Revista
Brasileira de
Ciência do Solo

Division - Soil Processes and Properties | Commission – Soil Pollution, Remediation and Reclamation of Degraded Areas

Cadmium and copper transport in alluvial soils in the Brazilian semiarid region: column percolation and modeling

Vitor Hugo de Oliveira Barros(1), Adriana Thays Araújo Alves(1), Severino Martins dos Santos Neto(1), Artur Paiva Coutinho(1)*, Laurent Lassabatere(2), Manuella Virgínia Salgueiro Gondim(3) and Antonio Celso Dantas Antonino(3)

(1) Universidade Federal de Pernambuco, Centro Acadêmico do Agreste, Departamento de Engenharia Civil, Caruaru, Pernambuco, Brasil.
(2) Université Claude Bernard Lyon, Vaulx-en-Velin, France.
(3) Universidade Federal de Pernambuco, Centro de Tecnologia e Geociências, Departamento de Energia Nuclear, Recife, Pernambuco, Brasil.

ABSTRACT: Regarding the Brazilian textile industry, part of the northeast region stands out as the second-largest textile manufacturing hub in the country. Despite its importance, this industrial activity has been bringing relevant environmental concerns regarding the disposal of textile effluents, especially from industrial laundries. This waste contains many chemicals and among them are various types of heavy metals. To assess environmental risks associated with heavy metals, pollutant transfer needs to be investigated. This study evaluated the retention and mobility of heavy metals Cd and Cu in alluvial soil, through soil column tests. The up-flow column percolation tests were performed using a nonreactive tracer (KBr) at a concentration of 0.3 mol L^{-1} and injecting a metallic solution containing Cu and Cd at 100 and 60 mg L^{-1}, respectively. The injection flow rate was 0.75 mL min^{-1}. The hydro-dispersive parameters were obtained by modeling the observed breakthrough curves with the convection-dispersion equation (CDE) and the two-region model, also referred to as the MIM (Mobile-IMmobile waters) model. The transport parameters were obtained from the two-site model (TSS). All elution curves were fitted to the models with the CXTFIT 2.0 program. The Two-Site Sorption Model was the best for the case studied, with R^2 of 0.985 and 0.995 for Cu and Cd, respectively. The values of R were considerably higher than the unit, presenting an average of 2.138 for Cu and 1.907 for Cd. This indicates a delay of these contaminants when leaving the column, which is caused by the interaction of these chemical compounds with the soil. The values obtained for parameter D were 3.469 for Cu and 5.205 for Cd. Thus, the metals in this study present a risk of groundwater contamination for the local alluvial aquifers. The main reason for that is the physicochemical features of the soil, such as high sand content (85 %) and low OM content (2.1 %). The results also indicated greater retention and less mobility for Cu than for Cd, pointing to a greater risk for Cd.

Keywords: alluvial aquifers, Arenosols, heavy metals, mobility.

*** Corresponding author:**
E-mail: arthur.coutinho@ufpe.br

Received: November 17, 2022

Approved: June 29, 2023

How to cite: Barros VHO, Alves ATA, Santos Neto SM, Coutinho AP, Lassabatere L, Gondim MVS, Antonino ACD. Cadmium and copper transport in alluvial soils in the Brazilian semiarid region: column percolation and modeling. Rev Bras Cienc Solo. 2023;47:e0220153
https://doi.org/10.36783/18069657rbcs20220153

Editors: José Miguel Reichert and João Tavares Filho.

INTRODUCTION

The increased pollution of water resources is a major environmental problem. It is reported that an increasing number of hazardous chemicals have been released into receiving waters and could reach the groundwater (Abbasi et al., 2021). The contamination of these waters by human activities is of concern due to the threat to public health (Won et al., 2019). In this case, heavy metal pollution has great relevance due to its toxic effects, non-biodegradability, and multiple releases by a wide range of anthropogenic activities.

Heavy metals are classified as persistent bio-accumulative toxicants (PBTs), in the same way as organo-metal compounds (Akindele et al., 2020). These compounds cannot be degraded, only converted to less toxic forms (Swarnkumar et al., 2020), and are generally toxic to animals and plants (Wang et al., 2020). Regarding adverse health effects, several neurological and functional disorders are reported (Swarnkumar et al., 2020; Liu et al., 2021).

The content of heavy metals exceeds safety standards in many rivers and groundwater (Qiu et al., 2021). Groundwater contamination by heavy metals can occur from different sources, such as leachate from mine tailings and landfills or discharge of domestic and industrial effluents (Abbasi et al., 2021). Within these sources, textile effluents are diversified in terms of chemical composition and highly characterized by heavy metals in high concentration, such as cadmium and copper (Swarnkumar et al., 2020).

In Brazil, the northeast region stands out as the second-largest textile manufacturing hub in the country (Alexandre et al., 2020). This region hosts the Textile Pole of Agreste of Pernambuco, an important local production arrangement of garments that involves more than 1200 production units in more than 10 municipalities (Sebrae, 2013). Despite all this industrial arrangement, the northeast region, which encompasses most of the Brazilian semiarid region, is marked by problems related to water scarcity. In the absence of surface water resources, many rural communities in this region obtain water through underground reservoirs, such as alluvial deposits. These reservoirs serve as natural water resource, from the excavation of wells in the dry bed of intermittent rivers (Braga et al., 2015).

In particular, these reservoirs are easy to recharge in short rainy periods, serving the diffuse rural population in long periods of drought. These deposits are an important source of water supply in the region (Alexandre et al., 2020; Caetano et al., 2020), with high potential for various purposes, such as domestic use, family agriculture, and animal and plant watering. In contrast, these formations have a high vulnerability because the textile economic activity has generated contamination risks by heavy metals and textile dyes. From a compositional point of view, the alluvial deposits in the Alto do Capibaribe region are highly heterogeneous geological formations, made of lithofacies with contrasting hydrodynamic properties, which are prone to preferential flows and pollutant dispersion (Slimene et al., 2017; Rabelo et al., 2021).

Contamination of alluvial soils by textile dyes, such as Remazol Black B and Direct Black 22, respectively, were investigated by Alves et al. (2020) and Alexandre et al. (2020) in the Alto Capibaribe region, Agreste of Pernambuco. They used the batch method to evaluate the retention capacity of local soils for such contaminants. Both authors concluded that these pollutants have enough mobility to contaminate the local aquifer, constituting a risk to the soil and groundwater quality. This case is an illustration of the risks associated with textile effluents, which are one of the sources of heavy metals in the environment and groundwater (Panigrahi and Santhoskumar, 2020).

To understand the environmental behavior and risks associated with heavy metals, column experiments combined with modeling constitute an efficient tool to accede to the transfer can be obtained through displacement experiments of solutions containing heavy metals in soil columns under laboratory conditions. According to Dong et al. (2018), soil column experiments' transport parameters can predict the contamination plumes in natural porous environments. Understanding the miscible displacement of non-reactive and reactive solutes in laboratory columns and the related estimation of transfer parameters applicable to real soils is fundamental to mitigating the environmental impacts caused by these pollutants. The hydrodispersive and hydrodynamic parameters play a significant role in the characterization of solute transfer and remain crucial for the prevention and remediation of pollutant impacts on the environment. The miscible displacement assays of contaminants are highlighted in the literature by several authors in different soil types for different types of pollutants (Lassabatere et al., 2004, 2007; Smaranda et al., 2017; Chotpantarat et al., 2018; Morsali et al., 2019; Shahmohammadi-Kalalagh and Taran, 2019; Abbasi et al., 2021; Alves et al., 2022).

Regarding the models used for solute transfer through soil columns, the convection–dispersion equation (CDE), also called the one-region model, is the classic model often used for the one-dimensional transport of solutes in homogeneous porous media, under isothermal conditions. Due to physical and chemical non-equilibria, many experiments have demonstrated the presence of nonequilibrium flow and transport conditions in soils (Šimůnek et al., 2008). In these cases, the CDE model no longer describes the transport adequately. For physical non-equilibrium (water fractionation into mobile and stagnant zones), the two-region non-equilibrium model (MIM) is required (Köhne et al., 2009a,b). This model accounts for the concomitancy of two regions, the mobile region hosting the mobile water and the immobile region hosting pockets of stagnant water (van Genuchten and Wierenga, 1976). Solutes are transported by convection and dispersion in the mobile region and diffuse to the immobile region by molecular diffusion at the interface between the two regions (Gaudet et al., 1977). On the other hand, for the chemical non-equilibrium, the two-site non-equilibrium model (TSS) considers different types of adsorption: type 1 (instantaneous sorption) and type 2 (first-order kinetically limited sorption) (Cao et al., 2021). The chemical non-equilibrium is a kinetic process attributed to a slow sorption reaction at the solid-solution interface or a slow diffusion to sorption sites (Sidoli et al., 2016).

