, and Mn in six different soil samples taken from alluvial deposits aged Quaternary were studied by means of batch tests. The test was conducted in two separate systems, that is, single and multicomponent solutions at constant temperature (24 ± 1 °C) in the laboratory condition. As anticipated, the amount of metal adsorption was determined by the sorption capacity of the soil, and the selectivity of this soil for different metal ions. In the batch test, in all cases, the rate of metal removal was relatively rapid at the beginning because of the greater availability of the soil surface area at the start.

In the single component batch test, sorption competition was tested by measuring Cu sorption alone to determine the time required to achieve equilibrium. In multisolution, all three heavy metals were mixed together (Cu^{+2}, Zn^{+2}, and Mn^{+2}) to study the effect of competition between heavy metals in soil samples. Mixed metal solutions were used rather than single metal solutions to simulate competition between metals for the sorption sites because metal-bearing wastes commonly contain a range of heavy metals. The

experiments were carried out with pH adjustment using very small amounts of nitric acid or sodium hydroxide to simulate measured pH in the boreholes (pH 7.15 ± 0.15). The batch experiments were performed in special 100 mL glass vials capped with a Teflon-coated silicon septum in order to minimize heavy metal loss. All soils were air-dried and passed through a 2-mm sieve. All experimental works were undertaken using the <2 mm size fraction. This size was selected in order to prevent a diffusion limited sorption and to reach equilibrium by making the external surface area to be much larger than the internal surface area (Xu and Wörman 1999).

In order to obtain the sorption capacity, the amount of ions adsorbed per unit mass of adsorbent (S_i) in milligrams of metal ions per gram of adsorbent) was calculated with the following equation:

$$S_i = \frac{\left(C_i - C_{aq}\right) \times V}{W} \qquad (2)$$

where S_i is the amount of contaminant removed from solution (MM^{-1}); C_i is the concentration of contaminant in the solution before mixing with soil (ML^{-3}); C_{aq} is the equilibrium concentration of contaminant left in the solution after the experiment (ML^{-3}); V is the solution volume (L^{-3}), and W is the weight of air-dried soil sample (M). The amount of contaminant removed from solution (S_i) was then plotted with the equilibrium concentration (C_{aq}) to determine the sorption response curves (i.e., sorption isotherms). There are three isotherm models that have been widely used to represent the response curves; namely linear, Freundlich, and Langmuir models. The decision to select the best model is based on the pattern of the sorption curves.

Single Component Batch Experiment

To estimate the time required to achieved equilibrium, solutions with Cu alone with initial concentrations of 10, 20, 30, 40, 50, 60, and 80 mg L^{-1}, were applied to soil 1 (borehole number: E-8, sampling depth from surface: 969.4 to 963.815 m) because of selective adsorption. Seven sets of 0.5 g air dry clay were exactly weighed into 100 mL glass bottles and mixed with 50 mL of each of Cu solutions. And all suspensions were placed immediately in a thermostated water bath. Then the suspensions were shaken manually three times a day (1 min each time) for 7 days and then allowed to equilibrate in the water bath (24 ± 1 °C) with intermittent shaking before sampling. Then 5 mL sample was taken from each solution for analysis after various periods of contact time (0, 90, 265, 1080, 2520, 9985, 12,865, and 15,745 min) to determine sufficient time for equilibrium condition. The initial and final solutions were analyzed with Atomic Absorption Spectrophotometer (Flame Atomic absorption) to determine Cu concentration before and after the batch experiment.

Multicomponent Batch Experiments

In multicomponent (element) batch-equilibrium experiments, all three heavy metals were mixed together (Cu,

Zn, and Mn) to study the effect of competition between heavy metals in soil and to determine the sorption isotherms for Cu, Mn, and Zn metals. A total of 33 batch tests were carried out for six types of soils (e.g., clay, silty clay, and sand) taken from the different depth (Table 1). For this purpose, 0.5 g of air-dried soils has been put into 100 mL glass bottles. Then, 50 mL of a solution containing three metals has been added into the bottle. Eight equilibrating solutions were used to determine the isotherms, and the concentration of each metal in each solution was approximately 10, 20, 30, 40, 50, 60, 80, and 100 ppm. Then all bottles were put into a thermostated water bath (24 ± 1 °C). All bottles were closed with paraffin, and then they were shaken manually for 1 min three times during 24 h to ensure sufficient time for solid-liquid equilibrium to be reached. Initial and final solutions were analyzed with Atomic Absorption Spectrophotometer to determine heavy metal concentrations (Cu, Mn, and Zn) before and after the batch experiment.

Dispersivity in the Column Experiments

In this study, the conservative column tracer experiments were done in order to determine the transport parameters (dispersion and dispersivity) for six different soil samples.

Table 1
Sampling Well and Depth

Well No.	Sample Depth (m)	
E1	973.11	972.11
E1	972.11	970.911
E1	969.51	968.66
E1	968.66	967.686
E2	970.63	963.325
E4	969.12	968.315
E4	968.015	967.715
E4	967.72	965.025
E4	965.03	964.525
E4	964.53	963.686
E7	969.45	966.81
E7	966.81	966.11
E7	966.11	962.9
E7	962.9	961.913
E7	961.253	960.453
E8	969.4	963.815
E8	963.815	962.155
E8	960.315	959.915
E10	967.52	966.85
E10	965.77	965.02
E10	965.02	964.22
E10	964.22	963.37
E10	962.43	961.41

The experiments were carried out in two different Plexiglas cylindrical columns vertically placed. The first column (C1) was 6.6 cm long and had 3.7 cm inner diameters, while the second column (C2) was 9.0 cm long and had 3.7 cm inner diameters (Table 2). The soil column apparatus consisted of the soil column itself, a column support structure, a pressure pump unit which supplies conservative tracer or water to the top of the column, two different storage tank with fill the sodium chloride (NaCl) solution and clean water, a tracer input/output line, output water container, and conductivity meter (EC meter) (Figure 2). In these experiments, NaCl was selected as conservative or nonreactive tracer in all experiments. At the top and bottom of the column, Whatman filter papers (0.7 μm) were used to prevent finest grains from flowing out of the column and to support the soil. The mesh size of the filters is adapted to the particle size distribution

