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DISTRIBUTION OF SOLUTES NO_3^- E Ca IN SOIL COLUMNS WITH VINASSE

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ABSTRACT

Simulation models can provide a better understanding of the processes occurring in the soil displacement relative to solutes, and is applicable to research tools to minimize impacts on the environment. Thus, this study aimed to determine the retardation factors, diffusive-dispersive coefficients involved in the transport and distribution of vinasse effluent curves for the ions Calcium and Nitrate in soil columns. The Alfisol was collected in the rural municipality of Piracicaba-SP, soil samples were collected at 0-0.20 m depth. For the manufacture of columns was used PVC tubing 0.25 m long and 0.05 cm in diameter, wire mesh, and fast filter paper at one end, fastened by a "cap" bottomless PVC screw. The volumes of 10 mL were collected, defined in terms of pore volume (related to the porosity of the soil, taken generally around 50%) and the amount required to be performed the analysis of chemical components NO_3^- (nitrate) and Ca (calcium). We used the computer program to calculate the DISP parameters of solute transport in soil miscible fluid displacement. The transport parameters showed the positive effects of adsorption and calcium ion present in the shift vinasse. For the nitrate ion, despite the breakthrough curve not have adjusted the parameters indicate low adsorption to soil may be moved to greater depths.

Keywords: absorption, convection, diffusion-dispersion.

DISTRIBUIÇÃO DE SOLUTOS NO_3^- E Ca EM COLUNAS DE SOLO COM VINHAÇA

RESUMO

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Modelos de simulação podem proporcionar um entendimento melhor dos processos que ocorrem no solo, relativos ao deslocamento de solutos, constituindo ferramentas aplicáveis a estudos de minimização de impactos ao meio ambiente. Dessa forma, o presente trabalho teve por objetivo determinar os fatores de retardamento, coeficientes dispersivos-difusivos envolvidos no transporte da vinhaça e distribuição das curvas de efluente para os íons Nitrato e Cálcio em colunas de solo. O Nitossolo Vermelho eutrófico (NVe) foi coletado na zona rural do município de Piracicaba-SP, as amostras de solo foram coletadas nas camadas de 0-0,20 m de profundidade. Para a confecção das colunas utilizou-se tubos de PVC com 0,25 m de comprimento, e 0,05 m de diâmetro, tela metálica, e papel de filtro rápido em uma das extremidades, presos por um "cap" PVC rosqueável sem fundo. Os volumes coletados foram de 10 mL, definidos em função do volume de poros (relacionados com a porosidade do solo, assumida em termos gerais em torno de 50%) e da quantidade necessária para serem realizadas as análises dos componentes químicos NO_3^- (Nitrato) e Ca (Cálcio). Utilizou-se o programa computacional DISP para cálculo dos parâmetros de transporte de solutos no solo em deslocamento de fluidos miscíveis. Os parâmetros de transporte evidenciaram positivamente os efeitos de adsorção e de deslocamento do íon cálcio presente na vinhaça. Para o íon nitrato, apesar da curva de eluição não ter se ajustado, os parâmetros indicam baixa adsorção ao solo podendo ser deslocado para maiores profundidades.

Palavras-chave: absorção, adsorção, convecção, difusão-dipersão.

INTRODUCTION

Vinasse is a waste liquid derived from the distillation of wine called an alcoholic solution obtained from the fermentation process for obtaining the alcohol. The wine is the product of fermentation of sugarcane juice, molasses or mixture of broth and molasses. Therefore, the vinasse is the residue of ethanol production, which can be the raw material sugar cane juice, molasses or mixing ratios, or dilutions thereof. To each liter of alcohol produced are generated between 10 and 15 liters of vinasse.

Since the initial work on solute transport in the soil in the early sixties (Nielsen & Biggar, 1961), the number of jobs has grown considerably, and with them the number of experimental situations and circumstances on which the convection equation -dispersão (CDE) is applied. Research involving the use of vinasse have been developed, most successfully completed, as the use of waste in fertigation areas planted with sugarcane, the raw material for the manufacture of alcohol (MIRANDA et al., 2005; BRITO & ROLIM, 2005; LELIS-NETO, 2008; SILVA et al; 2012 e MATOS et al, 2013).

