Mobility of Manganese in a Compacted Residual Gneissic Soil Under Laboratory Conditions

R. Nascentes, I.C.D. Azevedo, A.T. Matos, M.P.F. Fontes, R.F. Azevedo, L.M. Guimarães

Abstract. Given the shortage of information available in the literature on transport parameters of heavy metals in Brazilian tropical soils, the mobility of manganese (Mn^{2+}) in a residual gneissic compacted soil is studied in this work. Manganese can be found in toxic concentrations in landfill leachate, besides being one of the main contaminants from acid mine drainage. Column tests were performed in two groups of compacted soil samples to determine the manganese retardation factor. The sample groups presented slightly different soil compaction degrees and water contents. Soil samples were initially saturated by upward percolation of distilled water without applied counter pressure. A multi-species contaminant solution was then percolated through the soil columns. A different behavior of the hydraulic conductivity along time was observed between the two groups, during water as well as solution percolation. Manganese mobility was observed to be independent of soil hydraulic conductivity, *k*, for the range of *k*-values attained in this investigation, emphasizing the importance in evaluating the mobility of this metal in compacted soil barriers. Even when these barriers present low hydraulic conductivity values, this cation high mobility may cause it to reach soil layers below the compacted layer resulting in groundwater contamination.

Keywords: adsorption, hydraulic conductivity, manganese, mobility, tropical soils, column tests.

1. Introduction

Municipal solid waste (MSW) dump sites and areas surrounding mining activities are normally subjected to heavy metal contamination. The leachate produced by MSW generally contains high concentrations of metals, including manganese, while acid mine drainage exhibits low pH and high concentrations of iron, aluminum and manganese.

Heavy metals are chemical elements frequently associated with contamination since they may accumulate and cause disturbances in living organisms in a given environment. Studies concerning their behavior in soil have received considerable attention, and have helped to increase our understanding of the phenomena related to mobility and retention of these elements in the environment and their inclusion in the food chain.

Concern over manganese is relatively recent. However, like other essential elements such as zinc and copper, it can be responsible for soil and groundwater contamination when it is present above certain concentrations. Groundwater pollution below contaminated areas is related to contaminant mobility. When it is high, a greater risk exists.

Manganese, a plant and animal micronutrient, is a transition element of the iron family. It is among the most abundant elements (Group VII B), representing 0.09% of the weight of the Earth's crust (Wills, 1992). It is employed in metallurgy as well as in the production of fertilizers, electrolytic batteries, ceramics, varnish and paints, among other uses. According to Barceloux (1999), manganese is present in almost all types of soils in divalent and tetravalent forms and in concentrations varying between 40 and 900 mg kg^{-1}. In mining areas its concentration can reach levels of about 7000 mg kg^{-1}. The formation of Mn^{2+} complexes in the process of adsorption and the consequent mobility depend on the properties of that metal, the type and amount of ligands, the composition of soil solution and soil pH (Alleoni *et al.*, 2005).

Therefore, the main objective of this work was to evaluate Mn^{2+} mobility and determine its retardation factor when percolating a multi-species contaminant solution through compacted gneissic residual soil columns.

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2. Material and Methods

2.1. Soil

The soil used in this study, extracted from a slope of Visconde do Rio Branco, MG, sanitary landfill, was collected from the B horizon of a yellow red latosol classified, according to Unified System of Soil Classification (USCS), as inorganic silt of high compressibility (MH) and according to the Highway Research Board (HRB) system as A-7 soil with group index 12 (Azevedo *et al.*, 2006). The soil was characterized through geotechnical tests, clay fraction mineralogical analysis and chemical and physicochemical analyses. Soil characterization and compaction tests were performed according to the Brazilian Standards ABNT NBR-7181/84 for particle size; ABNT NBR-6459/84 and NBR-7180/84 for consistency limits; ABNT NBR-6508/84 for specific weight of solids; and ABNT NBR-6457/86 for compaction. The chemical and physicochemical analyses were determined according to EMBRAPA (1987).

Geotechnical properties are presented in Tables 1 and 2 while the results of chemical and physicochemical analyses are listed in Table 3.

X-ray analysis was conducted with a Rigaku D-Max diffractometer equipped with a cobalt tube (Co-Kα radiation) and a graphite curved crystal monochromator operated at 40 kV and 30 mA. The X-ray analysis of the soil clay fraction was performed in three different types of samples: (i) random-powder, prepared on a glass slide with a cavity in which the natural clay was packed in powder form; (ii) oriented-aggregate, prepared with natural clay by the paste method according to Theisen and Harward (1962) for better mineral preferential orientation; and (iii) oriented-aggregate, prepared after treating the clay to remove the iron oxides, to enhance the preferential orientation of the silicate layer species present (Fig. 1). Analysis of these three sam-

Table 1 - Soil grain size distribution and Atterberg limits.

Grain size distribution				Atterberg limits			
Clay (%)	Silt (%)	Sand (%)	Gravel (%)	w_L[1]	w_P[2]	PI[3]	Activity
42.0	10.0	47.1	0.9	52	30	22	0.52

[1]w_L - liquid limit; [2]w_P - plastic limit; [3]PI - plasticity index.

Table 2 - Soil physical indexes.

