

CATION CONCENTRATIONS AND DYNAMICS IN THE SURFACE PROFILE OF TWO OXISOLS AFTER THE APPLICATION OF VINASSE

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ABSTRACT

Vinasse is considered the main residue of the sugar and alcohol industry and its application in agriculture provides a considerable amount of potassium and other nutrients to the soil. However, care should be taken when using it for the fertigation of sugarcane fields owing to its high polluting potential. Based on the hypothesis that sandy textured soils promote a greater leaching of cations and therefore a lower cation availability for plants than other soils, the aim of the present study was to evaluate the dynamics and levels of cations along the profile of two Oxisols after vinasse application in elution columns. The experiment was conducted in the Hydraulics and Irrigation laboratory of the Federal Institute of Goiás - Rio Verde Campus, Goiás, Brazil. Two soils were used: Rhodic Hapludox with clayey texture and Oxisol-Typic Hapludox with sandy texture. Rigid polyvinyl chloride (PVC) columns with 0.20 m in height and 0.07 m in diameter were used. The columns were dismantled and the chemical analysis of K, Ca, Mg, Na, Cu, Zn, Fe, and Mn nutrient concentrations was performed in the 0.00-0.05, 0.05-0.10, 0.10-0.15, and 0.15-0.20 m layers of the PVC soil column. There was a large K concentration increase along the surface profile of both soils after vinasse application. The Rhodic Hapludox promoted a higher gradient of K concentration than the Oxisol-Typic Hapludox, as well as the highest concentrations along the profile. Conversely, the Oxisol-Typic Hapludox promoted a greater leaching of K than the Rhodic Hapludox. The increase in K concentrations promoted the transport, mainly of Ca and Mg, to deeper layers in both soils. In general, metallic ions had greater mobility in sandier soil, resulting in higher leached contents. Interactions between pH/organic matter and ions could be observed.

Keywords: leaching, potassium, cationic nutrients, metallic nutrients.

INTRODUCTION

Vinasse is one of the main by-products of sugarcane processing, originating from the ethanol production process. It is important because of its chemical composition, which includes nutrients and organic matter, with potassium (K) constituting around 20% of the total organic and mineral compounds (Marques, 2006). Therefore, vinasse is widely applied by sugar and alcohol mills in sugarcane plantations as a form of organic and mineral supplementation, mainly in the form of fertigation. However, despite its nutritional benefits to plants, vinasse is characterized as an effluent from distilleries with high polluting power (Freire

and Cortez, 2000), and it can damage the soil and surface and ground waters when used incorrectly (Santos et al., 2018a).

The main constituent of vinasse is organic matter, mainly formed by organic acids and, to a lesser extent, cations such as K⁺, Ca⁺² and Mg⁺² (Ribeiro et al., 2014). When applied to the soil, vinasse can improve fertility by increasing the levels of nutrients and organic matter (Ribeiro et al., 2019) and improve the physical characteristics of the soil (Melo et al., 2019). However, when used for this purpose, the quantities should not exceed their ion retention capacity. Therefore, the dosages should be measured according to the characteristics of each soil, since vinasse has different amounts of

mineral and organic elements, which may lead to leaching of several of these ions, especially nitrate and K (Silva et al., 2007).

The soil capacity to retain the applied K is highly dependent on the cation exchange capacity of the soil. Consequently, the quantities of organic matter and clay influence the degree of leaching. Soils with high cation exchange capacity have great ability to retain the applied K. However, the washing of this element is a frequent problem in sandy soils (Libardi, 2005).

In view of the above, the aim of the present study was to evaluate the distribution of Ca, Mg, and Na ions as a function of K, and metal ion (Cu, Zn, Fe, and Mn) concentrations as a function of pH and organic matter along the profile of two distinct oxisols (clay and sandy texture) after vinasse application in elution columns.

MATERIAL AND METHODS

The experiment was conducted in the Hydraulics and Irrigation laboratory of the Federal Institute of Education, Science, and Technology of Goiás - Campus Rio Verde, Goiás, Brazil.