The composition of vinasse is very variable depending on various factors. One of them relates to their source. When using the juice for fermentation the resulting stillage is always less concentrated than the stillage from molasses must or wine mixed. Furthermore, the concentration of the vinasse varies from plant to plant, and within each plant, there are many variations in the days of harvest, and even in one day, due to the grinding of different varieties, with varying subpopulations from different soils, different levels of fertility.

The characterization of hidrodispersivos parameters of a soil is of fundamental importance for the use of numerical simulation models of solute transfer processes to improve the handling and application of chemicals in the soil, thus minimizing the risk of salinization and pollution of groundwater (ANTONINO & NETTO, 2006).

Simulation models can provide a better understanding of the processes occurring in soil, for the displacement of solutes, forming applicable tools minimization studies of environmental impacts. The success of simulation and resolution of equations that predict the solute displacement in the soil is necessary for the determination of the transmission parameters that influence the soil-solute relationship; the most important parameters that must be determined for this purpose are the velocity the water in the pores, the diffusion-dispersion coefficients and the delay fator (SILVA et al., 2012).

The solute transport process comes down in two basics process, convection and diffusion-dipersão hydrodynamics. Convection and the method by which the groundwater carries the dissolved solutes, whose quantity transported depends on their concentration, the flowing water volume and speed of same. The hydrodynamic dispersion-diffusion mechanism includes the mechanical dispersion mechanism and transport by diffusion. As the solute moves through the porous medium, the dispersion process act diluting the solute, reducing its concentration.

In this context, according to Borges Junior & Ferreira (2006), concern about the behavior of certain chemicals in the subsoil has motivated researchers to develop theoretical models in order to describe the physical processes involved in solute transport in the soil profile.Thus, this study aimed to determine the retardation factors, dispersive-diffusive coefficients involved in the transport of vinasse and distribution of effluent curves for nitrate and calcium in soil columns.

MATERIALS AND METHODS

The experiment was conducted at the Soil Physics Laboratory of the Department of Biosystems Engineering from College of Agriculture "Luiz de Queiroz" - ESALQ, University of São Paulo - USP, in Piracicaba.

The soil was collected in rural Piracicaba-SP, classified and defined according to the Brazilian System of Soil Classification EMBRAPA (2006), as UDULT eutrophic (NVe). It is a ground made of mineral material with nitic B horizon below the horizon, with low activity clay or alítico character most of the B horizon within 1.5 m of the soil surface. It presents clayey, with clay content greater than 350 g kg^{-1} of soil from the horizon, and textural ratio equal to or less than 1.5.

Soil samples were collected at 0.0-0.20 m deep, and taken to the laboratory where they were screened in a mesh of 2 mm, prepared using the TFSA methodology (dried soil air), and subjected to analysis It is measured characteristics physical and chemical (Table 1) for subsequent filling of the columns.

Table 1 - Physical and chemical characteristics of Alfisol used in filling soil columns.

Macronutrients											
Layer	P[1]	O.M.[2]	pH[3]	K[1]	Ca	Mg	H+Al	S[4]	T[5]	Al	V[6]
(m)	$Mgdm^{-3}$	g dm^{-3}	$CaCl_2$	---------------------mmol dm^{-3}------------------							%
0 – 0.20	8.0	27.0	5.0	2.5	15	25.2	39.0	48.0	86.0	1.0	55.8

Texture			
Layer	Clay	Silt	Sand
(m)	----------------------------------g kg^{-1}------------------------------------		
0 – 0.20	410	209	381

[1]Extrator of P and K, Mehlich. [2]Organic matter, g dm^{-3}. [3]pH calcium chloride in g 100 cm^{-3} of soil.[4]sum of bases, Ca + Mg + K [5]Cation exchange capacity, S + H + Al. [6]Saturation per base, V = 100 S/T.

For the production of columns was used PVC tubes 0.25 m in length and 0.05 m in diameter, wire mesh, and fast filter paper at one end, locked by a "cap" PVC threaded no background. At the other end at 0.21 m, the side of the column was installed a drain for excess water output and maintaining a constant blade 0.01 cm. Then, the columns filled up with soil to a height of 0.20 m with a volume of 392.7 cm^3 keeping the surrounding soil density from 1.29 to 1.30 $g.cm^{-3}$, the closest possible to the found the field.