γ_s[0] (kN m^{-3})	γ_{dmax}[1] (kN m^{-3})	γ_{dmax}[2] (kN m^{-3})	γ_{dmax}[3] (kN m^{-3})	w_{opt}[1] (%)	w_{opt}[2] (%)	w_{opt}[3] (%)
27	16.45	15.97	15.82	22.3	23.9	24.1

[0]γ_s - solids unit weight; [1]γ_{dmax} and [1]w_{opt} - soil maximum dry unit weight and optimum moisture content for Standard Proctor; [2]γ_{dmax} and [2]w_{opt} - idem for 291 kJ/m^3; [3]γ_{dmax} and [3]w_{opt} - idem for 233 kJ/m^3.

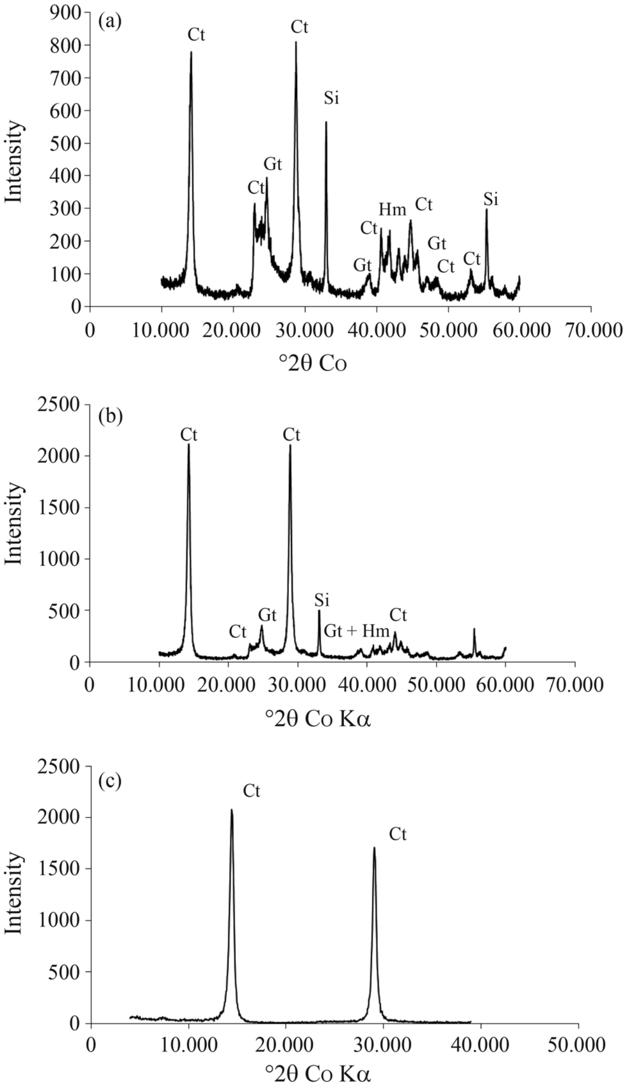

Figure 1 - Soil clay fraction X-ray: (a) random-powder, (b) oriented-aggregate, prepared with natural clay by the paste method, and (c) oriented-aggregate, prepared with the clay after removal of iron oxides. Ct - kaolinite, Gt - goethite, Si - silicon, Hm - hematite.

Table 3 - Chemical and physicochemical analyses.

Mn^{2+} (cmol$_c$ kg^{-1})	Ca^{2+} (cmol$_c$ kg^{-1})	Mg^{2+} (cmol$_c$ kg^{-1})	K^+ (cmol$_c$ kg^{-1})	Al^{3+} (cmol$_c$ kg^{-1})	H^++Al^{3+} (cmol$_c$ kg^{-1})	CEC$_{ef}$[1] (cmol$_c$ kg^{-1})	CEC$_{pot}$[2] (cmol$_c$ kg^{-1})	*OMC*[3] (%)	pH
0.046	1.23	0.11	0.026	0.0	0.7	1.37	2.07	0.0	6.01

[1]CEC$_{ef}$ - Effective Cation Exchange Capacity for natural soil pH; [2]CEC$_{pot}$ - Potential Cation Exchange Capacity for pH = 7; [3]*OMC* - organic matter content.

ple types allowed definition of the soil clay fraction composition as kaolinite, goethite and a very small amount of hematite (Nascentes, 2006).

The amount of iron was determined using the dithionite-citrate extraction method (Coffin, 1963) to quantify the presence of iron oxides. Iron oxides content was 13.3% in mass which was entirely allocated to goethite. It is important to determine the amount of iron oxides in the clay fraction of the soil since these mineral constituents exhibit a high energy retention capacity for heavy metals.

2.2. Heavy metals contaminant solution

An artificial contaminant solution (synthetic landfill leachate) consisting of six heavy metals was used in the column tests. This solution was prepared by addition of nitrate salts, available at the laboratory, which are water soluble, of manganese, zinc, cadmium, copper, lead and chromium, metals commonly encountered in landfill leachates (Azevedo *et al.*, 2006). The pH and heavy metal concentrations used (Table 4) are within the range of values for Brazilian landfill leachate (Oliveira & Jucá, 1999).

2.3. Column tests

The flexible-walled permeameter used in the column tests is similar to a triaxial cell and capable of simultaneously testing four soil samples of 0.05 m in diameter by 0.10 m in height. Each sample cell has an inlet for the percolating fluid and an outlet for effluent collection. Fluid flows upward through the soil samples. Each inlet is connected, by a latex hose, to a Mariotte bottle containing the contaminant fluid. The equipment also has an inlet for applying confining pressure that allows reproduction of *in situ* horizontal stresses (Azevedo *et al.*, 2003).

The tests were performed under controlled temperature conditions (17 to 21 °C). A confining pressure of 50 kPa was applied to the samples to simulate a 10 m deep urban solid waste layer over the liner.

