



Spatial variability of hydraulic conductivity and solute transport parameters and their spatial correlations to soil properties

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ABSTRACT

Spatial variation of the correlation among variables related to water flow and solute transport are important in the characterization of the spatial variability when performing uncertainty analysis and making uncertainty-qualified solute transport predictions. However, the spatial variation of the correlation between solute transport parameters and soil properties are rarely studied. In this study, the spatial correlation among laboratory-measured transport parameters dispersivity and coefficient of distribution of a reactive and a nonreactive solute and soil properties were studied at the scale of a few meters using a dense sampling design. In an area of 84 m² and a depth of 2 m, 55 undisturbed soil samples were taken to determine the soil properties. Column experiments were performed, and the transport parameters were obtained by fitting the experimental data to the analytical solution of the advection-dispersion equation using the computer program CFITM. Stepwise multiple linear regression (MLR) was performed in order to identify the statistically significant variables. The spatial correlation of the variables and between variables were determined using the Stanford Geostatistical Modeling Software. Soil properties presented a moderate coefficient of variation, while hydraulic conductivity and transport parameters were widely dispersed. The difference between its minimum and maximum value was quite large for most of the studied variables evidencing their high variability. Both dispersivity and retardation factor were higher than the expected and this result can be related to the preferential pathways and to the non-connected micropores. None of the physical soil property was strongly correlated to the transport parameters. Coefficient of distribution was strongly correlated to the cation exchange capacity and significantly correlated to mesoporosity and microporosity. Hydraulic conductivity presented significant positive correlation to the effective porosity and macroporosity. Stepwise multiple linear regression analysis indicated that further studies should be performed aiming to include other variables relevant for lateritic soils such as pH, electrical conductivity, the content of Al and Fe, CaCO₃ and soil structure and microstructure. The study of the spatial correlation among transport parameters and soil properties showed that the codispersion among the variables is not constant in space and can be important in dictate the behavior of the combined variables. Our results also showed that some variables that were identified as explanatory in the MLR were not significant in the spatial analysis of the correlation, showing the importance of this kind of analyses for a better decision about the most relevant variables and their relations. The present study was a first attempt to evaluate the spatial variation in the correlation coefficient of transport parameters of a reactive and a nonreactive solute, indicating the more relevant variables and the ones that should be included in future studies.

1. Introduction

The soil's ability to retard and filter solutes as well as water flow and solute movement in soils are significant themes in the earth and environmental sciences, and they are critical in the hydrological and

biogeochemical cycles (Keesstra et al., 2012; Kung et al., 2005). Solutes can migrate from the soil to the groundwater and cause its contamination (Arias-Estévez et al., 2008). That ability can be quantified after determining soil transport parameters such as dispersivity (α) and partition coefficient (K_d) (Dyck et al., 2005; Fetter, 1999). Knowledge

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of solute transport parameters is needed to improve the prediction of the groundwater contamination potential (Kazemi et al., 2008). These parameters depend on many factors such as the chemical characteristics of the contaminant and the soil physical, chemical, and physicochemical properties (Holland, 2004; Trangmar et al., 1986).

The transport parameters, the hydraulic conductivity, other soil properties and the relations among them are highly spatially variable following a structural pattern overlapped by an erratic component, also referred to as structured variation (Alletto and Coquet, 2009; Fu and Gómez-Hernández, 2009; Goovaerts, 1997; Isaaks and Srivastava, 1989; Mulla and Mc Bratney, 2002; Trangmar et al., 1986). The spatial variability of soil properties might be studied at the centimeter scale, as well as at a regional scale since the soil heterogeneity is present in all scales (Chapuis et al., 2005; DeGroot and Baecher, 1993; Lacasse and Nadim, 1996; Søvik and Aagaard, 2003). Additionally, since taking measurements of the properties of interest in an entire area is impractical, there is always an uncertainty component related to the locations where the properties were not measured (Erşahin et al., 2017; Fu and Gómez-Hernández, 2009).

The interest in quantifying the uncertainty in groundwater flow and solute transport predictions has increased in the last decades (Cassiraga et al., 2005; Fu and Gómez-Hernández, 2009; Goovaerts, 2001; Grunwald et al., 2004; Hoffmann et al., 2014; Lacasse and Nadim, 1996; Li et al., 2011; Teixeira et al., 2012). Performing an uncertainty analysis and making uncertainty-qualified solute transport predictions requires building a model of the spatial variability of the parameters controlling transport from a limited set of experimental data (laboratory or field). Such a model will allow estimating soil properties at unsampled locations (Goovaerts, 1999).

The study of the spatial variability in soil science is commonly performed using geostatistics (Alletto and Coquet, 2009; Erşahin et al., 2017; Goovaerts, 1999; Gwenzi et al., 2011; Marín-Castro et al., 2016). This technique is based on the random function model assumption, where variables are modeled as random variables usually spatially correlated. By assuming this model, the characterization of the spatial variability is reduced to the characterization of the correlations among the random variables of the random function (Goovaerts, 1997). Then, it is possible to perform coherent inferences about the variable using estimation (such as kriging and cokriging) or simulation techniques (such as sequential Gaussian simulation), and the spatial variability can be fully characterized.

Geostatistics has been widely used to study the spatial variability of several soil properties (Alletto and Coquet, 2009; Brocca et al., 2007; Goovaerts, 1998; Grego et al., 2006; Iqbal et al., 2005; Mbagwu, 1995; Tesfahunegn et al., 2011; Vieira, 1997; Wang and Shao, 2013; Zhao et al., 2011) and specifically of the hydraulic conductivity (Bohling et al., 2012; Gwenzi et al., 2011; Hu et al., 2008; Liu et al., 2017; Marín-Castro et al., 2016; Motaghian and Mohammadi, 2011; Sobieraj et al., 2002; Sudicky et al., 2010). On the other hand, the spatial characterization of solute transport parameters is still discrete (Huysmans and Dassargues, 2006; Jacques et al., 1999; Kazemi et al., 2008) due to the high cost and time-consuming efforts associated with solute transport studies (Erşahin et al., 2017).

Allen-King et al. (2006) determined the spatial geostatistical properties of the perchloroethene partition coefficient (K_d) and permeability (k) and found that K_d and k exhibited a statistically significant positive correlation. They concluded that additional studies were necessary since the statistics describing the horizontal autocorrelation behavior of $\ln K_d$ and its cross-correlation to $\ln k$ remained uncertain.

Gómez-Hernández et al. (2006) studied the impact of the cross-correlation between $\ln K_d$ and $\ln K$ in the upscaling of the retardation factor (R) in a synthetic two-dimensional isotropic aquifer. They found that the upscaled R was highly affected by the cross-correlation between $\ln K$ and $\ln K_d$. For a negative correlation, upscaled R for early times was smaller than that for late times. For a positive correlation, the result was the opposite and upscaled R for early times was larger than

that for late times.

