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DINÂMICA DO POTÁSSIO, CLORO E FÓSFORO EM SOLO DA REGIÃO DO SUBMÉDIO DO VALE DO RIO SÃO FRANCISCO

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1 RESUMO

Os modelos matemáticos podem ser usados para entender a dinâmica dos íons no solo, em função principalmente da mobilidade da fração liquida em ralação a fração sólida. O objetivo da pesquisa foi avaliar o deslocamento miscível dos íons potássio, cloro e fósforo, em colunas de PVC preenchidas com Argissolo Amarelo Distrófico típico (PAd) em diferentes densidades, utilizando como ferramenta adicional, o modelo matemático STANMOD (STudio of ANalytical MODels) para o ajuste numérico das *Breakthrough Curves* (BTC). Os ensaios foram realizados no Laboratório de Irrigação da UNIVASF Campus Juazeiro-BA, utilizando-se colunas de PVC nas profundidades (alturas) de 0,10; 0,20 e 0,30 m e nas densidades de 1,30; 1,50 e 1,70 g cm^{-3}. Utilizou-se solução com concentração de 1000 mg L^{-1} contendo os fertilizantes Cloreto de Potássio (58% de K_2O e 39% de Cl) e Superfosfato Simples (8% de P_2O_5, 16% de Cálcio (Ca) e 8% de Enxofre (S)). Os resultados permitiram concluir que os íons potássio, cloro e fósforo tiveram uma elevada mobilidade no Argissolo Amarelo Distrófico típico (PAd) apresentando um menor valor do fator de retardamento (R) e um maior número de Peclet (P). O modelo STANMOD apresentou desempenho satisfatório no ajuste numérico das Breakthrough Curves (BTC´s).

Palavras-chave: dispersividade, curvas de avanço de íons, dinâmica de solutos, STANMOD

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IONS DYNAMICS IN POTASSIUM, CHLORINE AND PHOSPHORUS IN SOILS IN THE SÃO FRANCISCO RIVER VALLEY

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2 ABSTRACT

Mathematical models can be used to understand the dynamics of ions in the soil, mainly due to the mobility of the liquid fraction in relation to the solid fraction. The objective was to measure the miscible displacement of potassium, chlorine and phosphorus ions in PVC columns filled with typical Dystrophic Yellow Argisol (PAd) in different densities, using the mathematical model STANMOD (Analytical Model Studio) as an additional tool Numeric Advance Curves (BTC). The tests were conducted at the Irrigation Laboratory of UNIVASF Campus Juazeiro-BA, using PVC columns at depths (heights) of 0.10; 0.20 and 0.30 m and densities of 1.30; 1.50 and 1.70 g cm^{-3}. A solution with a concentration of 1000 mg L^{-1} containing the fertilizers Potassium chloride (58% K2O and 39% Cl) and Simple Superphosphate (8% P2O5, 16% Calcium (Ca) and 8% Sulfur) was used. (S)). The results allowed to conclude that the potassium, chlorine and phosphorus ions had high mobility in the typical Yellow Dystrophic Argisol (PAd), reducing a lower value of the delay factor (R) and a greater number of Peclet (P). The STANMOD model presents satisfactory performance without numerical adjustment of Breakthrough Curves (BTC´s).

Keywords: dispersive, ion advance curves, solute dynamics, STANMOD

3 INTRODUCTION

The mobility and adsorption capacity of ions in the soil are influenced by several factors; that is, the displacement of miscible fluids is a process that occurs when a fluid mixes with another fluid and displaces it in the soil profile; therefore, the mobility of solutes in the soil is inversely related to their adsorption, the solid fraction or the environmental conditions that favor the precipitation of ions (OLIVEIRA et al., 2013).

The use of mathematical models to estimate ion retention and transport in soil has become an acceptable tool to aid in the analysis and simulation of ion displacement in soils. Soil column tests combined with mathematical models enable an understanding of the behavior of solutes in porous media and the processes of diffusion, dispersion, and changes during transport (OLIVEIRA et al., 2013). These studies are relevant in that they enable the estimation of ion retention and transport in soil, aiding in the improvement of current methods, as well as in the application of technologies that present some measurement errors, such as the calibration of electronic sensors.