Tests were performed on two groups of samples, with different compaction energies. Three samples from group I and eight from group II were dynamically compacted in a 0.05 m diameter metallic cylinder at 21.9% (group I) and 22.5% (group II) water content, corresponding to 95% of optimum specific dry density (15.63 kN m^{-3}). The compaction energy was such that all samples were compacted until they reached 0.10 m in height and 0.05 m in diameter. As the water content varied slightly, the compaction energy also varied, as shown in Fig. 2.

Tables 5 and 6 present a summary of molding and testing conditions for groups I and II, respectively.

Table 4 - Chemical characteristics of the contaminant solution.

pH	Cr^{3+} (mg L^{-1})	Cd^{2+} (mg L^{-1})	Pb^{2+} (mg L^{-1})	Cu^{2+} (mg L^{-1})	Mn^{2+} (mg L^{-1})	Zn^{2+} (mg L^{-1})
5.2	0.7	1.6	1.6	5.0	36.0	62.0

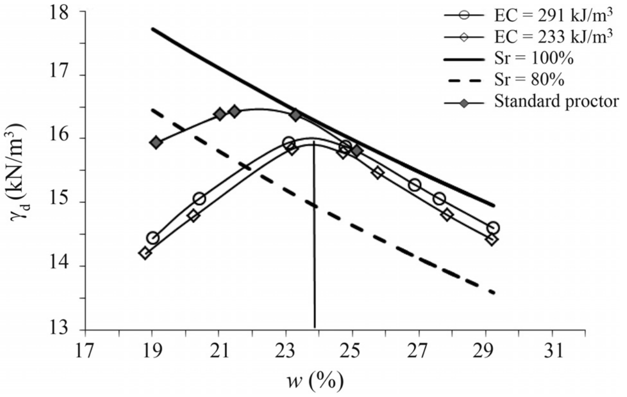

Figure 2 - Soil compaction curves.

The different gradients and, consequently, different percolation velocities, adopted for CP06, CP07, CP010 CP011 samples of group II, were adopted with the purpose of evaluating the diffusion coefficient, which was not possible.

The procedure used in this type of test is similar to that used in constant head permeability tests. The main differences are the need for measuring the effluent chemical concentration (C_e) and the generation of several pore volumes of chemical solution.

During the tests, both affluent and effluent chemical concentrations were determined at regular intervals. The relationship C_e/C_0 was calculated considering the value of C_0 read at the instant preceding the collection of the effluent.

The hydraulic gradient was maintained constant during the tests. Soil samples were initially saturated by upward percolation of distilled water, without applying counter pressure, prior to the percolation of the contaminant solution. Soil columns were considered saturated when constancy of flow was observed. The soil hydraulic conductivity coefficient was determined using Darcy's law (Lambe and Whitman, 1979).

Samples CP04 and CP09 from group II were percolated with distilled water to serve as reference for the other group II samples which were saturated with distilled water and then percolated with the contaminant solution.

Table 5 - Compaction tests - Sample characteristics: Group I - water content = 21.9% and compaction energy of 291 kJ/m³.

	CP01	CP02	CP03
GC (%)	98.7	99.0	98.4
Gradient	13.4	13.4	13.4
Void ratio	0.713	0.706	0.718
Porosity	0.416	0.414	0,418
Void volume (mL)	80.0	79.7	80.4
Saturation degree (%)	82.9	83.7	82.3
Water content deviation (%)	-2.0	-2,0	-2.0

Table 6 - Compaction tests - Sample characteristics: Group II - water content = 22.5% and compaction energy of 233 kJ/m^3.

	CP04	CP05	CP06	CP07
GC (%)	98.7	98.6	98.9	98.3
Gradient	13.4	13.4	7.3	7.3
Void ratio	0.729	0.731	0.726	0.737
Porosity	0.422	0.422	0.421	0.424
Void volume (mL)	81.4	81.4	80.7	82.0
Saturation degree (%)	83.2	83.0	83.6	82.4
Water content deviation (%)	-1.6	-1.6	-1.6	-1.6
	CP08	CP09	CP10	CP11
GC (%)	98.3	98.7	98.9	98.6
Gradient	13.4	13.4	7.3	7.3
Void ratio	0.737	0.729	0.726	0.731
Porosity	0.424	0.422	0.421	0.422
Void volume (mL)	81.7	81.5	81.0	81.3
Saturation degree (%)	82.4	83.3	83.6	83.0
Water content deviation (%)	-1.6	-1.6	-1.6	-1.6

Column effluents were collected daily from 50 mL burettes fixed to the base of the equipment and stored in bottles, previously washed with a solution of nitric acid, for subsequent determination of metal concentrations in an atomic absorption spectrophotometer. After measuring effluent concentrations of each metal (C_e), for each percolated pore volume (T), breakthrough curves (C_e/C_0 *vs.* T) were elaborated for manganese.