Erşahin et al. (2017) characterized the spatial variability of pore-water velocity (v), dispersivity, retardation factor and dispersion coefficient (D) and analyzed their statistical relations to other soil properties. They found that solute parameters were not correlated with the physical soil properties but were significantly correlated with soil chemical variables such as pH, electrical conductivity (EC) and cation exchange capacity (CEC). A pure nugget model was fitted to $\log \alpha$ and R indicating no spatial structure. On the contrary, $\log v$ and $\log D$ showed a moderate and strong spatial structure, respectively.

By analyzing many studies related to spatial variability in soil science, it can be noticed that a multivariate approach is used, in line with Goovaerts (1999), who points out that the soil information is generally multivariate. Usually, multivariate data are analyzed with statistical methods, such as principal component analysis or multiple linear regression (Ferreira da Silva et al., 2013; Rodríguez Martín et al., 2007) but without accounting for their possible spatial correlation (Erşahin et al., 2017; Kazemi et al., 2008). Ignoring the multivariate spatial correlations can be a waste of available and important information.

Some effort has been made to characterize the spatial variation of the correlation among variables and to use this information for estimation purposes (Benamghar and Gómez-Hernández, 2014; Bevington et al., 2016; Goovaerts, 1998; Guagliardi et al., 2013). Nevertheless, attempts to obtain the spatial variation of the correlation among solute transport and all statistically significant variables are rare (Jacques et al., 1999) and more studies need to be done.

Our first objective is to determine the linear statistical correlations among soils properties, K , α , and K_d for a reactive (potassium) and a nonreactive (chloride) solute. Second, in order to identify the more statistically significant variables that explain the variability of the variables of interest (K , α , and K_d), multiple linear regression is performed. The third objective is to model the spatial structures of soils properties and of the variables of interest. Aiming to study the spatial cross-correlation among variables, the fourth objective is to model the relations among the variables of interest and each one of the more statistically significant variables. To the best of our knowledge, this is the first time that the spatial correlations among α and K_d of a reactive and a nonreactive solute, and statistically significant variables are studied. Finally, although the characterization of the spatial variability of soil properties at the centimeter/m scale can affect the solute transport prediction at a bigger scale (Salamon et al., 2007), studies in this scale are scarce. In this context, we are interested in the small-scale variability using a dense sampling design.

2. Material and methods

2.1. Description of the study site

The study was carried out in São Carlos city (21°51'38" S, 47°54'14" W), which is located in the East-Center of the São Paulo State, Brazil (Fig. 1). As mentioned before, since we are studying the spatial variability at the scale of a few meters, the study site covers an area of 84 m² and a depth of 2 m. The pedologic soil type is classified as Oxisol according to US Soil Taxonomy (Soil Survey Staff, 1999) and medium textured, dystrophic, red-yellow Latosol according to the Brazilian classification system (Santos et al., 2014). Clayey fine sand is the predominant texture. The climate in this region is Köppen's Cwa type (Miranda et al., 2015; Peel et al., 2007). The mean annual temperature is 21.2 °C, having humid and hot summers and a dry winter, with an average annual rainfall of 1423 mm (Miranda et al., 2015). The parent material comprising Cenozoic sediments that cover the Botucatu Formation (Paraná Sedimentary Basin, São Bento Group), constituted by unconsolidated sands with the thickness ranging from 5 to 7 m and pebbles at the base, and are spread at all São Paulo interior region (de Azevedo et al., 1981; Giacheti et al., 1993). The action of weathering under tropical conditions makes the soil from the Cenozoic sediments

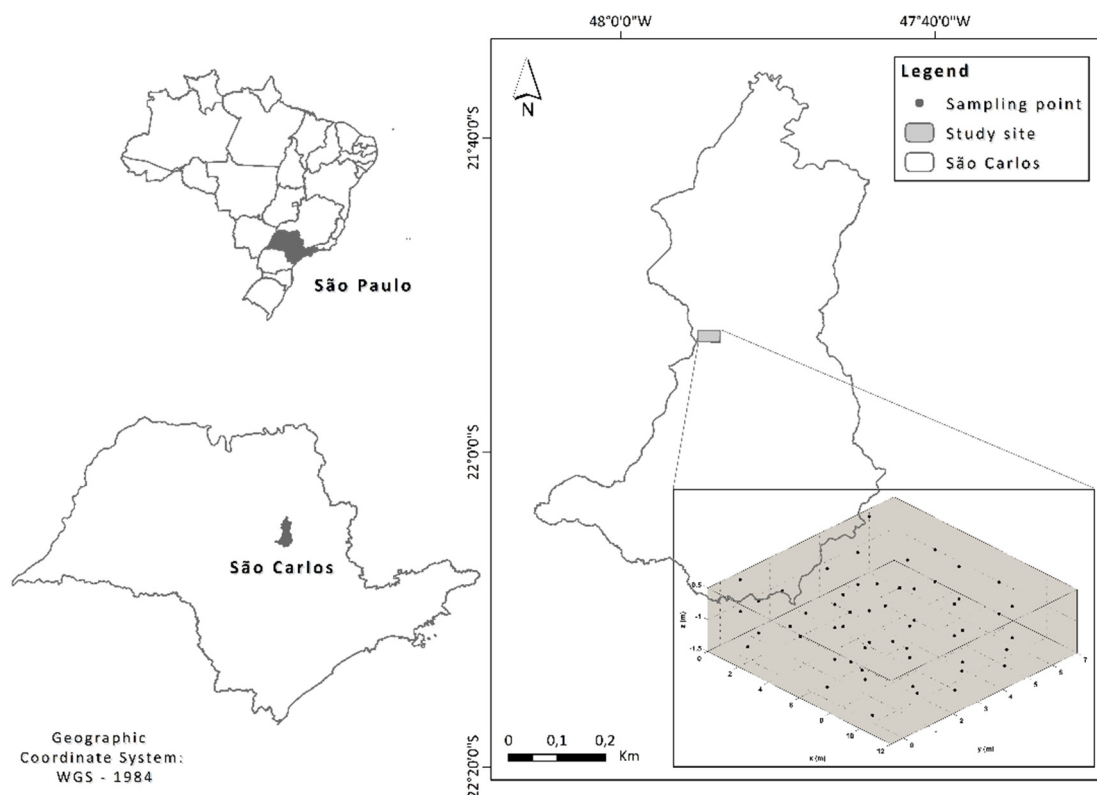


Fig. 1. Location of the study site and the position of the sampling points.

highly lateritized (Giacheti et al., 1993). The main constituents of the studied soil are quartz, oxides, and hydroxides of aluminum, kaolinite, and gibbsite. Macropores and dual-porosity are also characteristics of that soil (Rohm, 1992).

2.2. Soil sampling

Undisturbed soil samples were cautiously taken from hand-excavated trenches by carefully forcing rigid polyvinyl chloride (PVC) cylinders (150 mm in height and 97.2 mm in inner diameter) into the soil. Soil core sampling started by removing the grass (when present) and a thin and hard layer from the top of the soil. Sampling in the x-y plane was performed at 23 locations of the study site. For each x-y coordinate three samples were taken at different depths (z coordinate 0.5 m, 1.0 m and 1.5 m), resulting in a dense sampling design. Initially, 69 undisturbed soil samples were collected, but 14 samples presented defects or cracks and were discarded. The position of the 55 remaining samples in the study site is shown in Fig. 1. Additionally, disturbed soil samples were collected to characterize soil properties that were not spatially evaluated.

