MODELING VERTICAL MOBILITY OF P IN REGOSOLS OF THE BRAZILIAN SEMIARID REGION: LEACH COLUMN EXPERIMENT

MODELAGEM DA MOBILIDADE VERTICAL DE P EM NEOSSOLO REGOL DO SEMIÁRIDO BRASILEIRO: EXPERIMENTO DE COLUNA DE LIXIVIAÇÃO

MODELACIÓN DE MOVILIDAD VERTICAL DE P EN REGOSOLES DE LA REGIÓN SEMIÁRIDA BRASILEÑA: EXPERIMENTO DE COLUMNA DE LIXIVIACIÓN

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Abstract

Phosphorus (P) mobility can be high in sandy soils in tropical regions due to its high proportion of macropores, low levels of Fe and/or Al oxides, and low natural levels of organic matter. The aim of this study was to verify if the fit with convection-dispersion model (CDE) is adequate to analyze P vertical mobility in Regosols from the Brazilian semiarid region. Leaching columns were packed with two soils, fertilized with cattle manure. The columns were prepared based on the hydrodispersive parameters of the modeling with potassium bromide (KBr) and saturated flow. Soil samples were saturated with calcium chloride ($CaCl_2$) and potassium chloride (KCl), both 0.001 mol L^{-1}, and a pulse of 0.6 mmol L^{-1} of P. The hydrodispersive parameters (inverse method) were estimated using the CDE (CXTFIT). The soil samples packed in the columns, the delay factors (R) were around 1, the dispersivity values (λ) were very close, and the Péclet numbers (Pe) were greater than 10. In the P pulse transport assay, $P_{leached}$ contents were on average 270.8 mg L^{-1}, and it was observed that most of Pleached were translocated with 20 Vp, from 40 Vp the relationship between concentration and volume remains constant; hydrodynamic dispersion coefficients (D) ranged from 22.85 to 72.50 cm^2 h^{-1}, R ranged from 2.36 to 5.23, Damkohler number (ω) values were less than 1, and Pe ranged from 0.76 to 2.40. The adjustment with the CDE was efficient to demonstrate the vertical mobility of P in Regosols of the Brazilian semiarid region.

KEYWORDS: Hydrodispersive parameters. Elution curves. Convection-dispersion. Adsorption.

Resumo

A mobilidade do fósforo (P) pode ser elevada em solos arenosos em regiões tropicais devido à sua alta proporção de macroporos, baixos teores de óxidos de Fe e/ou Al e baixos teores naturais de matéria orgânica. Objetivou-se verificar se o ajuste com o modelo de convecção-dispersão (CDE) é adequado para analisar a mobilidade vertical de P em Neossolo Regolítico do Semiárido brasileiro. As colunas de lixiviação foram preenchidas com solos adubados com esterco bovino. As colunas foram preparadas com base nos parâmetros hidrodispersivos da modelagem com brometo de potássio (KBr) e fluxo saturado. As amostras de solo foram saturadas com cloreto de cálcio ($CaCl_2$) e cloreto de potássio (KCl), ambos 0,001 mol L^{-1}, e um pulso de 0,6 mmol L^{-1} de P. Os parâmetros hidrodispersivos foram estimados utilizando o CDE (CXTFIT). Nas amostras de solo acondicionadas nas colunas, os fatores de retardo (R) foram em torno de 1, os valores de dispersividade (λ) foram muito próximos e os números de Peclet (Pe) foram maiores que 10. No ensaio de transporte de P o teor médio de $P_{lixiviado}$ foi de 270,8 mg L^{-1}; observou-se que a maior parte do $P_{lixiviado}$ foi translocado com 20 Vp, a partir de 40 Vp a relação entre concentração e volume permanece constante; os coeficientes de dispersão hidrodinâmica (D) variaram de 22,85 a 72,50 cm^2h^{-1}, R variaram de 2,36 a 5,23; os valores do número de Damkohler (ω) foram menores que 1 e Pe variou de 0,76 a 2,40. O ajuste com o CDE foi eficiente para demonstrar a mobilidade vertical do P em Neossolo Regolítico do Semiárido brasileiro.

PALAVRAS CHAVE: Parâmetros hidrodispersivos. Curvas de eluição. Convecção-dispersão. Adsorção.