Two methods can be used for data analysis of the effluent concentration from column tests (traditional method and the cumulative mass method). The traditional method consists in measuring instantaneous concentrations *vs.* time, determining the breakthrough curve and applying an analytical model to determine the retardation factor and hydrodynamic dispersion coefficient. The concentration of solutes in any point of the column is calculated using Eq. (1) (Ogata & Banks, 1961), for the initial and boundary conditions given in Eq. (2), as follow:

$$C_r(x,t) = \frac{C_0}{2}\left\{ erfc\left[\left(\frac{R_d x - V_x t}{2\sqrt{D_h R_d t}}\right) + \exp\left(\frac{V_x x}{D_h}\right) \times erfc\left[\left(\frac{R_d x + V_x t}{2\sqrt{D_h R_d t}}\right)\right]\right\}\right] \tag{1}$$

$$\begin{aligned} &C_r(x,0) = 0 \quad \text{for} \quad x \geq 0 \\ &C_r(x,t) = C_0 \quad \text{for} \quad t \geq 0 \\ &\frac{\partial C_r(\propto,t)}{\partial x} = 0 \quad \text{for} \quad x \geq 0 \end{aligned} \tag{2}$$

where C_r is the solute resident concentration [ML^{-3}]; C_0 is the initial concentration [ML^{-3}]; R_d is the retardation factor; x is the direction coordinate; t is the time [T]; D_h is the hydrodynamic dispersion coefficient [L^{2}T^{-1}]; V_x is the percolation velocity in x direction [LT^{-1}] and *erfc* is the complementary error function.

When the length of the column is sufficiently long, the second term in the right side of Eq. (1) is negligible compared to the first, so that the effluent concentration at $x = L$ is given by (Shackelford, 1993):

$$C_e(L,t) = \frac{C_0}{2}\left\{ erfc\left(\frac{R_d L - V_x t}{2\sqrt{D_h R_d t}}\right)\right\} \tag{3}$$

or,

$$C_e(L,t) = \frac{C_0}{2}\left\{ erfc\left((R_d - T)\left(\frac{P_L}{4\,T\,R_d}\right)^{1/2}\right)\right\} \tag{4}$$

$$T = \frac{V_x t}{L} \tag{5a}$$

$$P_L = \frac{V_x L}{D_h} \tag{5b}$$

where C_e [ML^{-3}] is the effluent concentration at $x = L$; T is the number of pore volume; P_L is the column Peclet number; and L [L] is the soil column height.

The derivative of Eq. (4) with relation to T, at the point $T = R_d$, gives the value $b = \sqrt{P_L / 4\pi R_d^2}$. If the tangent to the experimental curve C_e/C_0 *vs.* T at the point $C_e/C_0 = 0.5$ is known and substituting P_L by the value given in Eq. (5), then the hydrodynamic dispersion coefficient, D_h, is determined from Eq. (6) as:

$$D_h = \frac{V_x L}{b^2 \, 4\pi \, R_d^2} \tag{6}$$

3. Results and Discussion

3.1. Percolation of distilled water

Soil hydraulic conductivity (k) *vs.* number of pore volumes (T) curves obtained from distilled water percolation through groups I and II sample columns are presented in Fig. 3. A significant variation in the hydraulic conductivity values for group II samples with time is evident, as shown in Fig. 3b. Since these samples were compacted with greater water content than those of group I, their structure was slightly more dispersed. Therefore, saturation with distilled water promoted greater variations in hydraulic conductivity of group II samples, which reached constant flow after percolation of almost ten times more number of pore volumes, compared to samples of group I. For these last samples, however, constant flow was reached more quickly (for a smaller number of pore volumes) because of a more flocculated soil structure after compaction, as compared to samples of group II. More flocculated soil structures facilitate the exit of air which in turn allows constant flow values to be reached for a smaller number of percolated pore volumes.

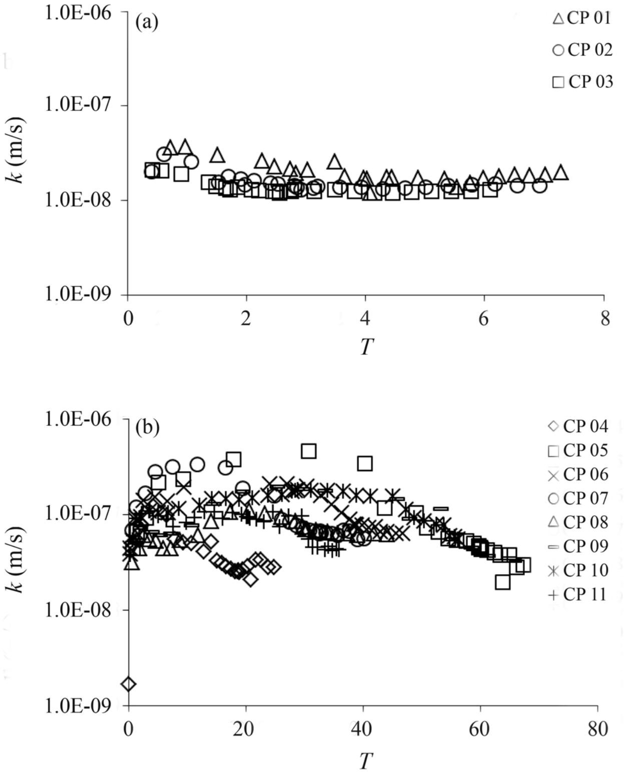

Figure 3 - Hydraulic conductivity for distilled water percolation in samples: (a) Group I and (b) Group II.