Before starting the test, saturated columns slowly with distilled water, the wicking process, using a plastic container with a volume of 20 L, in which the columns were placed at an angle, and with the aid of a pump peristaltic added dropwise to distilled water to a height of about 2/3 of the column, and allowed to rest for 24 hours to complete saturation. After this period, the columns were set in a metal support, being installed above them effluent reservoir containing distilled water, and began the test with the soil washing for a period of 24 hours, for removal of nutrients present in the same.

Reaching steady flow, with zero concentration for Ca, was replaced the supply of distilled water for vinasse, starting from that point the manual collect of the volumes of the solution after covering the soil column, and the timing time.

The degree of mixing of the two miscible fluids can be quantified by determining the relationship between the solute concentration in the effluent (C), collected in the output section of the control element and the concentration of the same solute in the solution displacer (Co). Generally, the ratio C/Co is unitary in non-reactive material, when it has passed a volume of displacer fluid equal to twice the number of pore volume (PV) that are contributing to the flow profile.

The volumes of 10 mL were collected, defined in terms of pore volume (related to the porosity of the soil, taken generally around 50%) and the amount required for the analyzes to perform. Thus each vial represented approximately 0.05 pore volumes (relative to the total volume of the column filled with ground), as Equation 1:

$$PV = \alpha V \quad (1)$$

em que: PV - pore volume, cm^3; α - soil porosity in question, $cm^3 cm^{-3}$, and V - column volume, cm^3.

Control of the collected sample volume was done by a balance of 0.1 g accuracy. Upon reaching approximately 10 g of vinasse solution and the bottle is exchanged tarava-abalança to give only the weight of the effluent.

The vinasse used in the experiment was derived from an ethanol plant in Piracicaba, being collected near the discharge spout before being allocated to transport channels in the field to prevent contamination or addition of soil particles, and all care They were taken that the sample obtained would be representative. The vinasse was analyzed in the laboratory to determine their composition, and their physicochemical characteristics shown in Table 2.

Table 2 - Physico-chemical characterization of vinasse used in soil column.

Description	Unit	Values
BDO[1]	mg L^{-1}	10974.5
COD[2]	mg L^{-1}	62085.5
TDS[3]	mg L^{-1}	14886
EC[4]	dS m^{-1}	11.5
pH	-	4.5
K	mg L^{-1}	2934
Na	mg L^{-1}	51
Ca	mg L^{-1}	450
NO_3^-	mg L^{-1}	140.7

[1]DBO - oxygen biochemical demand; [2]COD - chemical oxygen demand; [3]TDS - total dissolved solids; [4]EC - electrical conductivity.

Due to the presence of high amounts of organic matter, vinasse was homogenized constantly to prevent the solid decantasse the reservoir during application.

When the concentration of the effluent samples collected at the end of the column equaled the initial concentration of the reservoir, it was concluded that the test being carried out with four repetitions by using two columns of identical characteristics.

The samples were subjected to laboratory analysis, using the flame spectrophotometer for the determination of K, Na and Ca and it was used ultraviolet spectrophotometer for the determination of NO_3^-.

The computer program DISP was used for calculation of solute transport parameters in the soil displacement of miscible fluids, developed in the Department of Agricultural Engineering of the Federal University of Viçosa, by Borges Junior & Ferreira (2006), in obtaining the parameters: R (retardation factor), and D (Diffusion-dispersion), whose input parameters are: number of observations (observed values of relative concentration (c) as a function of volume number pores PV), total porosity (decimal), density flow (cm h^{-1}), and length of the soil column (cm).

Program output data are estimated values relative concentrations of (c) due to the number of pores volume (PV); graphical representation of the relative concentration and the volume of pores (observed and estimated); estimated parameters (R and D); sum squared residual (RS); and the coefficient of determination (R^2).