Resumen

La movilidad del fósforo (P) puede ser alta en suelos arenosos en regiones tropicales debido a su alta proporción de macroporos, bajos niveles de óxidos de Fe y/o Al y bajos niveles naturales de materia orgánica. El objetivo fue verificar si el ajuste con el modelo de convección-dispersión (CDE) es adecuado para analizar la movilidad vertical de P en Regosols del Semiárido Brasileño. Las columnas de lixiviación se llenaron con tierra fertilizada con estiércol bovino. Las columnas se prepararon en base a los parámetros hidrodispersivos del modelado con bromuro de potasio (KBr) y flujo saturado. Las muestras de suelo se saturaron con cloruro de calcio ($CaCl_2$) y cloruro de potasio (KCl), ambos 0.001 mol L^{-1}, y un pulso de 0.6 mmol L^{-1} de P. Los parámetros hidrodispersivos se estimaron mediante el CDE (CXTFIT). En las muestras de suelo empacadas en las columnas, los factores de retardo (R) estuvieron alrededor de 1, los valores de dispersividad (λ) fueron muy cercanos y los números de Peclet (Pe) fueron mayores a 10. En la prueba de transporte de P el $P_{leaachate}$ promedio el contenido fue de 270,8 mg L^{-1}; se observó que la mayor parte del Pleachate fue traslocado con 20 Vp, a partir de 40 Vp la relación entre concentración y volumen se mantiene constante; los coeficientes de dispersión hidrodinámica (D) oscilaron entre 22,85 y 72,50 cm^2h^{-1}, R entre 2,36 y 5,23; Los valores del número de Damkohler (ω) fueron inferiores a 1 y Pe osciló entre 0,76 y 2,40. El ajuste con el CDE fue eficiente para demostrar la movilidad vertical de P en Regosols del Semiárido Brasileño.

PALABRAS CLAVE: Parámetros hidrodispersivos. Curvas de elución. Convección-dispersión. Adsorción.

1. Introduction

Agricultural production has been limited due to the low phosphorus contents in soils from the Paraíba Agreste region, in Brazil, where the use of nitrogenous or phosphate fertilizers is rather restricted or nonexistent (MENEZES E SALCEDO, 2007). The problem is partially solved by the use of cattle manure in that region, but the amount applied varies according to the availability at each farm (AZEVEDO et. al, 2018).

The manure input in a smallholder farming system is often calculated based on the nitrogen requirement of the crop. Thus, the continuous use of manure can lead to the accumulation of phosphorus in soils (GALVÃO et. al, 2008), which can be leached to groundwater and may cause eutrophication of water sources in that region (BERGSTRÖM et. al, 2015).

Studies on the miscible displacement of P are useful to know the interaction of the solute in the porous medium, and, then, assess the delay factor. It can be performed indirectly, by sorption assay, or directly, by elution curve analysis in soil columns (MOREIRA et. al, 2010).

The soil hydrodynamic and hydrodispersive characteristics, combined with sorption-desorption experiments, allow for the evaluation of the P mobility in the soil. Such studies provide a better understanding of the soil solute displacement processes associated with the physiological models (BORGES JÚNIOR E FERREIRA, 2006). Most theoretical models were developed to describe the soil solute transport using differential equations. They describe the solute transport through the advanced interface between the displacer and displaced liquid and are based on the convection, diffusion, and dispersion components (VAN GENUCHTEN E WIERENGA, 1986).

The use of mathematical models to evaluate solute and water transport has been useful for agricultural and environmental studies. Such models are suitable to describe the physical processes involved in solute transport (JADOSKI et. al, 2010). The parameters involved in soil solute transport equations, such as the delay factor (R) and the dispersive-diffusive coefficient (D), express the ability of the solute to percolate in the soil and must be accurately determined (VAN GENUCHTEN E WIERENGA, 1986).

The retardation factor represents the discrepancy between the velocities of the solute advancement and the wetting front of the percolating solution. Therefore, it is a very important variable in the study of soil solute movement (OLIVEIRA et. al, 2013). This parameter indirectly expresses the soil's ability to retain ions, describing the interactions between the liquid phase and the solid phase on the solution percolation through the soil.

The dispersion-diffusion coefficient also called hydrodynamic dispersion coefficient, apparent diffusion coefficient, or longitudinal dispersion is a physical parameter of the solute transport equation (VAN GENUCHTEN et. al, 1974). It expresses two additive transport phenomena, namely: i) mechanical dispersion, which represents the distinct movement of solutes in the soil, provided by changes in the displacement velocity of the solution within individual pores and between pores of various shapes, diameters, and directions, and; ii) ionic diffusion, which is the natural thermal movement of dissolved constituents and occurs due to the existence of concentration gradients (MARTINEZ et. al, 2001).

The most appropriate method to estimate these parameters is the fitting of theoretical models to experimental laboratory and field data. This can be done by using computer programs such as STANMOD software (STudio of ANalytical MODels) (VILELA et. al, 2018). VAN GENUCHTEN et. al, (2012) report the effectiveness of applying the method to assess the transport of a wide variety of chemicals. The expansion of those programs brings essential results to the modeling, such as a huge level of knowledge and data, descriptions between hypotheses, and access to the methodology used, which allows modifications and improvements in the model, when necessary.

This research aimed to evaluate whether the Convection-Dispersion Model (CDE) adjustment using the KBr tracer is adequate to analyze the vertical transport of P in Regosols fertilized with bovine manure from the Brazilian semiarid region.

2. Material and Methods

2.1.Local Study

The experiment in leach columns was conducted throughout the year 2017 at the Centro de Ciências Agrárias (CCA) of the Universidade Federal da Paraíba (UFPB), Campus Areia, Paraíba State, Brazil. It consists of a laboratory experiment in leaching columns packed with soil samples with cattle manure.