Thus, the wide variety of models already developed in laboratories enables the improvement of computational tools, providing information for the reliable application of these models. For these models to accurately determine the movement of solutes in the soil, it is necessary to determine several transport parameters, such as the retardation factor (R), dispersion coefficient (D), and dispersivity (λ) (SILVA, 2013). These parameters can be obtained via the STANMOD (*studio of Analytical MODels*) model, which estimates the parameters through concentrations obtained in the laboratory or predicts solute concentrations under steady-state flow conditions via convection–dispersion equations (SILVA, 2013). The model uses the relative concentration (C/C_o) and the solution volume divided by the pore volume (P V) as input data. The output data are the Peclet number (P) and the retardation factor (R). With these values, the dispersion coefficient (D), dispersivity (λ) and pore water velocity (ν) are determined.

The Peclet number (P) is dimensionless and relates the advection velocity of a flow to its diffusion velocity, considering the length of the soil column. The retardation factor (R) represents the time lag between the solute advance velocity and the advance velocity of the wetting front of the percolating solution, therefore representing the interaction between the solute and the solid phase of the soil (SANTOS, 2014).

The research hypothesis is that the physical characteristics of the soils in the submiddle region of the São Francisco Valley, at great depths, interact differently with the chemical molecules of potassium, chloride, and phosphorus ions, affecting their dynamics. This particularly takes into account the differences in the soil solution displacement speed and chemical molecule displacement speed, considering both advection and diffusion.

Therefore, the objective of this work was to study the dynamics of the miscible displacement of potassium, chlorine and phosphorus ions in columns filled with soil classified as typical Dystrophic Yellow Argisol (P Ad) via the STANMOD mathematical model as an additional tool.

4 MATERIALS AND METHODS

The experiment was conducted at the Irrigation Laboratory of the Agricultural and Environmental Engineering course of the Federal University of Vale do São Francisco (UNIVASF), Juazeiro Campus/BA (9° 24' 46" S, 40° 30' 58" W).

The soil samples were collected from the 0.0 to 0.30 m depth layer in agricultural areas in the municipality of Petrolina, PE, and were classified as typical dystrophic yellow argisol (PAd) (EMBRAPA, 2018). PAd was collected at the Experimental Farm of UNIVASF – Campus of Agricultural Sciences of UNIVASF in Petrolina-PE.

The soil was homogenized, air-dried, crushed, and sieved through a 2 mm mesh. Physical characterization included granulometric analysis, which classified the PAd soil as having a medium sandy texture (EMBRAPA, 2018) (Table 1).

Table 1. Physicochemical characterization of the typical Dystrophic Yellow Argisol (PAd).

Parameter		PAd
Sand	kg kg $^{-1}$	0.81
Silt		0.05
Clay		0.14
pH		6.4
CE	dS m $^{-1}$	2.6
P	mg L $^{-1}$	10
K $^{+}$		76.9
Ca $^{2+}$		39.7
Mg $^{2+}$		17.1
In the $^{+}$		54.8
Ass		0.04
Faith		25.09
Mn		0.74
Zn		6.28

These samples were used to represent the different depths and were filled with soil material to obtain different densities and pore volumes in three replicates (Table 2). The different densities and pore volumes were calculated using the particle density and soil density as references (Table 2).

To achieve a homogeneous profile, the columns were filled with 3 cm layers, with each layer "accommodating" the previous layer. A piece of synthetic fabric, a screen, and a funnel were placed at the bottom of each column, and a polyester blanket disc (Bedim) was placed at the top to avoid disturbances on the soil surface (in the column) when connecting the column to the emission of the solution to be applied. The hydraulic head above ground was maintained at a constant value (2 cm) via an emitter and a Mariotte flask.

Table 2. Densities (ds) used for the typical dystrophic yellow argisol (PAd)

Soil	Densities (g cm $^{-3}$)		
	ds1	ds2	ds3
Typical Dystrophic Yellow Argisol (PAd)	1.30	1.50	1.70

*ds1 (density 1), ds2 (density 2) and ds3 (density 3)

The columns were slowly and incrementally saturated with deionized water and left undisturbed for 36 hours until complete saturation was achieved. After this stage, the columns were connected to the emitters and the Mariotte flask for the application of distilled water corresponding to twice the pore volume to leach all soluble ions from the soil.