The determination of transport parameters through the CDE, MIM, and TSS models has great importance for the prediction of pollutant transport in alluvial deposits. Each heavy metal has specific chemical, physical, and toxicological features (Suzaki et al., 2017). Consequently, it is necessary to analyze the transport of different metals that are present in textile effluents. To contribute to the issue, this study evaluates the retention and mobility of two heavy metals, cadmium (Cd) and copper (Cu), both already reported in textile effluents at high concentrations (Abdullahi and Ibrahim, 2019), in an alluvial soil of the dry bed of the Capibaribe River, Agreste de Pernambuco Brazil, through laboratory tests with saturated soil columns.

This study is part of a series of studies that analyzed the impact of the textile industry in northeastern Brazil. The series began with the analysis of the transport of the dye Remazol Black 5 (Alves et al., 2020) and Direct Black 22 (Alexandre et al., 2020), both widely used by the local textile industry. These studies demonstrated the great mobility of the dyes in the alluvial soils of the region and considered that the textile effluent is characterized by heavy metals (Swarnkumar et al., 2020). Meanwhile, other studies have evaluated the retention and mobility of heavy metals in alluvial soils of the location under study. A kinetics and sorption isotherm study was conducted for Cd and Cu (Barros et al., 2021) and chromium and zinc (in publication process). Other studies were conducted using the miscible displacement technique in soil columns saturated with the dye Remazol Black 5 (Alves et al., 2022) and Cd and Cu (present study). Thus, this study suggests a proposal to complement the study of kinetics and isotherm of Cd and Cu (Barros et al., 2021), which, despite being efficient for analyzing the solute-soil interaction, has the disadvantage of a high liquid-solid ratio (Alves et al., 2022). Therefore, the miscible displacement method provides a better analysis because it is closer to reality (Zhang et al., 2018). Because of that, it was possible, for example, to work with the apparent density of the experimental columns similar to the real one. This study aimed to evaluated the mobility of heavy metals Cu and Cd in alluvial soils of the Alto do Rio Capibaribe, in Pernambuco, Brazil, through laboratory tests with saturated soil columns.

MATERIALS AND METHODS

Study area

The studied soil belongs to the most superficial layer of an alluvial sediment deposit of the Capibaribe Basin, Pernambuco, Brazil, classified as *Neossolo Flúvico Psamítico* according to Santos et al. (2018) and Fluvisoil according to IUSS Working Group WRB (2015). The collection site is located in the macrozone of Alto Capibaribe, where the river is intermittent, in the division between the Pernambuco cities of Santa Cruz do Capibaribe and Brejo da Madre de Deus (Figure 1). The geographic coordinates are 7° 56’ 57” S and 36° 17’ 57” W. The samples were collected from the most superficial layer of the alluvial deposit profile of the dry bed of the Capibaribe River. Before sampling, a trench measuring 12 × 5 × 2 m was excavated and its layers haven inspected. The top layer with a maximum thickness of 0.52 m was chosen for this study. Sampling was carried out using a hand auger, resulting in disturbed samples. No additional preparation was undertaken for sample collection, except for removing surface debris.

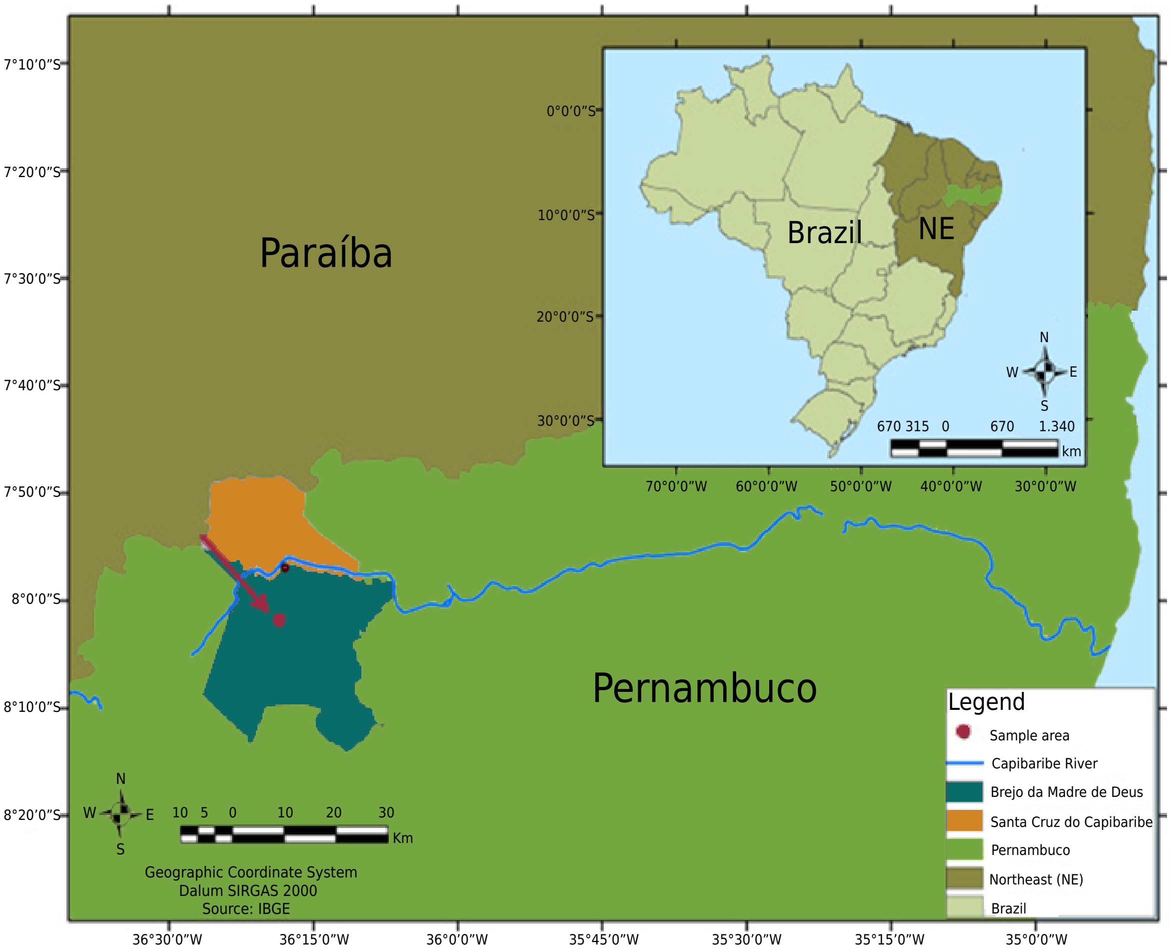

Figure 1. Study area sites adapted from Rabelo et al. (2021).

The region has an annual average rainfall of 600 mm and a potential evapotranspiration of 1900 mm per year. The climatic conditions are semiarid and the native vegetation cover is Caatinga (Braga et al., 2015). Geologically the study area is located over the Borborema Province and inserted on fissural domain hydrogeology, formed by rocky crystalline features (Beltrão et al., 2005).

Soil physical-chemical properties

Physicochemical properties of the soil are presented in table 1. The Point of Zero Charge (PZC) was obtained by Alexandre et al. (2020), and other physicochemical properties were determined by Rabelo et al. (2021).

The soil is sandy, having 82 % of sand and only 18 % of fine particles (silt and clay), and belongs to the soil class “loamy sand”. Clays, organic matter, and iron oxides are identified as the most reactive constituents in soils and sediments, playing an important role in the fate and transport of contaminants (Yin et al., 2019). Clay (7 %) and organic matter content (2.17 %) are of low concentrations.

Despite the low percentage of clay and OM, the soil presented an average value of cation exchange capacity (CEC) (7.0 $cmol_c$ dm^{-3}). Exchangeable cations include both basic cations (K^+, Ca^{2+}, Mg^{2+}, and Na^+) and acidic cations (H^+, Al^{3+} and Fe^{2+}). The soil CEC quantifies the capability of the soil to sorb exchangeable cation (Kalubi et al., 2017). The soil presents a pH(H_2O) of 8.26, higher than the PZC (5.02). The Point of Zero Charge PZC represents the value of pH(H_2O) corresponding to zero surface charge for particles. If the pH is lower than the PZC then the matrix has a positively charged surface, while if the pH is higher than the PZC, the surface is negatively charged (Bachratá et al., 2013). The first condition favors the sorption of anions, whereas the second condition favors the sorption of cations (Banerjee and Chattopadhyaya, 2017).

