

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

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11 **Highlights**

- 12 • We study reactive and non-reactive solute transport in a tropical soil.  
13 • Solute transport parameters and hydraulic conductivity display high variability.  
14 • Solute transport parameters and soil properties present spatial dependence.  
15 • Spatial correlation is important up to 2.5 m.

16  
17 **Abstract**

18 Spatial variation of the correlation among variables related to water flow and solute  
19 transport are important in the characterization of the spatial variability when performing  
20 uncertainty analysis and making uncertainty-qualified solute transport predictions.  
21 However, the spatial variation of the correlation between solute transport parameters  
22 and soil properties are rarely studied. In this study, the spatial correlation among  
23 laboratory-measured transport parameters dispersivity and coefficient of distribution of a  
24 reactive and a nonreactive solute and soil properties were studied at the scale of a few

25 meters using a dense sampling design. In an area of 84 m<sup>2</sup> and a depth of 2 meters, 55  
26 undisturbed soil samples were taken to determine the soil properties. Column  
27 experiments were performed, and the transport parameters were obtained by fitting the  
28 experimental data to the analytical solution of the advection-dispersion equation using  
29 the computer program CFITM. Stepwise multiple linear regression (MLR) was performed  
30 in order to identify the statistically significant variables. The spatial correlation of the  
31 variables and between variables were determined using the Stanford Geostatistical  
32 Modeling Software. Soil properties presented a moderate coefficient of variation, while  
33 hydraulic conductivity and transport parameters were widely dispersed. The difference  
34 between its minimum and maximum value was quite large for most of the studied  
35 variables evidencing their high variability. Both dispersivity and retardation factor were  
36 higher than the expected and this result can be related to the preferential pathways and  
37 to the non-connected micropores. None of the physical soil property was strongly  
38 correlated to the transport parameters. Coefficient of distribution was strongly correlated  
39 to the cation exchange capacity and significantly correlated to mesoporosity and  
40 microporosity. Hydraulic conductivity presented significant positive correlation to the  
41 effective porosity and macroporosity. Stepwise multiple linear regression analysis  
42 indicated that further studies should be performed aiming to include other variables  
43 relevant for lateritic soils such as pH, electrical conductivity, the content of Al and Fe,  
44 CaCO<sub>3</sub> and soil structure and microstructure. The study of the spatial correlation among  
45 transport parameters and soil properties showed that the codispersion among the  
46 variables is not constant in space and can be important in dictate the behavior of the  
47 combined variables. Our results also showed that some variables that were identified as

48 explanatory in the MLR were not significant in the spatial analysis of the correlation,  
49 showing the importance of this kind of analyses for a better decision about the most  
50 relevant variables and their relations. The present study was a first attempt to evaluate  
51 the spatial variation in the correlation coefficient of transport parameters of a reactive  
52 and a nonreactive solute, indicating the more relevant variables and the ones that  
53 should be included in future studies.

54 **Keywords:** cross-variogram, dispersivity, retardation factor, column experiment,  
55 undisturbed soil sample

## 56 1. Introduction

57 The soil's ability to retard and filter solutes as well as water flow and solute movement in  
58 soils are significant themes in the earth and environmental sciences, and they are critical  
59 in the hydrological and biogeochemical cycles (Keesstra et al., 2012; Kung et al., 2005).  
60 Solutes can migrate from the soil to the groundwater and cause its contamination (Arias-  
61 Estévez et al., 2008). That ability can be quantified after determining soil transport  
62 parameters such as dispersivity ( $\alpha$ ) and partition coefficient ( $K_d$ ) (Dyck et al., 2005;  
63 Fetter, 1999). Knowledge of solute transport parameters is needed to improve the  
64 prediction of the groundwater contamination potential (Kazemi et al., 2008). These  
65 parameters depend on many factors such as the chemical characteristics of the  
66 contaminant and the soil physical, chemical, and physicochemical properties (Holland,  
67 2004; Trangmar et al., 1986).

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

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

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

97 Geostatistics has been widely used to study the spatial variability of several soil  
98 properties (Alletto and Coquet, 2009; Brocca et al., 2007; Goovaerts, 1998; Grego et al.,  
99 2006; Iqbal et al., 2005; Mbagwu, 1995; Tesfahunegn et al., 2011; Vieira, 1997; Wang  
100 and Shao, 2013; Zhao et al., 2011) and specifically of the hydraulic conductivity (Bohling  
101 et al., 2012; Gwenzi et al., 2011; Hu et al., 2008; Liu et al., 2017; Marín-Castro et al.,

102 2016; Motaghian and Mohammadi, 2011; Sobieraj et al., 2002; Sudicky et al., 2010). On  
103 the other hand, the spatial characterization of solute transport parameters is still discrete  
104 (Huysmans and Dassargues, 2006; Jacques et al., 1999; Kazemi et al., 2008) due to the  
105 high cost and time-consuming efforts associated with solute transport studies (Erşahin et  
106 al., 2017) .

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

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

119 Erşahin et al. (2017) characterized the spatial variability of pore-water velocity ( $v$ ),  
120 dispersivity, retardation factor and dispersion coefficient ( $D$ ) and analyzed their statistical  
121 relations to other soil properties. They found that solute parameters were not correlated  
122 with the physical soil properties but were significantly correlated with soil chemical  
123 variables such as pH, electrical conductivity ( $EC$ ) and cation exchange capacity ( $CEC$ ).