To prepare the solutions for the application of potassium ($^{K+}$) and chloride (Cl^{-}) ions, a potassium chloride solution was used, and for the phosphorus (P) ions, a solution with simple superphosphate, both with a concentration of C0 = 1000 mg/L, $^{was\ used}$. These solutions were applied until the percolated volume corresponded to 3.5 times the pore volume (Santos et al., 2010).

The pore volume (Vp) for each column was calculated via Equation 5. For each column height (depth), there were three replicates; in each replicate, 10 volume aliquots were collected, representing leachate collections equivalent to 0.35 times the pore volume for each column.

$$Vp = \pi r^2 h \left(1 - \frac{Ds}{Dp}\right) \quad (1)$$

where:
Vp – pore volume
r – column radius (cm)
h – height from ground to column (cm)
Ds – soil density (g/cm ^{3})
Dp – particle density (g/cm ^{3}).

Chemical analyses of the leached solutions were performed at the Soil Chemistry Laboratory, Juazeiro Campus/BA. The potassium ion (K+) concentration was determined via flame spectrophotometry, the chloride ion concentration was determined via titrimetry, and the phosphorus ion concentration was determined via atomic absorption spectrometry to correlate the concentration of the aliquot solution with the concentration of the initial solution ($C/_{C^\circ}$).

Using the potassium, chloride, and phosphorus concentration values, advancement curves for their respective ions were developed. The aim was to adjust the solute transport parameters in the STANMOD model. The CFITIM option (VAN GENUCHTEN, 1981) was chosen to fit the curves. This code for the linear equilibrium adsorption model uses the relative solute concentration (C/C_o) and pore volume (P V) as input data. The output data of the STANMOD model are the Peclet number (P) and retardation factor (R), from which the dispersion coefficient (D) and dispersivity (λ) parameters are determined.

5 RESULTS AND DISCUSSION

Figures 1, 2 and 3 show the *breakthrough curves* obtained for the study of the miscible displacement of potassium, chloride and phosphorus ions in a typical Dystrophic Yellow Argisol (PAd) at three depths and three densities. Through these observed data, it was possible to determine the transport parameters of the respective ions via the *Studio of Analytical Models (STANMOD*) model, as discussed below**.**

The typical Dystrophic Yellow Argisol (PAd) is a medium-textured soil. Thus, observing the effect of soil density on the dynamics of potassium ions was possible. For densities of 1.5 and 1.7 g cm $^{-3,}$ a greater adsorptive effect was observed, demonstrating that the higher density provided a longer contact time between the solid part of the soil. Since the soil is composed of 81% sand and treated with a cation, greater displacement in the soil was expected. Therefore, the only factor that caused the delay in solution displacement and greater adsorption was the effect of the soil density, whose relative concentration did not reach 100%. This took approximately 3.5 VP. The lowest adsorptive effect was evidenced by the 10 cm column and lower density (1.3 g cm $^{-3}$). This condition reduced the interaction time between the cation and the soil matrix, facilitating its displacement.

Table 3 shows the potassium ion transport parameters. Notably, density influenced the retardation factor (R) values, demonstrating a greater adsorptive effect, i.e., providing a longer contact time between the potassium ion and the soil matrix. Pinho and Miranda (2014), studying potassium transport in soil columns, reported significant interactions between potassium ions and the clayey soil matrix. Interaction characteristics were also observed by Matos, Gariglio, and Lo Monaco (2013) in a ferric Eutrophic Red

Latosol with a very clayey texture when evaluating the miscible displacement of cations from vinasse in a soil column.

Another aspect that can be observed is the effect of the column size on the dispersion parameter. That is, as the possibility for the solution to travel in the soil increases, the dispersive effect increases, consequently decreasing the Peclet number (P). This shows that for this soil type, column size and soil density affect the dynamics and adsorption of potassium ions.

