3

Variation in Hydraulic Conductivity by the Mobility of Heavy Metals in a Compacted Residual Soil

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1. Introduction

There is a growing consciousness worldwide that progress must be linked to environmental preservation. However, in order to preserve the environment it is necessary to know it and only with an understanding of the mechanisms that regulate the integration of man with nature is it possible to use the environment resources without degrading or destroying it.

Heavy metals are important environmental contaminants that are toxic above a given concentration. Causes of soil contamination by metals include domestic and industrial solid waste disposal, atmospheric deposition of vehicular and industrial emissions, agricultural use of fertilizers, soil additives and pesticides and disposal of crop wastes (Alloway, 1995). Underground waters may be contaminated when metals levels exceed the maximum soil retention capacity.

Population growth and the consequent increase in waste generation has led to an increased demand for technologies that decrease the environmental impact of these wastes, especially with regard to barrier systems used to minimize the infiltration of waste leachates and contain migration of contaminants through soils and underground water in areas of waste disposal.

Tropical soils are common in Brazil. Compacted soils of this type is either used alone or associated with geomembranes have been used as liners in industrial and urban solid waste disposal areas. However a great deal of uncertainty exists with regard to use of these soils since few studies have been undertaken to evaluate their applicability. More studies on the interactions that occur between tropical soils and contaminant solutions are therefore necessary because these interactions may modify properties, such as hydraulic conductivity, which are important in controlling contaminant transport through soils.

The only legal requirements for liners are hydraulic conductivity limits. However, sensibility to contaminants of the soil used for impermeabilization may affect its structure and modify the liner layer by increasing its hydraulic conductivity, thus favoring contamination. Microscopic mechanisms responsible for thecha nges are of physico-chemical and/or purely chemical nature. Redistribution of the pore space driven by

dehydration of clay fraction, and rearrangement of clay particles (flocculation, peptization, andmicro-migration) togetherwith chemical reactions between contaminants and claymineral, such as dissolution of the solids are believed to be the most important causes of the permeability evolution (Kaczmarek, et al., 1997). Laboratory testing of soils used in liner layers should therefore be of long enough duration to allow for long term interactions to occur between soil and leachate.

Some of the most important parameters used to express solute mobility trough soil are diffusion, hydrodynamic dispersion coefficients and the retardation factor. Given the scarcity of information on these parameters in Brazilian tropical soils, especially in subsurface horizons and under compacted soil conditions, the main objectives of this study were to evaluate mobility of six heavy metals (Mn^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+} and Cr^{3+}) in residual compacted soil and to study the variation in soil hydraulic conductivity during percolation of a multispecies metal contaminant solution through the soil.

2. Background

Underground water deposits are generally more protected from pollution sources than surface water since in the former the overlying soil layer acts as a chemical and physical filter. The ease with which a contaminant reaches the underground water will depend on whether the aquifer is freatic or confined, on the aeration zone depth, the aeration zone and aquifer permeability, the level of organic matter present in the soil and on the types of oxides and minerals clay existing in the soil. Deeper aeration zones permit a longer filtration time and also increase the exposure time of contaminants to oxidizing and adsorbing agents present in this layer. Soil with a higher organic fraction has a higher capacity to adsorb heavy metals.

A contaminant may go through a series of chemical, biochemical and photochemical reactions and physical interactions with soil constituents before reaching underground water. These reactions may neutralize, modify or retard the polluting effect.

The main functions of liner systems are to minimize infiltration of percolates and contain migration of contaminants to the soil and underground water. To properly design liner systems, not only must contaminant flux be determined but the different physicochemical mechanisms that influence transport in contamination evolution must also be known. Although legal requirements for liner materials only establish limits for hydraulic conductivity (maximum value typically limited to 10-6 or 10-7 cm/s), at least four mechanisms control contaminant transport across impermeable layers: advection, diffusion, dispersion and sorption. For practical and economic reasons natural soils alone or combined with geomembranes are being used in these barrier systems in domestic and industrial waste disposal areas.

Soils in tropical climates have greatly different mineralogical compositions than those of temperate regions since they develop under hot humid conditions and minerals in more advanced stages of weathering are generally present. Kaolinite is the most abundant silicate mineral, goethite and hematite are the most abundant iron oxides and gibsite is almost the only aluminum oxide present in tropical soils.

Mineralogical composition has a profound affect on metals retention in soils. In most tropical soils the adsorption of metals is quite intense due to the oxide composition, since iron and aluminum oxides retain heavy metals with high energy in both specific and non-specific interactions.

Two important classes of tropical soils are the lateritic and saprolitic soils. Lateritic soils are often denominated as mature residual soils or red tropical clays while saprolitic soils are called young residual soils or soils from rock alteration.

The clay soil fraction of lateritic soils is essentially composed of clay minerals of the kaolinite group and of hydrated iron and/or aluminum hydroxides and oxides. A characteristic of lateritic soil structure is that macropores are formed in the empty spaces between soil aggregates and micropores are formed within the aggregates during the laterization process. Consequently, lateritic soils in their natural state have low density, high permeability and high porosity that are associated with the low support capacity of these soils. However, when compacted, these soils exhibit a high support capacity.

The variation in permeability of the impermeabilization layers is as important an aspect of soil and underground water contamination as are the soil components, their physicochemical properties and soil retention mechanisms. Contact between the contaminant solution and soil that can cause spatial redistribution because of clay particle rearrangement (flocculation, dispersion, peptization and micro-migration) together with chemical reactions between contaminants and clay minerals, such as solids dissolution and precipitation, are the most important causes of variations in permeability.

The initial soil structure varies with compaction humidity, energy and degree of compaction. According to Boscov (1997), significant variations in permeability may occur within a relatively small range of compaction humidity and density because of the formation of different structural arrangements.

In order to better understand the interactions that occur between tropical soils and contaminant solutions and how these interactions can alter soil properties it is necessary to perform laboratory tests for sufficient time so that long term interactions between soil and the percolating solution may occur.

3. Heavy metals

The meaning of the term heavy metals is controversial and a variety of definitions based on different criteria can be found in the literature. In the density based definition, heavy metals are high density (≥ 6.0 g/cm3) chemical elements and their ions belonging to the transition and non-transition groups of the periodic table (Matos et al., 1999). According to Guilherme et al. (2005), the term trace element has been preferred over heavy metal in several recent publications since the latter has never been formally defined by an official organization of chemistry professsionals.

Some heavy metals, such as Co, Cu, Fe, Mn, Mo, Ni and Zn, are essential human, animal and plant elements. Other elements, such as Cd, Hg and Pb, have no known biological function (Srivastava & Gupta, 1996). Both essential and non-essential metals can cause metabolic problems in living beings if absorbed above a certain amount (McBride, 1994). These elements´ capacities to accumulate in living tissue and to concentrate along the food chain increases the chance of their causing disturbances in ecosystems that may occur even after the release of the metals is stopped. (Tavares & Carvalho, 1992).

Studies on the behavior of heavy metals in soils have concluded that soil retention of these elements depends on the nature of the solid phase and the proportions of its constituents, the properties of the liquid phase and the metal species present in the soil solution (Sposito, 1984; Yuan & Lavkulich, 1997; Naidu et al., 1998).

The concentration of heavy metals in the soil solution results from equilibrium between precipitation, dissolution, complexation and adsorption reactions and is affected by various factors, such as soil type, climate, vegetative cover, and chemical form of the elements (Cooker & Matthews, 1983). However, given the equilibrium changes and chemicals forms of metals in wastes and soil and the possibility of exceeding the soil pollutant retention capacity, the metals may be leached, especially under acid conditions, and may thus reach the underground water. The specific surface area, texture, apparent density, temperature, pH, redox potential, cation exchange capacity (CTC), organic matter content, amount and type of clay minerals and metals and ion competition are among the soil properties that affect the metals reactions and their mobility in soil (Matos, 1995).

The existence of competition for adsorption sites between ions has been recognized by many researchers (Matos, 1995), and it has been observed that the rate of adsorption of any ionic species decreases with the increase in number of competing species. Factors such as solution pH, concentration and the nature of competing species affect the competitive adsorption.

Soils generally have a large variety of adsorption sites with different bonding properties and contain abundant aqueous ionic and non-ionic complexes capable of participating in adsorption processes and possibly in metals precipitation processes.