Table 2
Properties of the Two Soil Columns C1 and C2

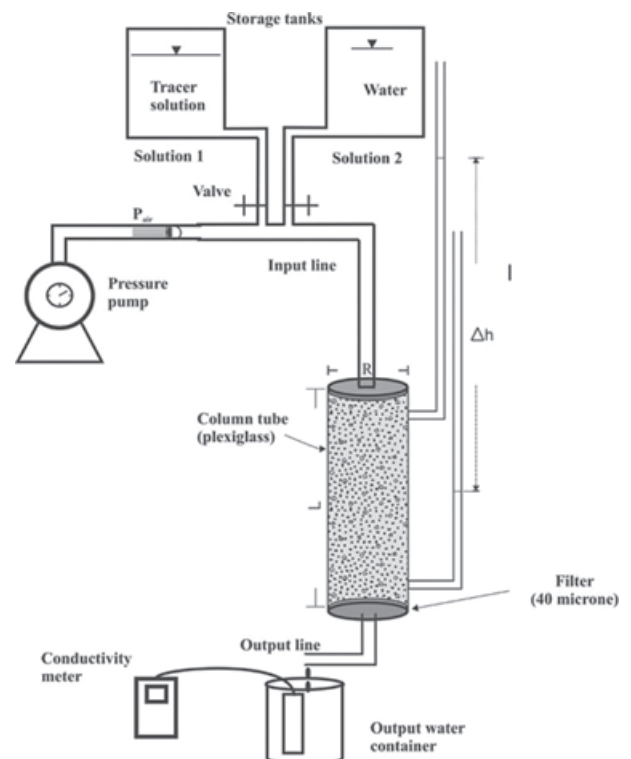|	Soil Column			
	Diameter (cm)	Length (cm)	Area (cm²)	Volume (cm³)
Soil 1	3.7	6.6	10.75	70.93
Soil 2	3.7	6.6	10.75	70.93
Soil 3	3.7	6.6	10.75	70.93
Soil 4	3.7	6.6	10.75	70.93
Soil 5	3.7	9	10.75	96.72
Soil 6	3.7	9	10.75	96.72

Figure 2. Schematic diagram of the soil column apparatus.

of the material tested. All column experiments were conducted at a room temperature of 23 ± 2 °C.

A sample from each soil was uniformly packed in a soil column and then all the soil columns were wet from the top very slowly with water by applying pressure between 1.25 and 2 Pa with pump until they were completely saturated steady-state flow conditions. After the steady state condition was achieved, for each run the conservative (NaCl) solution at concentrations with EC of about 10, 10.22, 10.25, 10.43, and 10.55 µS cm⁻¹ was pumped into the column inlet at a constant flow rate. Then, samples were collected from the start ($t = 0$) of the experiments and the electrical conductivity (EC) of the samples were measured using a pH meter with a glass electrode. The EC of the first sample was the same as that in water. Then, at a constant time interval equivalent to one pore volume for the whole experiment the effluents were collected and their electrical conductivities were measured. The experiments were continued up to the time when the concentration in the final sample reached the initial NaCl concentration. To this end, the column was then flushed with tap water until chemical concentrations in the effluent were reduced to the background level of the tap water. To this end, a series of displacement experiments were carried out, where distilled water was displaced by a weak chloride solution.

Results and Discussion

Soil Characteristics

The physical and chemical characteristics of the soils are summarized in Table 3, which indicates significant differences in the components and properties of the soils (Dişli 2007, 2008). These soils had pH values lay in the alkaline range (8.7 to 9.23), and low organic matter content (0.91% to 3.17%). The particle size distribution of soils exhibits a substantial variation in gravel, sand, silt, and clay contents ranging from 0% to 33.47% for gravel, 51.83% to 64.90% for sand, 12.67% to 72.66% for silt, and 0% to 30.8% for clay. Soil 1 had the highest specific surface area (450.75 m² g⁻¹), but soil 6 showed the lowest one (12.43 m² g⁻¹) .

Cation Exchange Capacity

The CEC values are calculated by ammonium acetate exchange and pedotransfer function are given in Table 3. The CEC values for soils varied from 33.59 to 7.4 meq/100 g for the method of ammonium acetate and varied form 13.85 to 9.99 cmol kg⁻¹ for pedotransfer function. The CEC generally decreased with increasing particle size of the fractions. The sand fraction had the lowest CEC (7.4 meq/100 g).

Batch Sorption Experiment

The sorption of heavy metals from single and multicomponent solutions as a function of their initial concentrations was studied at the constant temperature (24 ± 1 °C). In the batch test, in all cases, the rate of metal removal was relatively rapid at the beginning because of the greater availability of the soil surface area at the start. In the single component batch test, the maximum percent

Table 3
The Statistical Data of the Selected Soil Physico-Chemical Properties of the Studied Soil

Soil number	Sample number	ρ_B (g cm⁻³) Average	Stdev	Gs (g cm⁻³) Average	Stdev	O.M. (%) Average	Stdev	pH (soil/H₂O) Average	Stdev	Clay (%) Average	Stdev	Silt (%) Average	Stdev	Sand (%) Average	Stdev	Gravel (%) Average	Stdev	SSA m² g⁻¹	CEC meq/100 g	CEC1 cmol kg⁻¹
Soil 1	3	1.48	0.15	2.53	0.23	2.42	0.75	9.23	0.67	27.34	4.23	72.66	4.23	0	0	0	0	450.75	33.59	12.62
Soil 2	3	1.68	0.19	2.58	0.08	3.17	0.90	8.70	0.08	24.87	1.94	12.67	0.73	55.79	5.48	6.70	2.46	336.13	23.60	13.85
Soil 3	3	1.64	0.29	2.63	0.17	2.59	1.24	9.10	0.37	30.82	0.49	69.18	0.49	0.00	0.00	0.00	0.00	302.97	27.14	12.91
Soil 4	11	1.78	0.16	2.66	0.19	1.77	1.39	9.15	1.01	0.00	—	37.96	12.85	51.83	3.08	10.20	5.44	21.48	18.45	11.47
Soil 5	7	1.82	0.16	2.61	0.17	1.49	1.55	8.82	0.48	0.00	—	13.81	4.23	57.72	9.19	33.47	11.52	17.03	22.45	10.98
Soil 6	5	1.84	0.09	2.62	0.14	0.91	0.74	8.97	0.45	0.00	—	10.85	1.33	64.90	10.82	24.25	12.66	12.43	7.40	9.99

removal was attained after about 30 min and final equilibrium was reached after 9985 min in all cases (Figure 3). Figure 4 shows that Cu sorption occurred in two steps, that is, 97.61% of sorption occurred within 30 min followed by a very slow sorption up to 99.45% in 9985 min perhaps due to diffusion. After 9985 min, the removal percentage remained constant. As a consequence, most of the sorption is completed after about 9985 min (about 6.9 days) and therefore this time was properly chosen as the reaction time required observing equilibrium-controlled sorption parameters in the batch sorption experiments (Dişli 2007).