Figure 1. *Breakthrough curves* of potassium ions ($^{K+}$) in the soil columns at heights of 0.10 m (A, D and G), 0.20 m (B, E and H) and 0.30 m (C, F and I) and densities of 1.3 g.cm $^{-3}$ A, B and C), 1.5 g.cm $^{-3}$ (D, E and F) and 1.7 g.cm $^{-3}$ (G, H and I) for the typical dystrophic yellow argisol (PAd).

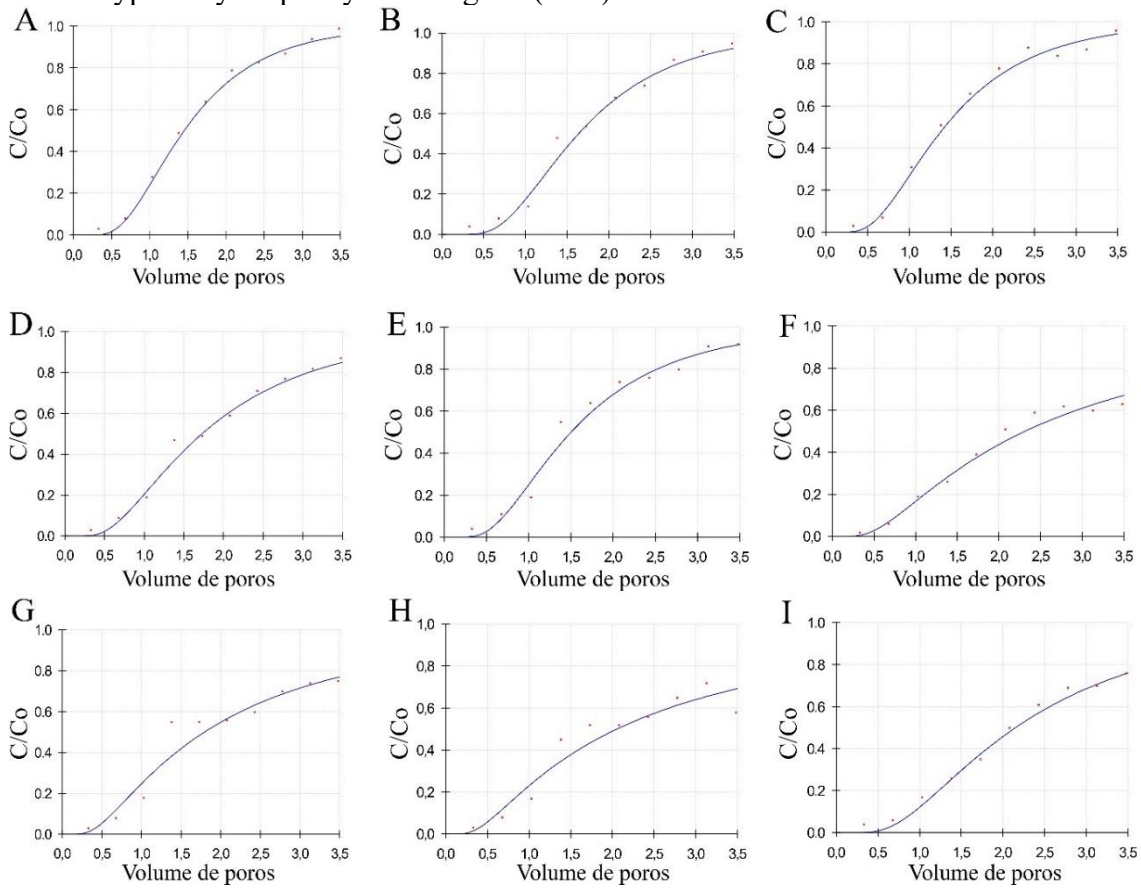


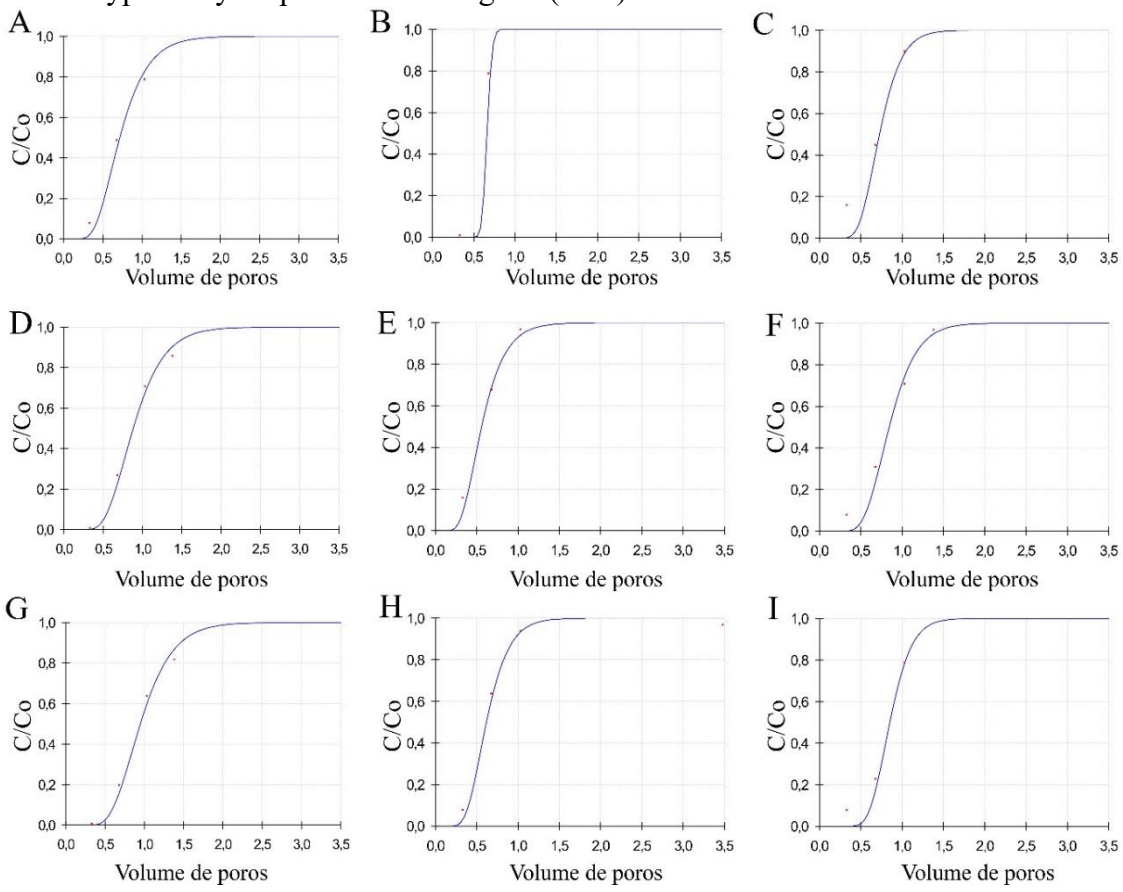
Table 3. Transport parameters for potassium ions from the retardation factor (R) and Peclet number (P), soil solution velocity (ν – cm min $^{-1}$), dispersivity (λ – cm) and dispersion coefficient (D – cm ^{2} min $^{-1}$) in typical Dystrophic Yellow Argisol (PAd) at different depths (H) and soil densities (ds)

	H (0.10 m)			**H (0.20 m)**			**H (0.30 m)**		
	ds1	ds2	ds3	ds1	ds2	ds3	ds1	ds2	ds3
P	6,548	3,841	2,000	6,563	4,865	1,338	5,597	1,823	3,761
R	1,665	2,161	2,647	1,800	1,800	3,504	1,667	3,517	2,697
N	0.088	0.075	0.062	0.176	0.150	0.124	0.265	0.226	0.186
Λ	0.015	0.026	0.015	0.013	0.014	0.015	0.015	0.017	0.018
D	1,130	1,200	1,310	1,540	1,620	1,185	1,420	1,720	1,490

*H - height of the soil columns; PAd-(ds1 - 1.3 g cm $^{-3}$, ds2 - 1.5 g cm $^{-3}$, ds3 - 1.7 g cm $^{-3}$)

In a study carried out by Santos (2014), in the Yellow Argisol and Red Latosol, the Latosol required a greater volume of pore mixture to reach the maximum relative concentration (C/C_o = 1), indicating that the Yellow Argisol presented the highest solute advance speed, whereas the Red Latosol had the greatest solute–soil interaction. In this sense, Pinho and Miranda (2014) studied the relationship between the solution flow velocity and the length of the soil column with respect to the potassium ion transport parameters in an Oxisol and a Neosol and reported that the potassium retardation factor ($^{K+}$) was greater in clayey soil than in clayey soil because of the greater cation exchange capacity, which was favored by the greater quantity of clay and organic matter.