Percolation of group II samples with distilled water, associated with colloidal dispersion and double layer expansion, lead to a decrease in soil solution ionic concentration (Na^+, Ca^{2+}, Mg^{2+}), as shown in Fig. 4. An expansion of this layer results in a narrower and more tortuous solution percolation path and, consequently, in lower soil hydraulic conductivity. In other words, there was more salt leaching and as a consequence, a larger double layer thickness, for a

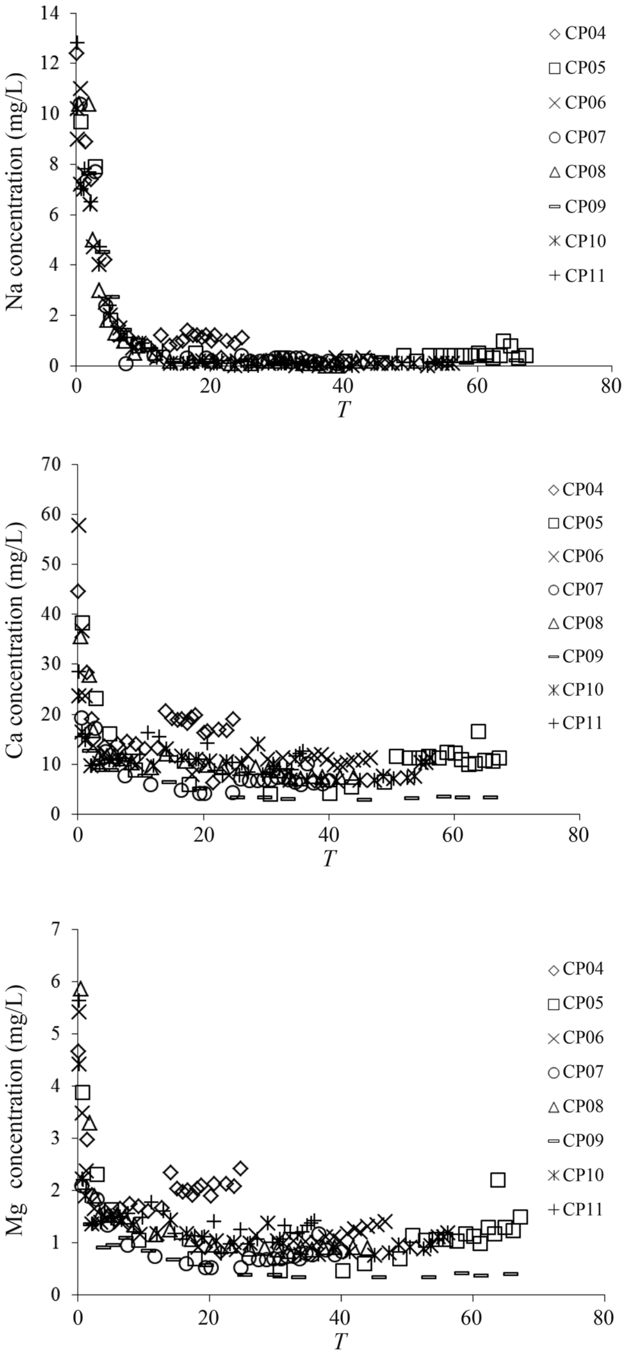

Figure 4 - Group II: Cation concentrations in effluent after distilled water percolation through soil columns. (a) Sodium, (b) Calcium, and (c) Magnesium.

greater number of distilled water pore volumes percolated through the samples.

The average final values of hydraulic conductivity were 1.5 x 10^{-8} m/s for group I and 5.0 x 10^{-9} m/s for group II. The heterogeneity of the soil samples tested and something in this particular testing procedure probably contributed to a slight difference in the final values of k between the two groups.

3.2. Percolation of contaminant solution

Soil hydraulic conductivity *vs.* number of pore volume curves for percolation of the contaminant solution through the two soil sample groups are shown in Figs. 5 and 6. The significant difference observed in hydraulic conductivity behavior for the two groups is attributed to the distinct double layer thicknesses attained by each after the saturation process. In other words, the soil hydraulic conductivity for contaminant solution percolation depended mainly on the compacted soil structure and the previous percolation with distilled water.

Group I samples exhibited an initial great increase in hydraulic conductivity followed by a pronounced decrease, while a monotonic significant decrease was observed for all group II samples. However, this decrease occurred in a distinct way for each sample, possibly as a result of the different structures formed after the saturation process. The large difference in number of distilled water pore volumes directly influenced the behavior of the hydraulic conductivity by the time the contaminant solution was percolated.

The small difference in the numbers of percolated distilled water pore volumes in samples CP07 and CP08 from group II (40.1 and 44.1, respectively), the approximate amount of leached cations and the same Standard Proctor compaction degree of 94.5% led to similar behaviors in hydraulic conductivity, when the contaminant solution was percolated through these samples.

The introduction of chemical substances to soil generally produces variations in its hydraulic conductivity. The contact between these substances and the soil may lead to redistribution of pore spaces as a result of clay particle rearrangement (flocculation or dispersion) and chemical reactions, such as dissolution or precipitation of solids, between these substances and clay minerals. As a result of this contact, ionic changes may occur that can cause double layer contraction or expansion. The thickness of the double layer and the magnitude of acting forces depend mainly on the dielectric constant, temperature, electrolytic concentration in the interstitial fluid and cation valence, and to a lesser extent on cation size, fluid pH and anion adsorption on clay particle surfaces (Boscov, 1997).

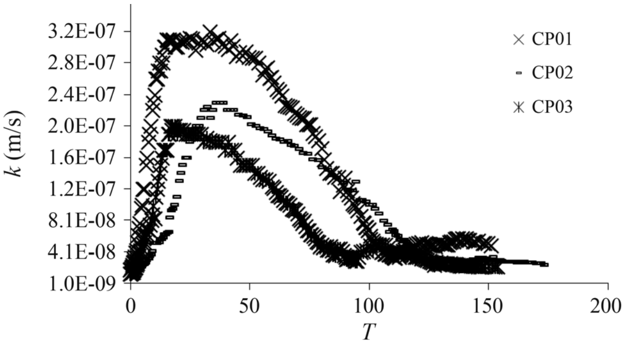

Figure 5 - Hydraulic conductivity for percolation of the contaminant solution through samples: Group I.