RESULTS AND DISCUSSION

The mean values of the ion transport parameters – retardation factor (R), transport-dispersion (D) and coefficient of determination (R^2) are in Table 3. For potassium ion, gave a higher value in retardation factor, which expresses the interactions between the solid and liquid phases that occur during the percolation of the soil displacing solution, showing the potassium ion as well as having a greater concentration in the stillage, have greater interaction with the ground added vinasse, the sodium, calcium nitrate and, in addition, potassium is the most nutrient accumulated in the culture of sugarcane after silicon, however, in this study commented above discussion that nitrate It did not behave so that we could compare it to other ions. However, the mobility of ions in the soil influence the efficiency of utilization of nutrients by plants and leaching. The greater or lesser mobility of the heavy metals in the soil is influenced by the soil characteristics and the metal content (OLIVEIRA & MATTIAZZO, 2001). Ions with high mobility can be easily lost by leaching and contaminate groundwater (SANGOI et al., 2003).

According to Nielsen & Biggar (1962), the number of pores volume corresponding to the relative concentration of 0.5 is a first indication in the sense of whether or not, solute-soil interactions. When the amount corresponding to 0.5, the relative concentration is 1 pore volume means that the solute is not interacting with the colloidal fraction of the soil; On the other hand, when the value is greater than 1, the effluent curve has shifted to the right means that, in drains through the soil profile of the solute is adsorbed, resulting in a greater retardation factor the unit. Therefore, the larger the delay factor, the greater the solution-soil interaction.

The delay factor for the calcium and nitrate (R) shown in Table 3, It was considered as the number of pore volume for C/Co = 0.5, as Genuchten & Wierenga (1986).

Although it is a clay soil (sand = 38% = 20% silt and clay = 41%), with predominance of kaolinite in the clay fraction composition, was interaction between the calcium and nitrate compared the colloids demonstrated by retardation factor, averaged for 0.942 VP to VP nitrate and 1.247 for calcium (Table 3), indicating that the study soil, it is necessary to apply the respective VP, in addition to irrigation blade to be applied to compensate for the delay of these four elements in relation to the front of the feed solution into the soil.

Table 3 - Transport parameters for both elements obtained for Alfisol under application of vinasse, using the computational model DISP.

Element	R	D (cm^2 min^{-1})	R^2

*Potassium	2.211	0.141	0.977
*Sodium	1.273	0.172	0.970
Nitrate	0.942	0.613	-
Calcium	1.247	0.108	0.644

* Source: (SILVA et al., 2012).

The nutrient losses caused by leaching phenomenon are important because mean low efficiency of utilization of nutrients by the crops and consequently lower yields. When leached, nutrients are incorporated into the groundwater by internal drainage process and thus are transported over long distances, contaminating the water table and also the drinking water sources (KONRAD, 2002).

The model provides important parameters, for example, the R and D parameter; when the model fits the experimental data, it is understood that he can describe the movement of the soil solute (ZHENG & BENNETT, 2002). However, the computer program DISP could not adjust the elution curve, not relating the observed and calculated values (Figure 1); a likely cause can not be of this adjustment of the curve due to a predominance of negative charges present on the clay particles, causing the repellency of this anion, promoting its rapid leaching when the soil was saturated with water, it can be observed by dispersive time delay factor-diffusive coefficients having higher values of relative concentration for the initial samples. Nitrate required an amount of at least 0.0 VP and at most 0.1 VP so that the initial concentration was reached (Figure 1).

However, with passage of time, and vinasse application containing high concentrations of organic matter, the nitrate was being retained in small quantities, such a fact is due to adsorption of nitrate be predominantly electrostatic, with lower relative concentration values thus such facts will have direct influence on the model fit.

The delay the leaching is proportional to the amount of positive charges in deep soil and subsoil rich in iron oxides (DONN & MENZIES 2005; ALCANTARA & CAMPBELL, 2005) found adsorption of nitrate by positive charges of soil, which delayed their movement in relation to the advancement of water. Indirectly, this factor being a parameter that expresses the soil's ability to retain ions, it is clear its dependence on the interactions between the liquid phase and the solid phase during the percolation of the soil solution (TITO et al, 2012).

According to Santos et al. (2008), the variation coefficients of the coefficients of dispersion-diffusion of ions with ranges between 10 and 20% are admitted as appropriate and indicate satisfactory data accuracy.