Up-flow column percolation test

The up-flow column percolation tests were performed in triplicate. The experimental device used was a cylindrical acrylic column 0.30 m high and 2.60 cm of internal diameter, a twelve-channel peristaltic pump, and a fraction collector (Figure 2). The column was filled with soil and was lightly compacted into 2 cm layers. The soil used was subjected to air-drying, disaggregation, and sieving through a 2 mm mesh sieve prior to being filled in the columns. The soil was saturated with a solution of $CaCl_2$ (Calcium chloride), purity ≥99 %, in an ascending flow with a concentration of 0.01 mol L^{-1}. A pore volume was applied for each type of displacer solution. Three different solutions were used. One tracing solution containing Potassium Bromide (KBr) at the concentration of 0.3 mol L^{-1}. This non-reactive tracer, aimed to determine physical transport parameters. The others

Table 1. Physicochemical properties of the soil

Sand	Silt	Clay	Soil classification		SS	pH(H_2O)	ZPC	BS	CEC	OM	OC	V^2
	%				m^2 g^{-1}			$cmol_c$ dm^{-3}			%	
82	11	7	Loamy sand		3.75	8.26	5.02	7	7.4	2.17	1.26	94
						Oxides						
Mn	Fe	Ni	Zn	Pb	Sr	Ti	Mg	Al	Si	K	Ca	V
						mg kg^{-1}						
231±29	13897±445	9±4.9	25±7	32±12	409±6	2356±93	7112 ±981	6476±1852	38491 ±11468	28185±633	7367±927	66±12

SS: specific surface; ZPC: zero charge point; BS: sum of bases; CEC: cation exchange capacity; OM: organic matter; OC: organic carbon; V^2: Base saturation, calculated as the ratio between effective CTC and total CTC.

solutions contained Cu Nitrate [$Cu(NO_3)_2.3H_2O$] and Cd Nitrate [$Cd(NO_3)_2.4H_2O$] at a concentration of 100 mg L^{-1} and 60 mg L^{-1}, respectively. The injection of each heavy metal occurred separately in its respective column. The average flow rate used was 4.5×10^{-6} m^3 h^{-1} (0.75 mL min^{-1}). The injection of $CaCl_2$ solution followed this step to leach each solution from the soil column. After column passage, the solution output was collected with the fraction collector. For the tests with the nonreactive solution, the electrical conductivity of each bottle was read on a Digimed DM-31 digital conductivity meter. The Agilent Atomic Absorption Spectrometry (AAS) apparatus was used to read Cu and Cd concentrations in the samples, following the manufactures' recommendations for wavelength and calibration curve (Agilent, 2017).

The progression of solute advancement was performed by measuring concentration (C) over time. The evolution of the parcel C/C_0 due to the number of pore volumes of the effluent collected (V/V_0) provided the elution curves (Moura et al., 2013).

The elution curves of KBr were adjusted according to the CDE model and the mobile-immobile convection-dispersion model (CDE-MIM). Contaminant elution curves (Cu and Cd) were fitted to the two Sorption sites (TSS). All adjustments were made using the STANMOD computer software CXTFIT 2.0 (*Code for Estimating Transport Parameters from Laboratory or Field tracer Experiments*) (Toride et al., 1995). The STANMOD is a software that allows the numerical solution of Equations for different initial and boundary conditions of column experiments: known concentration at the input, zero gradient concentration at column output, and initial solute concentration over time t = 0. The transfer parameters are estimated by the inverse method, fitting the calculated data to the experimental data and using the nonlinear least-squares optimization method based on the Levenberg-Maquard algorithm.

Convection-dipersion Model

The convection-dispersion (CDE) model, also called a region model, is the classic model of the one-dimensional transport of solutes in homogeneous porous media under isothermal conditions. The CDE model equation for the transfer of interactive solute with the soil matrix in homogeneous soils may be written as (Equation 1) (Radcliffe and Šimůnek, 2018):

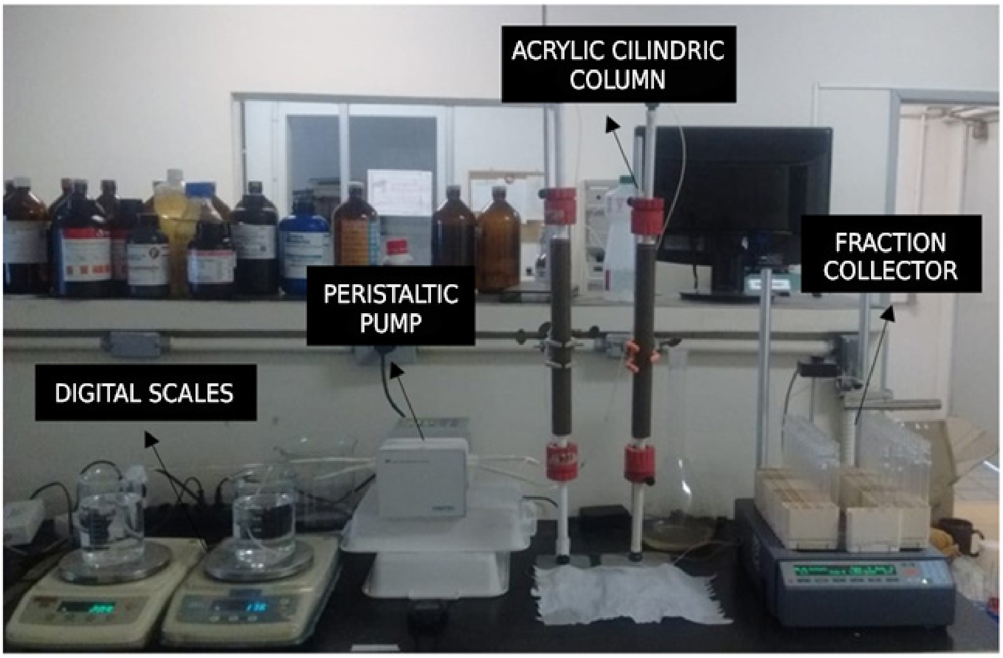

Figure 2. Picture of the experimental laboratory setup.

$$\frac{\partial}{\partial t}\left(\theta c + \rho_d S\right) = -\frac{\partial}{\partial z}\left[-\theta D \frac{\partial c}{\partial z} + qc\right] \qquad \text{Eq. 1}$$

in which: c is the dissolved solute concentration [M L^{-3}], t [T] is the time, z is the spatial coordinates [L], S is the concentration of adsorbed solute expressed as the solute mass per soil mass [M M^{-1}], ρ_d is the specific mass of the soil [M L^{-3}], D is the hydrodynamic dispersion coefficient [L^2 T^{-1}], q is the density of water flow [L T^{-1}], and θ is the volumetric water content [L^3 L^{-3}].

The convection-dispersion model equation (Equation 2) may be described in dimensionless form, considering that the displacement of the studied substance occurred with sorption under chemical equilibrium conditions (Barizon et al., 2006; Milfont et al., 2006, 2008):

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial z} \qquad \text{Eq. 2}$$

in which: v is the average of pore water velocity [L T^{-1}] and R is the delay factor, obtained according to equation 3:

$$R = 1 + \frac{\rho_d K_D}{\theta} \qquad \text{Eq. 3}$$

in which: K_D is the linear distribution coefficient [L^3 M^{-1}], representing the distributed concentrations between the liquid and adsorbed phases.

The equation is valid for the one-dimensional transport of reactive solutes subjected to adsorption, first-order degradation, and zero-order production in homogeneous and non-deformable soil.

Two region nonequilibrium model (MIM)

The MIM model consists of a conventional convection-dispersion equation for solute transport in the mobile region, coupled with a term describing solute mass transfer between mobile and immobile regions (Gao et al., 2009).

Mobile moisture is a moisture content that is located within the pores in the coarse aggregates, it has a dynamic state and the solute transport is done by convection and hydrodynamic dispersion. Stagnant moisture is a moisture content located within the microcosms' pores and is stationary.

Thus, the concentration c is the sum of the two components (mobile and immobile), resulting in equation 4:

$$\theta c = \theta_m c_m + \theta_{im} c_{im} \qquad \text{Eq. 4}$$

in which: *m* and *im* refer to the mobile and immobile region respectively.

The equations of the MIM model can be expressed by equations 5 and 6:

$$\theta_m \frac{\partial c_m}{\partial t} + \theta_{im}\frac{\partial c_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 c}{\partial x^2} - \theta_m v_m \frac{\partial c_m}{\partial x} \qquad \text{Eq. 5}$$

$$\theta_{im}\frac{\partial c_{im}}{\partial t} = \omega\left(c_m - c_{im}\right) \qquad \text{Eq. 6}$$

in which: ω is the mass exchange rate between mobile and immobile regions [T^{-1}].