The soil CTC is one of the most important indicators of heavy metals retention capacity in the soil solid phase. Soils with higher CTC values generally have greater metals adsorption capacity than those with lower CTC values (Lake, 1987).

4. Mass transport mechanisms in porous media

The accumulation of contaminants in soil is a consequence of soil-solute physicochemical interactions arising from transport through the soil. Physical, chemical and biochemical mechanisms can govern solute transport in hydrogeological environments. The most important mechanisms in contaminant transport across saturated clay soil layers are the physical mechanisms of advection and diffusion. In the case of transport in aquifers, advection and dispersion are usually the most important mechanisms.

The transfer of the solute from the interstitial fluid to the solid soil particles is as important as the physical mechanisms. The transfer processes depend on the chemical composition of the solute, its reactivity and organic and inorganic content as well as on soil constituents and characteristics and system pH. These processes may include ion exchange sorption reactions (adsorption and desorption), precipitation and complexation. Biodegradation and radioactive decay are other mechanisms that may be involved.

According to Rowe et al. (1995), the most important factor in soil-contaminant interaction processes and substance transport through soil is probably the diffuse double layer expansion-contraction phenomenon.

5. Diffuse double layer

The thickness of the diffuse double layer (Equation 1) depends on charge density, surface electric potential, electrolyte concentration, valence, pH, dielectric constant of the medium and temperature. Changes in any of these variables may cause alterations in system behavior since forces of repulsion and attraction depend on interaction between adjacent double layers. In general, an increase in thickness of the diffuse double layer corresponds to a lower tendency of the particles in suspension to flocculate. That is, the thicker the double

layer, the thinner and more torturous will be the path of percolating solutions in the soil and consequently, the lower the hydraulic conductivity will be.

$$\frac{1}{K} = \left(\frac{\varepsilon_0 \, D \, k \, T}{2 \, n_0 \, e^2 \, v^2} \right)^{\frac{1}{2}} \tag{1}$$

where $1/K$ is the electric double layer thickness; (= 8,8542 x 10-12C^{2}J-^{1}m-^{1}; D is the dielectric constant; k is the Boltzman constant; T is the temperature; n0 is the ionic concentration; v is the cationic valence and e is the electron charge.

For a constant void volume, contraction or flocculation of the diffuse double layer causes an increase in voids between soil particles, and increases the hydraulic conductivity and accelerates the advance of percolating fluid. If, on the contrary, an ion exchange reaction that favors expansion of the diffuse double layer takes place, the hydraulic conductivity will decrease and the percolating fluid will be slowed. At a constant void volume, substitution of monovalent cations by bivalent or trivalent cations on the clay particle surface and an increase in temperature are among the factors that cause diffuse double layer contraction and can lead to dramatic increases in hydraulic conductivity (Rowe et al, 1995).

Hydraulic conductivity is inversely proportional to resistance that the medium offers to fluid flow caused by a hydraulic gradient and depends on the characteristics of both the fluid and the porous medium. According to Lambe (1969), the factors with greatest effect on soil permeability are its composition, void index, structure, degree of saturation as well as fluid characteristics, including chemical composition, since the compounds present in the fluid interact with the minerals that form the soil (Mesri & Olson, 1971; Folkes, 1982).

6. Case study - city of Viscount of Rio Branco - Minas Gerais / Brazil

The material used in this study was collected from the B horizon of a red-yellow latosol classified according to Unified Soil Classification (USC) as high plasticity silt, located on line A (MH/CH), and according to the Highway Review Board (HRB) system as A-7 soil with group index 12 (Nascentes, 2005). The geotechnical soil characterization is presented in Tables 1 and 2.

Granulometry				Atterberg Limits		
Clay (%)	Silt (%)	Sand (%)	Rock (%)	LL (%)	LP (%)	PI (%)
42	10	47.1	0.9	52	30	22

LL– liquid limit; LP– limit of plasticity; PI– Plasticity index.

Table 1. Granulometry and Atterberg limits for the soil used in this study.

γ_S (kN.m^{-3})	Activity	γ_{dmax}[1] (kN.m^{-3})	$w_{optimum}$[1] (%)	γ_{dmax}[2] (kN.m^{-3})	$w_{optimum}$[2] (%)
27	0.52	16.45	22.3	15.82	24.1

γ_s – specific weight of solids; γ_{dmax} and $w_{optimum}$ – dry soil specific weight and optimum soil humidity: [1] at Normal Proctor energy; [2] at an energy of 233 kJ/m^3.

Table 2. Physical indexes of the soil used in this study.

X-ray analyses were performed on three sample types: (i) natural clay randomly placed in powdered form on a glass well slide, (ii) an oriented sample, prepared with natural clay spread as a paste to orient minerals and clay and (iii) an oriented sample, after treatment to remove ferric oxides in order to better identify clay silicates and aluminum oxides possibly present in the soil sample. Analyses were performed in the Mineralogy Laboratory of the Soils Department of the Federal University of Viçosa using a Rigaku D-Max X-ray difractometer. A cobalt tube and curved graphite monochromator was used to obtain Co-Kα radiation. The difractometer was operated at 40 kV and 30 mA.

The presence of various peaks that permit identification of kaolinite, goethite and small quantities of hematite can be observed in the difractogram of the random natural clay fraction (Figure 1a). Given its yellow color, it was assumed that only a very small amount of hematite was present in this soil since the presence of hematite, even in small quantities imparts a reddish color to the soil (Fontes & Carvalho Jr., 2005), which was not the case for the sample used.

The attempt to orient the clay minerals in the presence of ferric oxides was not successful, as can be seen in Figure 1b. Face to face alignment of kaolinite minerals was not possible due mainly to the presence of goethite, resulting in a large series of peaks characteristic of kaolinite. The difractogram of the clay fraction of the soil after removing ferric oxides is presented in Figure 1c. Only two large kaolinite peaks (1st and 2nd order) were observed proving that when the kaolinite is perfectly aligned only peaks characteristic of this mineral's base atomic planes will appear.

Through combined evaluation of the difractograms the soil's clay fraction composition was defined as kaolinite and goethite with very little hematite.

The Fe content was determined using the dithionite extraction method (Coffin, 1963) to quantify iron oxides. Iron oxides corresponded to 13.3% of the clay fraction and were assigned to goethite. It is important to determine the presence of iron oxides since they have the capacity to retain heavy metals with high energy even when present in small quantities. Important chemical and physicochemical characteristics of the soil are presented in Table 3.

Ca^{2+}	Mg^{2+}	K^+	Al^{3+}	H^++Al^{3+}	CTC_{ef}	CTC_{pot}	pH	MO
			cmol$_c$	kg^{-1}				dag kg^{-1}
1.23	0.11	0.026	0.0	0.7	1.37	2.07	6.01	0.0

CTC_{ef}- Effective cation exchange capacity at natural soil pH; CTC_{pot}- Cation exchange capacity at pH 7

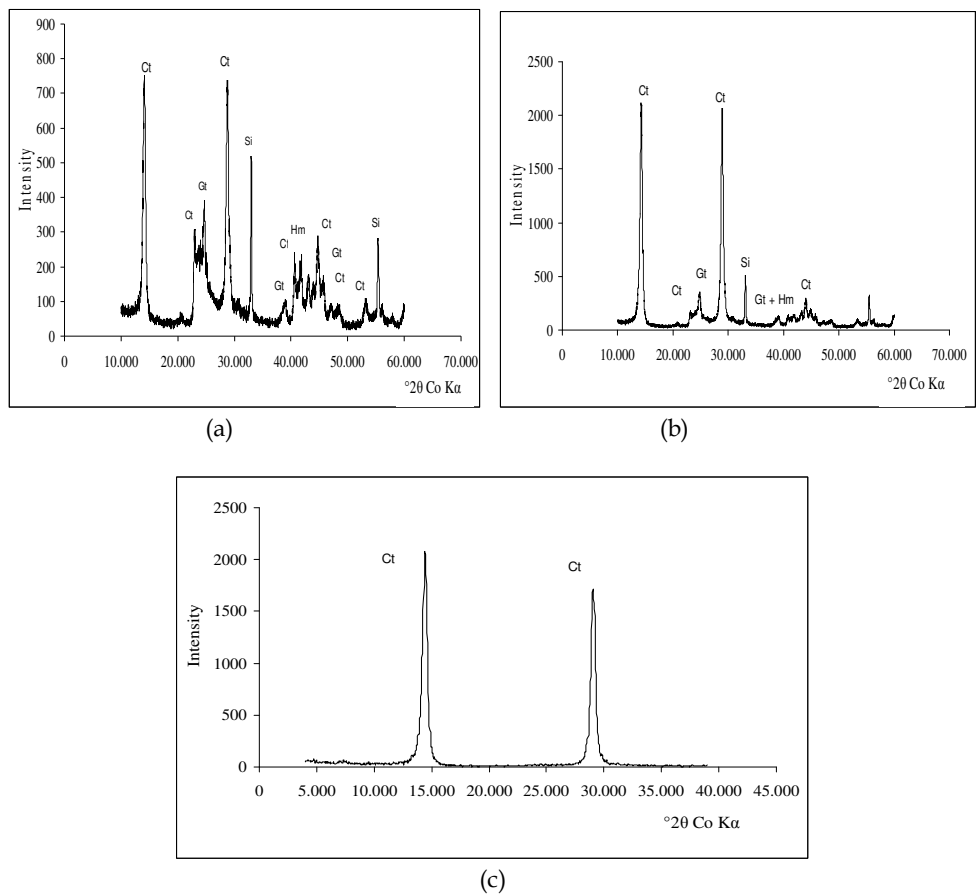Table 3. Results of chemical and physicochemical soil analyses.