124 A pure nugget model was fitted to  $\log \alpha$  and  $R$  indicating no spatial structure. On the  
125 contrary,  $\log v$  and  $\log D$  showed a moderate and strong spatial structure, respectively.  
126 By analyzing many studies related to spatial variability in soil science, it can be noticed  
127 that a multivariate approach is used, in line with Goovaerts (1999), who points out that  
128 the soil information is generally multivariate. Usually, multivariate data are analyzed with  
129 statistical methods, such as principal component analysis or multiple linear regression  
130 (Ferreira da Silva et al., 2013; Rodríguez Martín et al., 2007) but without accounting for  
131 their possible spatial correlation (Erşahin et al., 2017; Kazemi et al., 2008). Ignoring the  
132 multivariate spatial correlations can be a waste of available and important information.  
133 Some effort has been made to characterize the spatial variation of the correlation among  
134 variables and to use this information for estimation purposes (Benamghar and Gómez-  
135 Hernández, 2014; Bevington et al., 2016; Goovaerts, 1998; Guagliardi et al., 2013).  
136 Nevertheless, attempts to obtain the spatial variation of the correlation among solute  
137 transport and all statistically significant variables are rare (Jacques et al., 1999) and  
138 more studies need to be done.

139 Our first objective is to determine the linear statistical correlations among soils  
140 properties,  $K$ ,  $\alpha$ , and  $K_d$  for a reactive (potassium) and a nonreactive (chloride) solute.  
141 Second, in order to identify the more statistically significant variables that explain the  
142 variability of the variables of interest ( $K$ ,  $\alpha$ , and  $K_d$ ), multiple linear regression is  
143 performed. The third objective is to model the spatial structures of soils properties and of  
144 the variables of interest. Aiming to study the spatial cross-correlation among variables,  
145 the fourth objective is to model the relations among the variables of interest and each  
146 one of the more statistically significant variables. To the best of our knowledge, this is

147 the first time that the spatial correlations among  $\alpha$  and  $K_d$ , of a reactive and a  
148 nonreactive solute, and statistically significant variables are studied. Finally, although the  
149 characterization of the spatial variability of soil properties at the centimeter/meter scale  
150 can affect the solute transport prediction at a bigger scale (Salamon et al., 2007),  
151 studies in this scale are scarce. In this context, we are interested in the small-scale  
152 variability using a dense sampling design.

## 153 **2. Material and methods**

### 154 **2.1. Description of the study site**

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



169 tropical conditions makes the soil from the Cenozoic sediments highly lateritized  
170 (Giacheti et al., 1993). The main constituents of the studied soil are quartz, oxides,  
171 and hydroxides of aluminum, kaolinite, and gibbsite. Macropores and dual-porosity are  
172 also characteristics of that soil (Rohm, 1992).

173

174 **Fig. 1**

## 175 **2.2. Soil sampling**

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

## 186 **2.3. Soil properties characterization**

187 Silt, clay and sand content, cation exchange capacity (*CEC*), total porosity (*n*), effective  
188 porosity (*ne*), macroporosity (*Ma*), mesoporosity (*Me*), microporosity (*Mi*) and bulk  
189 density ( $\rho_d$ ) are referred to soil properties. These soil properties were analyzed spatially.  
190 In the laboratory, the moisture was determined in three replicates for each soil sample.

191 Subsequently, the soil was air-dried and sieved through a #10 mesh sieve (2 mm  
192 openings). Particle size distribution were determined according to ASTM D7928-17  
193 (ASTM, 2017a) and ASTM D6913 / D6913M-17 (ASTM, 2017b). in only one replicate for  
194 each soil sample. Particle density  $\rho_s$  was determined in five replicates using the ASTM D  
195 854-14 (ASTM, 2014a) and resulted in  $2.71 \text{ Mg}\cdot\text{m}^{-3}$  for all soil samples (arithmetic mean  
196 of all replicates).

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

200 Mercury intrusion porosimetry (MIP) (Washburn, 1921) and total porosity was calculated  
201 for each soil sample as  $n = 1 - \rho_d/\rho_s$ . When the total porosity calculated was different  
202 from the one obtained by MIP, we assumed that the difference was due to large pores  
203 that were not identified in the MIP due to the reduced sample size used. The effective  
204 porosity ( $n_e$ ) was considered as the total porosity minus the porosity that corresponds to  
205 the soil water content at 33 kPa, suction equivalent to the field capacity (Ahuja et al.,  
206 1984; Brutsaert, 1967; Corey, 1977; Dippenaar, 2014). It is important to mention that the  
207 field capacity is not precisely defined in soil science and we chose to use that value  
208 since it is widely used in the literature. The diameter of the pore equivalent to the suction  
209 at 33 kPa was calculated as  $8.9 \mu\text{m}$  from the capillary rise equation assuming a contact  
210 angle of  $0^\circ$ . Thus, based on the results of the MIP, the effective porosity was calculated  
211 as the total porosity minus the porosity correspondent to the pores with a diameter  
212 smaller than  $8.9 \mu\text{m}$ . From the MIP results,  $M_a$ ,  $M_e$ , and  $M_i$  were determined according  
213 to the classification proposed by Koorevaar et al. (1983), in which the diameters of  $M_i$ ,

214 *Me*, and *Ma* are, respectively, <30  $\mu\text{m}$ , 30-100  $\mu\text{m}$  and >100  $\mu\text{m}$ . The methylene blue  
215 adsorption test using the filter paper method described by Pejon (1992) was used to  
216 determine *CEC* in one replicate for each soil sample.