2.3. Soil properties characterization

Silt, clay and sand content, cation exchange capacity (CEC), total porosity (n), effective porosity (ne), macroporosity (Ma), mesoporosity (Me), microporosity (Mi) and bulk density (ρ_d) are referred to soil properties. These soil properties were analyzed spatially. In the laboratory, the moisture was determined in three replicates for each soil sample. Subsequently, the soil was air-dried and sieved through a #10 mesh sieve (2 mm openings). Particle size distribution were determined according to ASTM D7928-17 (ASTM, 2017a) and ASTM D6913/D6913M-17 (ASTM, 2017b). in only one replicate for each soil sample. Particle density ρ_s was determined in five replicates using the ASTM D 854-14 (ASTM, 2014a) and resulted in $2.71 \text{ Mg}\cdot\text{m}^{-3}$ for all soil samples (arithmetic mean of all replicates).

Bulk density was determined for each soil column as $\rho_d = M_d/V_t$, where V_t is the total volume of the soil sample (internal volume of each PVC cylinder) and M_d is the dry mass of the soil sample.

Mercury intrusion porosimetry (MIP) (Washburn, 1921) and total porosity was calculated for each soil sample as $n = 1 - \rho_d/\rho_s$. When the total porosity calculated was different from the one obtained by MIP, we assumed that the difference was due to large pores that were not identified in the MIP due to the reduced sample size used. The effective porosity (ne) was considered as the total porosity minus the porosity that corresponds to the soil water content at 33 kPa, suction equivalent to the field capacity (Ahuja et al., 1984; Brutsaert, 1967; Corey, 1977; Dippenaar, 2014). It is important to mention that the field capacity is not precisely defined in soil science and we chose to use that value since it is widely used in the literature. The diameter of the pore equivalent to the suction at 33 kPa was calculated as $8.9 \mu\text{m}$ from the capillary rise equation assuming a contact angle of 0° . Thus, based on the results of the MIP, the effective porosity was calculated as the total porosity minus the porosity correspondent to the pores with a diameter smaller than $8.9 \mu\text{m}$. From the MIP results, Ma , Me , and Mi were determined according to the classification proposed by Koorevaar et al. (1983), in which the diameters of Mi , Me , and Ma are, respectively, $< 30 \mu\text{m}$, $30\text{--}100 \mu\text{m}$ and $> 100 \mu\text{m}$. The methylene blue adsorption test using the filter paper method described by Pejon (1992) was used to determine CEC in one replicate for each soil sample.

In order to characterize average properties with no concern about spatial structure, the next parameters were determined in three replicates by using disturbed soil samples: pH in H_2O and in KCl, redox potential (Eh) and electrical conductivity (EC) (Donagema and Campos, 2011), ΔpH ($\text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$) (Mekaru and Uehara, 1972), point of zero charge (PZC) ($2\text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$) (Keng and Uehara, 1974), organic matter content according to the ASTM D 2974-14 (ASTM, 2014b), and mineralogical composition by X-ray diffraction (Azaroff and Buerger, 1953).

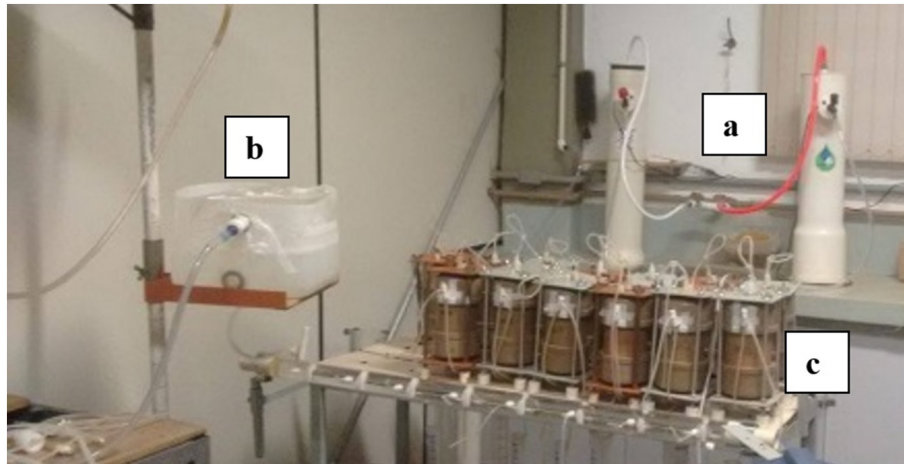


Fig. 2. Column experiments in progress: a) water deionizers, b) hydraulic head controller device, c) rigid-wall permeameters.

2.4. Column experiments

The PVC cylinders used for collecting the undisturbed soil samples were used as rigid-wall permeameters and 55 column experiments were conducted. Fig. 2 shows the column experiments in progress. First, the columns were sealed with a cap containing a stainless plastic plate with holes on both ends of the column, which allowed a uniform distribution of the inlet flow. Second, the soil samples were slowly saturated from the bottom with deionized water to remove entrapped air. Third, the flow was reversed, and the permeability test was performed under a constant hydraulic gradient of 1 and the flow rate (Q) was measured. We have taken two measures per day and we assumed that steady-state flow was achieved when Q variations were below 5% in a week. Water temperature was monitored throughout the test and, when necessary, corrections were made in the calculations of the hydraulic parameters. Fourth, the following water flow parameters were obtained from each soil sample: saturated hydraulic conductivity, K ; specific discharge, q ; flow rate, Q ; and average linear velocity, v (q/ne) (Freeze and Cherry, 1979). When the steady-state flow was reached, deionized water was replaced by a 2.56 mol m^{-3} KCl solution ($100 \text{ mg L}^{-1} \text{ K}^+$ and $90.7 \text{ mg L}^{-1} \text{ Cl}^-$ referred to as initial concentrations, C_0) continuously injected into the soil column. Solute displacement tests were carried out under constant hydraulic head and isothermal (20°C) conditions. The concentration, temperature, and pH of the initial solution were monitored throughout the test. Leachate samples were collected from the outlet of the columns at pre-set time intervals (defined for each column in accordance with the flow rate), stored in plastic bottles and refrigerated immediately after collection. Preferably, the tests were performed until the relative concentrations (C/C_0) reached 1, but this condition was not achieved in some samples. An ion-selective electrode (ISE) (Hanna instruments - HI 4107 model) was used to determine Cl^- concentration (C) at each time. K^+ concentration at each time was measured by a flame photometer (Micronal B462 model) at a 1:21 ratio. All ion concentrations were measured in one replicate and determined as the arithmetic mean of the replicates. The relative concentrations (C/C_0) of Cl^- and K^+ were determined by dividing the concentration of the ion in the leachate samples at each time by the concentration of the ion in the initial solution. Thereafter, a breakthrough curve (BTC) of each soil sample and each ion was plotted. The BTC's were expressed as C/C_0 and the number of pore volumes (T), where T is a dimensionless variable calculated as $T = vt/L$ (van Genuchten, 1980), where v is the average linear velocity, t is the time elapsed from the start of the solute application, and L is the length of the soil column (150 mm).