(a)

(b)

(c)

Fig. 1. Difractogram of the clay fraction. (a) Randomly oriented natural clay in a well slide; (b) Oriented natural clay (c) Oriented clay after iron removal.

6.1 Contaminant solution

A contaminant solution was prepared by mixing nitrates of manganese, zinc, cadmium, copper, lead and chrome since these are the metals most commonly found in urban landfill leachates. The pH and concentrations of the heavy metals in the leachate (Table 4) are within the range cited in the literature for Brazilian landfill leachates (Oliveira & Jucá, 1999; Barbosa & Otero, 1999).

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

Source: Azevedo et al. (2006)

Table 4. Contaminant solution.

6.2 Column tests

Column tests were performed on eight soil samples adjusted to 22.5% humidity to evaluate hydraulic conductivity of compacted soil leached by the contaminant solution and to determine the transport parameters of the metals studied.

All samples were compacted to a specific weight of approximately 15.63 kN/m³ (95% of the maximum normal Proctor compaction degree). Compaction energy was such that the samples were compacted until reaching 10 cm height and 5 cm diameter (233 kJ/m³). Compaction data for each sample are presented in Table 5.

Soil columns were saturated with distilled water until a constant flow was obtained before percolating the contaminant solution. A flexible walled permeameter that resembled a triaxial chamber (Azevedo et al., 2003), constructed in the Geotechnical Laboratory of the Civil Engineering Department of the Federal University of Viçosa was used for the tests. Tests were conducted in a temperature controlled room (17 to 20 °C).

	CP 01	CP 02	CP 03	CP 04	CP 05	CP 06	CP 07	CP 08
GC (%)	94.9	94.8	95.1	94.5	94.5	94.9	95.1	94.8
Gradient	13.4	13.4	7.3	7.3	13.4	13.4	7.3	7.3
Void index	0.729	0.731	0.726	0.737	0.737	0.729	0.726	0.731
Porosity	0.422	0.422	0.421	0.424	0.424	0.422	0.421	0.422
Void vol. (mL)	81.4	81.4	80.7	82.0	81.7	81.5	81.0	81.3
Degree of saturation (%)	83.2	83.0	83.6	82.4	82.4	83.3	83.6	83.0
Δh (%)	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6	-1.6

Table 5. Compaction assays.

6.2.1 Analyses

Chemical, physical and micromorphological analyses of the samples were performed at the end of the column tests to evaluate soil retention of the heavy metals and variation in hydraulic conductivity caused by the percolating contaminant solution. The following determinations were made: hydraulic conductivity when percolating distilled water; hydraulic conductivity when percolating contaminant solution; leachate cation (Na^+, Ca^{2+}, Mg^{2+}) concentrations; effluent pH; effluent electric conductivity; metals retardation factors of (R_d); metals hydrodynamic dispersion coefficients (D_h) of; sequential extraction; dispersed clay; scanning microphotography.

6.2.2 Chemical analyses

Samples from columns CP01 (control), CP03, CP05 and CP07 were sliced into five 2 cm thick layers, placed in plastic bags to avoid water loss and kept in a humidity chamber for up to 24h for chemical analyses. Sequential extraction was used to determine speciation of each heavy metal in the compacted samples (article in press).

At the end of the column tests three samples of distilled water were collected from each permeameter used to apply the confining pressure and analyzed for the six heavy metals (Mn, Zn, Cd, Cu, Pb and Cr). No differences were detected among the samples indicating that no contaminant migration occurred into the water chamber.

6.2.3 Physical analyses

Percentage of dispersed clay was determined in the upper half of samples CP02, CP04, CP06 (control) and CP08. Slow and fast mechanical dispersion were employed to examine the effect of type of dispersion on the results. The methodology used was described by Ruiz (2005).

6.2.4 Micromorphological analyses

The lower half of samples CP02, CP04, CP06 and CP08 were used for micromorphological analyses. Samples were oven dried at 60°C, for 48h and then impregnated with a mixture of acrylic resin (60%) and styrene (40%) plus 5 mL of catalyst for each 1000 mL of mixture. The samples were left to soak in a well vented environment for 20 days to permit penetration in all the sample pores. Thin slides were prepared for optical and scanning electron microscope observations. The microphotographs were taken in the Microscopy Laboratory of the Geology Department of the Federal University of Ouro Preto. Some microphotographs were also taken of carefully withdrawn 1 cm³ subsamples from the compacted samples. These subsamples were oven dried at 50°C and fixed on aluminum stubs using double faced adhesive tape, covered with about 20 nm of a gold-palladium mix using a model FDU 010 (Balzers, Inc, USA) metalizer and observed under a VP 1430 scanning electron microscope (LEO Electron Microscopy, Oberkochen, Germany) operated at a voltage of 15 kV. This procedure was performed at the Center for Microscopy and Microanalysis of the Federal University of Viçosa. The images obtained were used to observe changes in soil microstructure.

6.3 Results
6.3.1 Column tests

6.3.1.1 Distilled water percolation

Soil hydraulic conductivity curves (corrected to 20°C) for distilled water percolation are presented in Figure 2. Concentrations of Na^+, Ca^{2+} and Mg^{2+} in the column leachates are presented in Figures 3a, 3b and 3c. Electrical conductivity and pH values measured in the column leachates are presented in Figures 4 and 5, respectively. T is a dimensionless parameter corresponding to the ratio of effluent volume to column void volume and is equivalent to the pore volume.
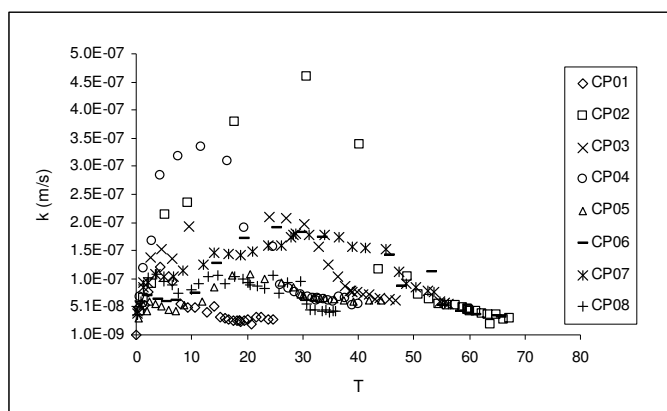
Fig. 2. Hydraulic conductivity in samples percolated with distilled water.