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

#### 224 **2.4. Column experiments**

225 The PVC cylinders used for collecting the undisturbed soil samples were used as rigid-  
226 wall permeameters and 55 column experiments were conducted. Figure 2 shows the  
227 column experiments in progress. First, the columns were sealed with a cap containing a  
228 stainless plastic plate with holes on both ends of the column, which allowed a uniform  
229 distribution of the inlet flow. Second, the soil samples were slowly saturated from the  
230 bottom with deionized water to remove entrapped air. Third, the flow was reversed, and  
231 the permeability test was performed under a constant hydraulic gradient of 1 and the  
232 flow rate (*Q*) was measured. We have taken two measures per day and we assumed  
233 that steady-state flow was achieved when *Q* variations were below 5% in a week. Water  
234 temperature was monitored throughout the test and, when necessary, corrections were  
235 made in the calculations of the hydraulic parameters. Fourth, the following water flow  
236 parameters were obtained from each soil sample: saturated hydraulic conductivity, *K*;

237 specific discharge,  $q$ ; flow rate,  $Q$ ; and average linear velocity,  $v$  ( $q/ne$ ) (Freeze and  
238 Cherry, 1979). When the steady-state flow was reached, deionized water was replaced  
239 by a  $2.56 \text{ mol m}^{-3}$  KCl solution ( $100 \text{ mg L}^{-1} \text{ K}^+$  and  $90.7 \text{ mg L}^{-1} \text{ Cl}^-$  referred to as initial  
240 concentrations,  $C_0$ ) continuously injected into the soil column. Solute displacement tests  
241 were carried out under constant hydraulic head and isothermal ( $20 \text{ }^\circ\text{C}$ ) conditions. The  
242 concentration, temperature, and pH of the initial solution were monitored throughout the  
243 test. Leachate samples were collected from the outlet of the columns at pre-set time  
244 intervals (defined for each column in accordance with the flow rate), stored  
245 in plastic bottles and refrigerated immediately after collection. Preferably, the tests were  
246 performed until the relative concentrations ( $C/C_0$ ) reached 1, but this condition was not  
247 achieved in some samples. An ion-selective electrode (ISE) (Hanna instruments - HI  
248 4107 model) was used to determine  $\text{Cl}^-$  concentration ( $C$ ) at each time.  $\text{K}^+$  concentration  
249 at each time was measured by a flame photometer (Micronal B462 model) at a 1:21  
250 ratio. All ion concentrations were measured in one replicate and determined as the  
251 arithmetic mean of the replicates. The relative concentrations ( $C/C_0$ ) of  $\text{Cl}^-$  and  $\text{K}^+$  were  
252 determined by dividing the concentration of the ion in the leachate samples at each time  
253 by the concentration of the ion in the initial solution. Thereafter, a breakthrough curve  
254 (BTC) of each soil sample and each ion was plotted. The BTC's were expressed as  $C/C_0$   
255 and the number of pore volumes ( $T$ ), where  $T$  is a dimensionless variable calculated as  
256  $T = vt/L$  (van Genuchten, 1980), where  $v$  is the average linear velocity,  $t$  is the time  
257 elapsed from the start of the solute application, and  $L$  is the length of the soil column  
258 (150 mm).

259

260 **Fig. 2**

## 261 **2.5. Transport parameter determination**

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

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

$$265 \quad R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}, \quad (1)$$

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

268 The hydrodynamic dispersion coefficient is related to the dispersivity by

$$269 \quad D = \alpha \cdot v, \quad (2)$$

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

$$271 \quad R = 1 + \frac{\rho_d}{n} K_d, \quad (3)$$

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

$$275 \quad \frac{C}{C_0} = \frac{1}{2} \left[ \operatorname{erfc} \left( \frac{RL-vt}{2\sqrt{DRt}} \right) \right] + \frac{1}{2} \exp \left( \frac{vL}{D} \right) \operatorname{erfc} \left( \frac{RL+vt}{2\sqrt{DRt}} \right), \quad (4)$$

276 where  $\operatorname{erfc}$  is the complementary error function.

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

## 282 **2.6. Statistical analysis**

283 Exploratory analysis of the  $K$ ,  $\ln K$ , soil properties and transport parameters (including  $P$ ,  
284  $R$ ,  $D$ ,  $\ln \alpha$  of  $K^+$  and  $\ln \alpha$  of  $Cl^-$ ) was performed. Global summary statistics such as mean,  
285 standard deviation, variance, minimum and maximum value, kurtosis, skewness, and  
286 coefficient of variation (CV) were computed. The CV were classified according to Wilding  
287 and Drees (1983): low variability for  $CV < 15\%$ ; moderate variability for  $15\% < CV <$   
288  $35\%$ ; and high variability for  $CV > 35\%$ . The normality of the data was tested by means  
289 of the Kolmogorov–Smirnov test (Massey, 1951). When necessary, the variables were  
290 standardized, and the subsequent studies were performed using standard normal  
291 variables. Outliers were analyzed in detail to investigate errors in the determination of  
292 the variables, and when deemed appropriate they were excluded from the dataset.  
293 Trends were also investigated and, if present, removed. The presence and strength of  
294 significantly linear associations between soil properties and the variables of interest ( $\ln$   
295  $K$ ,  $\ln \alpha$  ( $K^+$ ),  $\ln \alpha$  ( $Cl^-$ ),  $Kd$  ( $K^+$ ), and  $Kd$  ( $Cl^-$ )) were examined by computing Pearson  
296 correlation coefficients at 0.05 and 0.01 significance level. The natural logarithm ( $\ln$ ) of  $\alpha$   
297 and  $K$  were used as variables rather  $\alpha$  and  $K$  because they resulted in better  
298 correlations.