2.5. Transport parameter determination

Dispersivity (α) [L] and partition coefficient between liquid and solid phases (K_d) [L^3M^{-1}] are referred to as the transport parameters and were determined as explained next.

The advection-dispersion equation (ADE) used to interpret the BTCs is

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}, \quad (1)$$

where C is solute concentration [ML^{-3}], D is the hydrodynamic dispersion coefficient [M^2T^{-1}], R is the retardation factor [-], x is the distance [L], and t is time [T].

The hydrodynamic dispersion coefficient is related to the dispersivity by

$$D = \alpha \cdot v, \quad (2)$$

and the retardation factor is related to the partition coefficient K_d through the expression

$$R = 1 + \frac{\rho_d K_d}{n} \quad (3)$$

This equation has the following analytical solution (Lapidus and Amundson, 1952; Ogata and Banks, 1961), when the initial condition is $C_0 = 0$ for the entire sample, and the boundary conditions are $C=C_0$ at the inlet and $C = 0$ at an infinite distance from the inlet

$$\frac{C}{C_0} = \frac{1}{2} \left[\text{erfc} \left(\frac{RL - vt}{2\sqrt{DRt}} \right) \right] + \frac{1}{2} \exp \left(\frac{vL}{D} \right) \text{erfc} \left(\frac{RL + vt}{2\sqrt{DRt}} \right), \quad (4)$$

where erfc is the complementary error function.

This expression was fitted to the observed BTCs for each soil sample and values of D and R were obtained for both K^+ and Cl^- . The fitting was performed using the computer program CFITM (van Genuchten, 1980), that is part of the Windows-based computer software package Studio of Analytical Models (STANMOD) (Simunek, van Genuchten, Sejna, Toride, & Leij, 1999).

2.6. Statistical analysis

Exploratory analysis of the K , $\ln K$, soil properties and transport parameters (including P , R , D , $\ln \alpha$ of K^+ and $\ln \alpha$ of Cl^-) was performed. Global summary statistics such as mean, standard deviation, variance, minimum and maximum value, kurtosis, skewness, and coefficient of variation (CV) were computed. The CV were classified according to Wilding and Drees (1983): low variability for $\text{CV} < 15\%$; moderate variability for $15\% < \text{CV} < 35\%$; and high variability for

CV > 35%. The normality of the data was tested by means of the Kolmogorov–Smirnov test (Massey, 1951). When necessary, the variables were standardized, and the subsequent studies were performed using standard normal variables. Outliers were analyzed in detail to investigate errors in the determination of the variables, and when deemed appropriate they were excluded from the dataset. Trends were also investigated and, if present, removed. The presence and strength of significantly linear associations between soil properties and the variables of interest ($\ln K$, $\ln \alpha$ (K^+), $\ln \alpha$ (Cl^-), K_d (K^+), and K_d (Cl^-)) were examined by computing Pearson correlation coefficients at 0.05 and 0.01 significance level. The natural logarithm (\ln) of α and K were used as variables rather than α and K because they resulted in better correlations.

The quantification of the significance of the relationships between all the studied variables, i.e. soil properties and variables of interest, was analyzed separately using multiple linear regression (MLR) (Eq. 3). Stepwise regression analyses were carried out to avoid the possible collinearity effects in multiple regressions. Statistically significant differences were set with p values equal to 0.05.

A stepwise MLR as in Eq. (3)

$$y = b_0 + b_1 w_1 + b_2 w_2 + b_3 w_3 + \dots + b_n w_n \quad (3)$$

defines the best linear combination of the variables to predict the variables of interest and helps understand which variables have the highest influence on the variables of interest, where y is the dependent variable and w_1 to w_n are independent variables.

2.7. Geostatistical analysis

Based on the MLR results, the spatial dependence of the more statistically significant soil properties and the variables of interest was measured using direct experimental variograms.

The variogram can be defined as the mean-squared difference between the same variable at specified separation distances (Isaaks and Srivastava, 1989), and it was calculated using

$$\gamma(\mathbf{h}) = \frac{1}{2N} \sum_{aa=1}^{N(\mathbf{h})} [z(u_{aa}) - z(u_{aa} + \mathbf{h})]^2 \quad (5)$$

where $\gamma(\mathbf{h})$ is the variogram function, $z(u_{aa})$ is the measured value of the attribute under consideration taken at location aa , \mathbf{h} is the separation vector and $N(\mathbf{h})$ is the number of data-pairs separated by the vector \mathbf{h} . The variograms were obtained using the Stanford Geostatistical Modeling Software (SGeMS).

Almost all experimental variograms were best fitted to the isotropic spherical variogram model (Isaaks and Srivastava, 1989)

$$\gamma(\mathbf{h}) = c_0 + c_1 \text{sph}(|\mathbf{h}|/a) \quad (6)$$

where a is the range, i.e., is the separation distance beyond which observations are spatially independent of each other, c_0 is the nugget effect, c_1 is the covariance contribution or sill value, and \mathbf{h} is the directional lag distance.

The nugget effect model was also used in a situation, indicating that the variable was randomly spatially distributed.

$$\gamma(\mathbf{h}) = \begin{cases} 0 & \text{if } \mathbf{h} = 0 \\ 1 & \text{otherwise} \end{cases} \quad (7)$$

In multivariate geostatistics, to model the coregionalization between p variables requires modeling $p(p+1)/2$ direct and cross-variograms. In this paper, p corresponds to the variables of interest plus the set of variables that best explains its variability, according to the MLR results.

The cross-variogram function describes the way in which two variables are spatially related, and was used to quantify the structure of the spatial correlation between selected soil properties and $\ln K$, $\ln \alpha$ (K^+), $\ln \alpha$ (Cl^-), K_d (K^+), and K_d (Cl^-)

$$\gamma_{uv}(\mathbf{h}) = \frac{1}{2N(\mathbf{h})} \sum_{i=1}^{N(\mathbf{h})} [z_i(u_{aa}) - z_i(u_{aa} + \mathbf{h})] \cdot [z_j(u_{aa}) - z_j(u_{aa} + \mathbf{h})] \quad (8)$$

where $z_i(u_{aa})$ and $z_j(u_{aa})$ are the measured z_i and z_j regionalized variables, respectively, taken at location aa .