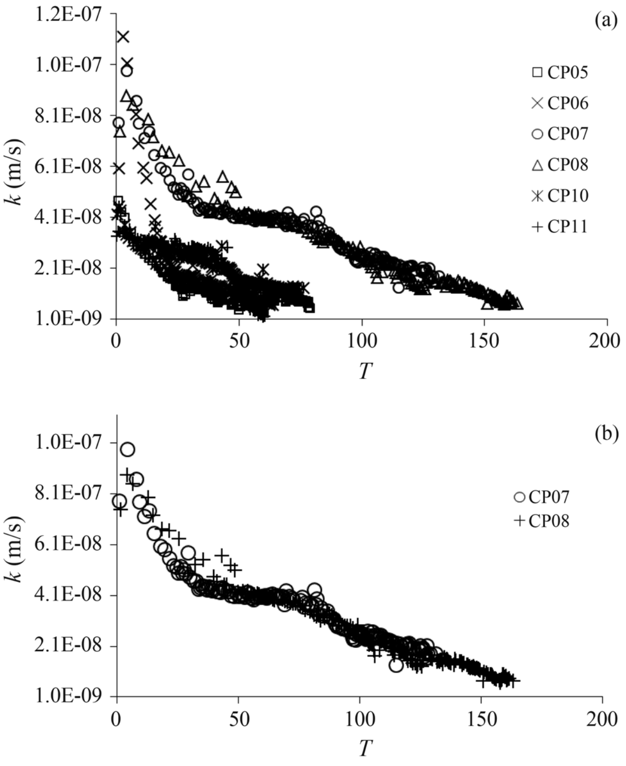

Figure 6 - Hydraulic conductivity for percolation of the contaminant solution through samples: (a) Group II and (b) Samples CP07 and CP08.

The samples in group I showed more flocculated structures (thinner double layer) than those in group II after percolation with distilled water. Thus, the initial increase in hydraulic conductivity probably occurred as a result of exchange of monovalent ions, naturally found in the soil, with divalent and trivalent cations present in the contaminant solution, leading to flocculation. Hydraulic conductivity started to decrease when the soil exhausted its capacity to retain zinc and manganese, precisely the metals present in high concentrations in the contaminant solution.

In group II samples, the increase in pH could have been a factor favouring metal precipitation and leading to a decrease in hydraulic conductivity, as a consequence of the obstruction of soil pores by metal precipitates. In this case the soil structure was more dispersed and the duration of contact between the contaminant solution and samples was greater, which also favours precipitation.

Effluent pH was measured for all samples and curves of pH *vs.* T are shown in Fig. 7a. In Fig. 7b, for the sake of clarity, only pH *vs.* T curves for soil columns CP10 and CP11 (group II) are presented.

When heavy metal solutions percolate through the soil columns, variations in the pH of the effluent, due to sorption and desorption reactions, are common. In these reactions, the cations naturally present in the soil are liberated and leached, usually associated to the hydroxyl (OH^-). In this way, the pH of the effluent varies according to the type and the leached amount of the cation, which could explain the oscillation of the pH value around the one that would be reached when reactions of sorption and desorption cease.

According to Fig. 6b, the hydraulic conductivity in sample CP10 was lower than that of CP11 for values of *T* between 13 and 50, approximately. In this range, effluent pH in CP10 was greater than in CP11, indicating a possible higher precipitation in the former sample. Both samples showed similar pH values as well as hydraulic conductivities between $T = 50$ and $T = 104$. From $T = 104$ on, effluent pH in sample CP11 increased in relation to that in sample CP10 and hydraulic conductivity in CP11 consequently decreased more than in CP10.

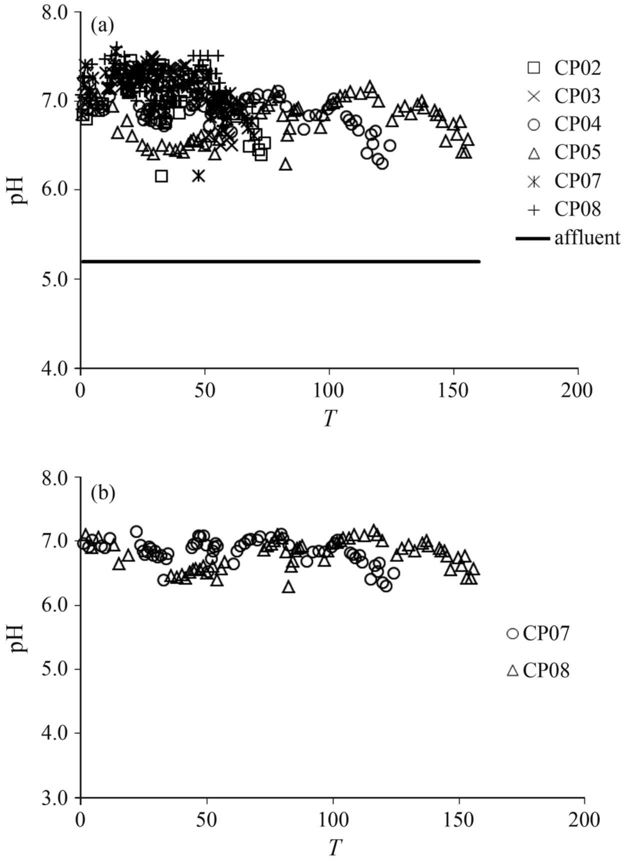

Figure 7 - Effluent pH *vs.* number of pore volumes - Group II (a) For all samples and (b) CP07 and CP08.