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

304 A stepwise MLR as in Equation (3)

305  $y = b_0 + b_1w_1 + b_2w_2 + b_3w_3 + \dots + b_nw_n$  (3)

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

## 310 **2.7. Geostatistical analysis**

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

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

317 
$$\gamma(\mathbf{h}) = \frac{1}{2N} \sum_{aa=1}^{N(\mathbf{h})} [z(u_{aa}) - z(u_{aa} + \mathbf{h})]^2$$
 (5)

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

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

324 
$$\gamma(\mathbf{h}) = c_0 + c_1 sph(|\mathbf{h}|, a)$$
 (6)

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

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

$$330 \quad \gamma(\mathbf{h}) = \begin{cases} 0 & \text{if } \mathbf{h} = 0 \\ 1 & \text{otherwise} \end{cases} \quad (7)$$

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

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

$$338 \quad \gamma_{uv}(\mathbf{h}) = \frac{1}{2N(\mathbf{h})} \sum_{i=1}^{N(\mathbf{h})} [z_i(u_{aa}) - z_i(u_{aa} + \mathbf{h})] \cdot [z_j(u_{aa}) - z_j(u_{aa} + \mathbf{h})] \quad (8)$$

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

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

$$344 \quad r_{uv}(\mathbf{h}) = \frac{\gamma_{uv}(\mathbf{h})}{\sqrt{\gamma_u(\mathbf{h})\gamma_v(\mathbf{h})}} \quad (9)$$



### 345 **3. Results and discussion**

#### 346 **3.1. Average soil properties**

347 The main minerals present in the studied soil are quartz, kaolinite, and gibbsite, in  
348 accordance with Giachetti *et al.* (1993) and Kronberg *et al.* (1979). Average values of  
349 5.71 and 5.19 for pH in H<sub>2</sub>O and in KCl, were obtained, respectively. These results show  
350 that the soil is strongly acid, which is a typical characteristic of Cenozoic sediments and  
351 lateritic soils (Fagundes and Zuquette, 2011; Giachetti *et al.*, 1993). The negative  $\Delta\text{pH}$  (-  
352 0.52) and a point of zero charge (PZC) (4.67) lower than the  $\text{pH}_{\text{H}_2\text{O}}$  indicate a  
353 predominance of negative charges, which can promote cation adsorption (Fagundes and  
354 Zuquette, 2011). This soil contains a small average amount of organic matter (2.40 %), a  
355 result suitable for lateritic acid soils (Mahapatra *et al.*, 1985). According to the soil  
356 salinity classification of the Food and Agriculture Organization of the United Nations  
357 (FAO), the electrical conductivity values indicate small amounts of dissolved salts (55.70  
358  $\text{mS m}^{-1}$ ) and a non-saline soil (Abrol *et al.*, 1988).

#### 359 **3.2. Soil properties statistical analysis**

360 The exploratory statistical results of the soil properties,  $v$  and  $K$  are shown in Table 1. In  
361 order to identify trends, all statistical results were also investigated for each depth  
362 (results not shown), and no significant influence of the depth was observed. Because of  
363 that, in further analysis the samples were considered as a unique dataset, regardless of  
364 the depth. Soil properties are slightly skewed, quantified by a skewness  $< |0.5|$  (Webster,  
365 2001), except  $Ma$  and  $CEC$ , which are moderately and highly skewed with a skewness  
366 of 0.75 and 1.06, respectively. The difference between its minimum and maximum value

367 was quite large for  $K$ ,  $\ln K$ ,  $v$ , silt content,  $Ma$ , and  $CEC$ . According to the CV  
368 classification of Wilding and Drees (1983), high CV were identified for  $K$ ,  $v$ , silt content  
369 and  $Ma$  (1.22, 1.23, 0.61 and 0.56, respectively) evidencing high variability in these  
370 variables. Our results confirm that soil heterogeneity is present even on a small scale,  
371 depending on the studied property (Chapuis et al., 2005; Lacasse & Nadim, 1996; Søvik  
372 & Aagaard, 2003).

373 Mercury intrusion porosimetry results indicated that the soil has dual-porosity and the  
374 predominant pore diameters correspond to  $Me$  and  $Mi$ . The multimodal pore size  
375 distribution is characteristic of well-structured soils (Hajnos, Lipiec, Świeboda,  
376 Sokołowska, & Witkowska-Walczak, 2006; Lipiec et al., 2007). The soil has a low  $CEC$   
377 (maximum value  $4.20 \text{ cmolc Kg}^{-1}$ ) and it suggests a low capacity to adsorb cations by  
378 electrostatic adsorption (Fagundes & Zuquette, 2011). Mean soil properties presented  
379 values in accordance with the typical characteristics of the studied soil (Giacheti et al.,  
380 1993; Zuquette & Palma, 2006), and are shown in Table 1.

381

## 382 **Table 1**

### 383 **3.3. Statistical analysis of the transport parameters**

384 The breakthrough curves (not shown) of  $K^+$  and  $Cl^-$  obtained from the 55 miscible  
385 displacement tests were analyzed, and transport parameters were determined. The  
386 goodness of fit of the experimental BTC to the ADE model was evaluated by its  $R^2$ . Most  
387 BTCs presented significant tailing,  $R^2$  ranged from 0.77 to 0.99 with a mean of 0.92 for  
388  $K^+$  and 0.95 for  $Cl^-$ , suggesting that the ADE model was suitable to describe the data.