Two types of soil were studied. The first one was collected in a farm area belonging to the Federal Institute of Goiás - Campus Rio Verde, Goiás and can be classified as Rhodic Hapludox (Latossolo Vermelho distroférico - LVdf) with clayey texture according to the Brazilian Soil Classification System (Santos et al., 2018b), with oxisol and ferrosol classifications in the Soil Taxonomy (USDA, 1999) and the WRB/FAO (2015), respectively. The second soil, collected at the Rio Preto farm, also in the municipality of Rio Verde, Goiás, can be classified as Oxisol-Typic Hapludox (Latossolo Vermelho distrófico - LVd) with sandy texture according to the Brazilian Soil Classification System (Santos et al., 2018b), with oxisol and ferrasol classifications in the Soil Taxonomy (USDA, 1999) and the WRB/FAO (2015), respectively. Both were cultivated with pasture. Deformed samples were collected from each soil in 0.00-0.20 m depth layers. Initially, soil physical and chemical parameters were determined following the methodologies described by Embrapa - Brazilian Company of Agricultural Research (Teixeira et al., 2017), with subsequent filling of the soil columns (Table 1).

Table 1. Physical and chemical characteristics of the Rhodic Hapludox (LVdf) and Oxisol-Typic Hapludox (LVd) in the 0.00-0.20 m layer

Soil	Ca	Mg	Ca+Mg	Al	H+Al	K	K	S	P	CaCl ₂
	----- cmol _c dm ⁻³ -----					----- mg dm ⁻³ -----			pH	
LVdf	2.00	0.80	2.8	0.05	6.9	0.08	31	3.9	1.8	4.76
LVd	1.06	0.22	1.3	0.15	2.6	0.14	56	6.0	2.0	4.57
Solo	Na	Fe	Mn	Cu	Zn	B	CTC ^a	SB ^b	V% ^c	m% ^d
	----- Micronutrients (mg dm ⁻³) -----					cmol _c dm ⁻³		Bases Saturation		Aluminum Saturation
LVdf	1.0	28.5	23.6	3.3	1.0	0.3	9.8	2.9	29	1.7
LVd	3.0	46.7	27.2	0.4	0.4	0.3	4.0	1.4	36	9.5
Soil	Texture (%)			OM ^e	Ca/Mg	Ca/K	Mg/K	Ca/CTC	Mg/CTC	K/CTC
	Clay	Silt	Sand	g dm ⁻³	----- Relationship between bases -----					
LVdf	60	10	30	44.4	2.5	25.3	10.0	0.20	0.08	0.01
LVd	10	3	87	14.2	4.9	7.4	1.5	0.74	0.15	0.10

P (Honey), K, Na, Cu, Fe, Mn, and Zn = Melich 1; Ca, Mg, and Al = KCl 1N; S = Ca(H₂PO₄)₂ in HOAc; M.O. = colorimetric method; B = BaCl₂.

^aCation exchange capacity; ^bsum of bases; ^cbases saturation; ^daluminum saturation; ^eorganic matter.

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The samples from each soil were taken to the laboratory, smashed, sieved in a 2 mm mesh, and prepared using the air-dried soil (ADS) methodology. We used Rigid polyvinyl chloride (PVC) columns with 0.25 m in height

and 0.07 m in diameter. They were filled up to a height of 0.20 m, resulting in a soil volume of 0.0008 m³. Columns were filled in order to maintain the soil density as close as possible to that found in the field (Table 2).

Table 2. Mean values of the characteristics of columns filled with Rhodic Hapludox (LVdf) and Oxisol-Typic Hapludox (LVd)

Column	PVC column	Column with soil kg	Soil	*Sd kg m ⁻³
LVdf	0.17	1.16	1.00	1290.00
LVd	0.16	1.32	1.16	1500.00

*Sd - soil density

The vinasse used in the experiment was collected at the Decal Rio Verde plant, in the municipality of Rio Verde, Goiás. Vinasse was collected in the output unit after passing through the production and cooling system and before being destined to the transport channels in the field, which avoided contamination or addition of soil particles.

Vinasse composition was analyzed at the Soil Chemistry Laboratory of the Federal Institute of Goiás - Campus Rio Verde, Goiás, according to the methodology described by Embrapa (Teixeira et al., 2017). The chemical characteristics of vinasse are presented in Table 3.

Table 3. Physical and chemical characteristics of the vinasse used in the soil column

Macronutrients (g L ⁻¹)							g L ⁻¹
N	P	K	Ca	Mg	Na	S-SO ₄	OM ^a
1.1	0.04	2.50	0.13	0.12	1.4	0.04	0.9
Micronutrients (mg L ⁻¹)					pH	Density	M.S. ^b
Fe	Mn	Cu	Zn	Fe	g L ⁻¹	%	
83.6	4.0	0.2	1.8	3.98	1000	0.6	

P (Honey), K, Na, Cu, Fe, Mn and Zn = Melich 1; Ca and Mg = KCl 1N; S = Ca(H₂PO₄)₂ in HOAc; M.O. = colorimetric method.