The results of applying the linear, the Langmuir, and the Freundlich isotherm models to the experimental values obtained from the multicomponent batch sorption experiments are shown in Figure 5, respectively. Sorption isotherms for these metals by the soils exhibited differences in shape and in the amount retained. The constants (the linear value K_d; the Langmuir values S_{max}, α; Freunlich values K_f, n) derived from these isotherms were calculated and are shown in Table 3, together with the corresponding correlation coefficient.

As results of multicomponents batch experiments carried out under the local chemical equilibrium assumption, for Zn and Mn the sorption process was described generally by the Langmuir and the Freundlich isotherm models whereas the linear model was better suited for Cu, obtaining favorable isotherms. In addition, sorption data of Zn onto
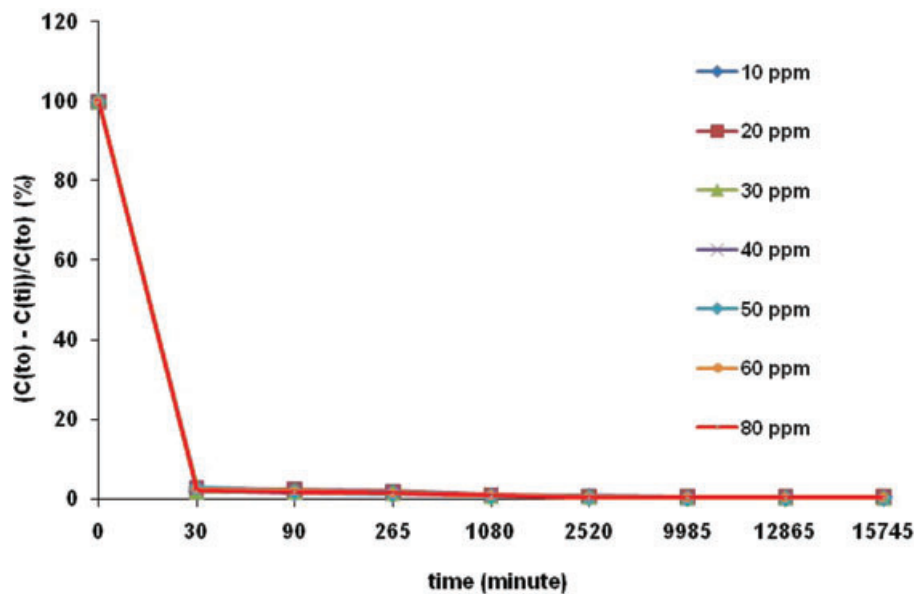

Figure 3. Changes of metal (Cu) solution concentrations over time for various initial concentrations during single component batch test.
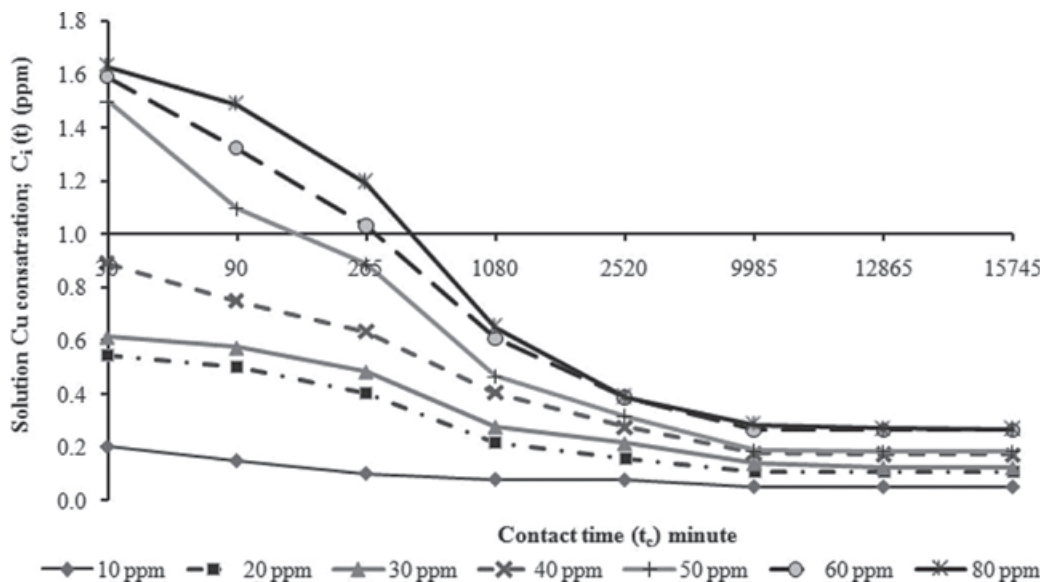