389 BTCs that presented low  $R^2$  were investigated to check for problems in the soil samples,  
390 but no problems were found.

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

396 All transport parameters show high CVs and the highest ones were obtained for the  
397 reactive solute ( $\text{K}^+$ ). The coefficients of variation of  $R$  and  $K_d$  for  $\text{K}^+$  shown that transport  
398 parameters are very variable. The values we obtained for  $\alpha$  were high when compared  
399 to other studies using samples of approximately the same dimensions (Erşahin et al.,  
400 2017). Also, mean  $\alpha$  values were high when compared to the typical values used in the  
401 literature ( $\alpha = 0.1L$ , where  $L$  in the distance) (Freeze & Cherry, 1979). These differences  
402 can be attributed to numerous factors such as the scale of the experiment, flow rate, and  
403 boundary conditions. Higher values of  $\alpha$  can also be indicative of preferential flow.

404 The maximum and minimum values were quite different for all transport parameters,  
405 evidencing, again, the large variability in these parameters. Peclet numbers ranged from  
406 0.11 to 13.41, showing that for some soil samples the advective transport prevailed,  
407 whereas for other samples, dispersive transport was the primary mechanism. These  
408 differences probably are related to heterogeneities between physical characteristics of  
409 soil samples.  $R$  ( $\text{K}^+$ ) ranged from 0.69 to 36.19, while  $R$  ( $\text{Cl}^-$ ) ranged from 0.33 to 5.20, as  
410 expected because reactive solute should have larger  $R$  values than nonreactive solutes.

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

421

## 422 **Table 2**

### 423 **3.4. Correlation among variables**

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

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

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

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

451 Almost no correlation was obtained among  $CEC$  and clay content, indicating that the  
452 clay mineral present in the soil is not relevant to adsorb cations, as mentioned before.  
453 Significant positive correlations among  $\ln K$ ,  $n$ ,  $ne$ , and  $Ma$  were verified, indicating that  
454 these properties dictate the values of  $\ln K$  and of the water flow in soils (Biswas & Si,  
455 2009). In a previous study, a high positive correlation was obtained among  $K$ ,  $Ma$ , and  $n$

456 (Mbagwu, 1995). A significant negative correlation was also found among  $\ln K$  and  $\rho_d$ ,  
457 results in accordance with other studies (Bevington et al., 2016; Botros, Harter, Onsoy,  
458 Tuli, & Hopmans, 2009; Mbagwu, 1995; Papanicolaou et al., 2015). These results show  
459 the higher  $ne$  (negatively related to  $n$  as shown in **Error! Reference source not**  
460 **found.**), higher  $v$ , as expected. No significant correlation between  $\ln K$  and texture was  
461 obtained. However, this result contrast with several previous studies in non-lateritic soils,  
462 showing the impact of the soil agglomerates in the relation among soil properties (M.  
463 Huang, Zettl, Lee Barbour, & Pratt, 2016; Igwe, 2005; Nemes, Timlin, Pachepsky, &  
464 Rawls, 2009; Pachepsky & Rawls, 2004; Søvik & Aagaard, 2003).

465

### 466 **Table 3**

467

468 Table 4 presents the results of the stepwise multiple linear regression analysis at a  
469 significance level of 95%. This analysis was used for investigating the significance of the  
470 relationships among all selected variables. The best model for  $K_d(K^+)$  was obtained by  
471 considering two variables,  $CEC$  and  $Ma$ , explaining 70% of the total variance in the  
472 model, with Pearson coefficient  $r$  equal to 0.84. The model that best represents  $K_d(Cl^-)$   
473 was found by combining  $CEC$ , clay content and  $Me$ , which explain 60% of the total  
474 variability with a moderate  $r$  equal to 0.70. These results suggest that other variables  
475 that were not considered in this study could be added to better explain the total  
476 variability of  $K_d$ . For example, several authors have suggested that pH, EC, the content  
477 of Al and Fe,  $CaCO_3$  and organic carbon have a strong influence on the total variability  
478 of  $K_d$  (Che, Loux, Traina, & Logan, 1992; Erşahin et al., 2017; Porfiri, Montoya,

479 Koskinen, & Azcarate, 2015). Additionally, some variables that were significantly  
480 correlated to  $K_d$  in the correlation analysis were not significant in the MLR. This can be  
481 related to possible collinearity effects of these variables, what is identified and excluded  
482 by using stepwise method.

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

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

499

500 **Table 4**

### 501 3.5. Spatial correlation among variables

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

513 The spatial structure was similar for all the studied variables. The largest range was  
514 obtained for  $\ln K$  (4.0 m), while silt content and  $M_i$  presented the smallest ones (2.5 m).  
515 Microporosity, as well as all studied solute transport parameters, displayed a nugget  
516 effect behavior, which accounts for short-scale spatial variability or measurement errors.  
517 These variables had a moderate spatial dependence classified by measuring the nugget  
518 ratio ( $R_b = \text{nugget/sill} \cdot 100\%$ ), which is strong if  $R_b < 25\%$ , moderate if  $25\% < R_b < 75\%$ ,  
519 weak if  $R_b > 75\%$  (Cambardella et al., 1994). Variograms of  $K_d$  resulted in a greater  
520 range than  $\ln \alpha$  variograms. Gupte et al. (1996), found a maximum range of 2.3 m for Br  
521 dispersivity. Contrary Erşahin et al. (2017) reported no clear spatial structure for  $\alpha$  and R  
522 under their sampling scheme. They argued that  $\alpha$  is distance and time-dependent at  
523 both the column and field scale, which complicates its spatial structure. Jacques et



524 al.(1999) found pure nugget effect in the variogram of  $K_f$  (Freundlich partition  
525 coefficient). Spatial structure of the  $Cl^-$  mass recovery was studied in a 2 m x 2 m x 2 m  
526 cube and a range of 0.37 m was found. With these results, we can argue that the range  
527 of the studied variables may vary depending on the sampling scheme and on the size of  
528 the studied site.