Figure 2. *Breakthrough curves* of chloride ions (Cl^-) in soil columns with heights of 0.10 m (A, D and G), 0.20 m (B, E and H) and 0.30 m (C, F and I) and densities of 1.3 g.cm $^{-3}$ (A, B and C), 1.5 g.cm $^{-3}$ (D, E and F) and 1.7 g.cm $^{-3}$ (G, H and I) for the typical Dystrophic Yellow Argisol (PAd)



On the other hand, Santos (2014) reported that the lower the solution advancement speed (v) in the soil column is, the longer the contact time between the solution ions and the soil colloids, promoting greater retention of the solute ions and increasing the retardation factor.

In the case of chloride ions, lower values of the retardation factor (R) were observed, indicating greater mobility of this ion in this type of soil. Second, Basso and Kiang (2017) concluded that chloride ions have a relatively high retardation factor (R_d) in clayey soils. This mobility may be because the soil already has a higher concentration of potassium relative to the other ions, and by adding more potassium from potassium chloride, the "drag" effect of the chlorine ions accompanying it (in this case, potassium) becomes more evident. Figure 2 shows that density or column height had no effect on the chloride ion content. The chloride exhibited greater displacement in the soil in question, requiring 1.0 to 1.5 VP to reach a relative concentration of 100%. This fact is related to the high mobility and leaching due to the high solubility and chemical characteristics of the chloride ions.

Table 4 shows the chloride ion transport parameters. The soil density had virtually no effect on mobility, according to the retardation factor (R) values, unlike potassium ions. Because it is an anion with a lower atomic weight than potassium and because of the physical characteristics of the soil in question, it is "dragged" by the accompanying ion. Thus, the dispersive

effect was smaller in the soil in question, and consequently, it presented higher Peclet number (P) values.

With respect to the phosphorus ion (Figure 3), the nonmobility of this anion is evident. In other words, the phosphorus remained concentrated in the soil, as it should not be considered for retention, as the soil has a greater number of positive charges (sandy soil), which strongly adsorbs this anion. This process also influences the displacement of chlorine, as it is also an anion. Notably, at depths (column heights) of 0.20 and 0.30 m, the retardation of phosphorus was quite pronounced, which shows that for this ion, soil depth and density influence its mobility (PINHO; MIRANDA, 2014).

This result is related to the fact that phosphorus has low mobility in the soil and is not subject to nutrient loss through percolation. In phosphate fertilizers in the form of water-soluble phosphate, phosphorus can be solubilized upon contact with the soil solution.

One way to explain the soil–solute interaction relationship for the chloride ion, which can directly influence the advancing front, is that for the PAd soil, it was possible to reach the maximum relative concentration (C/C_o), which indicates a low interaction (MELO; ALLEONI, 2009).

With respect to the slopes of the advancement curves for potassium and phosphorus ions, similar results are observed in relation to the variables column height and soil density. According to Basso and Kiang (2017), this is an indication of greater soil–solute interaction, resulting in higher retardation values.