Figure 4. Cu concentration removal from the solution during sorptive uptake.
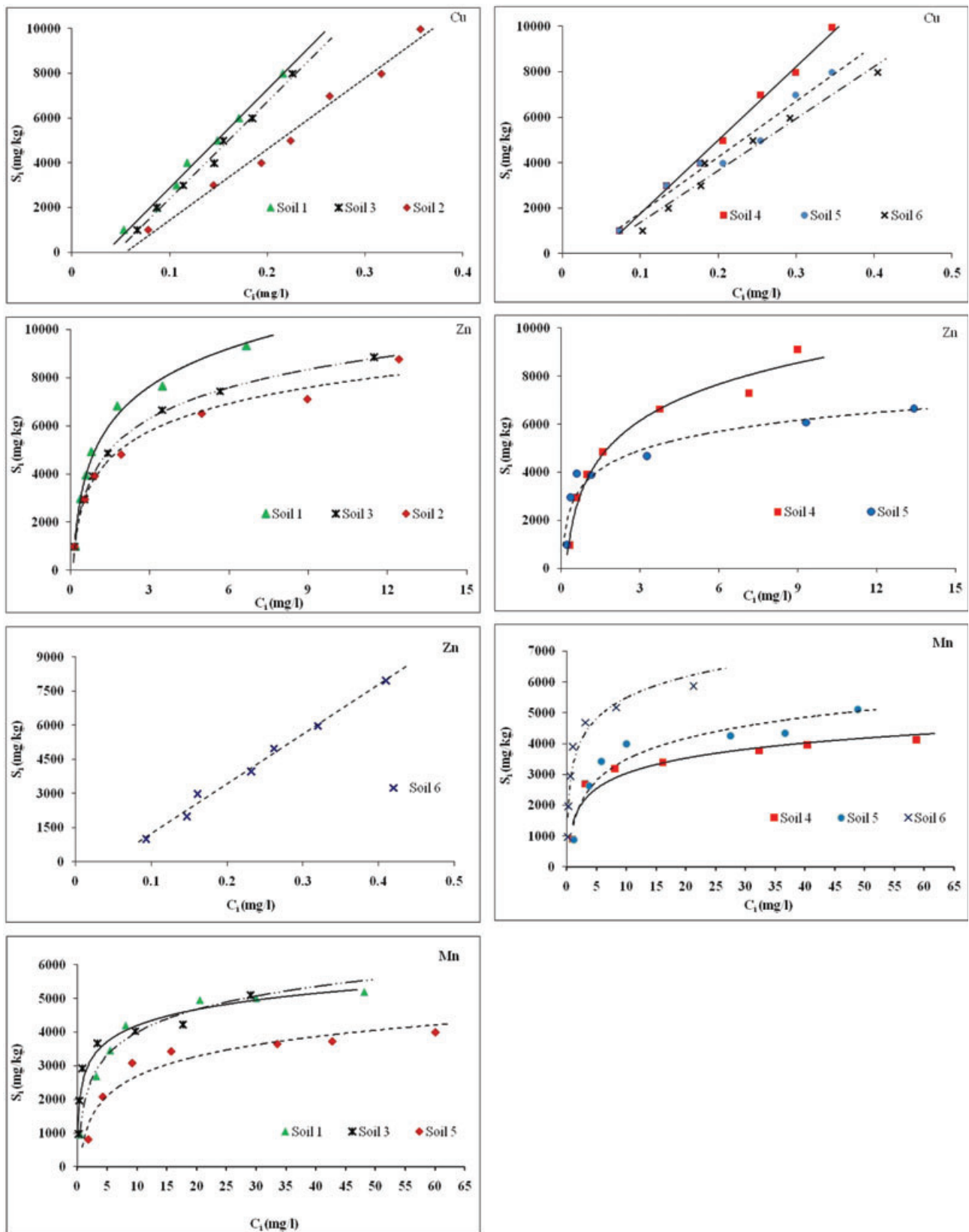
Figure 5. Linear and nonlinear sorption isotherms for the selected metals (Cu, Zn, and Mn) on different soil at pH 7.15 ± 0.15.

sandy soil were described by the linear isotherm model. The correlation coefficients (r) were better fitted to the Langmuir equation than the Freundlich equation with r values ranging from 0.955 to 0.998 (Table 3). The adsorption selectivity sequence of the heavy metals by the studied soils was derived based on isotherm parameters values and shown in Table 4. According to these values in Table 4 metal adsorption affinities to the studied soils can be arranged in the following relative adsorption sequences: Cu > Zn > Mn for six different soils.

Table 4

Isotherm Parameters and Statistics for Selected Heavy Metals, Sorption from Multicomponent Solutions at pH 7.15 ± 0.15

Soil Type	Heavy Metal	Number of Samples	Linear Equilibrium Isotherm K_d (L kg^{-1})	r	Langmuir Nonlinear Equilibrium Isotherm S_{max} (mg kg^{-1})	α (L mg^{-1})	r	Freundlich Nonlinear Equilibrium Isotherm N	K_f (L kg^{-1})	r	Selective Sequence
Soil 1	Cu	3	32550.35	0.925							
	Zn	3			10985.148	0.807	0.98	0.236	5876.246	0.97	Cu > Zn > Mn
	Mn	3			7587.391	0.513	0.985	0.36	3086.978	0.94	
Soil 2	Cu	2	21602.29	0.935							
	Zn	2			8597.14	1.075	0.978	0.28	4300.32	0.975	Cu > Zn > Mn
	Mn	2			5267.564	0.4	0.994	0.318	1938.032	0.872	
Soil 3	Cu	3	25828.62	0.925							
	Zn	2			9559.206	1.4	0.982	0.302	4625.576	0.99	Cu > Zn > Mn
	Mn	2			5083.984	0.518	0.989	0.282	2049.71	0.85	
Soil 4	Cu	5	24403.03	0.958							
	Zn	2			10730.383	0.62	0.955	0.404	4373.631	0.935	Cu > Zn > Mn
	Mn	4			5733.185	0.292	0.987	0.378	1596.464	0.953	
Soil 5	Cu	7	18170.76	0.95							
	Zn	6			8963.366	1.316	0.98	0.291	5310.624	0.89	Cu > Zn > Mn
	Mn	6			4908.695	0.295	0.987	0.364	1391.294	0.897	
Soil 6	Cu	1	19370.16	0.942							
	Zn	1	18397.29	0.962							Cu > Zn > Mn
	Mn	1			6032.819	1.238	0.998	0.133	3996.449	0.991	

K_d, distribution coefficient; α, Langmuir affinity constant; S_{max}, maximum adsorption capacity of the soil matrix; K_f, Freundlich sorption constant; N, Freundlich exponent, r, correlation coefficient.