The codispersion coefficient, r_{uv} , between the variables v and u , r_{uv} , for each vector \mathbf{h} was computed for any pair of variables as the ratio of the cross-variogram between v and u to the square root of the product of the variograms of u and v (Goovaerts, 1994)

$$r_{uv}(\mathbf{h}) = \frac{\gamma_{uv}(\mathbf{h})}{\sqrt{\gamma_u(\mathbf{h})\gamma_v(\mathbf{h})}} \quad (9)$$

3. Results and discussion

3.1. Average soil properties

The main minerals present in the studied soil are quartz, kaolinite, and gibbsite, in accordance with Giacheti et al. (1993) and Kronberg et al. (1979). Average values of 5.71 and 5.19 for pH in H_2O and in KCl, were obtained, respectively. These results show that the soil is strongly acid, which is a typical characteristic of Cenozoic sediments and lateritic soils (Fagundes and Zuquette, 2011; Giacheti et al., 1993). The negative ΔpH (−0.52) and a point of zero charge (PZC) (4.67) lower than the pH_{H_2O} indicate a predominance of negative charges, which can promote cation adsorption (Fagundes and Zuquette, 2011). This soil contains a small average amount of organic matter (2.40%), a result suitable for lateritic acid soils (Mahapatra et al., 1985). According to the soil salinity classification of the Food and Agriculture Organization of the United Nations (FAO), the electrical conductivity values indicate small amounts of dissolved salts (55.70 $mS\ m^{-1}$) and a non-saline soil (Abrol et al., 1988).

3.2. Soil properties statistical analysis

The exploratory statistical results of the soil properties, v and K are shown in Table 1. In order to identify trends, all statistical results were also investigated for each depth (results not shown), and no significant influence of the depth was observed. Because of that, in further analysis the samples were considered as a unique dataset, regardless of the depth. Soil properties are slightly skewed, quantified by a skewness < |0.5| (Webster, 2001), except Ma and CEC , which are

Table 1

Descriptive statistics of soil properties, hydraulic conductivity and linear average velocity at the study site.

	Mean	SD	CV	Skew	Kurt	Min	Max
K [$m\ d^{-1}$]	1.35	1.65	1.22	2.39	5.84	0.03	7.46
v [$m\ d^{-1}$]	5.40	6.57	1.23	2.20	4.61	0.13	27.71
$\ln K$ [$\ln(m\ d^{-1})$]	−0.37	1.25	n.d	−0.29	−0.12	−3.68	2.03
n []	0.51	0.04	0.08	−0.24	−0.39	0.42	0.58
ne []	0.24	0.02	0.08	−0.39	−0.14	0.20	0.28
ρ_d [$g\ cm^{-3}$]	1.34	0.10	0.07	0.28	−0.32	1.14	1.59
CEC [$cmol_c\ Kg^{-1}$]	2.51	0.64	0.25	1.06	0.39	1.60	4.20
Sand (%)	56.20	3.24	0.06	−0.36	−0.52	48.50	61.50
Silt (%)	4.62	2.82	0.61	0.16	−0.06	1.40	11.40
Clay (%)	39.18	3.51	0.09	0.10	−0.87	32.50	46.10
Ma []	0.072	0.04	0.56	0.75	−0.58	0.031	0.152
Mi []	0.262	0.06	0.23	−0.25	−0.96	0.141	0.361
Me []	0.172	0.05	0.29	0.21	−0.92	0.091	0.263

SD: standard deviation, CV: coefficient of variation, Skew: Skewness, Kurt: Kurtosis, Min: minimum value, Max: maximum value, n.d: undetermined, K : hydraulic conductivity; v : linear average velocity, ρ_d : bulk density, n : total porosity, ne : effective porosity Ma : macroporosity, Me : mesoporosity, Mi : microporosity, CEC : cation exchange capacity.

moderately and highly skewed with a skewness of 0.75 and 1.06, respectively. The difference between its minimum and maximum value was quite large for K , $\ln K$, v , silt content, Ma , and CEC . According to the CV classification of Wilding and Drees (1983), high CV were identified for K , v , silt content and Ma (1.22, 1.23, 0.61 and 0.56, respectively) evidencing high variability in these variables. Our results confirm that soil heterogeneity is present even on a small scale, depending on the studied property (Chapuis et al., 2005; Lacasse and Nadim, 1996; Søvik and Aagaard, 2003).

Mercury intrusion porosimetry results indicated that the soil has dual-porosity and the predominant pore diameters correspond to Me and Mi . The multimodal pore size distribution is characteristic of well-structured soils (Hajnos et al., 2006; Lipiec et al., 2007). The soil has a low CEC (maximum value $4.20 \text{ cmolc Kg}^{-1}$) and it suggests a low capacity to adsorb cations by electrostatic adsorption (Fagundes and Zuquette, 2011). Mean soil properties presented values in accordance with the typical characteristics of the studied soil (Giacheti et al., 1993; Zuquette and Palma, 2006), and are shown in Table 1.

3.3. Statistical analysis of the transport parameters

The breakthrough curves (not shown) of K^+ and Cl^- obtained from the 55 miscible displacement tests were analyzed, and transport parameters were determined. The goodness of fit of the experimental BTC to the ADE model was evaluated by its R^2 . Most BTCs presented significant tailing, R^2 ranged from 0.77 to 0.99 with a mean of 0.92 for K^+ and 0.95 for Cl^- , suggesting that the ADE model was suitable to describe the data. BTCs that presented low R^2 were investigated to check for problems in the soil samples, but no problems were found.

Basic statistics of the transport parameters are shown in Table 2. Almost all transport parameters were high right-skewed. Moderate right-skewness was obtained only for $R (Cl^-)$ and $K_d (Cl^-)$. Slightly right-skewness was obtained for $\ln \alpha (K^+)$ and $\ln \alpha (Cl^-)$. High right-skewness bromide (Br^-) α and D , and moderate $\ln \alpha$ left-skewness was found in the work of Erşahin et al. (2017).

All transport parameters show high CVs and the highest ones were obtained for the reactive solute (K^+). The coefficients of variation of R and K_d for K^+ shown that transport parameters are very variable. The values we obtained for α were high when compared to other studies using samples of approximately the same dimensions (Erşahin et al., 2017). Also, mean α values were high when compared to the typical values used in the literature ($\alpha = 0.1 L$, where L is the distance) (Freeze and Cherry, 1979). These differences can be attributed to numerous factors such as the scale of the experiment, flow rate, and boundary conditions. Higher values of α can also be indicative of preferential flow.

Table 2
Descriptive statistics of transport parameters.

	Mean	SD	CV	Skew	Kurt	Min	Max
$P (K^+)$ []	2.07	2.12	1.02	2.15	5.61	0.11	10.80
$R (K^+)$ []	5.37	5.10	0.95	4.51	25.31	0.69	36.19
$K_d (K^+)$ [$\text{cm}^3 \text{g}^{-1}$]	1.71	2.27	1.33	5.61	36.75	0.01	16.75
$D (K^+)$ [$\text{m}^2 \text{d}^{-1}$]	1.07	1.77	1.65	2.64	7.42	0.02	8.77
$\alpha (K^+)$ [m]	0.18	0.19	1.06	1.82	3.32	0.01	0.88
$\ln \alpha (K^+)$ [ln (m)]	-2.21	1.11	n.d.	-0.45	0.71	-5.79	-0.12
$P (Cl^-)$ []	2.82	2.78	0.99	2.08	4.25	0.44	13.41
$R (Cl^-)$ []	2.35	1.29	0.55	0.61	-0.60	0.33	5.20
$K_d (Cl^-)$ [$\text{cm}^3 \text{g}^{-1}$]	0.55	0.51	0.93	0.66	-0.81	0.03	1.64
$D (Cl^-)$ [$\text{m}^2 \text{d}^{-1}$]	0.61	1.14	1.87	3.43	12.26	0.01	5.62
$\alpha (Cl^-)$ [m]	0.10	0.08	0.80	1.23	1.43	0.01	0.34
$\ln \alpha (Cl^-)$ [ln (m)]	-2.61	0.93	n.d.	-1.18	2.80	-6.18	-1.07

SD: standard deviation, CV: coefficient of variation, Skew: Skewness, Kurt: Kurtosis, Min: minimum value, Max: maximum value, n.d.: undetermined, P : Peclet number, R : retardation coefficient, K_d : partition coefficient, D : hydrodynamic dispersion coefficient, α : dispersivity, (K^+) potassium, (Cl^-): chloride.