(a)

b)

(c)
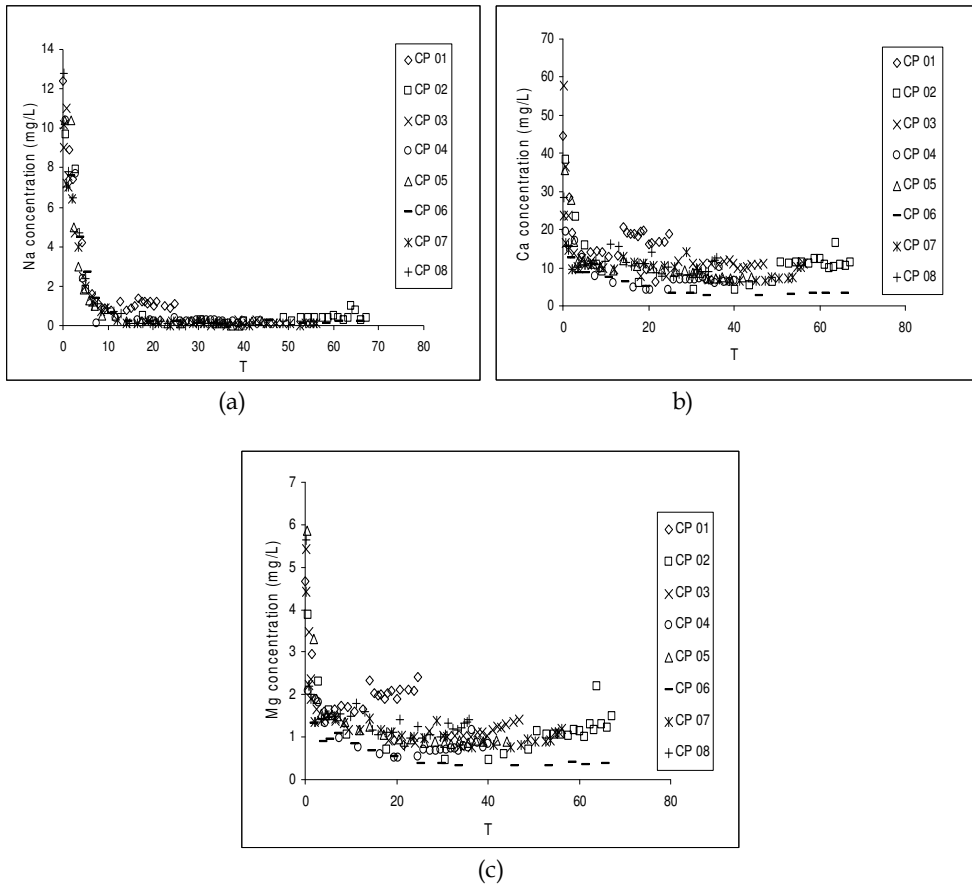
Fig. 3. Cations in soil column leachates percolated with distilled water (a) sodium, (b) calcium, (c) magnesium.
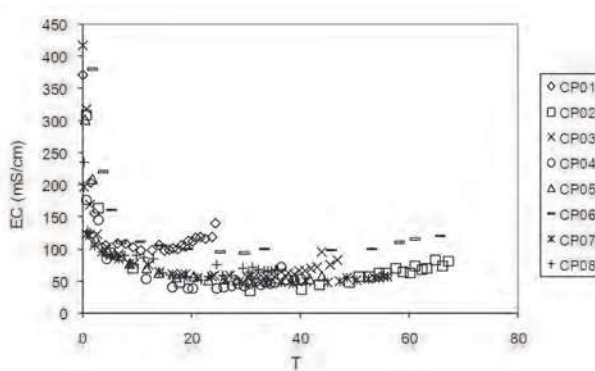

Fig. 4. Electrical conductivity (EC) in soil columns percolated with distilled water.
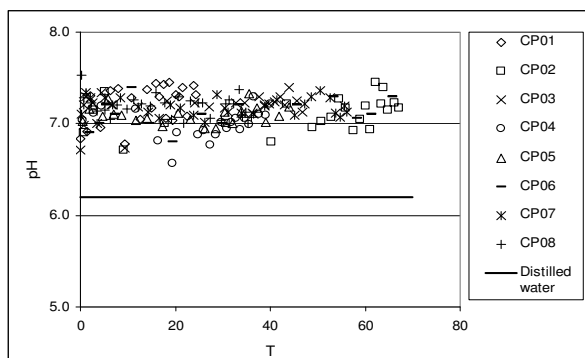
Fig. 5. Leachate pH of soil column percolated with distilled water.

The significant variation (up to one order of magnitude) in hydraulic conductivity with the number of pore volumes percolated (T) is shown in Figure 2. The increase in hydraulic conductivity at the beginning of the test may have been caused by the gradual increase in degree of sample saturation due to expulsion of air from the voids.

Distilled water percolated through the soil led to a decrease in ionic concentration (Na^+, Ca^{2+}, Mg^{2+} etc.) of the soil solution (Figures 3 (a), (b), (c)) as a result of expansion of the diffuse double layer. This expansion may have contributed to colloidal dispersion including that of material that acted as cementing agent of primary particles. The dispersion of cementing agents led to partial disaggregation of the soil structure, causing the greatest effect on soil macroporosity. Given the high correlation between soil hydraulic conductivity and macroporosity, it is clear that a decrease in macroporosity would lead to a proportional reduction in hydraulic conductivity.

Values of electrical conductivity were higher at the beginning of the column test (Figure 4) when greater leaching of basic cations occurred.

Leachate pH values varied somewhat during soil saturation with distilled water. All sample leachate pH values were higher than the influent water (pH=6.2) due to leaching of the bases Na^+, Mg^{2+}, Ca^{2+} adsorbed on the soil exchange complex. Their leaching to the aqueous solution resulted in an increase in hydroxide concentration (OH^-), and consequently in leachate pH.

6.3.1.2 Percolation of contaminant solution

Soil hydraulic conductivity curves for all samples percolated with the contaminant solution are presented in Figure 6. Control samples CP01 and CP06 were percolated with distilled water and served as references. Concentration curves for the leached cations versus pore volumes are presented in Figures 7a, 7b and 7c. Graphs of effluent electrical conductivity and pH versus pore volumes are presented in Figures 8 and 9, respectively.
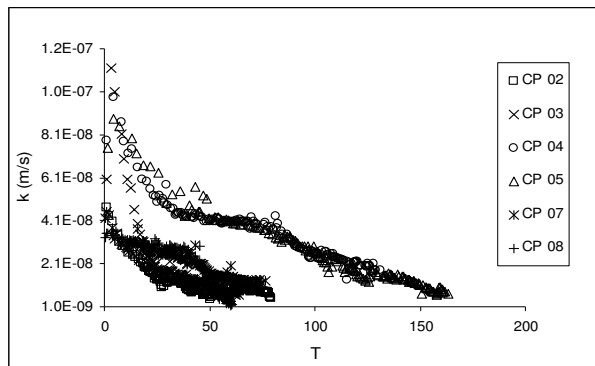
Fig. 6. Hydraulic conductivity in soil samples percolated with contaminant solution.
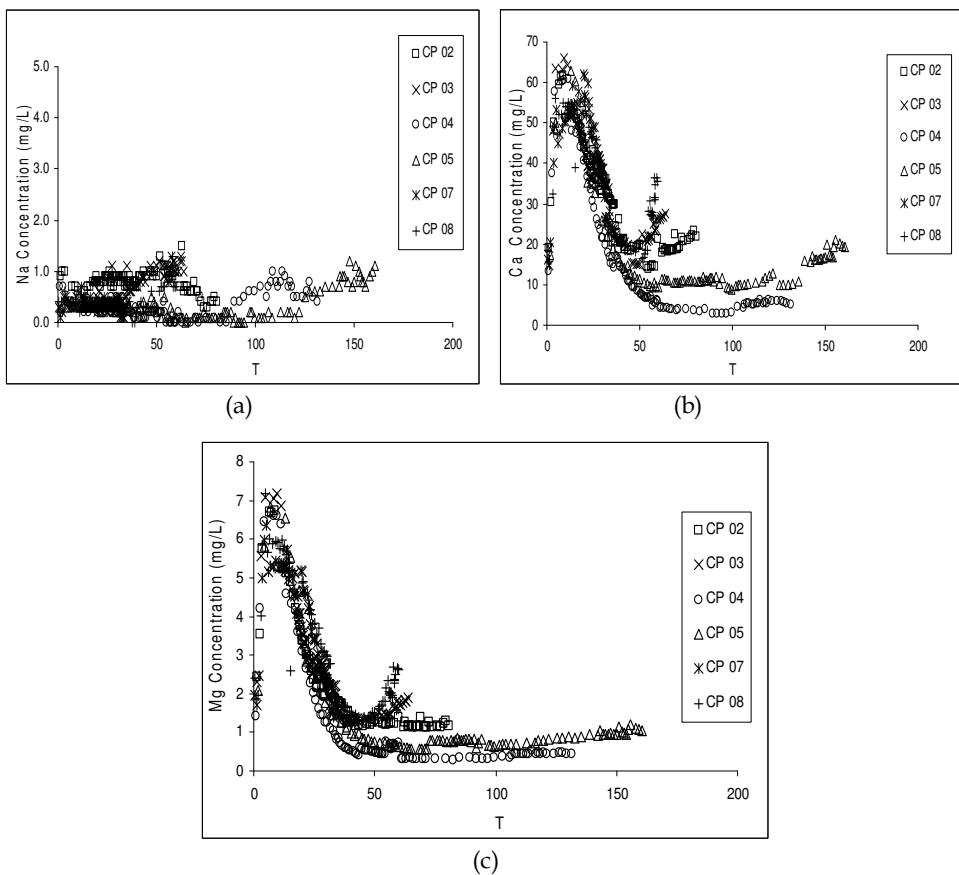