In the case of alluvial sediments found for multicomponent solutions, the maximum adsorption capacities (S_{max}) for Zn studied soils varied from 10985.148 and 8597.14 mg kg^{-1} and for Mn from 7587.391 and 4908.695 mg kg^{-1}. For soil 1 the maximum sorption capacity S_{max} was obtained for Zn, that is, 10985.14 mg kg^{-1}, which decreased to 7587.391 mg kg^{-1} for Mn. Similarly, for soil 3, the maximum sorption capacity S_{max} was obtained for Zn, that is, 8963.366 mg kg^{-1} which decreased to 5083.984 mg kg^{-1} for Mn. The sorption sequence of metal ions on the other alluvial sediments was the same as follows: Zn > Mn (Table 4). The sequence of the maximum adsorption capacity for Zn was: soil 1 > soil 4 > soil 3 > soil 5 > soil 2; for Mn was: soil 1 > soil 6 > soil 4 > soil 2 > soil 3 > soil 5. The bonding energy coefficient (α) varied with soil type and metal solution and all soils showed greater affinity for Zn than Mn (Table 4). Higher bonding energy coefficient values have been related to specifically sorbed metals at high energy surfaces with low dissociation constants (Serrano et al. 2005). Lower bonding energy coefficient values appear to be related to sorption on low energy surfaces with high dissolution constants (Ma and Rao 1997). Freundlich distribution coefficients for Zn ranged from 3996.449 to 5876.246 L kg^{-1}, for Mn 1391.294 from 3996.449 L kg^{-1} (Table 4). The sequence of the Freundlich sorption constant (K_f) for Zn was: soil 1 > soil 5 > soil 3 > soil 4 > soil 2 > soil 6; for Mn was: soil 6 > soil 1 > soil 3 > soil 2 > soil 4 > soil 5.

Distribution coefficient (K_d) for Cu ranged from 18170.76 to 32550.35 L kg^{-1} (Table 4). For Zn onto soil 6, K_d was 18397.29 L kg^{-1}. When comparing soils, soil 1 had the highest K_d value. Its high specific surface area and particle size fractions (especially soil 1 and silt) were responsible for the highest sorption capacity among the soils considered. Among the other soils, soil 5 showed the lowest sorption capacity for Cu. The sequence of distribution coefficient was: soil 1 > soil 3 > soil 4 > soil 2 > soil 6 > soil 5 (Table 4). The metal selectivity observed for Cu being higher than those of Zn and Mn might be owing to the physical aspects of the adsorption process. According to different authors, this different behavior between Cu, Zn, and Mn could be explained on basis on ionic properties such as electronegativity and ionic radius. The result trend is also matched with the order of the electronegativity of the metal cations, which is, according to Evans (1989), Cu (1.9), Zn (1.6), and Mn (1.5). This means that Cu ions interact more strongly electrostatically with the surface groups present on the surface of the adsorbent. Another factor, which may determine the adsorption capacity of the

ions is the ionic radius itself, especially, since a smaller ionic radius implies that more molecules can sorb onto a fixed surface area of sorbent. Having in mind, the ionic radius of the three metals ions are 0.72 Å for Cu, 0.70 Å for Zn, and 0.46 Å for Mn (Marcus 1988). The higher affinity of the six soils for Cu is expected at the adsorption sites on the soils.

Relationship Between CEC, SSA, and Sorption Isotherm Parameters

CEC, SSA, and sorption isotherm parameters (K_d, S_{max}, and K_f), are presented in Tables 3 and 4. It was found that K_d, S_{max}, and K_f values was positively correlated with CEC and SSA. Correlations of sorption values for all soil samples used in this study against various soil properties (CEC,

SSA), which greatly affect the sorption of heavy metals, are depicted in Figures 6 and 7. The plot shows good correlations between soprtion isotherm parameter (K_d, S_{max}) and basic soil properties SSA and CEC, with r values higher than 0.73. Correlation coefficients (r) between SSA and K_d, CEC and K_d for Cu metal were 0.85 and 0.73, between SSA and S_{max}, CEC and S_{max} for Zn were 0.78 and 0.77, respectively. However, in all soil sample (Figures 7 and 8) there is weak relationship between SSA and S_{max}, CEC and S_{max}, SSA and K_f, CEC and K_f for Mn⁻ (r = 0.37, 0.15, 0.001, and 0.12).

In order to evaluate the influence of soil properties on the metal sorption capacities, the single correlation coefficients (r) between K_d, S_{max}, and K_f values and the physico-chemical properties of soils were calculated and
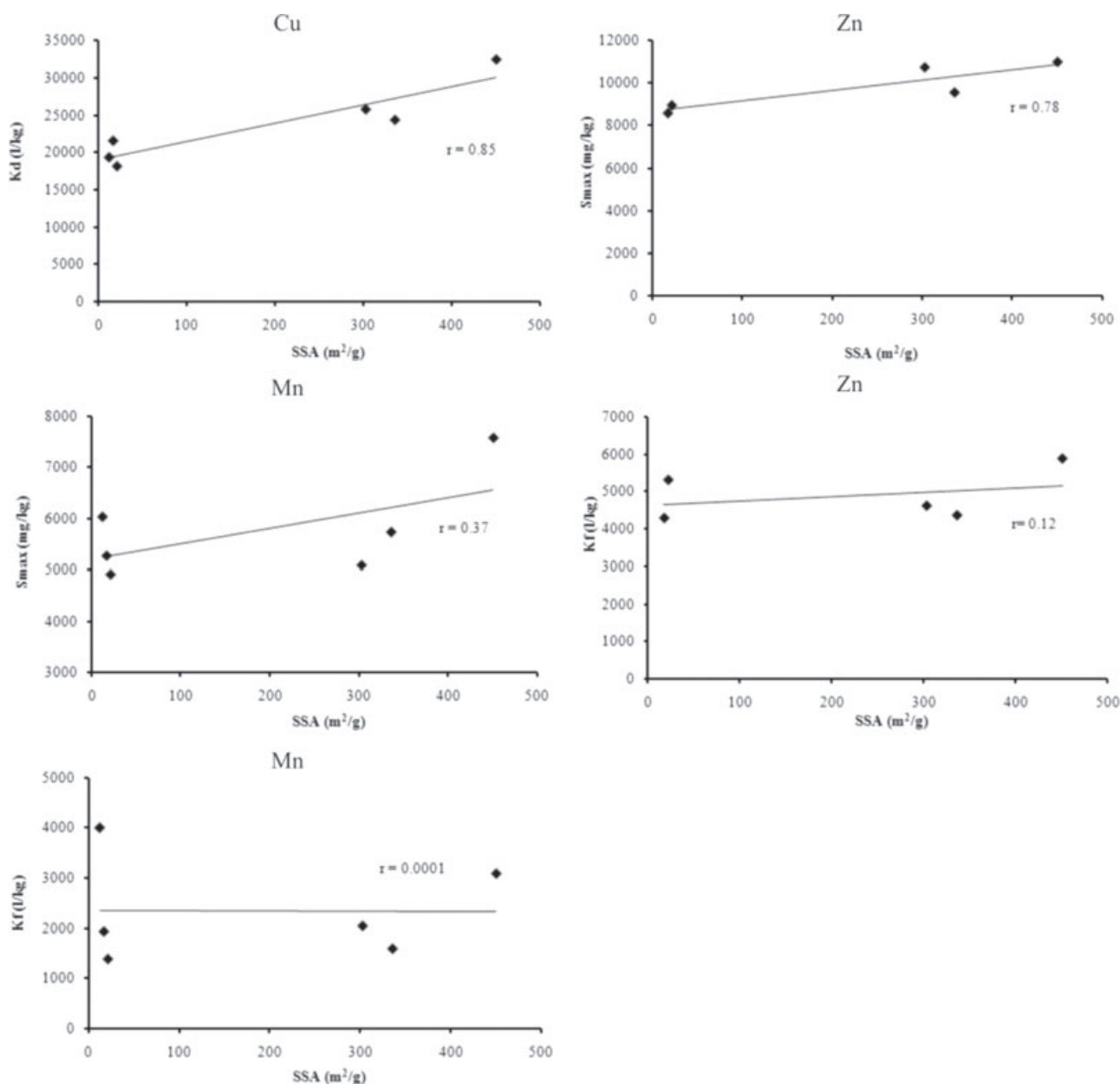