^aOrganic matter; ^bdry matter.

Before starting the analysis, the soil columns were slowly saturated with distilled water by the capillarity process using a 0.02 m³ plastic container. To complete the saturation by capillarity, the columns were set in a tilted position with distilled water up to 2/3 of its height and remained at rest for 24 hours. Then, the columns were fixed in a metallic support and the effluent reservoir containing distilled water was installed above them. Afterwards, the test with washing of the soil started and it took 4 hours to remove all nutrients present. The supply of distilled water was replaced by vinasse, and the test of saturated columns

started, with vinasse column passage through the lasting for 30 hours.

After passage of vinasse, the PVC columns with soil were disassembled and the physical and chemical characteristics of both oxisols were analyzed in the 0.00-0.05, 0.05-0.10, 0.10-0.15, and 0.15-0.20 m layers to obtain the concentrations of K, Ca, Mg, Na, Cu, Fe, Mn, and Zn. SigmaPlot[®] software was used to prepare surface graphs, which assess the relationships between Ca/K, Mg/K, K/CEC, and Na/K; and to prepare graphs showing the depth profiles of soil pH, Cu, Fe, Zn, Mn, and organic matter components.

RESULTS AND DISCUSSION

Table 4 presents the physical and chemical characteristics of the Rhodic Hapludox (LVdf) and the Oxisol-Typic Hapludox (LVd) after application of vinasse in the 0.00-0.05, 0.05-0.10, 0.10-0.15, and 0.15-0.20 m layers of PVC columns. As compared with the initial

soil analysis (before vinasse application), there was an average increase in the K content of 1000 and 400% in LVdf and LVd, respectively, after vinasse application (Table 1). This reduced base ratios by 30 and 53% (Na/K), 36 and 65% (Ca/Mg), 91 and 82% (Ca/K), and 87 and 43% (Mg/K) in LVdf and LVd, respectively.

Table 4. Physical and chemical characteristics of the Rhodic Hapludox (LVdf) and Oxisol-Typic Hapludox (LVd), after application of vinasse in the 0.00-0.05, 0.05-0.10, 0.10-0.15, and 0.15-0.20 m soil column layers

Soil (m)	Texture (%)			K mg dm ⁻³	pH		Relationship between bases			
	Clay	Silt	Sand		CaCl ₂	Na/K	Ca/Mg	Ca/K	Mg/K	K/CEC
LVdf 0.00-0.05	63	13	24	470	4.18	0.03	1.2	1.4	1.2	0.28
LVdf 0.05-0.10	46	13	40	380	4.33	0.02	1.5	1.7	1.2	0.26
LVdf 0.10-0.15	63	13	24	390	4.70	0.02	1.8	2.4	1.3	0.21
LVdf 0.15-0.20	60	13	27	330	4.87	0.02	1.9	3.2	1.6	0.17
LVd 0.00-0.05	10	7	83	270	4.25	0.03	1.2	1.2	1.1	0.30
LVd 0.05-0.10	10	3	87	230	4.25	0.03	2.7	1.7	0.6	0.30
LVd 0.10-0.15	10	3	87	230	4.23	0.02	1.3	1.3	1.0	0.30
LVd 0.15-0.20	10	3	87	250	4.35	0.02	1.7	1.2	0.7	0.33

K, Na = Melich 1; Ca and Mg = KCl 1N.

Agreeing with the behavior of K observed by Brito et al. (2005), when studying the K content in the leachate after vinasse application in different soils, we observed an increase in the levels of Ca, Mg and Na after vinasse application, as can be seen in Figures 1, 2, 3, and 4. However, given that K concentration in vinasse is much higher than that of other components (Table 3), it resulted in changes in the balance between bases in the Oxisols.

The clayey texture and higher CEC of the LVdf (Table 1) promoted the highest concentrations of K along the soil profile (Table 4). In LVdf, K concentration in the soil profile showed large heterogeneity among the evaluated layers, with a 30% K concentration decrease in the 0.15-0.20 m layer from the more superficial layer (0.00-0.05 m). Contrastingly, LVd showed only a 7% decrease in K concentration from the superficial layer.