The maximum and minimum values were quite different for all transport parameters, evidencing, again, the large variability in these parameters. Peclet numbers ranged from 0.11 to 13.41, showing that for some soil samples the advective transport prevailed, whereas for other samples, dispersive transport was the primary mechanism. These differences probably are related to heterogeneities between physical characteristics of soil samples. $R (K^+)$ ranged from 0.69 to 36.19, while $R (Cl^-)$ ranged from 0.33 to 5.20, as expected because reactive solute should have larger R values than nonreactive solutes.

Even though clay content was significant, high $R (K^+)$ and $R (Cl^-)$ values were not expected since the combination of the clay minerals identified, the low CEC values and the predominance of negative charges do not favor the retardation of K^+ and Cl^- . We believe that the structure of the soil played an essential role on the retardation. Moreover, the results of P and R can be explained by the distribution of the diameter of the pores in the soil, since the maximum Ma and Mi values were 0.15 and 0.36, respectively. Because of that, part of the solutes can move fast because of advection (in macropores) and part of them can be retarded due to the percolation through micropores and non-interconnected pores, behavior also stated by others (Jarvis, 2007; Silva, van Lier, Correa, Miranda, & Oliveira, 2016; van Genuchten and Wierenga, 1976).

3.4. Correlation among variables

To examine the relationship among soil properties, hydraulic conductivity and transport parameters, correlation coefficients were computed. Outliers were removed before the coefficients were computed and the analyses were performed using 50 values for each variable. As none of the variables was normally distributed, correlation analyses were performed using the original data (results not shown) as well as the standardized normal distributed transformed values. As the best correlation coefficients were obtained with standardized variables, all analyzes hereafter were performed using these variables. Variables that are not intrinsic properties of the media such as P , D , R , and v , were not considered in the analysis of correlations.

None of the physical soil property was strongly correlated to the transport parameters. According to Vanderborght and Vereecken (2007), texture has no significant effect in α and this result is also verified in our study. Since the studied soil has a structure characteristic of lateritic soils by forming agglomerates, texture itself may not show much about dispersivity.

It was obtained a statistically significant positive correlation between $\ln \alpha (Cl^-)$ and ρ_d and a negative correlation with n . This result is in accordance with the equation that relates dispersivity to D and v ($D = \alpha v$, where $v = q/ne$). Since n is slightly negatively related to ne , as shown in Table 3, when v increases α decreases, justifying the relations obtained. The only variable significantly positively correlated to $\ln \alpha (K^+)$ was $\ln \alpha (Cl^-)$, suggesting that higher D smaller the influence of other soil properties.

A strong positive correlation was obtained between $K_d (K^+)$ and CEC and $K_d (Cl^-)$, showing the importance of the physico-chemical adsorption and the relation between the ions studied. A low, but still significant, positive correlation among $K_d (K^+)$ and Me was obtained. A negative correlation was obtained between $K_d (K^+)$ and Mi , indicating that neither Ma nor Mi contributed to higher R , contrary to our initial assumptions. A low positive correlation was presented by $K_d (Cl^-)$ with silt content and a strong positive correlation with CEC and $K_d (K^+)$ and no correlation with pore size was observed.

Almost no correlation was obtained among CEC and clay content, indicating that the clay mineral present in the soil is not relevant to adsorb cations, as mentioned before. Significant positive correlations among $\ln K$, n , ne , and Ma were verified, indicating that these properties dictate the values of $\ln K$ and of the water flow in soils (Biswas and Si, 2009). In a previous study, a high positive correlation was obtained among K , Ma , and n (Mbagwu, 1995). A significant negative correlation

Table 3
Correlation coefficients among standardized variables.

	$\ln \alpha (\text{Cl}^-)$	$\ln \alpha (\text{K}^+)$	$K_d (\text{K}^+)$	$K_d (\text{Cl}^-)$	CEC	$\ln K$	ρ_d	n	ne	sand	silt	clay	Mi	Me	Ma
$\ln \alpha (\text{Cl}^-)$	1.00														
$\ln \alpha (\text{K}^+)$	0.71**	1.00													
$K_d (\text{K}^+)$	-0.03	0.06	1.00												
$K_d (\text{Cl}^-)$	-0.09	0.10	0.63**	1.00											
CEC	-0.04	0.15	0.70**	0.81**	1.00										
$\ln K$	0.13	0.11	-0.02	-0.14	-0.10	1.00									
ρ_d	0.33*	0.11	-0.22	-0.20	-0.26	-0.34*	1.00								
n	-0.32*	-0.10	0.23	0.19	0.26	0.33*	-0.99**	1.00							
ne	0.25	0.12	0.06	0.02	-0.01	0.44**	0.06	-0.06	1.00						
Sand	0.21	0.18	-0.27	-0.13	-0.17	0.01	0.22	-0.22	-0.28	1.00					
Silt	-0.07	-0.10	0.16	0.30*	0.21	0.05	-0.10	0.08	0.11	-0.29*	1.00				
Clay	-0.14	-0.10	0.15	-0.09	0.01	-0.05	-0.11	0.13	0.16	-0.69**	-0.48**	1.00			
Mi	-0.21	-0.18	-0.39**	-0.25	-0.26	-0.02	0.04	-0.03	-0.22	0.10	-0.37**	0.18	1.00		
Me	0.08	0.06	0.36*	0.28	0.12	-0.19	0.18	-0.20	0.22	-0.15	0.40**	-0.14	-0.68**	1.00	
Ma	0.10	0.03	-0.16	-0.20	0.03	0.38**	-0.22	0.24	0.10	0.14	-0.02	-0.12	0.28	-0.63**	1.00

α : dispersivity, (K^+) potassium, (Cl^-): chloride, K_d : partition coefficient, CEC: cation exchange capacity, K : hydraulic conductivity; ρ_d : bulk density, n : total porosity, ne : effective porosity, Mi : microporosity, Me : mesoporosity, Ma : macroporosity.

* Significant at 0.01 level of significance.