The average pore of water velocity (ν), dispersivity (λ) [L], and the dimensionless number of Peclet (Pe) was defined as equations 7, 8 and 9:

$$v = \frac{q}{\theta} \qquad \text{Eq. 7}$$

$$\lambda = \frac{D}{V} \qquad \text{Eq. 8}$$

$$Pe = \frac{L}{\lambda} \qquad \text{Eq. 9}$$

Convection Two-Sorption sites Dispersion Model

The Convection-Two-Sorption sites Dispersion Model (TSS) also called the two-site sorption model, is a model that represents the chemical non-equilibrium between the solute and soil. The interaction of the solute with the soil matrix can be considered instantaneous or not. Where, in the dimensionless form, the model that represents the chemical non-equilibrium at two sorption sites is represented by equations 10 and 11 (Toride et al., 1995):

$$\beta R\frac{\partial C_1}{\partial T} + \left(1-\beta\right)R\frac{\partial C_2}{\partial T} + \mu_1 c_1 = \frac{\partial^2 C_1}{P\partial z^2} - \frac{\partial C_1}{\partial z} \qquad \text{Eq. 10}$$

$$\left(1-\beta\right)R\frac{\partial C_2}{\partial T} = \omega\left(C_1 - C_2\right) \qquad \text{Eq. 11}$$

in which: C_1 and C_2 are the equilibrium and non-equilibrium site concentrations, respectively; T is the dimensionless time; T is equal to vt/L; z spatial coordinate; P_e is the number of Peclet (Equation 9); μ_1 is the degradation rate; β is the partition coefficient between the two sorption sites; ω is the number of Damköhler, representing the dimensionless mass-transfer coefficient. The parameters β and ω are defined by equations 12 and 13.

$$\beta = \frac{\theta + \rho_d f K_d}{\theta + p_d K_d} \qquad \text{Eq. 12}$$

$$\omega = \frac{\alpha\left(1-\beta\right)RL}{v} \qquad \text{Eq. 13}$$

in which: *f* is the fraction of sites in equilibrium; *α* is the first-order kinetics rate for non-equilibrium sites; *L* is the column length; *θ* is the volumetric humidity; *v* is the average water velocity in the pores; and ρ_d is the specific mass of the soil.

Statistical criteria

After adjusting for these models, a statistical analysis was performed to determine which of these models best fit the data. This analysis was based on four statistical criteria: Mean Square Error (MSE), Deviation Ratio (DR), Modeling Efficiency (ME), and Residual Mass Coefficient (RMC). Besides these, the determination factor (R^2) was also analyzed. The equations of these parameters are shown below (Equations 14, 15, 16, and 17):

$$MSE = \left(\frac{\sum_{i=1}^{N}\left(T_i - M_i\right)^2}{N}\right)^{\frac{1}{2}} \cdot \frac{100}{M} \qquad \text{Eq. 14}$$

$$DR = \frac{\sum_{i=1}^{N}\left(M_i - \underline{M}\right)^2}{\sum_{i=1}^{N}\left(T_i - M\right)^2} \qquad \text{Eq. 15}$$

$$ME = \frac{\sum_{i=1}^{N}\left(M_i - \underline{M}\right)^2 - \sum_{i=1}^{N}\left(T_i - M_i\right)^2}{\sum_{i=1}^{N}\left(M_i - M\right)^2} \qquad \text{Eq. 16}$$

$$RMC = \frac{\sum_{i=1}^{N} M_i - \sum_{i=1}^{N} T_i}{\sum_{i=1}^{N} M_i} \qquad \text{Eq. 17}$$

in which: T_i is the values calculated by the model; M_i is the experimental values; M is the average of the experimental values; and N is the number of determinations.

The DR describes the dispersion ratio of the values calculated by the theoretical model, and it tends to be one. In the absence of systematic deviations between the theoretical and experimental values, the RMC tends to zero. It indicates whether the model tends to overestimate or underestimate, with negative or positive RMC values, respectively. The MSE indicates the deviation degree between the experimental determinations and the values calculated by the theoretical model. Its expected value tends to zero. The ME indicates whether the theoretical model provides a better estimation of the experimental determinations than the mean value of these determinations, and its value tends to be the ones determined by Rabelo et al. (2021).

RESULTS AND DISCUSSION

Hydrodispersive Characterization of Soil Assay with KBr

Table 2 shows the physical characteristics of the column assembly and the KBr tracer passage. For each repetition, a pore volume was applied with an average flow of 0.75 mL min^{-1}. One observed homogeneous experimental conditions, since the coefficients of variation were small. Besides, the respective values for the standard deviation, the respective parameters were also small when taking into account their order of magnitude. It is important to highlight that the density used in the test was close to the real density of the soil in the field. In tables 3 and 4 can be observed the adjusted hydrodispersive parameters and statistics, respectively, for the CDE and CDE-MIM models.

Table 2. Initial parameters and experimental conditions for column assays of KBr

Statistic	ρ_d	V_p	θ	q	v	T_{pulse}
	Mg m^{-3}	cm^3	m^3 m^{-3}	cm h^{-1}		h
Values$^{(1)}$	1.543±0.012	54.430±2.138	0.343±0.012	6.850±0.848	19.587±2.379	1.543±0.188
CV (%)	0.748	3.928	3.363	12.378	12.145	12.162

$^{(1)}$ Average ± standard deviation (n = 3). CV: coefficient of variation (%).

Table 3. Adjusted parameters of elution curve according to CDE model

Statistic	D	R	R^2	λ	P_e	MSE	DR	ME	RMC
	cm^2 h^{-1}			cm					
Values$^{(1)}$	3.495±0.350	1.099±0.033	0.989±0.005	0.181±0.038	169.930±33.521	13.419±2.389	0.965±0.031	0.989±0.005	0.049±0.024
CV (%)	10.003	3.003	0.525	20.703	19.727	-	-	-	-

$^{(1)}$ Average ± standard deviation (n = 3). CV: coefficient of variation (%).

Table 4. Adjusted parameters of elution curve according to CDE-MIM model

Statistic	D	R	β	ω	R^2	λ	MSE	DR	ME	RMC
	cm^2 h^{-1}					cm				
Values$^{(1)}$	1.752±0.391	1.045±0.039	0.869±0.018	0.013±0.005	0.996±0.003	0.091±0.025	6.709±3.272	0.993±0.007	0.997±0.003	0.010±0.005
CV (%)	22.331	3.708	2.081	39.970	0.323	27.175	-	-	-	-

$^{(1)}$ Average ± standard deviation (n = 3). CV: coefficient of variation (%).

Analyzing the coefficients of determination (R^2) from table 3, it may be considered that the MIM model was better adjusted to the experimental data since for CDE the R^2 was 0.989, and for CDE-MIM the R^2 was 0.996. Analyzing the statistical parameters presented in table 4, it ca state that the CDE-MIM model had the best fit for the elution curve of the KBr tracer, especially when comparing with the MSE values.

The elution curves adjusted for the CDE and CDE-MIM models are shown in figure 3. The experimental curves of KBr are slightly shifted to the right relative to the point V/Vo = 1.0 and C/Co = 0.5, as considered a theoretical condition for an ideal tracer. An asymmetry of the rising part regarding the downward of the curves is also observed. Comparing the experimental elution curves with the adjustment curves, it can be seen that both models agree adequately with the ascending part of the curves, while for the descending part, it is noticed that the CDE model did not reproduce the “tail”. Similar behavior was verified by Dousset et al. (2007) on bromide ion transport in columns of soil classified as silty clay loam. The authors suggest that the tail of a BTC from a tracer is an indication of physical imbalance. Based on the values of R^2, it is possible to verify that this physical imbalance is due to the occurrence of a behavior in two regions of mobile and immobile water. Similar conclusions were reached by Costa et al. (2006) in the analysis of experimental elution curves of KBr transport in columns of alluvial soil. Certainly, a more careful analysis of these questions is allowed based on the transport parameters (Table 4).

Regarding the transport parameters in tables 3 and 4, values for the R coefficient are slightly higher than the unity for both, the adjustment of CDE and CDE-MIM. The R values are slightly higher than the unit for Bromide ion displacement reported in several studies (Milfont et al., 2006; Carmo et al., 2010, 2013; Moura et al., 2013). This result indicates that these ions are subject to a slight adsorption in soil minerals. On the other hand, the delay factor value (R) was slightly closer to the unit in the CDE-MIM model setting than in the CDE model setting. This outcome indicates that there was no considerable interaction between the tracer and the soil, but only a physical non-equilibrium. In any case, it can be said that the delay factor, R, was close to one in both settings, which validates the use of KBr to track water flow and that the conservative nature of the bromide was fully respected (Prédélus et al., 2014).