529

530 **Table 5**

531

532 Since the correlation among variables may depend on the spatial structure, the variation  
533 of the correlation coefficient among variables with the spatial scale was quantified. Fig.3  
534 (A to D) shows these results for the correlations between  $\ln K$ ,  $\ln \alpha (K^+)$ ,  $\ln \alpha (Cl^-)$ ,  $K_d$   
535 ( $K^+$ ), and  $K_d (Cl^-)$  and the variables which explained their variability, according to the  
536 MLR results. As stated by Wackernagel (1995), if the codispersion among the variables  
537 is constant in space, the structure of correlation of the variables is not affected by spatial  
538 scale.

539 The correlation coefficient among  $\ln K$  and  $Ma$  (Fig.3 A) decreases until 2.2 m and from  
540 then on presents a variation around zero, showing that for distances larger than 2.2 m  
541 these variables are no longer correlated. The spatial correlation among  $\ln K$  and  $ne$   
542 (Fig.3 A) showed that until 1.1 m the relationship became stronger and negative,  
543 changing completely the kind of relation between these variables since it is recognized  
544 that the increase in  $ne$  favors the water flow in soils. After that, the values became more  
545 positive (an expected relation) but the correlation weaker until 2.8 m, when the variation  
546 remained near zero. Similar behavior was also verified for the relation between  $\rho_d$  and

547  $Ma$  and between  $ne$  and  $Ma$  (Fig.3 A), but the correlations were not statistically  
548 significant. Contrarily, the correlation coefficient between  $\ln K$  and  $\rho_d$  became weaker  
549 and positive until 3.3 m and then the variables seem to be not related in space. The  
550 relation between  $ne$  and  $\rho_d$  was around zero for all studied distances (Fig.3 A).

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

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

569

570 **Fig. 3**

#### 571 **4. Conclusions**

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

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

588 Our findings show that the use of geostatistical methods was efficient to evaluate the  
589 spatial variation in the correlation coefficients. However, for the conditions analyzed, the  
590 use of the spatial correlation among transport parameters and soil properties would  
591 probably improve the estimation only in a small-scale study, since the spatial correlation

592 were only observed up to 2.5 m. It is important to mention that the study was performed  
593 for a specific field site and the results obtained may explain the spatial relation to the  
594 studied soil. However, the application of the statistical parameters to estimate transport  
595 parameters and predict solute transport in other soil is thus questionable.

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

602

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611

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950 **List of Figures**

951

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

953

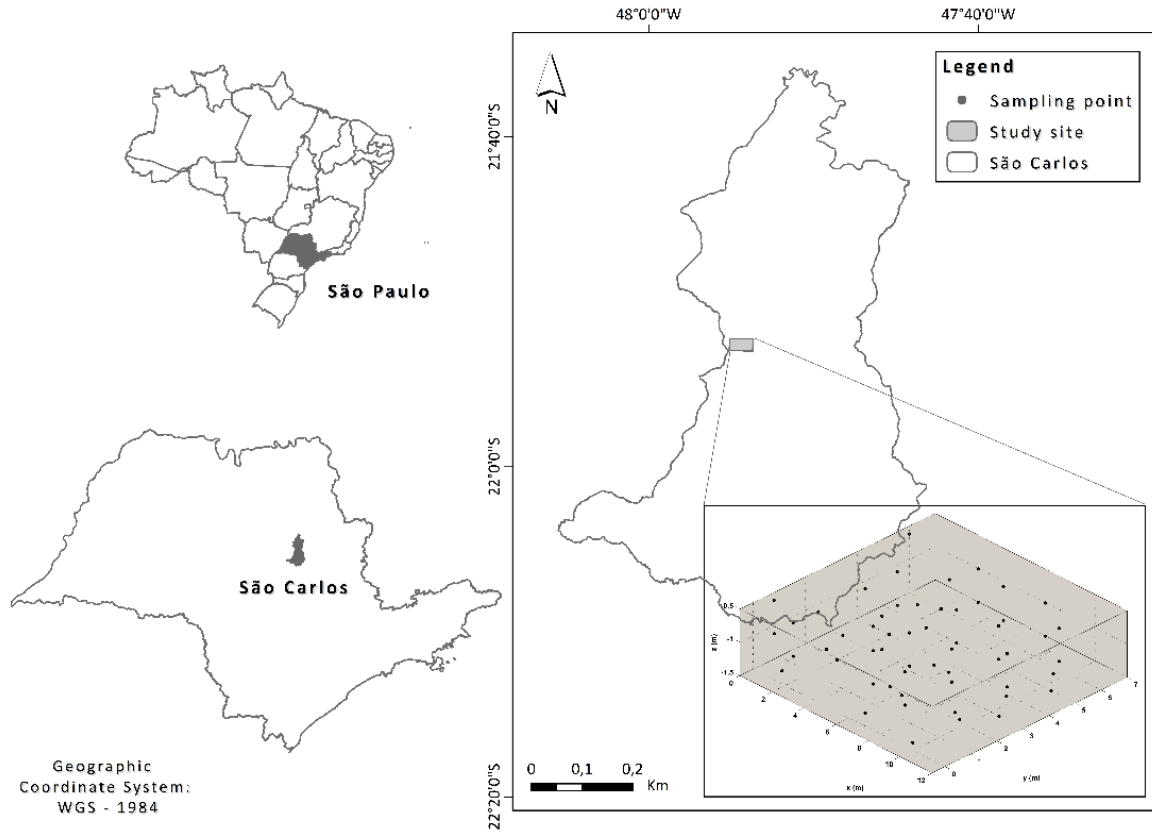
954 **Fig. 2 Column experiments in progress: a) water deionizers, b) hydraulic head**  
955 **controller device, c) rigid-wall permeameters**