Table 4. Chlorine ion transport parameters from the retardation factor (R) and Peclet number (P), soil solution velocity (ν – cm min $^{-1}$), dispersivity (λ – cm) and dispersion coefficient (D – cm ^{2} min $^{-1}$) in typical Dystrophic Yellow Argisol (PAd) at different depths (H) and soil densities (ds)

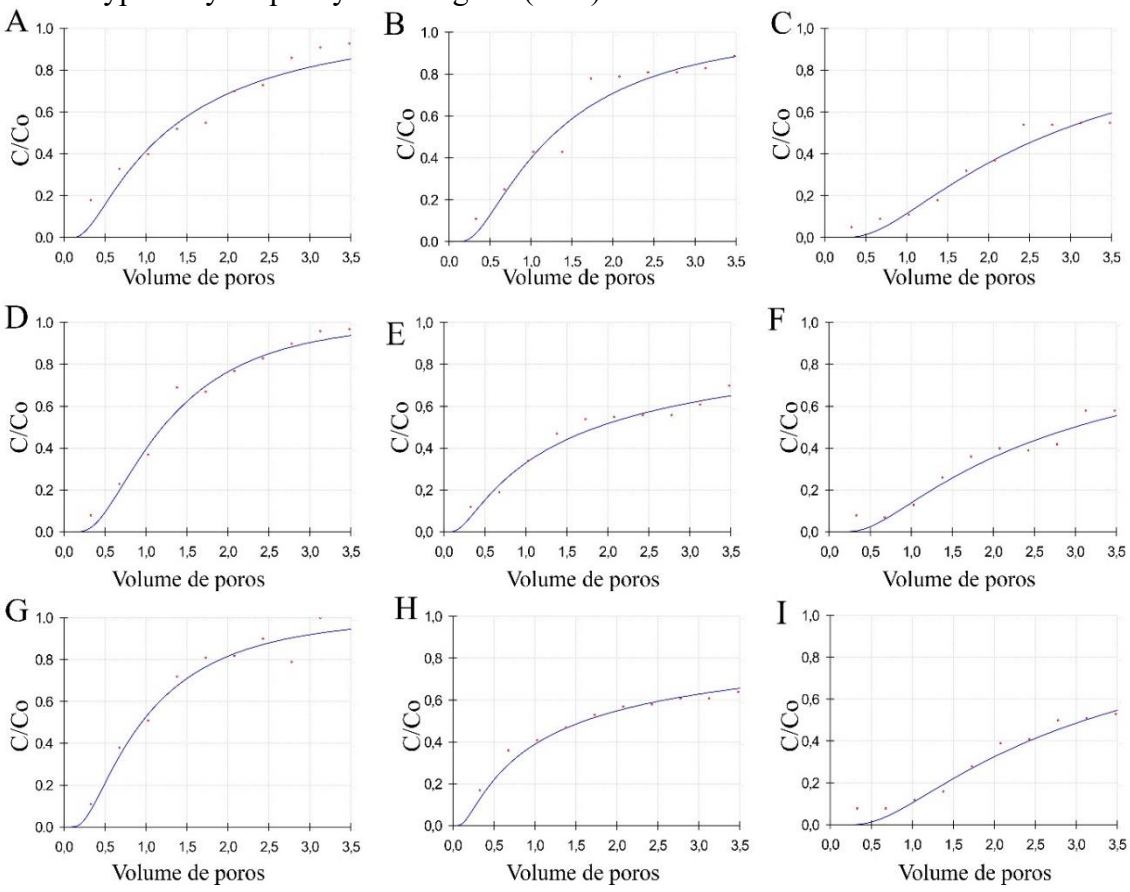
	H (0.10 m)			**H (0.20 m)**			**H (0.30 m)**		
	ds1	ds2	ds3	ds1	ds2	ds3	ds1	ds2	ds3
P	12.96	16.22	17.27	12.10	12.34	16.65	24.12	28.16	33.80
R	0.77	0.93	1.00	0.66	0.60	0.65	0.75	0.88	0.87
V	0.099	0.095	0.092	0.167	0.214	0.224	0.275	0.229	0.286
Λ	0.008	0.006	0.006	0.017	0.016	0.012	0.012	0.011	0.009
D	0.680	0.462	0.359	0.2913	0.2434	0.1490	0.3296	0.2408	0.1864

*H - height of the soil columns; PAd-(ds1 - 1.3 g cm $^{-3}$, ds2 - 1.5 g cm $^{-3}$, ds3 - 1.7 g cm $^{-3}$)

Its dispersive effect was slightly lower than that of chlorine, thus demonstrating lower Peclet number values. This indicates low mobility, greater adsorptive effects, and less dispersion. This is especially true when considering column heights of 10 and 20 cm.