Soil samples were collected (January 2016) in four areas fertilized with tanned cattle manure (15% moisture) with doses ranging from 12 to 20 t ha^{-1} yr^{-1}). Two of these areas received organic fertilization annually until 2016 (F1 and F2), while the other two areas received annual fertilization until 2011 (NF1 and NF2), that is, they did not receive any type of fertilization between 2011 and 2016.

The soil was classified as Regosol (IUSS - WRB, 2022), collected at municipality of Remígio, in the Curimataú Ocidental microregion of the Paraíba State (6º59'0.4"W and 6º59'0.8"S), 495 m of altitude and smoothly wavy to wavy relief. The local climate is characterized as hot and humid (As), with a concentrated rainy season from March or April to July or August. The average annual precipitation is 941 mm, the average temperature is 25°C and the relative humidity is 80% (ALVARES et. al, 2013).

2.1.1.Characterization of the soil

The samples were collected at the soil surface (0-10 cm layer), air dried, and passed through a 2 mm opening sieve. Then, they were submitted to soil physical (Table 1) and chemical (Table 2) analysis.

Table 1. Physical attributes(1) of a Regosol, annually fertilized (F1 and F2) and non-fertilized since 2011 (NF1 and NF2) with cattle manure, collected in the municipality of Remígio, Brazilian semiarid region.

	Unit	Collected soils
Very coarse sand	g kg^{-1}	109.5
Coarse sand	g kg^{-1}	211.0
Medium sand	g kg^{-1}	239.0
Fine sand	g kg^{-1}	198.5
Very fine sand	g kg^{-1}	61.5
Total sand	g kg^{-1}	819.5
Silt	g kg^{-1}	138.0
Clay	g kg^{-1}	43.0
Water Dispersible Clay	g kg^{-1}	6.5
Texture classification	_	Sandy loam
Flocculation Degree	%	75.9
Silt/Clay ratio		3.9
Bulk density	g cm^{-3}	1.4
Particle density	g cm^{-3}	2.6
Total porosity	%	46.5

(1) Soil analyses were performed as described in Teixeira et al., 2017.

Table 2. Chemical attributes(1) of a Regosol, annually fertilized (F1 and F2) and non-fertilized since 2011 (NF1 and NF2) with cattle manure, collected in the municipality of Remígio, Brazilian semiarid region.

	Unit	F1	NF1	F2	NF2
pH_{H2O}	1:2.5	7.1	6.3	6.4	6.9
pH_{KCl}	1:2.5	5.5	5.4	5.6	5.7
ΔpH	------	-1.6	-0.9	-0.7	-1.2
TOC	$mg\ g^{-1}$	1.3	1.2	0.5	0.3
Ca^{2+}	$cmol_c\ kg^{-1}$	0.8	0.6	0.5	0.7
Mg^{2+}	$cmol_c\ kg^{-1}$	0.8	0.8	0.9	0.7
$H+Al^{3+}$	$cmol_c\ kg^{-1}$	6.0	7.8	5.2	3.6
Al^{3+}	$cmol_c\ kg^{-1}$	0.1	0.2	0.2	0.1
K^{+}	$cmol_c\ kg^{-1}$	0.2	0.1	0.1	0.2
Na^{+}	$cmol_c\ kg^{-1}$	0.0	0.0	0.0	0.0
CEC	$cmol_c\ kg^{-1}$	7.9	9.4	6.6	5.3
P_{M1}	$mg\ kg^{-1}$	4.5	7.8	7.3	8.8
P_{H2O}	$mg\ kg^{-1}$	0.9	1.0	0,5	3.8
P_{Tot}	$mg\ kg^{-1}$	170	120	100	90
P_{res}	$mg\ kg^{-1}$	0.2	0.2	21.3	6.0
Fe_{ox}	$mg\ g^{-1}$	0.27	0.36	0.45	0.19
Al_{ox}	$mg\ g^{-1}$	0.10	0.57	0.45	0.11
$Fe+Al_{ox}$	$mg\ g^{-1}$	0.38	0.93	0.90	0.30
Fe_{dcb}	$mg\ g^{-1}$	0.89	0.94	0.67	0.41
Al_{dcb}	$mg\ g^{-1}$	0.40	0.44	0.47	0.18

(1) Soil analyses were performed as described in Teixeira et. al, 2017.

Mineralogical analysis (Figure 1) shows that the soil used has illite and kaolinite clay minerals. Through the dithionite-citrate-bicarbonate extraction, it is possible to verify the presence of Fe and Al oxides (Table 2) probably coming from the weathering of goethite and/or hematite, which it is not possible to perform the identification by the diffractometer.