The value of λ is an indication of the distance traveled by the solute (Tan et al., 2016). Masipan et al. (2016), in the displacement of the bromide ion in sandy loam soil columns (71 % sand, 25 % silt, and 4 % clay), found λ ranging from 0.37 to 0.98 cm. Lin and Xu (2020) obtained values of 0.24 cm for loam and 0.31 cm for sandy loam. Therefore, one can indicate that the average value found in the present study is low. Small value for dispersivity indicates that the analyzed soil is a homogeneous porous medium (Jellali et

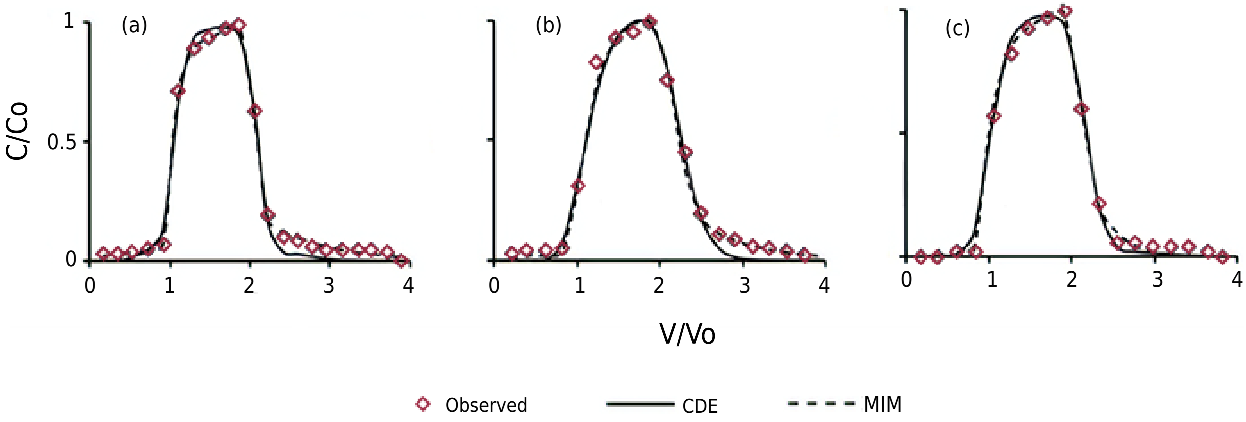

Figure 3. The elution curves adjusted according to the CDE and CDE-MIM models of KBr (a) R1, (b) R2 e (c) R3.

al., 2010; Lin and Xu, 2020). The results presented also show that the values of λ in the CDE model are higher than in the CDE-MIM model. Tan et al. (2016) conclude that the λ value in the CDE-MIM only partially concerns the dispersion phenomenon, whereas the λ value in the CDE includes two parts. These are the dispersion phenomenon and the mass transfer, thus leading the λ value in the CDE-MIM to be smaller than the λ value obtained by the CDE.

The Peclet number (P_e) is the ratio of advective to diffusive transfer (Simhayov et al., 2018), and the value obtained was 169.93. In the diffusion-dominated regime, $P_e \leq 0.1$, advection is negligible, $P_e > 300$ corresponds to the mechanical dispersion regime and for the intermediate values, $10 < P_e < 100$, the power-law dispersion regime is present (Afshari et al., 2018, 2020). Therefore, the P_e value for the KBr transport moves away from the intermediate condition, tending towards a transport in which diffusion is considered negligible.

The parameters ω and β can be used to indicate the equilibrium and non-equilibrium transport conditions. The β is the dimensionless non-equilibrium partitioning coefficient and ω is the dimensionless transfer coefficient. The β value equal to 1 indicates for a non-reactive solute the lack of stagnant water and the existence of physical equilibrium, while β value less than 1 indicates the inverse condition, stagnant water fraction and non-physical equilibrium (Shahmohammadi-Kalalagh and Taran, 2019). The mean value found for β was 0.869, indicating a physical non-balance. The dimensionless transfer coefficient (ω) is a parameter that has a minimum influence on the CDE-MIM (Tan et al., 2016). The dimensionless parameter ω incorporates in its definition the coefficient α, describing the diffusive transfer between two regions of water (Parker and van Genuchten, 1984). The resistance to diffuse solute transfer between the two water regions is influenced by the value of ω, the higher the value of ω, the lower the resistance to the occurrence of diffuse transfer of solute between the two regions (Schlindwein, 1998). The parameter ω assumes a very low value (0.013), indicating that the system deviated from local equilibrium, demonstrating that CDE-MIM model has more coherent adjustments.

TSS model of Cu and Cd

Table 5 presents the parameter values for the TSS model fitted to the Cu and Cd elution curves. Figure 4 shows Cu and Cd elution curves, fitted to the two-site sorption model. In table 5, the coefficient of determination was good for Cu ($R^2 = 0.985$), and even better for Cd curves ($R^2 = 0.995$). The MSE and RMC statistics, whose expected value is 0, and DR and the ME, whose expected value is 1, also validate the two-site model to describe the experimental elution curves. Besides, all values of the standard deviations were small regarding the order of magnitude of the respective parameters. However, the standard deviation for the Dispersion Coefficient (*D*) was 1.2 for adjusting the Cu elution curves, being an exception. It may be seen that the two-sorption site model adjusted the CD elution curves very well and the Cu curves reasonably well because it was difficult

Table 5. Adjusted parameter values for the Cu and Cd elution curves for the two-sorption site model

Statistic	D	R	β	ω	μ_1	R^2	K_d	MSE	DR	ME	RMC
	$cm^2\ h^{-1}$				h^{-1}		$L\ kg^{-1}$				
					Copper						
Values[1]	3.469±1.199	2.138±0.058	0.522±0.079	0.106±0.030	0.045±0.028	0.985±0.006	0.248±0.011	13.094±1.343	1.028±0.019	0.986±0.005	0.000±0.049
					Cadmium						
Values[1]	5.205±0.179	1.907±0.080	0.525±0.022	0.156±0.036	0.005±0.003	0.995±0.004	0.203±0.019	6.135±1.775	1.017±0.008	0.997±0.002	0.020±0.027

[1] Average ± standard deviation (n = 3). CV: coefficient of variation (%).

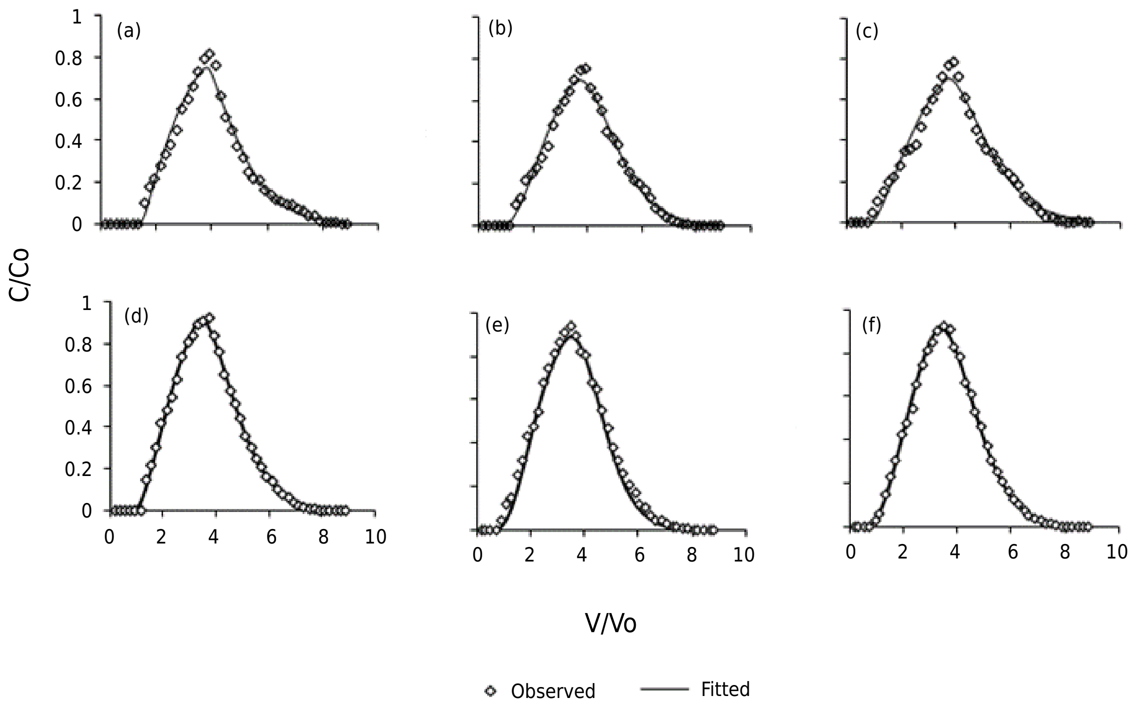

Figure 4. Cupper elution curves adjusted according to the TSS model for the repetition (a) R1, (b) R2 and (c) R3 and Cd elution curves adjusted according to the two-sorption site model for the repetition (d) R1, (e) R2 and (f) R3.

to adjust the curve peaks (Figure 4). These results indicate that the two-site model is satisfactory to describe the transport of Cd and Cu in the analyzed soil.

The values of *R* were considerably higher than the unit, presenting an average of 2.138 for Cu and 1.907 for Cd. This indicates a delay in the output of these contaminants from the column, caused by their interaction with these chemical compounds with the soil. The values obtained for parameter *D* were 3.469 for Cu and 5.205 for Cd. Based on the validation of this model, these results for parameters *D* and *R*, which have an inverse tendency, confirm the peak values of relative concentration. These outcomes indicate high retention and low mobility for Cu metal and the inverse trend for Cd metal. Therefore, in this configuration, the risks of groundwater contamination are greater for Cd metal than for Cu. Other studies also observed greater mobility of Cd metal than Cu metal (Sayyad et al., 2010; Fonseca et al., 2011). A parameter that directly helps in this analysis is K_d, which indicates the tendency for sorption and whose values for Cu and Cd were 0.248 and 0.203 L kg^{-1}, respectively.