Figure 6. Relationship between SSA with sorption parameters (K_d, S_{max}, K_f) for the different heavy metals.
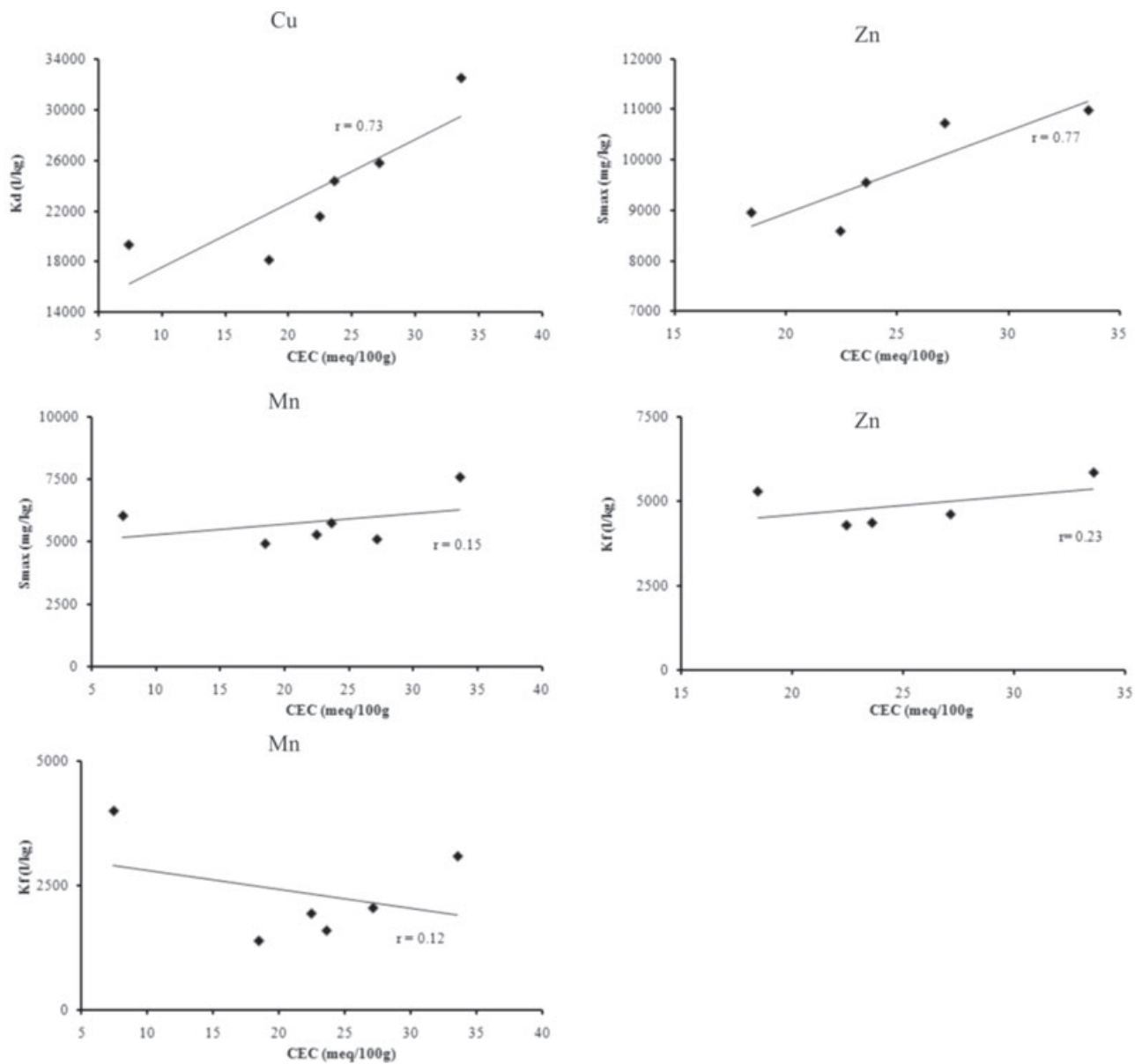
Figure 7. Relationship between CEC with sorption parameters (K_d, S_{max}, K_f) for the different heavy metals.

listed in Table 5. Highly significant positive correlations between the K_d-Cu values and SSA, CEC and S_{max}-Zn were found, indicating that the K_d and S_{max} were influenced mainly by SSA and cation exchange capacity of soils. The results indicated that K_d-Cu was strongly negatively related to Gs—the sediment density (Table 5) and no significant correlation with organic matter was observed. Usman (2008) reported an important factor regulating the adsorption of heavy metals by soils are the type and the amount of soil 1, as well as the CEC. The correlation of the heavy metals with the cation exchange capacity was expected. The CEC is directly related to the capacity of the soil to adsorb heavy metals, since these metals occur as cations adsorbed onto the soil exchange complex. The greater the CEC value, the more exchange sites on soil minerals will be available for metal retention. In general, the soil pH and CEC can be considered as most important factors responsible for the adsorption capacity of soils for heavy metals.