According to Melo et al. (2006), K, due to its cationic character, is more easily adsorbed to the soil matrix the higher the cation exchange capacity (CEC) of the soil. Our results corroborated this when LVdf and LVd were compared in this study. When vinasse is applied to sandy soils, leaching of K to deeper layers is predicted as the wetting front advances. Moreover, Brito et al. (2007) and Silva et al. (2018) found an association between soil type and vinasse doses, which interfered with the cation concentration of the drained solution (leachate).

Cherubin et al. (2015) studied the chemical properties of Brazilian tropical soils and observed that the increase in clay content determined greater accumulation of K after vinasse application in soils cultivated with sugarcane.

The Ca contents were different in the profile of each oxisol as a function of K concentrations. In LVdf, the decrease in K

concentration with the deepening of the soil layer promoted the increase in Ca content (Figure 1A). In LVd, the highest levels of

Ca were observed in the 0.00-0.15 m soil layer, which coincided with the lowest concentrations of K (Figure 1B).

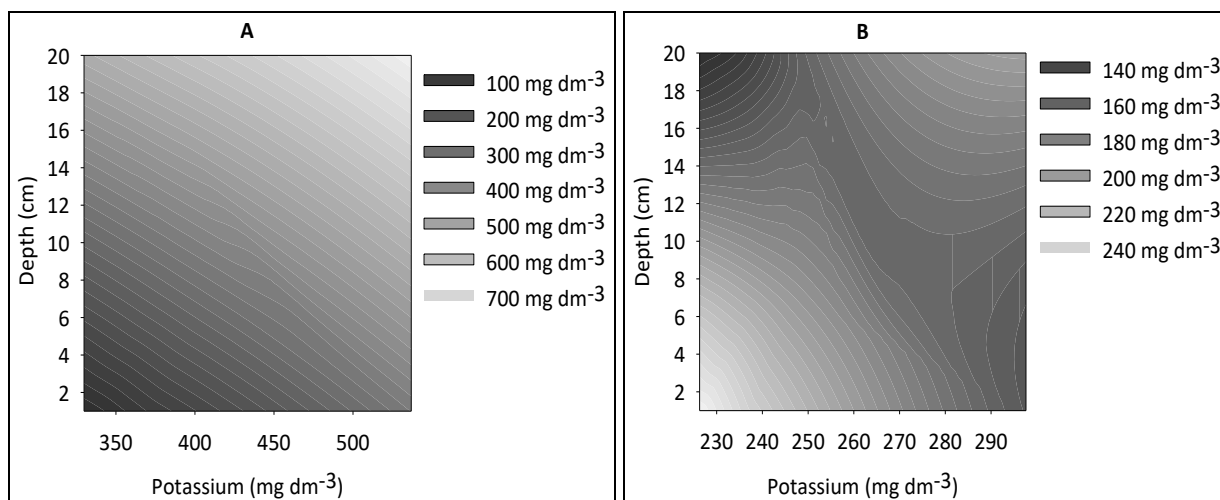


Figure 1. Calcium concentrations as a function of depth soil and potassium concentration in LVdf (A) and LVd (B) after application of vinasse

The highest concentration of Ca, 530 mg dm^{-3} , was observed in the deepest layer of LVdf. When this layer was compared to the initial and intermediate layers there were Ca concentration decreases of 39 and 25%, respectively. Ca concentrations were higher in LVdf than in LVd, around 47, 41, 67, and 70% in the 0.00-0.05, 0.05-0.10, 0.10-0.15, and 0.15-0.20 m layers, respectively.

Silva et al. (2016) observed that excess of K from vinasse application can displace other cations ($\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$) of the exchange

complex in a greater proportion than soils with lower base saturation, enabling greater leaching. In this sense, a greater displacement of Ca may cause a deficit of this nutrient in plants (Lelis Neto, 2008).

Mg showed the opposite behavior of Ca in both soils. The decrease in K concentrations as depth increased reduced Mg concentrations in LVdf (Figure 2A). In LVd (Figure 2B), the highest concentrations of K were found in the 0.00-0.10 and 0.15-0.20 m layers, resulting in the highest concentrations of Mg.