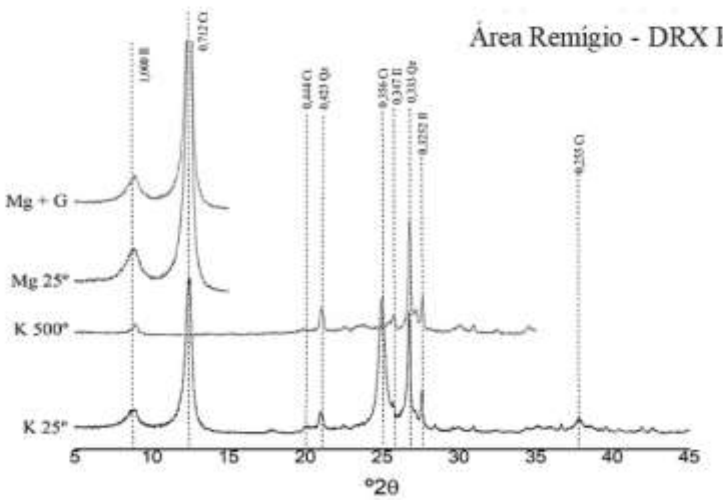

Figure 1: X-ray diffractometry of clay particles of a Regosol, annually fertilized (F1 and F2) and non-fertilized since 2011 (NF1 and NF2) with cattle manure, collected in the municipality of Remígio, Brazilian semiarid region. Source: The authors.

Ct: Kaolinite; Qz: Quartz; Il: Illite. Pretreatments: Mg+G - Magnesium and glycerol; Mg - Magnesium; K - Potassium.

2.1.2. Phosphorus transport in soil columns

The experiment of phosphorus transport in soil columns was performed in two steps: i) Hydrodispersive soil characterization test using potassium bromide (KBr); ii) P leaching test with a pulse of 0.6 mmol L^{-1} phosphorus into the soil column until complete at least 20 pore volumes (VP). After that, the leaching continued until no phosphorus elution was detected.

The experiment was set in 2.56 cm internal length and 10 cm long acrylic columns with PVC bases internally constituted by rubber rings for perfect sealing repair of the system. At the top and bottom of the column is a 3 mm thick perforated brass plate (2 mm diameter holes) and then a nylon filter to prevent soil loss during the test. A flow rate of 2.90 cm^3 min^{-1} was used. The value was established according to the average annual precipitation of the place where the soil samples were collected and ensured that the volume of water used was enough to initiate the vertical displacement of P.

2.1.3. Soil column filling

The column and lower base were weighed before and after filling to determine soil density. The columns were packed by placing the sample layers of approximately 2 cm into the column and lightly compacted with a glass stick. The columns were prepared in duplicates.

After the package of the column, a slow upward saturation process was performed for about 24 hours, with 0.001 M $CaCl_2$ and KCl solutions, to expel the air from the pores until it reached 10 cm of the soil column. After 24 hours, a phosphorus pulse with 0.6 mmol L^{-1} up to 20 Vp was applied, initiating the miscible displacement process of downwards using an 8-channel IPC Ismatec peristaltic pump connected by capillaries to the upper end of the column using saline with an average flow rate of 2.90 cm^3 min^{-1}.

Aliquots of the effluents were collected using a Gilson FC206 automatic fraction collector. The P contents in the aliquots ($P_{leached}$) were quantified according to MURPHY and RILEY (1962).

The following parameters were quantified in every column: soil (ρ_s) and particle (ρ_p) densities, pore volume (Vp), porosity (ε), flow (Q), flow (q), and average velocity of the solution in the pores (v). The pore volume (PV) was determined for every 2 cm soil layer, for five layers per column, according to Equation 1.

$$Vp = P = V_c * \varepsilon = \pi r^2 h\left(1 - \frac{\rho_s}{\rho_p}\right) \qquad \text{(Equation 1)}$$

In which, Vp: pore volume at the soil column (L^3); V_c: column volume (L^3); ε: porosity (L^3 L^{-3}); r: internal radius of the column (L); h: height of soil in the column (L); ρ_s: bulk density (M L^{-3}); ρ_p: particle density (M L^{-3}).

The flow (Q) was calculated according to the Equation 2.

$$Q = \frac{V}{t} \qquad \text{(Equation 2)}$$

In which, Q: flow (L^3 T^{-1}); V: solution volume (L^3); t: time (T).

The flux, was calculated using Equation 3.

$$q = \frac{Q}{A} \qquad \text{(Equation 3)}$$

In which, q: flux (L T^{-1}); Q: flow (L^3 T^{-1}); A: column cross section (equal to 5.14 cm^2).

The average pore water velocity, was determined with Equation 4.

$$v = q/\varepsilon \qquad \text{(Equation 4)}$$

In which, v: average pore water velocity (L T^{-1}); *q:* flux (L T^{-1}); ε: porosity (L^3 L^{-3}).

2.1.4. Hydrodispersive characterization of the soil columns using Kbr

For hydrodispersive characterization of the soil, and columns, a 0.5 M potassium bromide tracer solution (KBr) was applied, following the miscible displacement technique described by MILFONT et. Al, (2008).