** Significant at 0.05 level of significance.

was also found among $\ln K$ and ρ_d results in accordance with other studies (Bevington et al., 2016; Botros et al., 2009; Mbagwu, 1995; Papanicolaou et al., 2015). These results show the higher ne (negatively related to n as shown in Table 3), higher v , as expected. No significant correlation between $\ln K$ and texture was obtained. However, this result contrast with several previous studies in non-lateritic soils, showing the impact of the soil agglomerates in the relation among soil properties (Huang et al., 2016; Igwe, 2005; Nemes et al., 2009; Pachepsky and Rawls, 2004; Søvik and Aagaard, 2003).

Table 4 presents the results of the stepwise multiple linear regression analysis at a significance level of 95%. This analysis was used for investigating the significance of the relationships among all selected variables. The best model for $K_d (\text{K}^+)$ was obtained by considering two variables, CEC and Ma , explaining 70% of the total variance in the model, with Pearson coefficient r equal to 0.84. The model that best represents $K_d (\text{Cl}^-)$ was found by combining CEC, clay content and Me , which explain 60% of the total variability with a moderate r equal to 0.70. These results suggest that other variables that were not considered in this study could be added to better explain the total variability of K_d . For example, several authors have suggested that pH, EC, the content of Al and Fe, CaCO_3 and organic carbon have a strong influence on the

total variability of K_d (Che et al., 1992; Erşahin et al., 2017; Porfiri et al., 2015). Additionally, some variables that were significantly correlated to K_d in the correlation analysis were not significant in the MLR. This can be related to possible collinearity effects of these variables, what is identified and excluded by using stepwise method.

The only variables that were significant to model $\ln \alpha (\text{K}^+)$ and $\ln \alpha (\text{Cl}^-)$ were $\ln \alpha (\text{Cl}^-)$ and $\ln \alpha (\text{K}^+)$, respectively, and both have explained only 50% of the total variability, with a moderate r equal to 0.70 and 0.72, respectively. It demonstrates that other variables should be considered to better explain total variability in $\ln \alpha$. As α has some scale and spatial dependence (Erşahin et al., 2017; Freeze and Cherry, 1979), it could be interesting to take into account its spatial relationship with other parameters and not only the parameter itself.

Only 40% of the total variability of $\ln K$ was explained by the combination of ne , ρ_d , and Ma with a moderate r equal to 0.63. Contrary to the correlation analysis, where the correlation between n and $\ln K$ was statistically significant, in the MLR, n had not explained $\ln K$ variability when combined with other variables. In future studies, it would be valuable to include other explanatory variables, such as soil structure and microstructure that in previous studies were recognized as direct drivers of K (Benegas et al., 2014; Beven and Germann, 2013; Burke et al., 1999; Hillel, 2004; Nanzyo et al., 1993; Narwal, 2002; Zimmermann and Elsenbeer, 2008) and can be even more important for lateritic soils.

3.5. Spatial correlation among variables

As the correlation among variables in Table 3 neglects the spatial component of the sample points, in this section, the direct and the cross-variograms are used to explore further the spatial correlation among variables. The spatial structure of the standardized variables was evaluated using variograms functions. Table 5 summarizes the parameters of the models that were used to fit the experimental variograms. Only clay content shows no spatial dependence (pure nugget effect), indicating that this variable is spatially random, despite being correlated to sand and silt content, which display spatial dependence. This result can be related to the more or less uniform distribution of the clay content in the studied site, with a CV of only 9%. Experimental variograms of all the remaining variables were fitted with a spherical model, indicating that abrupt changes in space may occur, while preserving an overall spatial structure.

The spatial structure was similar for all the studied variables. The largest range was obtained for $\ln K$ (4.0 m), while silt content and Mi presented the smallest ones (2.5 m). Microporosity, as well as all

Table 4
Stepwise multiple linear regression results.

	$K_d (\text{K}^+)$	$\ln \alpha (\text{K}^+)$	$K_d (\text{Cl}^-)$	$\ln \alpha (\text{Cl}^-)$	$\ln K$
$\ln K$	–	–	–	–	–
n	–	–	–	–	–
ne	–	–	–	–	26.4
ρ_d	–	–	–	–	-3.90
CEC	0.68	–	0.48	–	–
Sand	–	–	–	–	–
Silt	–	–	–	–	–
Clay	–	–	0.03	–	–
Ma	-0.03	–	–	–	0.09
Mi	–	–	–	–	–
Me	–	–	0.02	–	–
$K_d (\text{K}^+)$	–	–	–	–	–
$\ln \alpha (\text{K}^+)$	–	–	–	0.63	–
$K_d (\text{Cl}^-)$	–	–	–	–	–
$\ln \alpha (\text{Cl}^-)$	–	0.79	–	–	–
Intercept	-0.29	-0.26	-2.34	-1.15	-2.25
R^2	0.70	0.50	0.60	0.50	0.40
r^a	0.84	0.70	0.77	0.72	0.63

All results were significant at $p \leq 0.05$.

^a Pearson's coefficient.

Table 5
Parameters of the variogram models used to fit the isotropic direct experimental variograms.

Variable	Model	Nugget (c_0)	Sill (c_1)	Range (m) (a)
$\ln K$	Spherical	0.0	1.0	4.0
n	Spherical	0.0	1.0	3.0
ne	Spherical	0.0	1.0	3.0
ρ_d	Spherical	0.0	1.0	3.5
CEC	Spherical	0.0	1.0	3.0
Sand	Spherical	0.0	1.0	3.0
Silt	Spherical	0.0	1.0	2.5
Clay	Pure nugget effect	1.0	0.0	–
Ma	Spherical	0.0	1.0	3.5
Mi	Spherical	0.45	0.55	2.5
Me	Spherical	0.00	1.0	3.0
$K_d(K^+)$	Spherical	0.40	0.60	3.6
$\ln \alpha(K^+)$	Spherical	0.50	0.50	3.0
$K_d(Cl^-)$	Spherical	0.55	0.45	3.3
$\ln \alpha(Cl^-)$	Spherical	0.30	0.70	2.7

studied solute transport parameters, displayed a nugget effect behavior, which accounts for short-scale spatial variability or measurement errors. These variables had a moderate spatial dependence classified by measuring the nugget ratio ($R_b = \text{nugget/sill} \times 100\%$), which is strong if $R_b < 25\%$, moderate if $25\% < R_b < 75\%$, weak if $R_b > 75\%$ (Cambardella et al., 1994). Variograms of K_d resulted in a greater range than $\ln \alpha$ variograms. Gupta et al. (1996), found a maximum range of 2.3 m for Br^- dispersivity. Contrary Erşahin et al. (2017) reported no clear spatial structure for α and R under their sampling scheme. They argued that α is distance and time-dependent at both the column and field scale, which complicates its spatial structure. Jacques et al. (1999) found pure nugget effect in the variogram of K_f (Freundlich partition coefficient). Spatial structure of the Cl^- mass recovery was studied in a $2\text{ m} \times 2\text{ m} \times 2\text{ m}$ cube and a range of 0.37 m was found. With these results, we can argue that the range of the studied variables may vary depending on the sampling scheme and on the size of the studied site.