3.3. Determination of transport parameters

Breakthrough curves (curves of relative concentration (C_e/C_0) *vs.* number of percolated pore volumes) were constructed for manganese for both sample groups and are presented in Figs. 8 and 9.

Manganese is a metal that happens naturally in great amount in tropical soils. The easily exchangeable concentration of this element in the studied soil is approximately 0.046 $\text{cmol}_c\ \text{kg}^{-1}$, obtained by sequential extraction method with $CaCl_2$, which accounts for the total amount of Mn^{2+} released into solution when in competition with other ions for adsorption sites. The largest Mn^{2+} desorption in CP03 of group I and in all samples of group II, as shown in Figs. 8c and 9, may be explained by the greater time of contact between the solution and the soil particles, as indicated by the hydraulic conductivity variations observed during the tests. According to Azevedo *et al.* (2006) and Nascentes (2006), manganese (Mn^{2+}) was least sorbed by soil when compared to the other metals (Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} and Cr^{3+}) present in the contaminant solution. The mobility sequence obtained from test column and soil sequential extraction was $Mn^{2+} > Zn^{2+} > Cd^{2+} > Cu^{2+} > Cr^{3+} > Pb^{2+}$.

The behavior of Zn^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+} and Cr^{3+} was also studied and published in Nascentes *et al.* (2008). Their

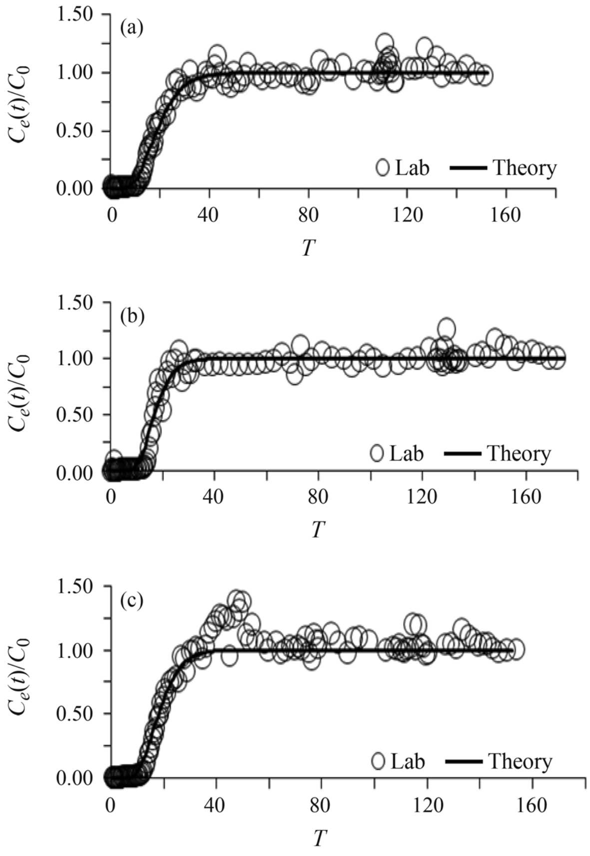

Figure 8 - Breakthrough curves for manganese - Group I (a) CP01; (b) CP02 and (c) CP03.