After saturation, a pore volume (1 Vp) of the 0.001 mol L^{-1} $CaCl_2$ and KCl (solution-1) was pumped down into the column at 2.90 cm^3 min^{-1} flow rate. Then solution-1 was replaced by the tracer solution 0.5 M KBr, which was pumped at 1 Vp and then replaced by solution-1 again. In the effluent aliquots, collected with an automatic fraction collector, were determined the electrical conductivities with a TECHNICAL 4MP digital conductivity meter.

2.1.5. Hydrodispersive parameters calculations (inverse method) - Convection-Dispersion Model (CDE)

Solute transport in porous media can be conceptualized by the convection-dispersion model (CDE) (Coat & Smith, 1964). Convective transport refers to the passive displacement of the solute together with the water forming the solution, which when moving in the soil, carries with it the solute dissolved in it at a certain concentration, moving at the same speed, while dispersion occurs only at dynamic conditions, that is, when there is a movement of the solution. In its dimensionless form, is given by Equation 5.

$$R\frac{\partial C}{\partial z} = D\frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} \qquad \text{(Equation 5)}$$

In which, C: solute concentration expressed as mass of solute per volume of solution (M L^{-3}); D: hydrodynamic dispersion coefficient (L^2 T^{-1}); v: average pore water velocity, given by the ratio (v = q/ε), where q is Darcy flux density, and θ is volumetric water content; z: spatial coordinate (L); t: time (T); R: retardation factor, given by Equation 6.

$$R = \left(1 + \frac{\rho_S K_d}{\theta}\right) \qquad \text{(Equation 6)}$$

In which, K_d: linear distribution coefficient (K_d = S/C) (M L^{-3}), representing the concentrations distributed between the liquid phase (C) and the adsorbed phase (S); θ volumetric water content (L^3 L^{-3}); and ρ_s: specific mass of dry soil (M L^{-3}).

The hydrodispersive parameters were estimated by the CDE model with CXTFIT code (TORIDE et. al, 1995) from the KBr transport data in the miscible displacement experiments (Table 3) using the STANMOD for Windows (version 2.0) software.

3. Results and Discussion

3.1.Hydrodispersive characterization of soil columns using potassium bromide

The physical characterization of soil columns is presented in table 3. The fitting (Figure 2) of the CDE model to the KBr elution curve data at a flow rate of 2.90 cm^3 min^{-1}, provided adequate hydrodispersive parameter values in all tests.

The quality of KBr as a chemical tracer was considered good, and of hydrodispersive parameters obtained in the present study (Table 3) are in agreement with data from OLIVEIRA et. al, (2004) and CARMO et. al, (2010).

Table 3. Physical characterization of soil columns by KBr miscible misplacement experiment of a Regosol, annually fertilized (F1 and F2) and non-fertilized since 2011 (NF1 and NF2) with cattle manure, collected in the municipality of Remígio, Brazilian semiarid region.

Sample	Soil mass	Ds	Vp	ε	Q	q	v
	g	*g* cm^{-3}	cm^3		cm^3 h^{-1}	*cm* h^{-1}	*cm* h^{-1}
F1	83.24	1.65	18.7	0.35	60	11.92	32.23
NF1	79.99	1.58	18.7	0.38	65	12.82	34.68
F2	83.38	1.65	17.8	0.35	54	10.76	30.54
NF2	83.38	1.65	17.8	0.35	64	12.75	36.18

Ds = bulk density; VP = pore volume; ε = total porosity; Q = flow; q = water flux density and v = average pore water velocity.

In addition, symmetry in the ascending and descending stretch was observed for all elution curves. This means that the chemical equilibrium was achieved during the process of miscible bromide displacement (NIELSEN E BIGGAR, 1962). In some soil columns, the elution curves, fitted to the CDE model, reached 1.0 V/V_0 for the point 0.5 C/C_0, resulting in a retardation factor near to unit (Figure 2).