With respect to the characteristics of the physical processes involving the Peclet number (P), for P less than 0.01, diffusive flow predominates; for P between 0.01 and 50, the flow is diffusive and advective; and for P greater than 50, the flow is advective (MONCADA, 2004). Thus, a physical process involving the Peclet number occurs in the range between 0.01 and 50, indicating the dominance of diffusive and advective flow (LIBARDI, 2005). For the respective research, homogenization of the porous medium occurred to obtain high values of soil density, which explains the low values of dispersivity (λ).

Figure 3. *Breakthrough curves* of phosphorus $_{ions\ (P2O5)}$ in the soil columns at heights of 0.10 m (A, D and G), 0.20 m (B, E and H) and 0.30 m (C, F and I) and densities of 1.3 g cm $^{-3}$ (A, B and C), 1.5 g cm $^{-3}$ (D, E and F) and 1.7 g cm $^{-3}$ (G, H and I) for the typical dystrophic yellow argisol (PAd)



The speed of the soil solution is proportional to the dispersion coefficient (D) because of the dispersivity variable (λ) (SANTOS, 2014). Thus, the results obtained in this research are within the theory of solute transport.

The results of this research also agree with the theory described by Nielsen and Biggar (1962) that higher values of the dispersion–diffusion coefficients (D) are associated with lower slopes of the effluent curves and, consequently, with the widening of the mixing range between the displacing and displaced solutions in the soil profile, making the increases in relative concentration (C/C $_{o}$) low for increases in the number of pore volumes.

On the other hand, Engler et al. (2008) mentioned that the dispersion–diffusion coefficient can be indicative of the soil's capacity to retain a given solute as the wetting front of the applied solution advances through the soil profile. According to this theory, for chloride ions, the curves are highly inclined and, consequently, have a narrow mixing range, which also indicates low values of dispersion–diffusion coefficients (D).

The ions studied exhibited both diffusive and advective flux effects. However, the chloride ions most closely approximated the advective flux and exhibited the lowest soil–solute interaction, as measured by the slope of the advance curves. Compared with potassium, it presented higher retardation factor values, indicating greater soil retention.

Table 5. Transport parameters for phosphorus ions from the retardation factor (R) and Peclet number (P), soil solution velocity (ν – cm min $^{-1}$), dispersivity (λ – cm) and dispersion coefficient (D – cm ^{2} min $^{-1}$) in typical Dystrophic Yellow Argisol (PAd) at different depths (H) and soil densities (ds)

Typical Dystrophic Yellow Argisol (PAd)									
	H (0.10 m)			H (0.20 m)			H (0.30 m)		
	ds1	ds2	ds3	ds1	ds2	ds3	ds1	ds2	ds3
P	1.60	3.56	2.45	2.21	1.28	1.58	1.80	1.04	1.45
R	1.97	1.53	1.32	1.78	8.06	6.80	4.28	5.71	2.70
N	0.088	0.075	0.062	0.077	0.038	0.024	0.026	0.023	0.086
Λ	0.006	0.003	0.004	0.009	0.018	0.003	0.017	0.029	0.021
D	0.553	0.211	0.254	0.595	0.701	0.270	0.265	0.226	0.186

*H - height of the soil columns; PAd-(ds1 - 1.3 g cm $^{-3}$, ds2 - 1.5 g cm $^{-3}$, ds3 - 1.7 g cm $^{-3}$).

6 CONCLUSIONS

On the basis of the results obtained for the soil in the submiddle São Francisco Valley region, potassium and phosphorus ions behaved similarly on the basis of the transport parameters obtained via the STANMOD model. Both an adsorptive effect and low mobility in the soil in question were evident. The effect of soil density was more evident for potassium ions but not for the other ions (chlorine and phosphorus). The effect of column length was not evident.

The chloride ions presented high mobility in the typical Dystrophic Yellow Argisol, with a lower retardation factor (R) and greater dispersive effect, resulting in lower *Peclet number* (P) values. The STANMOD model presented satisfactory performance in the numerical adjustment of the breakthrough curves (BTCs).

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