956

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

959

960 **Figure 1**

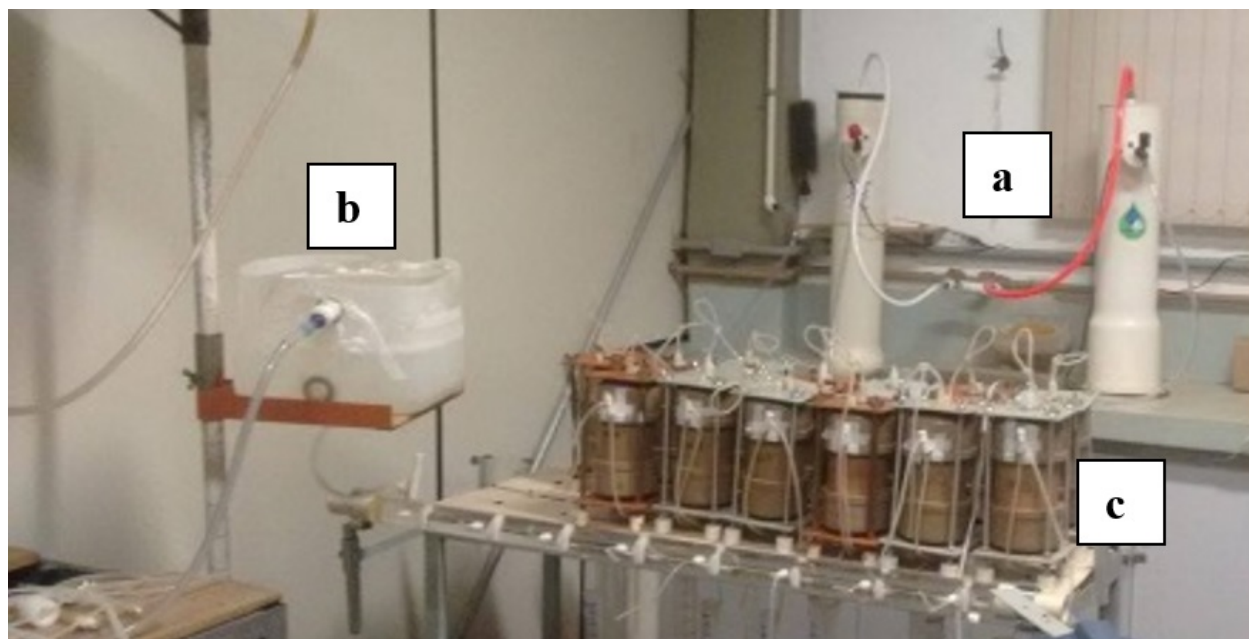


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963 **Figure 2**

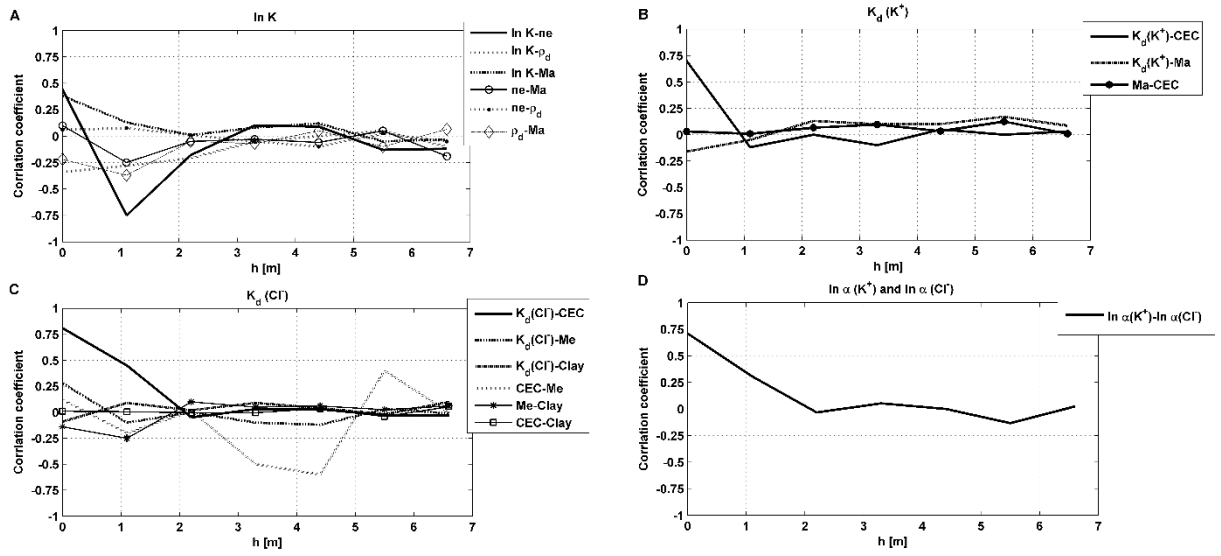
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967 **Figure 3**