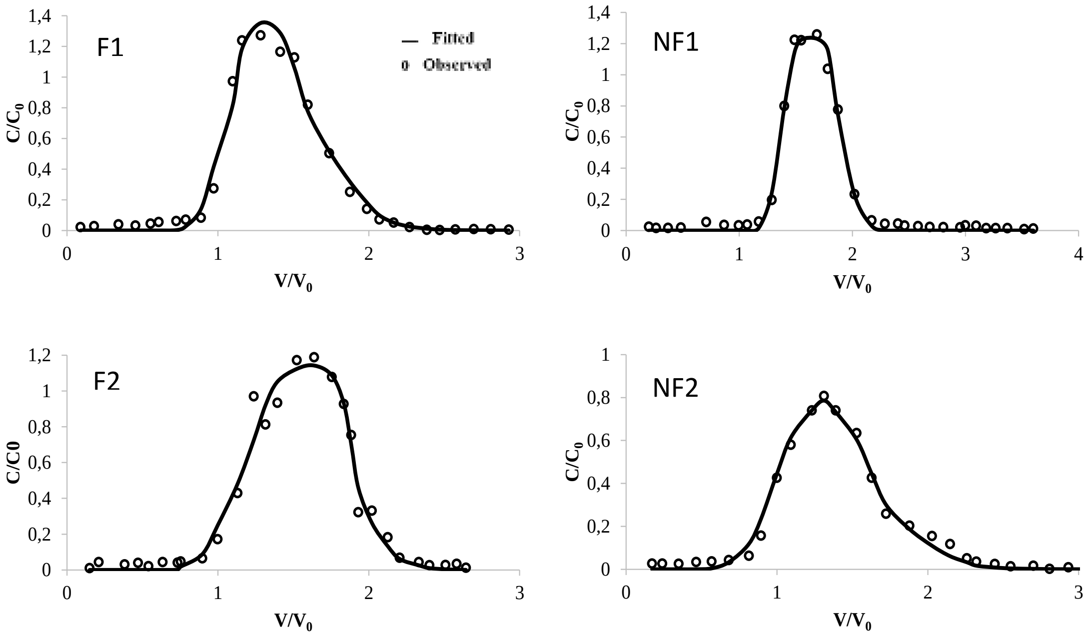

Figure 2. KBr elution curves fitted to the CDE model in saturated soil columns of a Regosol, annually fertilized (F1 and F2) and non-fertilized since 2011 (NF1 and NF2) with cattle manure, collected in the municipality of Remígio, Brazilian semiarid region.

Values of retardation factor (R), at a flow of 2.90 cm^3 min^{-1}, were near to unit, indicating that the KBr suffered low interactions (adsorption or exclusion) in all soil samples (Table 4). Such values corroborate the data from Kang et al. (2011) and Carmo et al. (2010), who also found factors for the KBr solution close to the unit, R = 1.19 ± 0.01 and R = 1, respectively.

We also observed the occurrence of preferential flux, probably due to the columns filling and flowing near the walls of the columns, causing leaching of the solute present there (BASSO E KIANG 2017).

According to van GENUCHTEN E WIERENGA (1986), R lower than the unit, indicate that only a fraction of the liquid phase is acting on the transport process. It could be the case where a chemical substance is submitted to regions with stagnated water that do not participate at the convective transport.

Table 4. Hydrodispersive parameter values from KBr miscible displacement experiment in soil columns of a Regosol, annually fertilized (F1 and F2) and non-fertilized since 2011 (NF1 and NF2) with cattle manure, collected in the municipality of Remígio, Brazilian semiarid region.

Sample	**R**	**Tvalue R**	**D** *cm^2h^{-1}*	**Tvalue D**	**R^2**	***Pe***	**λ** *cm*
F1	0.83	0.11	3.14	0.145	0.98	103	0.097
NF1	1.24	115.7	1.08	4.62	0.98	323	0.031
F2	1.18	37.4	4.29	3.909	0.97	71	0.14
NF2	1.16	43.76	2.23	3.698	0.93	162	0.062

R – Retardation factor; T value R- significance of R; D – Hydrodynamic dispersion coefficient; T value D - significance of D; R^2 – determination coefficient; P_e – Peclet number (P_e = L.v/D); λ – dispersivity (λ= D/v).

There were no significant differences in dispersivity values for all soil samples (T value D <0.05) because the texture of the soil is homogeneous, since dispersivity is related to the average soil particle size (MILFONT et. al, 2006). In Regosol there is a predominance of macropores that favor a higher distribution and speed of water.

Regarding the Peclet number (P*e*), the values were greater than 10 for all soil samples (Table 4). These results indicate that the predominant transport process of KBr elution curves is convective.

3.2.Transport of phosphorus by miscible displacement in soil columns

The elution curves of P, applied by pulse, show that most of the leached P has been translocated with 20 PV (Figure 3).