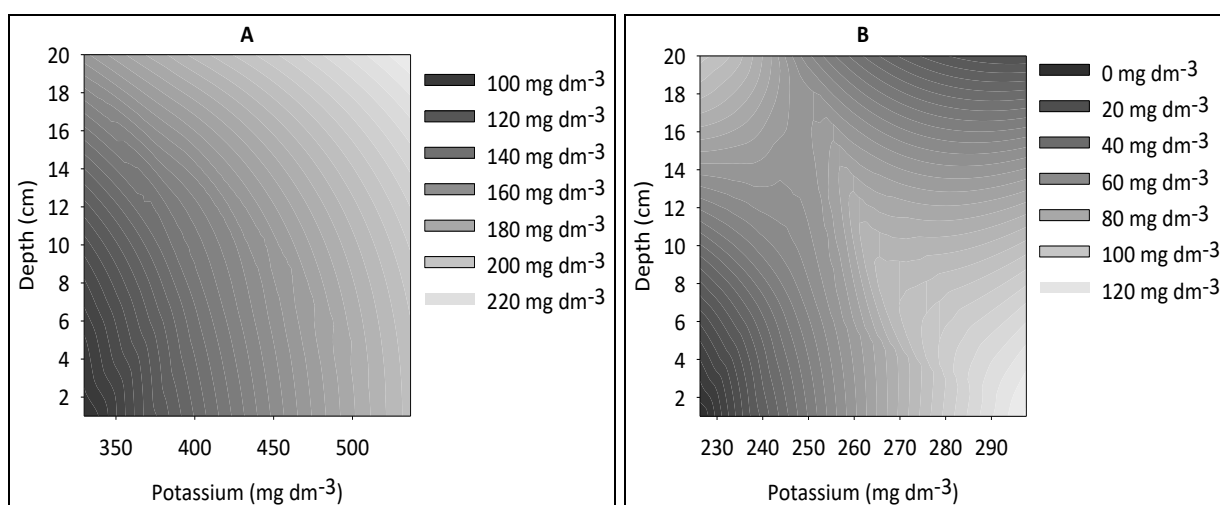


Figure 2. Magnesium concentrations as a function of depth soil and potassium concentration in the in LVdf (A) and LVd (B) after application of vinasse

The concentrations of Mg were higher in LVdf than in LVd, with around 47, 41, 67, and 70% in the 0.00-0.05, 0.05-0.10, 0.10-0.15 and 0.15-0.20 m layers, respectively.

Bebé et al. (2009), evaluating soils under different periods of application of vinasse, found a negative correlation between K contents and soil depth, with a reduction of concentration in soil depth. Camargo et al. (1983) observed an increase in cations (K, Ca, Mg, and Na) at the evaluated depths due

to the amount of these elements supplied by vinasse application.

In LVdf and LVd, the deepening of the layers as a function of the decrease in K concentrations reduced Na concentrations (Figure 3A and 3B). The highest concentrations of Na, 13, 9, 9 and 8 mg dm⁻³, were found in LVdf when compared to LVd. Reductions of 46, 33, 44 and 25% were observed in 0.00-0.05, 0.05-0.10, 0.10-0.15 and 0.15-0.20 m layers, respectively.