(a)

(b)

(c)

Fig. 7. Cation concentrations concentration in leachates from soil columns percolated with contaminant solution: a) sodium, b) calcium e c) magnesium.
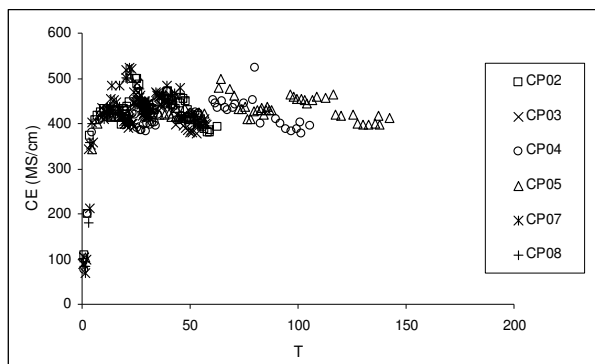
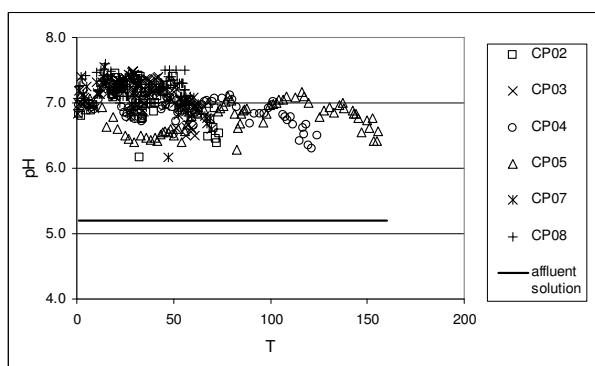Fig. 8. Electrical conductivity in leachate from soils columns percolated with contaminant solution.

Fig. 9. pH of leachate from soil columns percolated with contaminant solution.

A significant decrease in hydraulic conductivity with percolation of contaminant solution was seen for all samples (Figure 6). The decrease was not homogeneous among samples due to the different structures formed after the initial percolation with distilled water (Figure 2). The large difference in water volume percolated directly influenced the hydraulic conductivity behavior when percolating the contaminant solution. In samples CP04 and CP05, the small difference observed between number of pore volumes and amount of leached cations when percolating water led to a similar hydraulic conductivity behavior when the contaminant solution was percolated through these columns.

The decrease in hydraulic conductivity in all samples was caused by obstruction of soil pores by heavy metals precipitation. According to Alloway (1995), the solubility of Cr^{3+} decreases at pH values greater than 4, with complete precipitation of the metal at values above 5.5. Evidence of metals precipitation from the contaminant solution are indicated by the pH versus T curves in Figure 9. Curves obtained for samples CP04 and CP05 are shown in Figure 10 because of the large amount of data overlay in Figure 9. Hydraulic conductivity *versus* T curves presented the same trend in variation as the pH *versus* T curves in all samples tested.

Column CP04 presented lower hydraulic conductivity than CP05 for number of pore volumes between 13 and 50 (Figure 6). CP04 leachate pH was greater than that of CP05 over this pore volume interval, indicating greater precipitation in CP04. From that point on the pH values approached the hydraulic conductivity values up to T=104. At that point CP05 leachate pH increased compared to that of CP04 and consequently the hydraulic conductivity of CP05 decreased more than that of CP04. This occurred in all samples.

Column CP08 presented the highest leachate pH value (Figure 11) and lowest final hydraulic conductivity (Figure 6) of all samples. Higher pH values were observed at the beginning of the test (maximum of 7.6) for T values up to about 17, decreasing afterwards to T=38. From that point on, the pH increased indicating an increase in metals precipitation and consequent decrease in hydraulic conductivity.

More colloidal dispersion also occurred in the samples after percolation with contaminant solution than after percolation with distilled water. Microphotographs of sample CP06 (control) and CP02 are presented in Figures 12 and 13. It can be seen that the soil mass was more uniform in sample CP02 than in sample CP06, indicating more clay dispersion in the former. It is therefore possible to conclude that clay dispersion occurred during contaminant solution percolation and the dispersion contributed to the decrease in hydraulic conductivity.
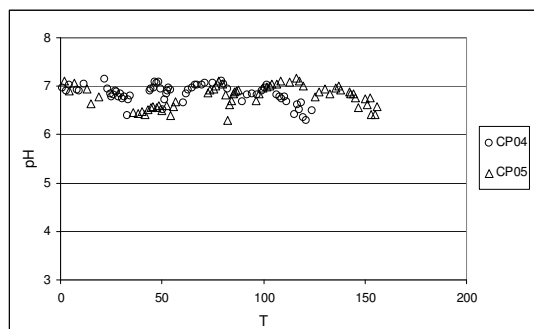
Fig. 10. Comparison of pH values of leachate collected from soil columns CP04 and CP05 percolated with contaminant solution.
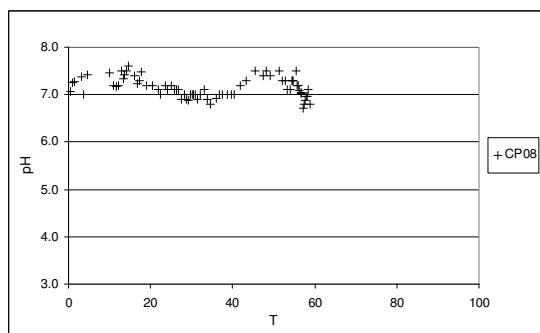
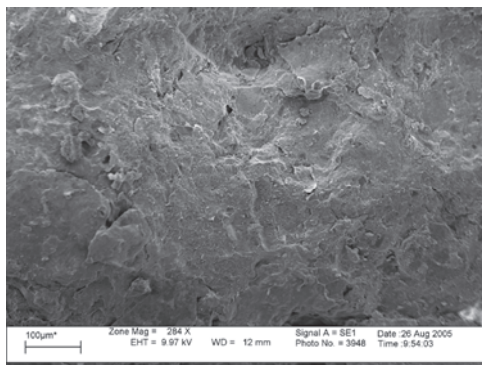Fig. 11. pH values of leachate collected from soil column CP08 percolated with contaminant solution.

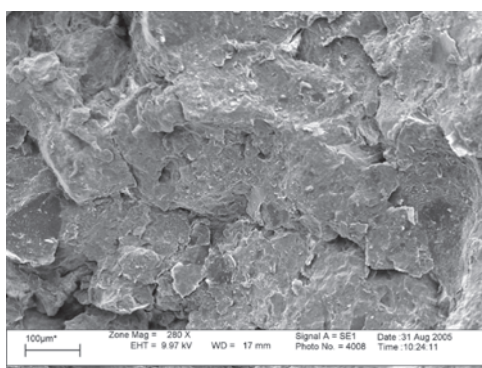Fig. 12. Microphotograph of sample CP02.

Fig. 13. Microphotograph of sample CP06 (control).

Alterations in of all sample leachate pH values were attributed to an initial washing of the bases Na^+, Mg^{2+}, Ca^{2+} (distilled water percolation increased the concentration of OH^- in the leachate because the bases are accompanied by hydroxyl) present in the soil solution exchange complex (Figures 7a, 7b and 7c).