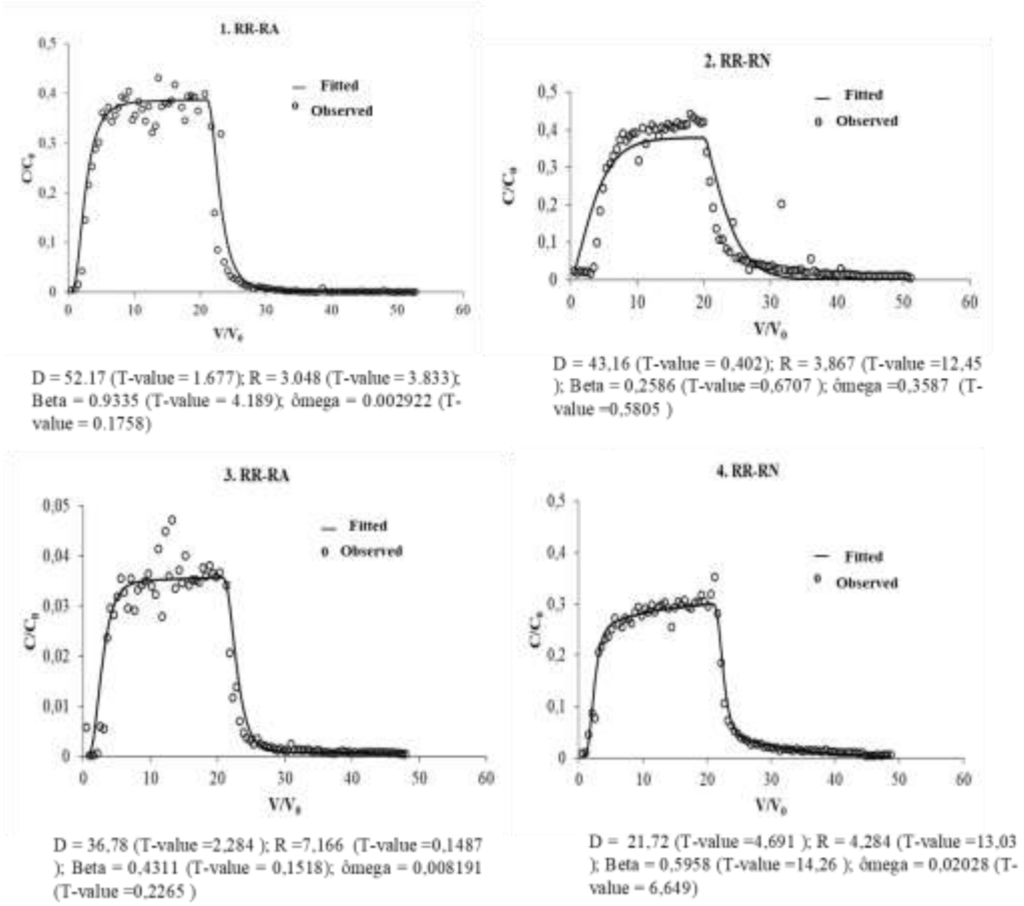

Figure 3. Elution curve of pulse of P by miscible displacement with saline solution of a Regosol, annually fertilized (F1 and F2) and non-fertilized since 2011 (NF1 and NF2) with cattle manure, collected in the municipality of Remígio, Brazilian semiarid region.

(-) Fitted data; (o) Observed data.

The initial P concentration in the first aliquot sampled, corresponded to the equilibrium concentration in the column. It is assumed a homogeneous concentration throughout it. From 30 to 40 VP, the relation between P concentration and pore volume starts to become relatively constant. The variation in P leaching in the samples is related to the Fe and Al oxyhydroxide contents (Table 2).

Tabela 5. $P_{leached}$ of a Regosol, annually fertilized (F1 and F2) and non-fertilized since 2011 (NF1 and NF2) with cattle manure, collected in the municipality of Remígio, Brazilian semiarid region.

$P_{leached}$ (mg L^{-1})			
F1	**NF1**	**F2**	**NF2**
212.6	273.5	289.5	307.7

Was observed a lower P leaching in sample F1 than in F2, both fertilized annually with cattle manure (Figure 3), can be ascribed to its higher oxalate extractable Fe and Al contents, (Table 2). However, P leaching was not significantly different (T value R < 0.05) for samples NF1 and NF2, non-fertilized with cattle manure since 2011 (Figure 3) despite their quite different contents of both, oxalate and dithionite extractable Fe and Al (hydr)oxides (Table 2).

That is, our data demonstrate that in addition to the P content added by organic fertilization, the P leaching in these sandy soils is influenced by the Fe and Al contents, corroborating the report of (FINK et. al, 2016).

The hydrodispersive parameters (D, R, P*e*, and λ) were influenced by the contents of amorphous Fe and Al oxides, the samples with close contents of Fe_{ox} and Al_{ox} (F1-NF2 and F2-NF1) (Table 2) were also those that had similar values of hydrodispersive parameters (Table 6). Samples F2 and NF1 have the highest values of these oxides, on average 0.41 mg g^{-1} of Fe_{ox} and 0.51 mg g^{-1} of Al_{ox}, resulting in the following average values: D = 23.25, R = 4.94, P*e* = 39.80 and λ = 0.77. Samples F1 and NF2 have the lowest contents of these oxides, on average 0.23 mg g^{-1} of Fe_{ox} and 0.11 mg g^{-1} of Al_{ox}, resulting in the following mean values: D = 67.28, R = 2.85, P*e* = 6.51, and λ = 2.26.

Table 6. Hydrodispersive parameters obtained by CDE model fitting without equilibrium at two sorption sites from soil phosphorus leaching experiment at a flow of 2.90 cm^3 $min^{-1}$with Regosol, annually fertilized (F1 and F2) and non-fertilized since 2011 (NF1 and NF2) with cattle manure, collected in the municipality of Remígio, Brazilian semiarid region.