Since the correlation among variables may depend on the spatial structure, the variation of the correlation coefficient among variables with the spatial scale was quantified. Fig. 3(A to D) shows these results for the correlations between $\ln K$, $\ln \alpha(K^+)$, $\ln \alpha(Cl^-)$, $K_d(K^+)$, and $K_d(Cl^-)$ and the variables which explained their variability, according to

the MLR results. As stated by Wackernagel (1995), if the codispersion among the variables is constant in space, the structure of correlation of the variables is not affected by spatial scale.

The correlation coefficient among $\ln K$ and Ma (Fig. 3A) decreases until 2.2 m and from then on presents a variation around zero, showing that for distances larger than 2.2 m these variables are no longer correlated. The spatial correlation among $\ln K$ and ne (Fig. 3A) showed that until 1.1 m the relationship became stronger and negative, changing completely the kind of relation between these variables since it is recognized that the increase in ne favors the water flow in soils. After that, the values became more positive (an expected relation) but the correlation weaker until 2.8 m, when the variation remained near zero. Similar behavior was also verified for the relation between ρ_d and Ma and between ne and Ma (Fig. 3A), but the correlations were not statistically significant. Contrarily, the correlation coefficient between $\ln K$ and ρ_d became weaker and positive until 3.3 m and then the variables seem to be not related in space. The relation between ne and ρ_d was around zero for all studied distances (Fig. 3A).

The spatial correlation between $K_d(K^+)$ and CEC (Fig. 3B) presented a fast decrease until 1 m and then these variables are no longer statistically significant. The spatial correlation among $K_d(K^+)$ and Ma and among CEC and Ma (Fig. 3B) was not significant even for the distance equal to zero, but these variables were identified as explanatory in the MLR, illustrating the importance of the spatial analyses for a better decision about the most relevant variables and their relations.

Until a distance of 1 m, only a slight decrease (become more negative) was observed in the spatial correlations among $K_d(Cl^-)$ and Me , Me and clay content, and CEC and Me (Fig. 3C). Contrarily, the correlation between $K_d(Cl^-)$ and clay content (Fig. 3C) showed a slight increase until 1 m. From 1 m, those correlations increased slightly and ranging near zero, except the correlation between CEC and Me , which showed an erratic behavior that may be related to its poor spatial correlation. The correlation among $K_d(Cl^-)$ and CEC (Fig. 3C) became weaker and negative until 2 m but was statistically significant just until 1.5 m. No spatial correlation was obtained between CEC and clay content, result different from that obtained by Jacques et al. (1999) who observed a strong spatial correlation between CEC and clay content until 2.03 m. Statistically significant correlation was verified between $\ln \alpha(K^+)$ and $\ln \alpha(Cl^-)$ (Fig. 2D) until 1.5 m, and from 2 m these variables were no longer correlated.

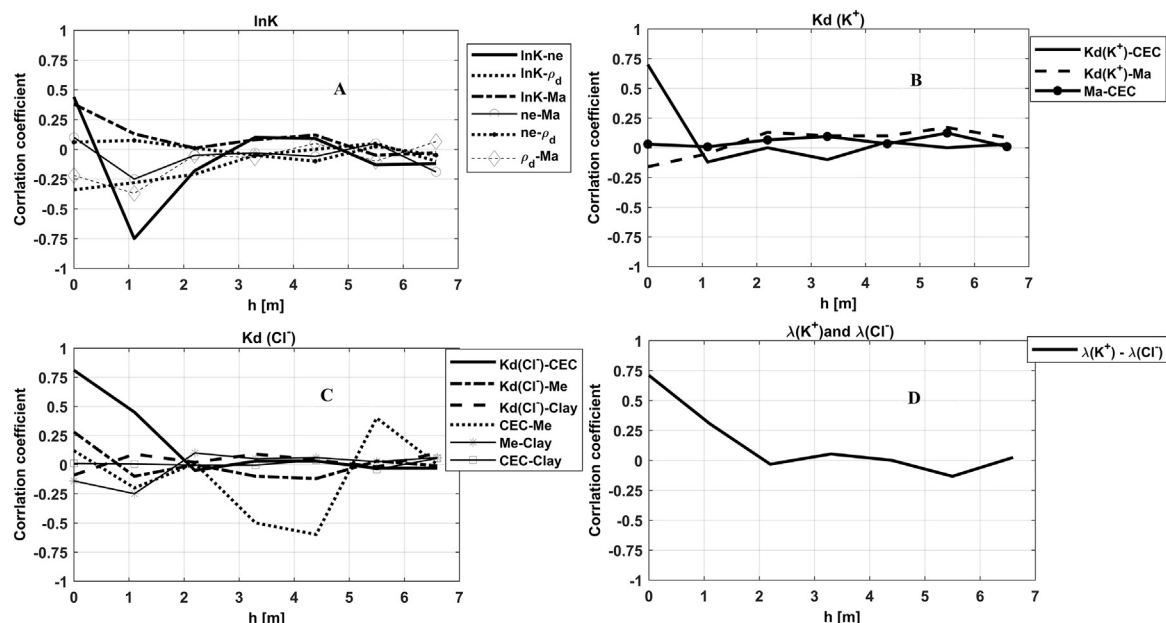


Fig. 3. Variation of the correlation coefficient among variables with the spatial scale.

4. Conclusions

In this study, the spatial correlation among soil properties (total porosity, effective porosity, cation exchange capacity, macroporosity, microporosity, mesoporosity, bulk density, silt, clay and sand content) and the variables of interest (hydraulic conductivity, partition coefficient and dispersivity of a reactive (K^+) and for a nonreactive solute (Cl^-) was studied at the scale of a few meters using a dense sampling design. The soil was characterized as acid with low cation exchange capacity and composed of minerals commons for lateritic soils.

None of the variables studied were normally distributed. Soil properties presented a moderate coefficient of variation (CV) while hydraulic conductivity and transport parameters were widely dispersed. None of the physical soil property was strongly correlated to the transport parameters. Nevertheless, some parameters such as cation exchange capacity and partition coefficient presented exhibits a statistically significant positive correlation with transport parameters. Stepwise multiple linear regression (MLR) analysis indicated that further studies should be performed aiming to include other explanatory variables such as pH, electrical conductivity, the content of Al and Fe, $CaCO_3$ and soil structure and microstructure, that are relevant variables for lateritic soils.

Our findings show that the use of geostatistical methods was efficient to evaluate the spatial variation in the correlation coefficients. However, for the conditions analyzed, the use of the spatial correlation among transport parameters and soil properties would probably improve the estimation only in a small-scale study, since the spatial correlation were only observed up to 2.5 m. It is important to mention that the study was performed for a specific field site and the results obtained may explain the spatial relation to the studied soil. However, the application of the statistical parameters to estimate transport parameters and predict solute transport in other soil is thus questionable.

The present study was a first attempt to evaluate the spatial correlation of transport parameters of a reactive and a nonreactive solute. We showed the soil properties that may exert greater influence and suggested the one that should be included in future studies. Understanding the spatial relations between variables can be useful in perform reliable prediction of flow and solute transport and contribute to reducing uncertainties when studying groundwater contamination.

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