In aqueous solution the bases promoted an increase in hydroxide concentration (OH^-), and thus an increase in solution pH. The fact that the leachate pH value remained above that of the influent solution may be due to the fact that ion exchange of metals by the bases adsorbed in the soil solid phase continued over the course of the test. It is believed that when sample saturation with all the metals is reached the leachate pH will tend to equal the influent pH, as was observed by Azevedo et al. (2005).

Cation leaching occurred due to substitution by heavy metals added to the soil. The initially high exchange of Ca^{2+} and Mg^{2+} decreased as the exchange sites occupied by these cations were occupied and their soil concentration decreased. Na^+ was leached in small concentrations during almost the entire test. The concentrations of Ca^{2+}, Mg^{2+} and Na^+ in the leachate of some samples tended to increase at the end of the test, indicating greater leaching of these cations caused by adsorption of metals with greater affinity for the soil matrix.

Electrical conductivity values presented fluctuations. The final portion of the curve in Figure 8 presented a decline that indicates that a greater adsorption and/or precipitation of metals occurred.

6.4 Determination of transport parameters

Only the metals Mn (in all samples) and Zn (only in CP04) reached a steady state concentration (Figures 16 and 17c) in the column tests, that is they saturated the soil adsorption sites. Therefore it was only possible to determine the retardation factor (R_d) and hydrodynamic dispersion coefficient (D_h) using the cumulative mass method (Shackelford, 1995) for these two these metals. The curves of cumulative mass ration (CMR) *versus* theoretical and experimental T values are presented in Figures 14 and 15.
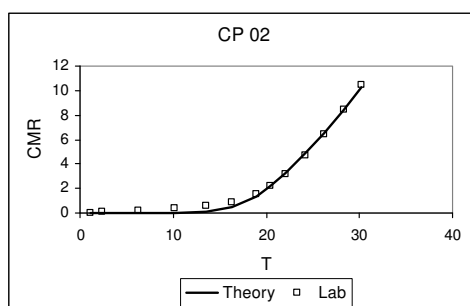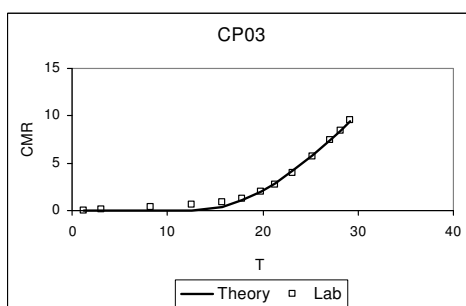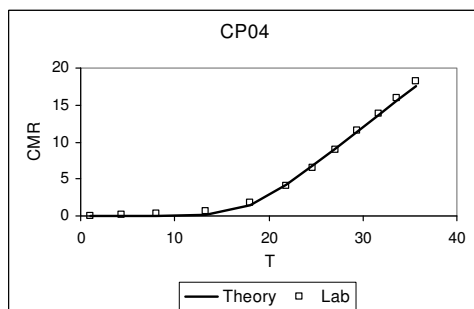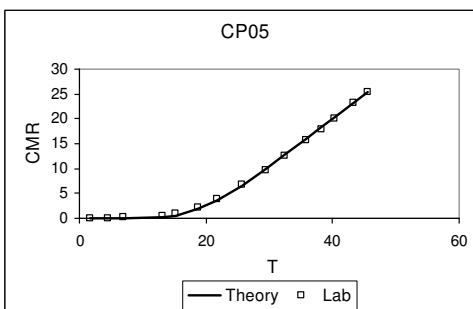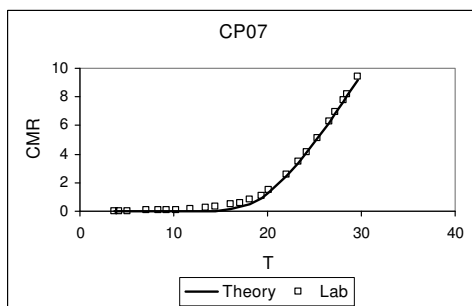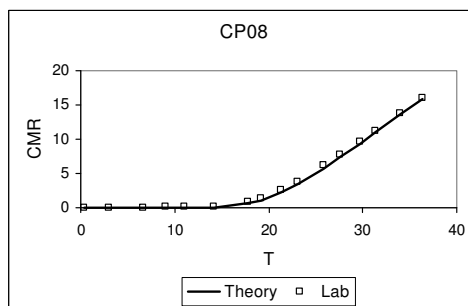
Fig. 14. Manganese cumultative mass ratio curves. CP02, (b) CP03, (c) CP04, (d) CP05, (e) CP07 e (f) CP08.
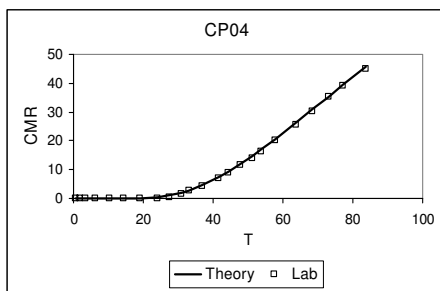
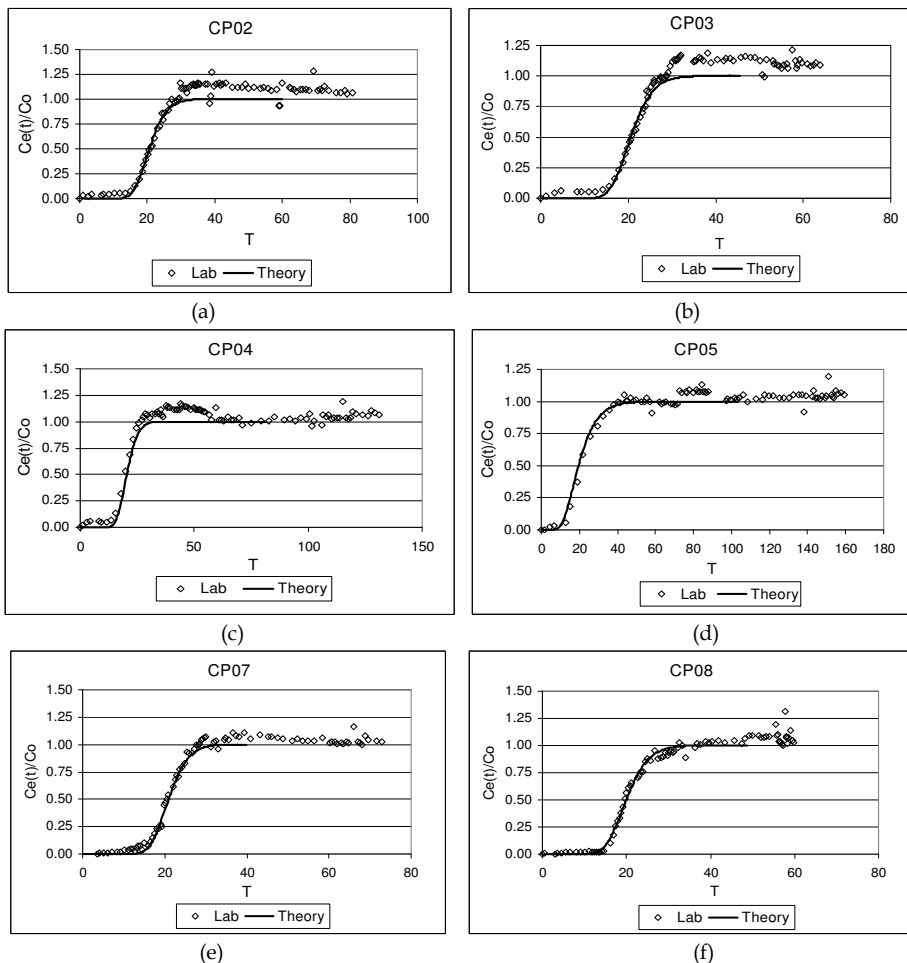Fig. 15. Zinc cumultative mass ratio curve (CP04).