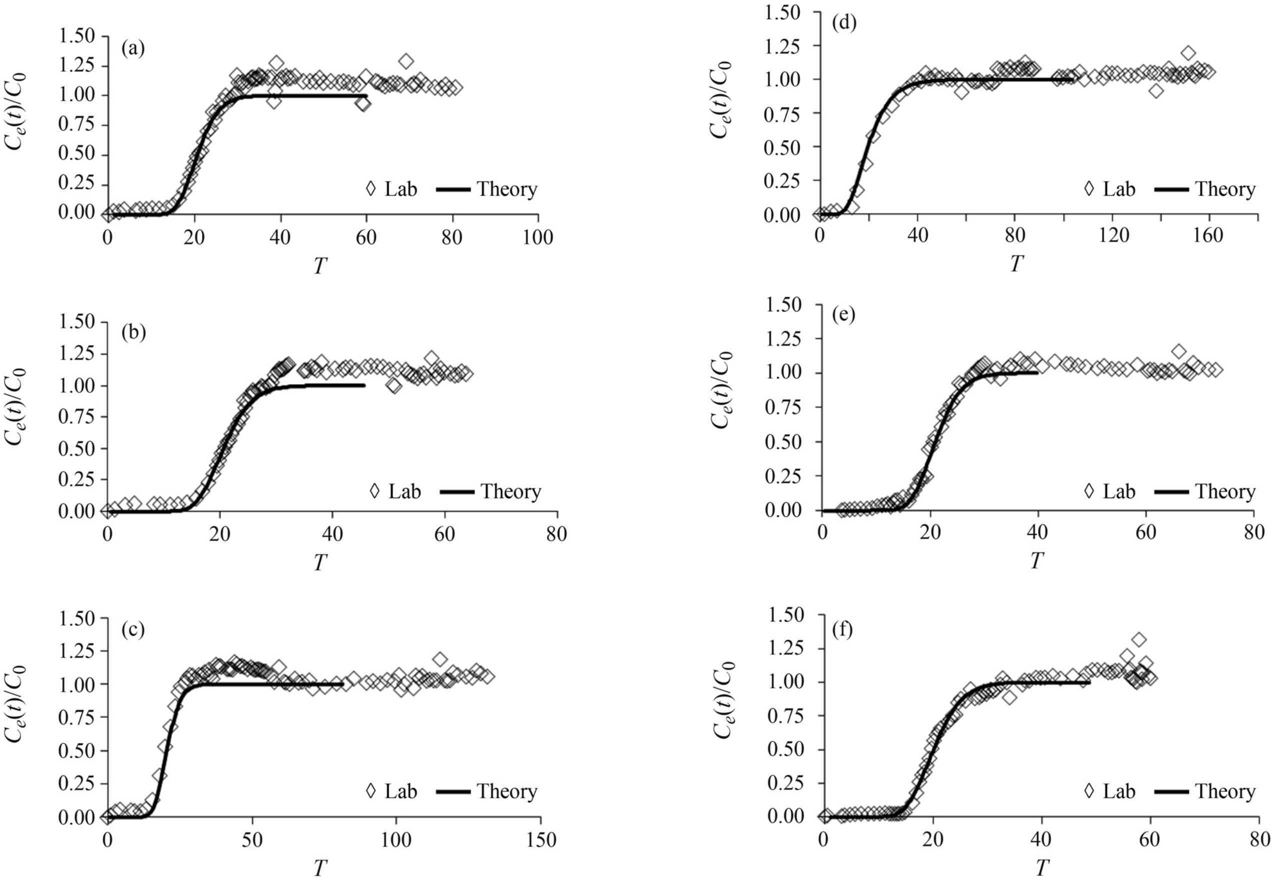

Figure 9 - Breakthrough curves for manganese - Group II (a) CP05; (b) CP06; (c) CP07; (d) CP08; (e) CP10 and (f) CP11.

mobility differed from that of manganese and was shown to depend on soil hydraulic conductivity.

The Peclet number is a parameter that helps in determining the predominant type of transport. This number for each column was calculated using Eq. (5b), considering the average percolation velocity of each test, up to $C_e/C_0 = 1$, as shown in Table 7. A mean value of 54.2 was determined for group II samples implying, according to the classification proposed by Sun (1995), that the predominant transport processes in column tests were advection and mechanical dispersion, since P_L was higher than 10 and less than 100, which depend on hydraulic conductivity.

Table 7 - Peclet numbers for each column.

Sample	V_{xm} (cm/min)	L (cm)	D_h (cm^2/min)	V/D_h (1/cm)	P_L
CP05	3.63E-03	10.00	6.55E-04	5.54	55.42
CP06	2.88E-03	10.00	5.21E-04	5.52	55.42
CP07	5.97E-03	10.00	1.08E-03	5.53	55.46
CP08	9.89E-03	10.20	2.10E-03	4.71	48.03
CP10	2.92E-03	10.00	5.27E-04	5.54	55.43
CP11	3.04E-03	10.00	5.49E-04	5.54	55.37

V_{xm} - average percolation velocity; L - column length; D_h - hydrodynamic dispersion coefficient.

The retardation factor (R_d) values shown in Table 8 were determined using the traditional method (Rowe *et al.*, 1995) with R_d given by the value of T for C_e/C_0 equal to 0.5.

Korf *et al.* (2008) conducted column tests in an undisturbed clayey soil, which was percolated by a synthetic multispecies solution composed of Cu^{2+} (20 mg/L), Cr^{3+} (20 mg/L), Mn^{2+} (1 mg/L), and Zn^{2+} (10 mg/L), and obtained an average value of 10.1 for the retardation factor.

It can be noted that the breakthrough curves for the two sample groups shown in Figs. 7 and 8 are quite similar as are the R_d values presented in Table 8. These similarities indicate that the mobility of manganese (Mn^{2+}) did not depend on hydraulic conductivity, for the range of *k* values of this investigation, which was markedly different for the two

Table 8 - Retardation factor for manganese.

	Group I*			Group II					
Test	01	02	03	04	06	07	08	10	11
R_d	19.5	18.0	18.5	20.0	20.0	18.0	20.0	20.5	20.4

*Azevedo *et al.* (2006).

groups when the contaminant solution was percolated through the soil columns.

The importance of test duration must be emphasized since the reactions between the soil and the contaminant solution did not occur in the same way for the manganese and the remaining heavy metals. Long term tests allow the development of chemical interactions of each heavy metal in competition with soil particles since a great number of pore volumes of contaminant solution are allowed to percolate through the soil column. In both sample groups, more than 60 pore volumes of the multi-species solution percolated through the soil columns, but in spite of significant differences in the values of hydraulic conductivities, the mobility of manganese in the soil was nearly the same in both groups.

4. Conclusion

The main conclusions drawn from this study can be summarized as follows.

Hydraulic conductivity behavior of a compacted clay layer saturated with distilled water and subsequently leached with a heavy metal solution is sensitive to the number of percolated pore volumes in the saturation process as well as to the compaction energy which can promote significant alterations in the structure of the material.

A mean value of 54.2 for Peclet number was determined for group II samples implying that the predominant transport processes in the column tests were advection and mechanical dispersion.

The mobility of manganese in test columns was not influenced by the compaction water content varying in the range of ±0.5% around the optimum value, indicating the potential of this metal to contaminate soil and groundwater, even for low values of saturated hydraulic conductivity.

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