To understand the processes involved in the transport of metals, it is necessary to consider the characteristics of the soil (Table 1). In the batch experiments, Lin and Xu (2020) observed that the loam soil with high OC and CEC exhibited strong sorption for Cd and Zn, and sandy loam with high pH exhibited strong sorption for Cu. Studies have also confirmed that Cd sorption was greater at higher pH than lower pH (Tahervand and Jalali, 2017; Rezaei et al., 2021). The analyzed soil presents low OC (1.26 %), median CEC value (7.4 $cmol_c$ dm^{-3}), and high pH (8.26). Then, except for the high pH, the other values do not favor any sorption process. According to Tahervand and Jalali (2017), at high pH values, metal sorption occurs along with the release of H^+, resulting in specific sorption due to the formation of inner-sphere complex via Si-O and Al-O groups. Furthermore, it is important to highlight that the soil presents pH(H_2O) (8.26) greater than PZC (5.02). So, the analyzed soil surface has a negative surface charge (Bachratá et al., 2013), being able to attract cations (Banerjee and Chattopadhyaya, 2017), such as Cu and Cd.

Regarding CEC, based on the high values for the different soil samples, Defo et al. (2017) concluded that net negative charges on the soil exchange complex attract and fix positively charged elements, such as heavy metals. Thus, it is possible to verify from the CEC that the analyzed soil does not present favorable conditions for a considerable retention of both metals in the soil, which justifies the high mobility and low retention verified. Organic content is also an important constituent of soils that affects heavy metal transport. For example, Defo et al. (2017), comparing organic matter, CEC, and clay content of tropical soils, found that organic matter exerted a greater influence on Cd retention than CEC and clay content. Regarding the organic component, the soil has a low value. This is consistent with the typical value of sandy soils, being, another factor that explains the high mobility and low retention observed.

The parameters β and ω represented the non-equilibrium degree of the packed column. The estimated β values are small, 0.522 for the Cu and 0.525 for the Cd. In the two-site sorption model, the parameter β is a partition coefficient that actually represents the fraction of the sites available for instantaneous sorption (Florido et al., 2010). Values of β near the unit could indicate a chemical equilibrium (Radcliffe and Šimůnek, 2018). This did not occur for any of the curves presented, and thus the application of the two-site sorption model is consistent. The β values derived from the breakthrough curve of Cu and Cd suggest that about 52 % of the sorption sites were instantaneous, and the rest were rate limited. The mass transfer coefficients are significantly small, 0.106 for Cu and 0.156 for Cd, and point to a non-equilibrium process (ω<1) (Fonseca et al., 2011) for the transport of both metals.

Compared to KBr transport, the metals Cd and Cu migration patterns in the soil column differed significantly. The curves are asymmetric by their format, mainly due to the trail formed, which indicates chemical non-equilibrium. Thus, approximately nine pore volumes are required to restore the curve. The relative concentration peak (C/C_0) for Cu was approximately 0.8, while the peak for Cd was 0.9, approximately. The peaks of the curves shifted well to the right when compared to the elution curve of KBr (Figure 3). These findings indicate a reactivity with the soil and, consequently, a delay in the displacement of the flow of these solutes in the column. Lin and Xu (2020) analyzed the transport of Cd, Zn and Cu metals. They verified that the initial breakthrough for Cd occurred after over ten pore volumes, while for Cu it appeared later in the effluent, after 20 pore volumes. The peak BTCs for Cd was 0.88 and much higher than for Cu, which was 0.35. These differences, mainly regarding Cu, can be attributed to the different experimental conditions of the referred study in relation to the present one. The main reason is the fact that the authors analyzed the transport of metals Cd, Zn and Cu coexisting in the same solution. Nevertheless, based on these and other results, the authors suggest that, comparing the metals Cd and Cu, shallow water resources may be more exposed to contamination risk by Cd. This finding could be determined according to the analysis of the non-equilibrium transport parameters (Table 5).

CONCLUSIONS

The KBR is a good chemical tracer, not suffering interaction (adsorption or exclusion) in the analyzed soil. For this non-reactive tracer, the presence of physical unbalance was indicated by the best adjustment of the MIM model.

The Cu and Cd transport results indicated a chemical non-equilibrium due to the good adjustment of the elution curves to the TSS model. The results show that the alluvial aquifer is more subject to contamination by Cd than by Cu. However, both metals were very mobile in the studied soil, which showed a low capacity to retain such metals. In addition, the results of these adjustments indicated that about 52 % of the sorption sites were instantaneous, and the rest were rate limited.

This study is part of a series of research that analyzed the textile industry's environmental impact in northeastern Brazil and aimed to complement the kinetics and isotherm study of the metals Cadmium and Copper, which despite being efficient in analyzing the solute-soil interaction, has the disadvantage of a high liquid-solid ratio. Meanwhile, the miscible displacement method provides a more complete analysis. Considering the soil structure, it is possible to represent the real apparent density of the soil in the experimental columns, approaching the reality of the soil in the environment. Thus, the tests carried out in this study promote an expansion of the scale of observation of the contaminants behavior in these soils and, consequently, the risk of contamination of aquifers. The determination of the transport parameters of the studied contaminants is the starting point to propose two-dimensional numerical simulations that can map the advance of the contamination plume of these heavy metals in the studied soil.

Our results represent a significant contribution to the studied region, evaluating the contamination possibility of the only water source of the population residing in the area.

For future studies, it is ideal to analyze the other soil layers in the same place and simulate the dispersion in the soil. These actions will allow the assessment of the mobility of these pollutants and a more accurate evaluation of the aquifer contamination.

ACKNOWLEDGMENTS

Acknowledgments: This work was carried out with the support of the following projects: Regional Scientific Development Program (FACEPE process DCR-0003-3.01/20 APQ-0236-3.01/19, CNPq process 316047/2020-1); Innovation Locus (FACEPE APQ-0169-3.01/22); ONDACBC Project (CNPq process N° 465764/2014-2; FACEPE process APQ-0498-3.07/17); Productivity Scholarship Project (CNPq process 315927/2021-6).

AUTHOR CONTRIBUTIONS

Conceptualization: Artur Paiva Coutinho (equal), Severino Martins dos Santos Neto (equal) and Vitor Hugo de Oliveira Barros (equal).

Data curation: Adriana Thays Araújo Alves (equal) and Vitor Hugo de Oliveira Barros (equal).

Formal analysis: Vitor Hugo de Oliveira Barros (equal).

Funding acquisition: Antonio Celso Dantas Antonino (equal) and Artur Paiva Coutinho (equal).

Investigation: Manuella Virgínia Salgueiro Gondim (lead).

Methodology: Adriana Thays Araújo Alves (equal), Manuella Virgínia Salgueiro Gondim (equal), Severino Martins dos Santos Neto (equal), and Vitor Hugo de Oliveira Barros (equal).

Project administration: Antonio Celso Dantas Antonino (equal) and Artur Paiva Coutinho (equal).

Resources: Artur Paiva Coutinho (equal) and Severino Martins dos Santos Neto (equal).

Software: Artur Paiva Coutinho (equal) and Vitor Hugo de Oliveira Barros (equal).

Supervision: Antonio Celso Dantas Antonino (equal), Artur Paiva Coutinho (equal) and Laurent Lassabatere (equal).

Validation: Adriana Thays Araújo Alves (equal), Artur Paiva Coutinho (equal) and Vitor Hugo de Oliveira Barros (equal).

Visualization: Vitor Hugo de Oliveira Barros (lead).

Writing – original draft: Laurent Lassabatere (lead).

Writing – review & editing: Artur Paiva Coutinho (equal), Laurent Lassabatere (equal) and Vitor Hugo de Oliveira Barros (equal).

REFERENCES

Abbasi M, Safari E, Baghdadi M, Janmohammadi M. Enhanced adsorption of heavy metals in groundwater using sand columns enriched with graphene oxide: lab-scale experiments and process modeling. J Water Process Eng. 2021;40:101961. https://doi.org/10.1016/j.jwpe.2021.101961

Abdullahi UA, Ibrahim S. Heavy metals analysis and toxicity evaluation of some textile and dyeing effluents in Kano, Nigeria using Allium cepa bioassay. Bayero J Pure Appl Sci. 2019;12:344-51. https://doi.org/10.4314/bajopas.v12i1.52S

Afshari S, Hejazi SH, Kantzas A. longitudinal dispersion in heterogeneous layered porous media during stable and unstable pore-scale miscible displacements. Adv Water Resour. 2018;119:125-41. https://doi.org/10.1016/j.advwatres.2018.06.005

Afshari S, Hejazi SH, Kantzas A. Pore-scale modeling of coupled thermal and solutal dispersion in double diffusive-advective flows through porous media. Int J Heat Mass Transf. 2020;147:118730. https://doi.org/10.1016/j.ijheatmasstransfer.2019.118730

Agilent Technologies. Flame atomic absorption spectrometry: Analytical methods. 14th ed. Victoria, Australia: Agilent Technologies; 2017.