Fig. 16. Manganese elution curves from soil columns: (a) CP02, (b) CP03, (c) CP04, (d) CP05, (e) CP07, (f) CP08.
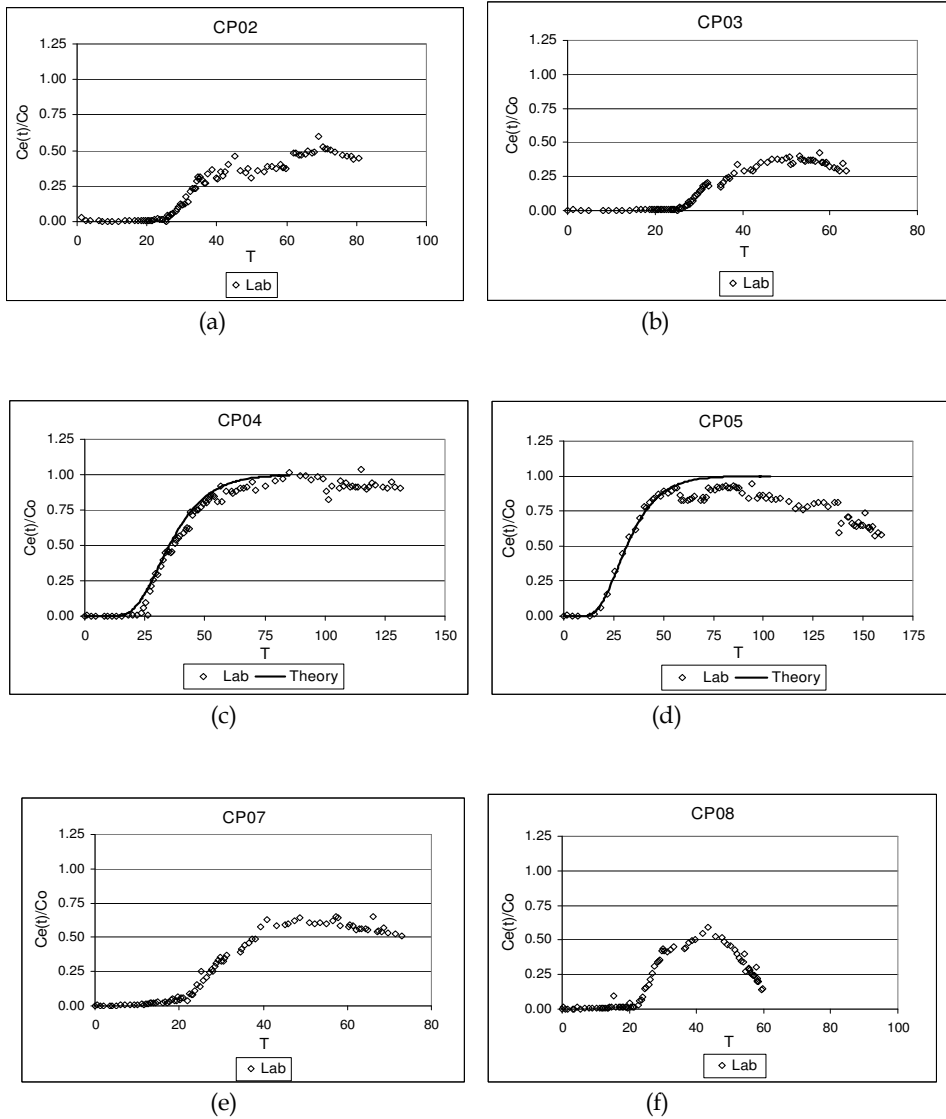
Fig. 17. Zinc elution curves from soil columns: (a) CP02, (b) CP03, (c) CP04, (d) CP05, (e) CP07, (f) CP08.
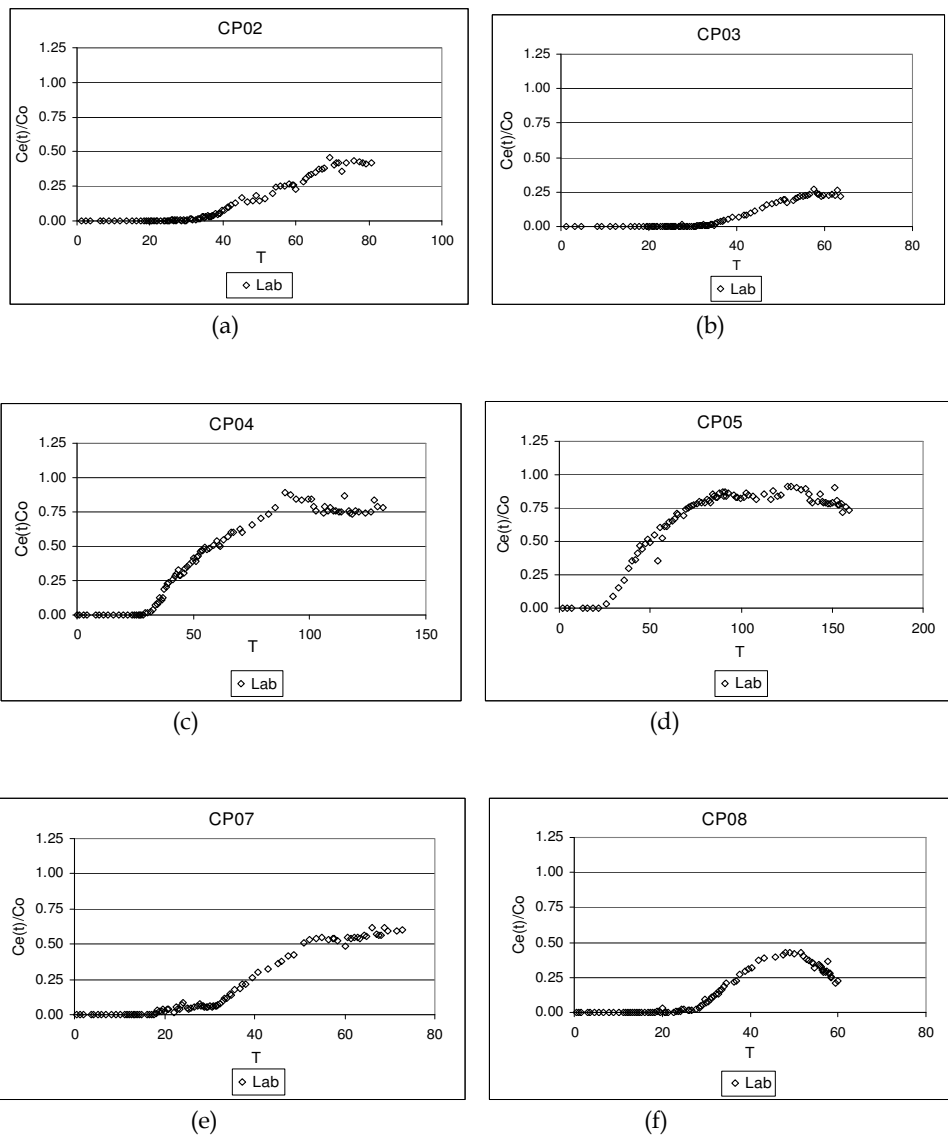
(a)

(b)

(c)

(d)

(e)

(f)

Fig. 18. Cadmium elution curves from soil columns: (a) CP02, (b) CP03, (c) CP04, (d) CP05, (e) CP07, (f) CP08.

Mn, Zn and Cd elution curves are presented in Figures 16 to 18. The desorption of Mn (Figure 16) and the increase in adsorption of Zn (Figures 17a, b, d, e, f) and Cd (Figures 18c, d, f) at the end of the column tests were observed in some samples.

The metals Cu, Pb and Cr remained totally retained in the soil, since these metals have low mobility and high affinity for iron oxides present in the soil. These elements can also form precipitates depending on their concentrations as well as on soil and solution pH.

No large data dispersion was observed in the CMR *versus* T curves (Figures 14 and 15) and the experimental curves adjusted well to the theoretical curves. The transport parameters R_d and D_h are presented in Table 6.

The relative Mn concentration (C/Co) in the elution curve (Figure 16) was greater than unity, evidence of desorption. For Zn (except CP04) and Cd, the C/Co ratio never reached unity (and decreased in some cases), due to the decrease in hydraulic conductivity, principally in CP08. It is thus possible to conclude that Zn and Cd replaced the desorbed Mn on the soil adsorption sites.

A Mn retardation factor of 18.8 was reported by Azevedo et al. (2005), close to the average value presented in Table 6. Given the greater hydraulic conductivity values (10^{-5} to 10^{-6} cm s^{-1}) in the work by Azevedo et al. (2005) as compared to those in the present study (10^{-6} to 10^{-7} cm s^{-1}), the mobility of Mn was found to be practically independent of soil hydraulic conductivity. The average D_h value equal to 4.3E-04 cm^2 min^{-1} (Table 6) was a little lower than the 8.64E-03 cm^2 min^{-1} presented in Azevedo et al. (2006), probably because the lower average percolation velocity used in that study caused less Mn dispersion.