Sample	**F1**	**NF1**	**F2**	**NF2**
D (cm^2 h^{-1})	72.50±28.74	22.85±28.72	23.65±18.58	62.06±57.05
Tvalue of D	1.09±0.84	0.81±0.57	1.26±1.44	2.88±2.57
R	2.36±0.98	4.64±1.09	5.23±2.74	3.33±1.35
Tvalue of R	5.57±2.46	15.82±4.77	9.57±13.33	11.54±2.11
ω	0.06 ± 0.09	0.20 ± 0.22	0.08 ± 0.01	0.20 ± 0.25
Pe	4.52±1.80	60.86±76.31	18.65±14.73	8.50±8.01
λ (cm)	2.4 ±0.95	0.76 ±0.96	0.77 ±0.61	2.12 ±2.00
r^2	0.92	0.92	0.94	0.97

D – Dispersion coefficient; T value of D - significance of D; R – retardation factor; T value of R - significance of R; ω - Damkhöler number; Pe – Peclet number ± standard deviation; λ – dispersivity ± standard deviation; r^2 – determination coefficient. Averages of two repetitions ± mean square error, calculated by CDE.

It is observed that soil samples F1 and NF2 presented the highest values of dispersion coefficient. These results prove the direct dependence between the hydrodynamic dispersion coefficient (D) and the average pore water velocity (v), because the higher the values of v obtained, the higher the values of D.

The dependence between D and v is corroborated by VAN DER ZEE E VAN RIEMSDIJK (1986). These authors studied the phosphorus leaching in soil columns at a velocity of 0.18 cm h^{-1} simulating precipitation and obtained D values of about 9.10^{-5} cm^2 h^{-1}.

High dispersion coefficient values were also found by OLIVEIRA et al. (2004) in a sandy Regosol (Quartzarenic Neossol) at 20 cm depth. They used deformed soil samples, with lower pH (4.8), higher zero point of charge (ZPC), and lower clay content (around 0.10 g kg^{-1}) compared to our samples. They added seven pore volumes of a phosphate solution, at a velocity of 557 cm h^{-1} and flow of 267 cm h^{-1}, and obtained a high dispersion coefficient (D = 7386 cm^2 h^{-1}) and a low retardation factor (R = 7.04). This D value was much higher than the ones obtained in our study, where as the highest dispersion coefficient value was 72.50 cm^2 h^{-1} for sample F1. This can be described to the predominance of negative charges despite higher clay content in our soil samples.

The pH for our samples were from 6.26 to 7.11 and clay contents from 27 and 59 g kg^{-1} (Table 1 and 2). These data suggest a lower ZPC and then a predominance of negative charges in our samples compared to more positive charges in samples from those authors. It is well known that adsorption of phosphate anions (HPO_4^{-2} and $H_2PO_4^-$) decreases as the pH and negative charges increase in soils (BARROW, 2017).

It is worthy of note that no precipitation of P can be considered in our soil samples despite alkaline pH since Ca^{2+} and Mg^{2+} contents can be considered quite low (Table 2). Therefore, we consider that Fe and Al oxyhydroxide are still enough protonated to influence P sorption, even at these high pH values.

The Damkohler number (ω) averaged 0.07 for the F1 and F2 samples, and 0.20 for the NF1 and NF2 samples. This number is related to the mass transfer coefficient. He highlights the importance of diffusive transfer phenomena between the mobile and immobile phases of water. The higher the Damkohler number ($\omega > 1$), the lower the resistance to solute transfer between the two regions, that is, the values obtained for the fertilized areas indicate that the flow in the leaching columns occurred without any interruption, this is due to to the fact that these samples have received a greater load of P over the years.

Thus, from the results presented in Tables 5 and 6, it can be inferred that the CDE model can be used to evaluate the destination of P in the 0-10 cm layer in the Regosol studied under saturation conditions.

The results for samples with levels of Fe_{ox} and Al_{ox} similar (F1-NF2 and F2-NF1) show the direct dependence between the hydrodynamic dispersion coefficient (D) and the average pore water velocity (v), because the higher the values obtained, the higher the D values.

In samples F1 and NF2, P diffusive movement predominated in the soil, due to values $Pe < 10$, confirming that lower levels of Fe_{ox} and Al_{ox} imply lower P.

Different values of λ and P_e for sandy soils have been reported in the literature, from $\lambda = 13.28$ cm and $Pe = 1.5$ (OLIVEIRA et. al, 2004) to $\lambda = 0.005$ cm and $Pe = 0.002$ (VAN DER ZEE E VAN RIEMSDIJK, 1986). These differences are due to several factors such as column length, average pore solution velocity, initial P concentration in the soil, and percolating solution.

Therefore, data from the modeling of P leaching in Regosols via cattle manure demonstrated the influence of physicochemical properties on the vertical displacement of P. It is also verified that poorly managed rainfall and irrigation can lead to deep percolation and leaching of this nutrient.

4. Conclusion

The convection-dispersion (CDE) model adequately represents the experimental data of the KBr elution curves and the vertical transport of P in Regosols fertilized with bovine manure in the Brazilian semiarid region.

Column leaching experiments using the CDE analytical model are useful to provide approximate data of P excess pollution scenarios in Brazilian semiarid region Regosols.

Organic fertilization via cattle manure, even if discontinued, under the evaluated conditions, saturates the P adsorption sites, resulting in its vertical transport in the soil.

The hydrodispersive parameters are influenced by the chemical and physical attributes of the soil, especially the content of Fe and Al oxides of low crystallinity, affecting the vertical transport of P.

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