The mobility of solutes in soil is inversely related to the adsorption thereof, the solid fraction or to environmental conditions that favor the precipitation of ions (MATOS et al., 2001; CHAVES et al., 2008). Although the vinasse can promote improvement in soil fertility, amounts used should not exceed their ability to ion exchange, that is, doses should be defined according to the characteristics of each soil, so as not to provide the imbalance of mineral elements (SILVA et al., 2006).

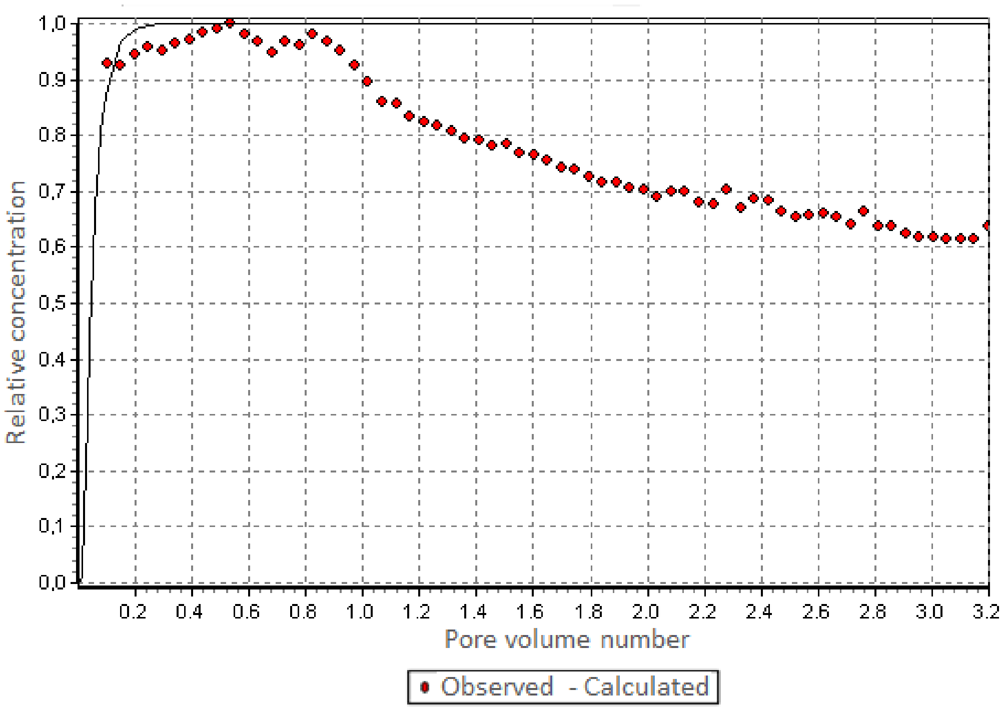

Figure 1 - Effluent distribution curves produced with vinasse for nitrate ion.

The delay factor expresses the ability of soil to retain solutes extent that the mass flow advances and depends on the interactions between the solid and liquid phases that occur during percolation (MELO et al., 2006). The dispersive-diffusion coefficient translates the additive effect of blending two phenomena, namely, diffusion, which is a spontaneous process that follows the thermal motion of ions and molecules in solution, and dispersion, which arises from the movement of solutes differentiated soil, provided by variations in the displacement velocity of the solution within the pores and between individual pores of different shapes, sizes, and directions (FERREIRA et al., 2006).

The calcium elution curve (Figure 2), there was a similar displacement to the displacement sodium, greater displacement of the elution curve to the right when compared to potassium, indicating that the calcium ion as the sodium was retained in the soil with less intensity than potassium, and sodium and potassium behavior as observed by Silva et al. (2012), with the application of vinasse excess potassium began to move other cations (Ca^{2+} and Na^{+}) complex in exchange for greater proportion than lower soil base saturation enabling you faster leaching, which is verified observing the curves.

The displacement of these inputs to the deepest parts of the profile, threatens the quality of groundwater, and make them unavailable to crops; therefore the adequate application of agricultural inputs contribute to the preservation of the environment, while optimizing the financial profile of the project as it allows higher productivity and minimizes waste (BORGES JUNIOR & FERREIRA, 2006).