Akindele EO, Omisakin OD, Oni OA, Aliu OO, Omoniyi GE, Akinpelu OT. Heavy metal toxicity in the water column and benthic sediments of a degraded tropical stream. Ecotox Environ Safe. 2020;190:110153. https://doi.org/10.1016/j.ecoenv.2019.110153

Alexandre JIS, Santos Neto SM, Coutinho AP, Melo TAT, Gonçalves EAP, Gondim MVS, Antonino ACD, Rabelo AECGC, Oliveira AL. Sorption of the Direct Black 22 dye in alluvial soil. Rev Ambient Agua. 2020;15:e2483. https://doi.org/10.4136/ambi-agua.2483

Alves ATA, Coutinho AP, Barros VHO, Lassabatere L, Santos Neto SM, Lima JRS, Antonino ACD. Transport Behavior of RB5 dye in alluvial soil in the northeast of Brazil. Water. 2022;14:1000. https://doi.org/10.3390/w14071000

Alves ATA, Silva LTMS, Alcântara LRP, Barros VHO, Santos Neto SM, Lima VF, Lima JRS, Coutinho AP, Antonino ACD. Sorption of remazol black B dye in alluvial soils of the Capibaribe River Basin, Pernambuco, Brazil. Rev Ambient Agua. 2020;15:e2491. https://doi.org/10.4136/ambi-agua.2491

Bachratá M, Šuňovská A, Horník M, Pipíška M, Augustín J. Sorption of synthetic dyes onto river sediments: A laboratory study. Nova Biotechnol Chim. 2013;12:12-29. https://doi.org/10.2478/nbec-2013-0002

Banerjee S, Chattopadhyaya MC. Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. Arab J Chem. 2017;10:S1629-38. https://doi.org/10.1016/j.arabjc.2013.06.005

Barizon RRM, Lavorenti A, Regitano JB, Prata F, Tornisielo VL. Simulação do transporte e da sorção de imazaquin em colunas de solo. Rev Bras Cienc Solo. 2006;30:615-23. https://doi.org/10.1590/S0100-06832006000400002

Barros VHO, Coutinho AP, Alves ATA, Santos Neto SM, Assis FX, Lima VF, Lima JRS, Antonino ACD. Sorption studies of Cd and Cu, on Brazilian alluvial soils. Rev Ambient Agua. 2021;16:e2717. https://doi.org/10.4136/ambi-agua.2717

Beltrão BA, Mascarenhas JC, Miranda JLF, Souza Junior LC, Galvão MJTG, Pereira SN. Projeto de cadastro de fontes de abastecimento por água subterrânea: Estado de Pernambuco. Diagnóstico do município de Santa Cruz do Capibaribe. Recife: CPRM/PRODEEM; 2005.

Braga RAP, Farias CO, Silva S, Cavalcanti ER. Gestão e educação socioambiental na Bacia do Capibaribe. Recife: Editora Clã; 2015.

Caetano TO, Paiva ALR, Silva SR, Coutinho AOP, Cirilo JA, Cabral JJSP. Abastecimento rural de água: Uso e demanda em comunidades do semiárido e a disponibilidade hídrica das aluviões. Rev Gestão Água da América Latina. 2020;17:e8. https://doi.org/10.21168/rega.v17e8

Cao Y, Dong S, Dai Z, Zhu L, Xiao T, Zhang X, Yin S, Soltanian MR. Adsorption model identification for chromium (VI) transport in unconsolidated sediments. J Hydrol. 2021;598:126228. https://doi.org/10.1016/j.jhydrol.2021.126228

Carmo AI, Antonino ACD, Martins JMF, Silva VL, Morel MC, Gaudet JP. Lixiviação de naftaleno em solos urbanos da região metropolitana do Recife, PE. Rev Bras Cienc Solo. 2013;37:1415-22. https://doi.org/10.1590/S0100-06832013000500030

Carmo AI, Antonino ACD, Netto AM, Corrêa MM. Caracterização hidrodispersiva de dois solos da região irrigada do Vale do São Francisco. Rev Bras Eng Agric Ambient. 2010;14:698-704. https://doi.org/10.1590/S1415-43662010000700003

Chotpantarat S, Kiatvarangkul N. Facilitated transport of cadmium with montmorillonite KSF colloids under different ph conditions in water-saturated sand columns: Experiment and transport modeling. Water Res. 2018;146:216-31. https://doi.org/10.1016/j.watres.2018.09.010

Costa CT, Antonino ACD, Maciel Netto A. Ensaios de deslocamento de líquido miscível na determinação dos parâmetros hidrodispersivos de um solo aluvial. Rev Bras Recur Hídricos. 2006;11:111-22. https://doi.org/10.21168/rbrh.v11n2.p111-122

Defo C, Yerima BPK, Bemmo N. investigating soils retention ratios and modelling geochemical factors affecting heavy metals retention in soils in a tropical urban watershed. Environ Dev Sustain. 2017;19:1649-71. https://doi.org/10.1007/s10668-016-9819-2

Dong Z, Wei L, Xu S, Sun J, Shi X, Qiu Y. Transport of imidazolium-based ionic liquids with different anion/cation species in sand/soil columns. Ecotox Environ Safe. 2018;147:480-6. https://doi.org/10.1016/j.ecoenv.2017.09.00

Dousset S, Thevenot M, Pot V, Šimůnek J, Andreux F. Evaluating equilibrium and non-equilibrium transport of bromide and isoproturon in disturbed and undisturbed soil columns. J Contam Hydrol. 2007;94:261-76. https://doi.org/10.1016/j.jconhyd.2007.07.002

Florido A, Valderrama C, Arévalo JA, Casas I, Martínez M, Miralles N. Application of two sites non-equilibrium sorption model for the removal of Cu(II) onto grape stalk wastes in a fixed-bed column. Chem Eng J. 2010;156:298-304. https://doi.org/10.1016/j.cej.2009.10.020

Fonseca B, Figueiredo H, Rodrigues J, Queiroz A, Tavares T. Mobility of Cr, Pb, Cd, Cu and Zn in a loamy sand soil: A comparative study. Geoderma. 2011;164:232-7. https://doi.org/10.1016/j.geoderma.2011.06.016

Gao G, Zhan H, Feng S, Huang G, Mao X. comparison of alternative models for simulating anomalous solute transport in a large heterogeneous soil column. Hydrol. 2009;377:391-404. https://doi.org/10.1016/j.jhydrol.2009.08.036

Gaudet JP, Jegat H, Vachaud G, Wierenga PJ. Solute transfer, with exchange between mobile and stagnant water, through unsaturated sand. Soil Sci Soc Am J. 1977;41:665-71. https://doi.org/10.2136/sssaj1977.03615995004100040009x

Jellali S, Diamantopoulos E, Kallali H, Bennaceur S, Anane M, Jedidi N. Dynamic sorption of ammonium by sandy soil in fixed bed columns: Evaluation of equilibrium and non-equilibrium transport processes. J Environ Manage. 2010;91:897-905. https://doi.org/10.1016/j.jenvman.2009.11.006

Kalubi KN, Mehes-Smith M, Spiers G, Omri A. Variation in whole DNA methylation in red maple (*Acer Rubrum*) populations from a mining region: association with metal contamination and cation exchange capacity (CEC) in Podzolic soils. Ecotoxicology. 2017;26:405-14. https://doi.org/10.1007/s10646-017-1773-8

Köhne JM, Köhne S, Šimůnek J. A review of model applications for structured soils: a) Water flow and tracer transport. J Contam Hydrol. 2009a;104:4-35. https://doi.org/10.1016/j.jconhyd.2008.10.002

Köhne JM, Köhne S, Šimůnek J. A review of model applications for structured soils: b) Pesticide transport. J Contam Hydrol. 2009b;104:36-60. https://doi.org/10.1016/j.jconhyd.2008.10.003

Lassabatere L, Spadini L, Delolme C, Février L, Galvez-Cloutier R, Winiarski T. Concomitant Zn-Cd and Pb retention in a carbonated fluvio-glacial deposit under both static and dynamic conditions. Chemosphere. 2007;69:1499-508. https://doi.org/10.1016/j.chemosphere.2007.04.053

Lassabatere L, Winiarski T, Galvez-Cloutier R. Retention of three heavy metals (Zn, Pb, and Cd) in a calcareous soil controlled by the modification of flow with geotextiles. Environ Sci Technol. 2004;38:4215-21. https://doi.org/10.1021/es035029s