Table 5
Simple Linear Correlation Coefficients (r) Between K_d, S_{max}, and K_f and Selected Physical-Chemical Characteristics of Studied Soils

		K_d-Cu	S_{max}-Zn	S_{max}-Mn	K_f-Zn	K_f-Mn
Soil characteristics	Gs	−.931**	−.306	−.404	−.428	−.404
	O.M.	.636	.656	−.451	−.003	−.451
	pH	.220	.266	.055	.685	.055
	Clay	.801	.449	−.131	.093	−.131
	Silt	.589	.544	−.175	.497	−.175
	Sand	−.712	−.504	.121	−.344	.121
	Gravel	−.599	−.530	.218	−.471	.218
	SSA	.928**	0.518**	.004	.357	.004
	CEC	.829*	.852*	−.377	.420	−.377

**Correlation is significant at the 0.01 level; *correlation is significant at the 0.005 level.

Determination of the Dispersivity

The most general one-dimensional (1D) advection-dispersion equation for a nonreactive solute transport in saturated, homogeneous, and isotropic porous media under steady-state conditions is as follows:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D_L \frac{\partial C}{\partial x}\right) - V_x \frac{\partial C}{\partial x} \qquad (3)$$

where C is the dissolved aqueous concentration (ML^{-3}), varying as a function of time t (T) and distance x (L), V_x is the average pore water velocity (LT^{-1}), D_L is the longitudinal dispersion coefficient (L^2T^{-1}), t is the time, and x is the longitudinal distance in the 1D coordinate system considered. This assumes that mechanical dispersion can be described as a Fickian process, with the fitted dispersion coefficient D (L^2T^{-1}) providing a measure of solute spreading and D is
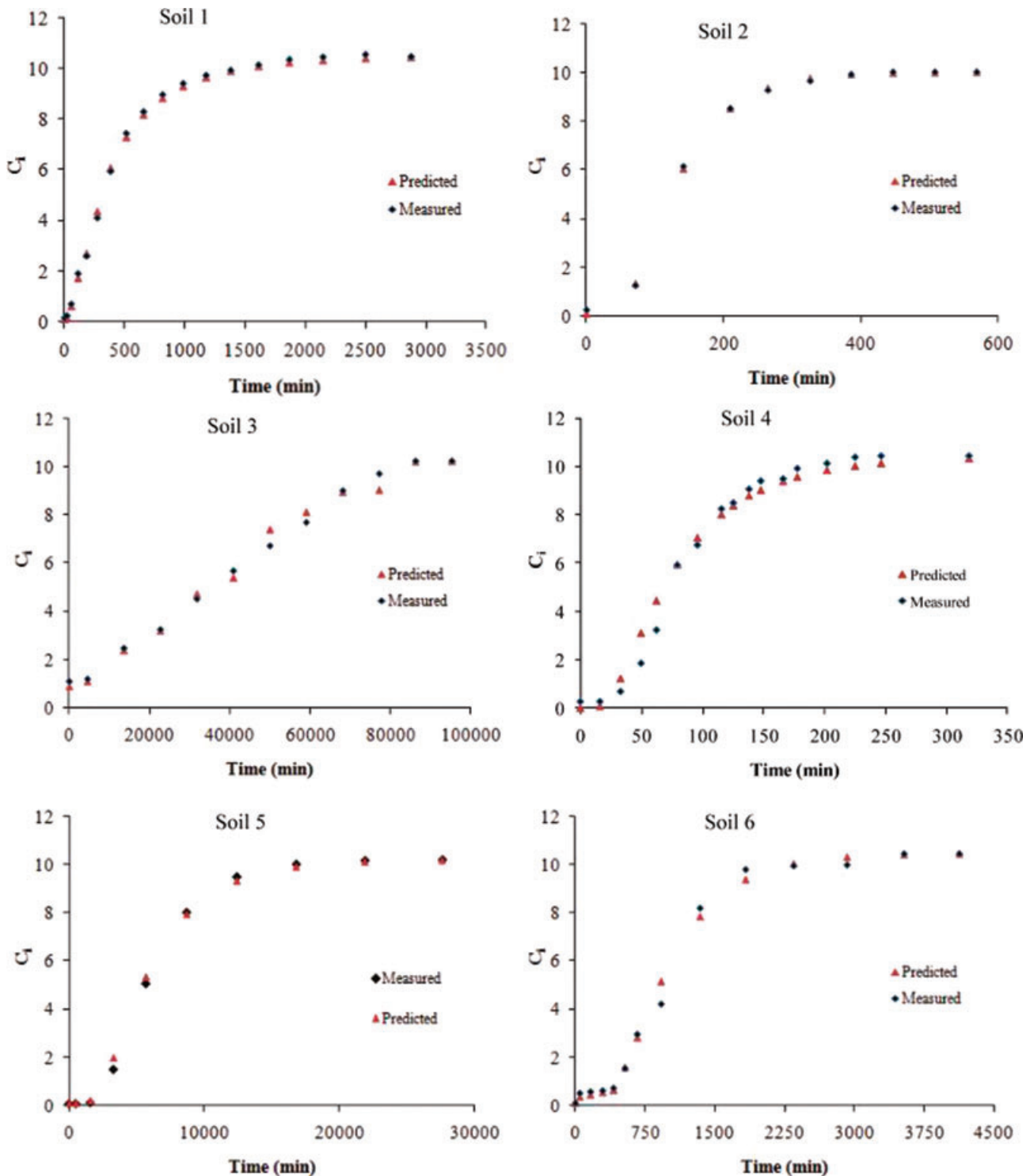

Figure 8. Comparison of measured and predicted chloride breakthrough curves (BTC) for six different soil samples (soil 1, soil 2, soil 3, soil 4, soil 5, and soil 6).

given empirically by $D = \alpha V^n + D^n$ where α is the longitudinal dispersivity (L) and D^* is molecular diffusion coefficient of solute in porous media. At low flow velocities, molecular diffusion is the dominant transport process. As a result, in such cases, the hydrodynamic dispersion coefficient will be equal to the molecular diffusion coefficient ($D \approx D^*$). At high flow velocities, mechanical dispersion process will be the dominant process and $D = \alpha_L^{V}$