In plants, lack of calcium, increase of the acidity and the excess aluminum results in reduced root growth, with consequent holding of small volumes of soil, leading to poor uptake of nutrients and water, making the crops subject to deficiencies minerals and susceptible to water deficits (LELIS NETO, 2008).

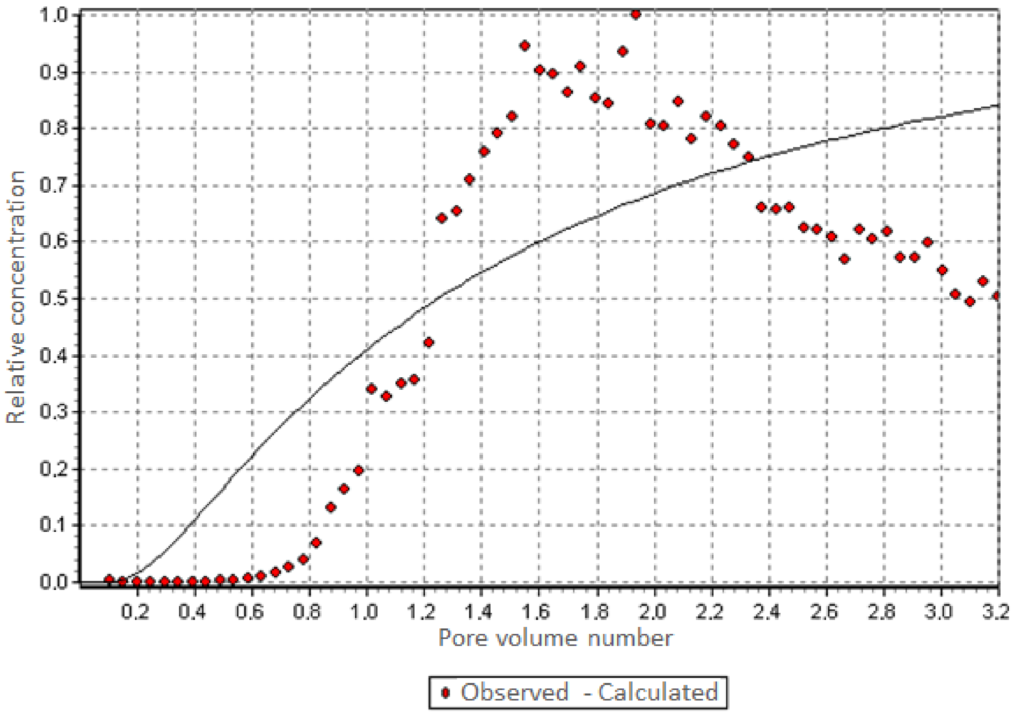

Figure 2 - Effluent distribution curves produced with vinasse for calcium ion.

The transport parameters of ions studied were obtained using the DISP software, whose highest value of dispersion-diffusion coefficient was observed for nitrate. Higher values of the diffusion-scattering coefficients are related to the lower slopes of the curves effluent, and consequently the enlargement of the mixture range between the displacing solutions in the soil profile, making increases in relatively low concentrations compared to increases the number of pore volume (NIELSEN & BIGGAR, 1962).

The lower calcium forward speed is one of the possible causes for its smaller dispersion-diffusion coefficient values for this soil. According to Gonçalves et al. (2008), sandy soils, which have a high percolation rate, provided greater dispersion-diffusion coefficient than the clayey soils.

The coefficient of dispersion-diffusion may be indicative of the ability of soil to retain certain solute as the front of the wetting solution applied advances in the soil profile (Engler et al., 2008).

The coefficients of determination (R^2) for the effluent curves were greater than 97%, for potassium and sodium and 64% for calcium, indicating adequate correlation between the experimental values and the values set by the DISP program, despite the values for calcium, although above the unit, are very close to this, characterizing solute-poor soil or strong shift provided by other cations added to the soil with the vinasse.

CONCLUSION

The transport parameters showed the positive effects of adsorption and calcium ion present in the shift vinasse.

For the nitrate ion, despite the breakthrough curve does not have adjusted the parameters indicate low adsorption to soil can be moved to greater depths.

According to the study conditions, the calcium absorption was observed corresponding to a volume of pores to 1.247 showing ion retention capacity Ca in the soil.

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