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972 **Table 1 Descriptive statistics of soil properties, hydraulic conductivity and linear**  
973 **average velocity at the study site**

974

975 **Table 2 Descriptive statistics of transport parameters**

976

977 **Table 3 Correlation coefficients among standardized variables**

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979 **Table 4 Stepwise multiple linear regression results**

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981 **Table 5 Parameters of the variogram models used to fit the isotropic direct**  
982 **experimental variograms**

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986 **Table 1**

	Mean	SD	CV	Skew	Kurt	Min	Max
<i>K</i> [m d <sup>-1</sup> ]	1.35	1.65	1.22	2.39	5.84	0.03	7.46
<i>v</i> [m d <sup>-1</sup> ]	5.40	6.57	1.23	2.20	4.61	0.13	27.71
<i>ln K</i> [ln (m d <sup>-1</sup> )]	-0.37	1.25	n.d	-0.29	-0.12	-3.68	2.03
<i>n</i> [ ]	0.51	0.04	0.08	-0.24	-0.39	0.42	0.58
<i>ne</i> [ ]	0.24	0.02	0.08	-0.39	-0.14	0.20	0.28
$\rho_d$ [g cm <sup>-3</sup> ]	1.34	0.10	0.07	0.28	-0.32	1.14	1.59
<i>CEC</i> [cmol <sub>c</sub> Kg <sup>-1</sup> ]	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
<i>Ma</i> [ ]	0.072	0.04	0.56	0.75	-0.58	0.031	0.152
<i>Mi</i> [ ]	0.262	0.06	0.23	-0.25	-0.96	0.141	0.361
<i>Me</i> [ ]	0.172	0.05	0.29	0.21	-0.92	0.091	0.263

987 SD: standard deviation, CV: coefficient of variation, Skew: Skewness, Kurt: Kurtosis,  
988 Min: minimum value, Max: maximum value, n.d: undetermined, *K*: hydraulic conductivity;  
989 *v*: linear average velocity,  $\rho_d$ : bulk density, *n*: total porosity, *ne*: effective porosity *Ma*:  
990 macroporosity, *Me*: mesoporosity, *Mi*: microporosity, *CEC*: cation exchange capacity.  
991

992 Table 2  
993

	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
$K_d(K^+)$ [cm <sup>3</sup> g <sup>-1</sup> ]	1.71	2.27	1.33	5.61	36.75	0.01	16.75
$D(K^+)$ [m <sup>2</sup> d <sup>-1</sup> ]	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
$K_d(Cl^-)$ [cm <sup>3</sup> g <sup>-1</sup> ]	0.55	0.51	0.93	0.66	-0.81	0.03	1.64
$D(Cl^-)$ [m <sup>2</sup> d <sup>-1</sup> ]	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

994 SD: standard deviation, CV: coefficient of variation, Skew: Skewness, Kurt: Kurtosis,  
995 Min: minimum value, Max: maximum value, n.d.: undetermined,  $P$ : Peclet number,  $R$ :  
996 retardation coefficient,  $K_d$ : partition coefficient,  $D$ : hydrodynamic dispersion coefficient,  $\alpha$ :  
997 dispersivity, ( $K^+$ ) potassium, ( $Cl^-$ ): chloride.  
998

999 **Table 3**

	$\ln \alpha (\text{Cl}^-)$	$\ln \alpha (\text{K}^+)$	$\alpha$	$K_d (\text{K}^+)$	$K_d (\text{Cl}^-)$	CEC	$\ln K$	$\rho_d$	$n$	$ne$	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										
$\rho_d$	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	

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1001  $\alpha$ : dispersivity, ( $\text{K}^+$ ) potassium, ( $\text{Cl}^-$ ): chloride,  $K_d$ : partition coefficient, CEC: cation exchange capacity,  $K$ :  
 1002 hydraulic conductivity;  $\rho_d$ : bulk density,  $n$ : total porosity,  $ne$ : effective porosity,  $Mi$ : microporosity,  $Me$ :  
 1003 mesoporosity,  $Ma$ : macroporosity  
 1004 \* significant at 0.01 level of significance.  
 1005 \*\* significant at 0.05 level of significance.  
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**Table 4**

	$K_d(K^+)$	$\ln \alpha (K^+)$	$K_d(Cl^-)$	$\ln \alpha (Cl^-)$	$\ln K$
$\ln K$	-	-	-	-	-
$n$	-	-	-	-	-
$ne$	-	-	-	-	26.4
$\rho_d$	-	-	-	-	-3.90
CEC	0.68	-	0.48	-	-
sand	-	-	-	-	-
silt	-	-	-	-	-
clay	-	-	0.03	-	-
$Ma$	-0.03	-	-	-	0.09
$Mi$	-	-	-	-	-
$Me$	-	-	0.02	-	-
$K_d(K^+)$		-	-	-	-
$\ln \alpha (K^+)$	-		-	0.63	-
$K_d(Cl^-)$	-	-		-	-
$\ln \alpha (Cl^-)$	-	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
$r^*$	0.84	0.70	0.77	0.72	0.63

1009 \* Pearson's coefficient

1010 All results were significant at  $p \leq 0.05$

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1015 **Table 5**

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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
$\rho_d$	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

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