Metal	Sample	R_d	D_h (cm^2 min^{-1})
	CP02	20	4.6E-04
	CP03	20	3.9E-04
	CP04	18	4.4E-04
Manganese	CP05	20	8.0E-04
	CP07	20.5	2.0E-04
	CP08	20.4	2.7E-04
	Average	19.8	4.3E-04
Zinc	CP04	38	1.4E-03

Table 6. R_d and D_h obtained by the cumulative mass method.

6.5 Soil physical analyses

Results of dispersed clay in samples withdrawn from the soil columns were quite similar for both fast and slow dispersal methods. Average results are indicated in Table 7. The values of dispersed clay indicated little dispersion of fine material in the soil samples analyzed. Greater values were expected since the hydraulic conductivity results indicated that clay dispersion occurred when distilled water was percolated through the columns. However the samples were stored for two months and 23 days (justified by the time necessary to decide on the appropriate sample analyses) and it is believed that they suffered a tixotropic effect. Compacted clays may exhibit a considerable tixotropic effect (increase in resistance and rigidity with time) leading to a natural tendency to flocculate during storage. According to Boscov (1997), the structure of adsorbed water may change in stored compacted samples and can be detected by measurements that show the decrease in neutral pressure with time after compaction.

Sample	CP02	CP04	CP06	CP08
Dispersed clay (kg/kg)	0.002	0.002	0.005	0.003
FI*	0.99	0.99	0.988	0.99

*Floculation index

Table 7. Dispersed clay in samples withdrawn from the soil columns.

6.6 Micromorphological analyses

Mosaics were prepared from 50% of the photos of slides taken in the optical microscope to better visualize pores. The photos taken with the scanning electron microscope (SEM) permitted visualization of a greater quantity of sample fissures in the control (CP06) than in the columns percolated with contaminant solution (CP02, CP04 and CP08). Mosaics of samples CP02, CP04 and CP06 are presented in Figure 19. No mosaic was made of CP08 due to insufficient sample quantity for evaluation.
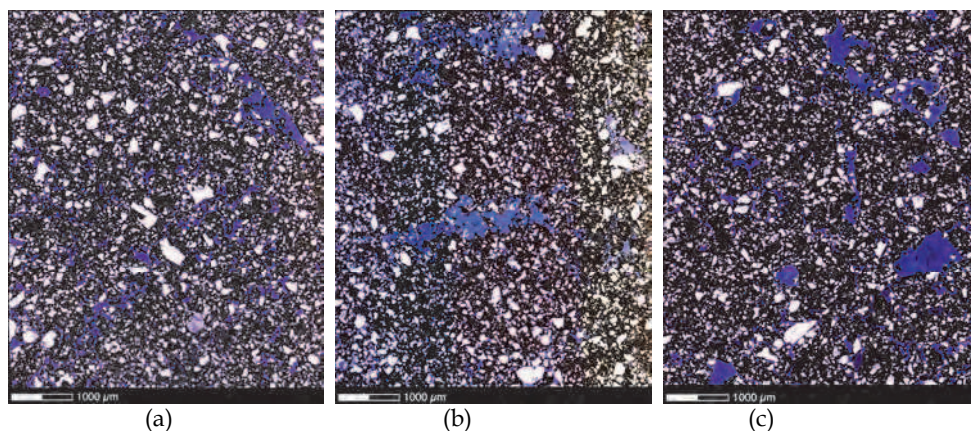

(a)   (b)   (c)

Fig. 19. Optical microscope mosaic of samples withdrawn from soil column: (a) CP02; (b) CP04; (c) CP06 (control)

A greater quantity of dark stained macropores can be observed in control column CP06 that had the greatest hydraulic conductivity. Sample CP04 presented larger pores than sample CP02, consistent with the larger final hydraulic conductivity of sample CP04, which could be attributed to less plugging of macropores.

The presence of fissures in photos of samples CP06 (control) and CP08 obtained by SEM are indicated by arrows in Figures 20 and 21. More fissures are present in CP06 (Figure 20) than in the other samples. The fissures in the other samples may possibly have been blocked by precipitates formed during the percolation of the contaminant solution in the soil columns and also by particle washout during the test (Figure 21).
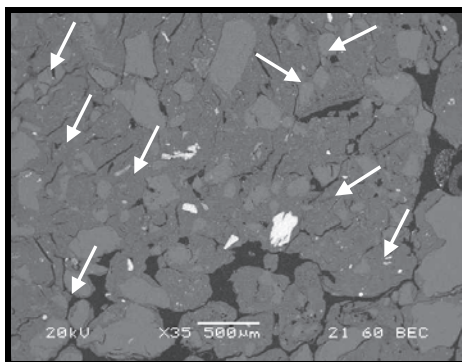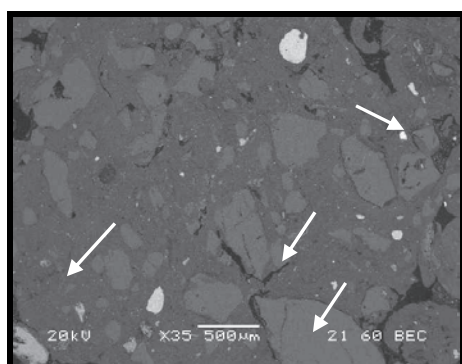
Fig. 20. Various fissures present - CP06

Fig. 21. Few fissures present - CP08.

7. Conclusions

Of the various conclusions to be drawn, it should be emphasized that initial percolation of distilled water to saturate the soil without counter pressure influenced the column test results since the soil structure was altered, especially when a large pore volume was percolated.

Hydraulic conductivity values decreased significantly in all soil columns, although the difference differed among the samples.

The difference in number of pore volumes percolated (T) and the amount of cations leached during percolation of distilled water in the soil columns directly affected hydraulic conductivity when the contaminant solution was percolated possibly because of an alteration in soil structure caused by initial percolation with distilled water.

Evidence of pore obstruction caused by heavy metal precipitation was observed, explaining in part the decrease in hydraulic conductivity. The decrease was also partially attributed to dispersion of colloidal material

Greater leaching of Ca^{2+}, Mg^{2+} and Na^+ was observed at the end of the soil column tests resulting in greater adsorption of some metals.

At the end of the column test, Mn was desorbed and a proportionally greater amount of Zn (except for CP04) and Cd were adsorbed due to decrease in hydraulic conductivity (especially in CP08), suggesting that Zn and Cd dislocated Mn from the adsorption sites.

Dispersed clay measurements indicated high flocculation indexes but the results may have been influenced by a trixotropic effect occurring in the stored samples.

Comparison of Mn transport parameters determined in the present study with those obtained in a previous study showed that Mn mobility was practically independent of soil hydraulic conductivity when all other factors were held constant. Hydraulic conductivity affected metal mobility of the other five metals studied.

8. Acknowledgments

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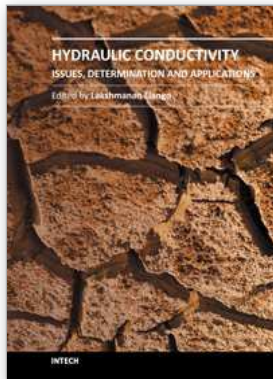
Hydraulic Conductivity - Issues, Determination and Applications

Edited by Prof. Lakshmanan Elango

There are several books on broad aspects of hydrogeology, groundwater hydrology and geohydrology, which do not discuss in detail on the intrigues of hydraulic conductivity elaborately. However, this book on Hydraulic Conductivity presents comprehensive reviews of new measurements and numerical techniques for estimating hydraulic conductivity. This is achieved by the chapters written by various experts in this field of research into a number of clustered themes covering different aspects of hydraulic conductivity. The sections in the book are: Hydraulic conductivity and its importance, Hydraulic conductivity and plant systems, Determination by mathematical and laboratory methods, Determination by field techniques and Modelling and hydraulic conductivity. Each of these sections of the book includes chapters highlighting the salient aspects and most of these chapters explain the facts with the help of some case studies. Thus this book has a good mix of chapters dealing with various and vital aspects of hydraulic conductivity from various authors of different countries.

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