The initial and boundary conditions used for the solution of Equation (3) are:

$$C(x, 0) = 0, x > 0$$
$$C(0, t) = C_{imp}, t \geq 0$$
$$C(\infty, t) = 0, t \geq 0$$

where C_{imp} is the constant inlet concentration, lead to an exact solution for Equation (3). The analytical solution of the dispersion model by using initial and boundary conditions is given by Ogata and Banks (1961):

$$\frac{C}{C_{imp}} = \frac{1}{2}\text{erfc}\left(\frac{x-Vt}{2\sqrt{Vt\alpha_L}}\right) + \frac{1}{2}\exp\left(\frac{x}{\alpha_L}\right)\text{erfc}\left(\frac{x-Vt}{2\sqrt{Vt\alpha_L}}\right) \quad (4)$$

where erfc is the complementary error function given by:

$$\text{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}}\int_0^x \exp(-t^2)\,dt \quad (5)$$

Table 6
Dispersion and Dispersivity Coefficient of Chloride for the Six Soil Types

Soil Type		Estimated Value	95% Confidence Limits	
			Lower	Upper
	V_x (cm s^{-1})	2.25×10^{-4}	2.07×10^{-4}	2.44×10^{-4}
	D_L (cm s^{-2})	8.33×10^{-4}	6.78×10^{-4}	9.88×10^{-4}
Soil 1	α (cm)	3.7	—	—
	V_x (cm s^{-1})	2.60×10^{-6}	2.12×10^{-6}	3.09×10^{-6}
	D_L (cm s^{-2})	5.35×10^{-6}	1.65×10^{-6}	9.0510^{-6}
Soil 2	α (cm)	2.06	—	—
	V_x (cm s^{-1})	1.24×10^{-3}	1.15×10^{-3}	1.35×10^{-3}
	D_L (cm s^{-2})	2.08×10^{-3}	1.27×10^{-3}	2.81×10^{-3}
Soil 3	α (cm)	1.68	—	—
	V_x (cm s^{-1})	1.67×10^{-5}	1.40×10^{-5}	1.98×10^{-5}
	D_L (cm s^{-2})	2.17×10^{-5}	4.48×10^{-6}	3.90×10^{-5}
Soil 4	α (cm)	1.3	—	—
	V_x (cm s^{-1})	1.07×10^{-3}	1.06×10^{-3}	1.10×10^{-3}
	D_L (cm s^{-2})	1.33×10^{-3}	1.15×10^{-3}	1.51×10^{-3}
Soil 5	α (cm)	1.25	—	—
	V_x (cm s^{-1})	1.39×10^{-4}	1.27×10^{-4}	1.51×10^{-4}
	D_L (cm s^{-2})	1.91×10^{-4}	1.26×10^{-4}	2.55×10^{-4}
Soil 6	α (cm)	1.37	—	—

Analysis of Measured Chloride Breakthrough Curves

There are several methods used for the determination of the dispersivity coefficient, but all the reviewed methods (Bear 1961, Scheidegger 1974) rely on the determination of the breakthrough curve induced by a step input in the concentration. The dispersion coefficient D_L is then estimated by fitting an analytical solution of the advection-dispersion equation to the observed breakthrough curve (BTCs).

Measured and predicted BTCs of NaCl concentrations in the effluent for each of the six experiments plotted as a function of time (Figure 8) were fitted to Equation (4) using program CXTFIT (Toride et al. 1995) to estimate the values of dispersion coefficient (D_L) of the soil samples. The dispersivities were computed using and $D = \alpha_L^{v}$ from the estimated pore water velocities and fitted dispersion coefficients.

The dispersion coefficient that was judged to provide the best fit to the experimental profile for each soil was selected as the experimental NaCl dispersion coefficient (Table 6). As it is shown in Table 4, the minimum dispersivity value obtained for soil 2 is 1.25 cm and maximum dispersivity value is 3.7 cm which belongs to soil 1.

Conclusions

The distribution coefficient represents the sorption affinity of the metal cations in solution for the soil solid phase and can be used to characterize the mobility and retention of trace elements in a soil system. A distribution coefficient can be related to both plant uptake and environmental pollution. Low distribution coefficients indicate that most of the metals present in the system remain in the solution and are available for transport, chemical processes, and plant uptake (Morera et al. 2001); whereas higher values indicate lower mobility and higher retention of metals in the soil.

According to sorption of Cu, Zn, and Mn from the multicomponent batch experiments that followed different trends shows that Cu had a slightly higher affinity for sorption on these soil texture than Zn and Mn. The sorption process of Zn and Mn onto the surface of six different soil samples was described well by the Langmuir isotherm and the Freundlich isotherm, whereas sorption of Cu was better described by the Linear. The calculated maximum adsorption capacity (S_{max}) of Zn and Mn studied soil samples varied from 10985.148 and 8597.14 L kg^{-1} and from 7587.391 and 4908.695 L kg^{-1}, respectively. Freundlich distribution coefficients for Zn ranged from 3996.449 to 5876.246 L kg^{-1}, for Mn from 1391.294 to 3996.449 L kg^{-1}. Distribution coefficient (K_d) for Cu ranged from 18170.76 to 32550.35 L kg^{-1}. The selective sequences of the metal adsorption based on the distribution coefficient was Cu > Zn > Mn indicating that Cu is the most strongly sorbed metal by these soils, whereas Zn and Mn are the least sorbed ones. In the multicomponent batch experiments for Cu, Zn, and Mn at pH 7.15 ± 0.15 apparent up take by the solid was due to precipitation because the precipitation of metal at higher pH produces artificially high sorption values. In general, metal cations are highly stable in solution under acidic conditions and sorption increases with pH, with maximum sorption taking

place at a slightly different pH for each metal (Forstner and Wittmann 1983). The study also concludes that there is a positive correlation between the sorption isotherm parameters and the basic properties of the soil samples. The main soil properties that are important in the metal sorption in these soils are the type and the amount of CEC, as well as the SSA.

For the conditions examined in column tests the dispersion coefficient on samples of soil 1, soil 3, soil 5, soil 4, soil 2, and sand ranged from 5.35×10^{-6} to 2.08×10^{-3} cm^2 s^{-2}. The values obtained are found to agree with the values reported in the literature.

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