Lin Q, Xu S. Co-Transport of heavy metals in layered saturated soil: Characteristics and simulation. Environ Pollut. 2020;261:114072. https://doi.org/10.1016/j.envpol.2020.114072

Liu C, Lin H, Li B, Dong Y, Menzembere ERGY. Endophyte *Pseudomonas putida* enhanced *Trifolium repens* L. growth, and heavy metal uptake: A promising in-situ non-soil cover phytoremediation method of nonferrous metallic tailing. Chemosphere. 2021;272:129816. https://doi.org/10.1016/j.chemosphere.2021.129816

Masipan T, Chotpantarat S, Boonkaewwan S. Experimental and modelling investigations of tracer transport in variably saturated agricultural soil of Thailand: Column study. Sustain Environ Res. 2016;26:97-101. https://doi.org/10.1016/j.serj.2016.04.005

Milfont ML, Antonino AC, Martins JM, Netto AM, Corrêa MM. Caracterização hidrodispersiva de dois solos do Vale do Rio São Francisco. Rev Bras Cienc Agrar. 2006;1:81-7. https://doi.org/10.5039/agraria.v1i1a186

Milfont ML, Antonino ACD, Martins JMF, Maciel Netto A, Gouveia ER, Correa MM. Transporte do paclobutrazol em colunas de solos. Rev Bras Cienc Solo. 2008;32:2165-75. https://doi.org/10.1590/S0100-06832008000500037

Morsali S, Babazadeh H, Shahmohammadi-Kalalagh S, Sedghi H. Simulating Zn, Cd and Ni transport in disturbed and undisturbed soil columns: Comparison of alternative models. Int J Environ Res. 2019;13:721-34. https://doi.org/10.1007/s41742-019-00212-w

Moura AESS, Carvalho J, Montenegro SMGL, Carmo AI, Magalhães A, Sousa C, Antonino ACD, Araujo J, Melo R. Determinação de parâmetros hidrodispersivos em solos da zona da mata de Pernambuco. Rev Bras Recur Hídricos. 2013;18:109-15. https://doi.org/10.21168/rbrh.v18n3.p109-115

Panigrahi T, Santhoskumar AU. adsorption process for reducing heavy metals in textile industrial effluent with low cost adsorbents. Prog Chem Biochem Res. 2020;3:135-9. https://doi.org/10.33945/SAMI/PCBR.2020.2.7

Parker J, van Genuchten MT. Determining transport parameters from laboratory and field tracer experiments. Blacksburg: Virginia Agricultural Experiment Station; 1984. (Bulletin 84-3).

Prédélus D, Lassabatere L, Coutinho AP, Louis C, Brichart T, Slimène E, Winiarski T, Angulo-Jaramillo R. Tracing water flow and colloidal particles transfer in an unsaturated soil. J Water Resour Prot. 2014;6:696-709. https://doi.org/10.4236/jwarp.2014.67067

Qiu B, Tao X, Wang H, Li W, Ding X, Chu H. Biochar as a low-cost adsorbent for aqueous heavy metal removal: A review. J Anal Appl Pyrolysis. 2021;155:105081. https://doi.org/10.1016/j.jaap.2021.105081

Rabelo AECGC, Santos Neto SM, Coutinho AP, Antonino ACD. Sorption of sulfadiazine and flow modeling in an alluvial deposit of a dry riverbed in the Brazilian Semiarid. J Contam Hydrol. 2021;241:103818. https://doi.org/10.1016/j.jconhyd.2021.103818

Radcliffe DE, Šimůnek J. Soil physics with HYDRUS: Modeling and applications. Boca Raton: CRC Press; 2018.

Rezaei MJ, Farahbakhsh M, Shahbazi K, Marzi M. Study of cadmium distribution coefficient in acidic and calcareous soils of Iran: Comparison between low and high concentrations. Environ Technol Innov. 2021;22:101516. https://doi.org/10.1016/j.eti.2021.101516

Sayyad G, Afyuni M, Mousavi SF, Abbaspour KC, Richards BK, Schulin R. Transport of Cd, Cu, Pb and Zn in a calcareous soil under wheat and safflower cultivation - A column study. Geoderma. 2010;15:311-20. https://doi.org/10.1016/j.geoderma.2009.10.019

Schlindwein S. Parametrização do transporte dispersivo de solutos em solos estruturados: Heterogeneidade do meio, percurso de transporte e modelagem. Rev Bras Cienc Solo. 1998;22:173-9. https://doi.org/10.1590/S0100-06831998000200001

Serviço Brasileiro de Apoio às Micro e Pequenas Empresas - Sebrae. Estudo econômico do arranjo produtivo local de confecções do Agreste Pernambucano, 2012. Recife: Sebrae Pernambuco; 2013.

Shahmohammadi-Kalalagh S, Taran F. Effect of initial concentration and input flux on equilibrium and non-equilibrium transport of Zn in soil columns. Int J Environ Sci Technol. 2019;16:7565-72. https://doi.org/10.1007/s13762-018-2159-z

Sidoli P, Baran N, Angulo-Jaramillo R. Glyphosate and AMPA adsorption in soils: Laboratory experiments and pedotransfer rules. Environ Sci Pollut Res. 2016;23:5733-42. https://doi.org/10.1007/s11356-015-5796-5

Simhayov RB, Weber TKD, Price JS. Saturated and unsaturated salt transport in peat from a constructed fen. Soil. 2018;4:63-81. https://doi.org/10.5194/soil-4-63-2018

Šimůnek J, van Genuchten MT. Modeling nonequilibrium flow and transport processes using HYDRUS. Vadose Zone J. 2008;7:782-97. https://doi.org/10.2136/vzj2007.0074

Slimene EB, Lassabatere L, Šimůnek J, Winiarski T, Gourdon R. The role of heterogeneous lithology in a glaciofluvial deposit on unsaturated preferential flow-a numerical study. J Hydrol Hydromech. 2017;65:209-21. https://doi.org/10.1515/johh-2017-0004

Smaranda C, Popescu MC, Bulgariu D, Malutan T, Gavrilescu M. Adsorption of organic pollutants onto a Romanian soil: Column dynamics and transport. Process Saf Environ Prot. 2017;108:108-20. https://doi.org/10.1016/j.psep.2016.06.027

Suzaki PYR, Munaro MT, Triques CC, Kleinübing SJ, Klen MRF, Bergamasco R, Jorge, LMM. Phenomenological mathematical modeling of heavy metal biosorption in fixed-bed columns. Chem Eng J. 2017;326:389-400. https://doi.org/10.1016/j.cej.2017.05.157

Swarnkumar R, Osborne WJ. Heavy metal determination and aquatic toxicity evaluation of textile dyes and effluents using Artemia salina. Biocatal Agric Biotechnol. 2020;25:101574. https://doi.org/10.1016/j.bcab.2020.101574

Tahervand S, Jalali M. Sorption and desorption of potentially toxic metals (Cd, Cu, Ni and Zn) by soil amended with bentonite, calcite and zeolite as a function of pH. J Geochem Explor. 2017;181:148-59. https://doi.org/10.1016/j.gexplo.2017.07.005

Tan S, Zhou B, Wang Q. Effects of nanocarbon on the hydraulic parameters and the solute transport process for disturbed loessial soil. Arab J Geosci. 2016;9:4. https://doi.org/10.1007/s12517-015-2018-x

Toride N, Leij F, van Genuchten MT. The CXTFIT code for estimating transport parameters from laboratory or filed tracer experiments. Riverside: US Salinity Laboratory; 1995.

Van Genuchten MT, Wierenga PJ. Mass transfer studies in sorbing porous media I. Analytical solutions. Soil Sci Soc Am J. 1976;40:473-80. https://doi.org/10.2136/sssaj1976.03615995004000040011x

Wang C, Jin H, Zhong C, Wang J, Sun M, Xie M. Estimating the contribution of atmosphere on heavy metals accumulation in the aboveground wheat tissues induced by anthropogenic forcing. Environ Res. 2020;189:109955. https://doi.org/10.1016/j.envres.2020.109955

Won J, Wirth X, Burns SE. An experimental study of cotransport of heavy metals with kaolinite colloids. J Hazard Mater. 2019;373:476-82. https://doi.org/10.1016/j.jhazmat.2019.03.110

Yin X, Jiang Y, Tan Y, Meng X, Sun H, Wang N. Co-transport of graphene oxide and heavy metal ions in surface-modified porous media. Chemosphere. 2019;218:1-13. https://doi.org/10.1016/j.chemosphere.2018.11.089

Zhang X, Tong J, Hu BX, Wei W. Adsorption and desorption for dynamics transport of hexavalent chromium (Cr(VI)) in soil column. Eviron Sci Pollut Res. 2018;25:459-86. https://doi.org/10.1007/s11356-017-0263-0