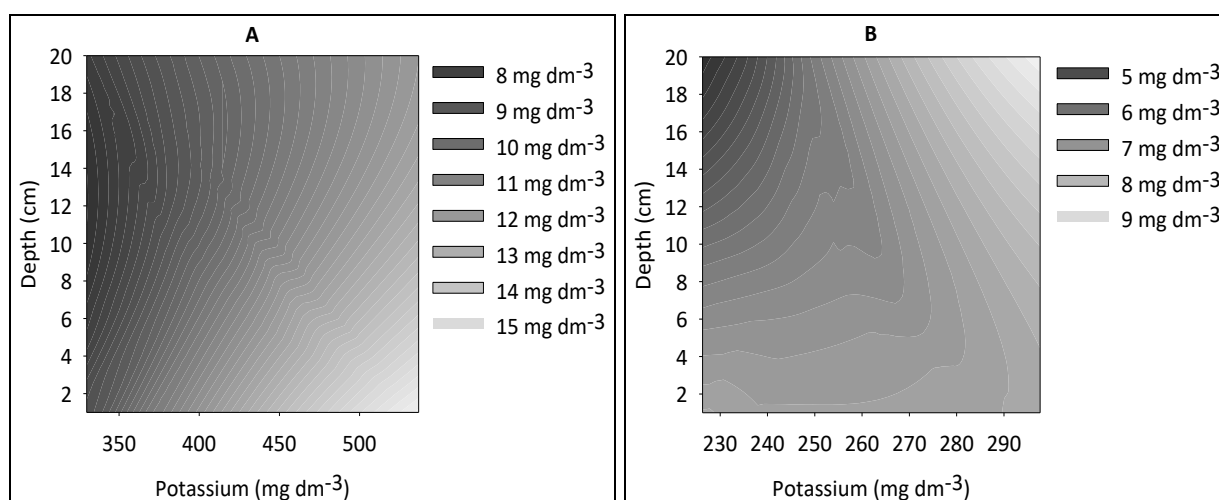


Figure 3. Sodium concentrations as a function of depth soil and potassium concentration in the in LVdf (A) and LVd (B) after application of vinasse

A lower gradient in Na contents is observed along the profile as a function of K concentrations in the two Oxisols, when compared to Ca and Mg (Figures 1 and 2). According to Silva et al. (2012), highly mobile ions can easily be lost through leaching and contaminate groundwater. For example, K⁺ and Na⁺, which have good mobility in the soil, mainly due to their monovalent character compared to the other bases and, salinizing potential of soils and waters.

As expected, there was an increase in the CEC of both soils due to the increase in soil bases. CEC values varied according to soil depth and K concentrations. In LVdf and LVd, the highest concentrations of K, and, therefore, of CEC, were observed in the 0-5 cm layer (Figure 4A and 4B). According to Martins et al. (2016), the highest effective CEC is related to the increase in pH and cation concentrations (K, Ca, Mg, and Na).

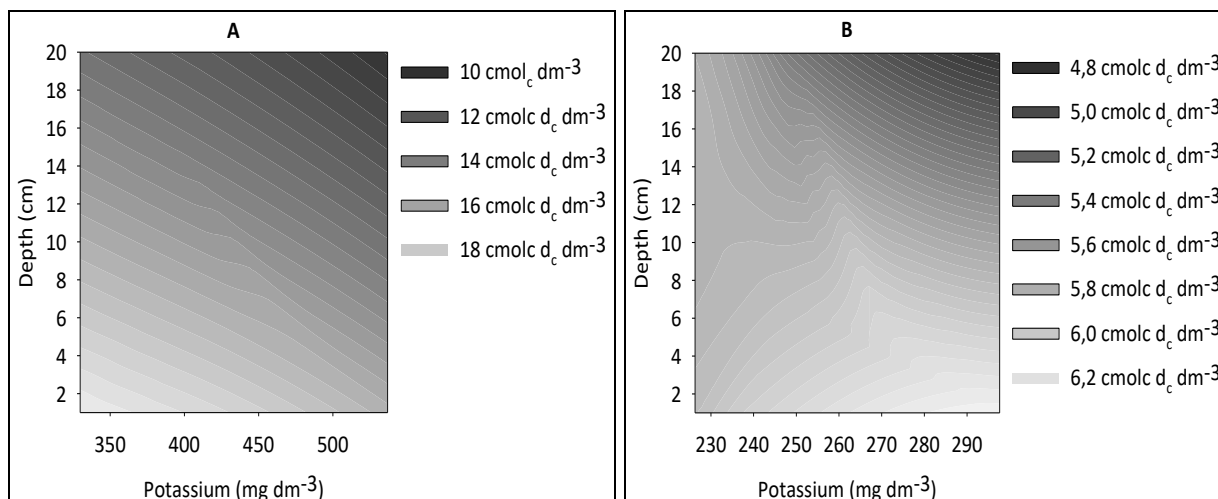


Figure 4. CEC values as a function of depth soil and potassium concentration in the in LVdf (A) and LVd (B) after application of vinasse

The highest values of CEC were observed in LVdf, 16, 16, 14 and 13 $\text{cmol}_c \text{dm}^{-3}$, in the 0.00-0.05, 0.05-0.10, 0.10-0.15, and 0.15-0.20 m layers, respectively. They were on average 60% higher than the values found in LVdf. Silva et al. (2007) analyzed the effects of vinasse application on soil properties and groundwater and concluded that the dosage to be applied with lower chances of contaminating groundwater depends on soil texture, since it exerts an influence on soil CEC. This can be observed in the relationship between the CEC values, depth, and K concentrations and by comparing the LVdf and LVd under study.

Surface profile K concentrations being higher in LVdf than in LVd (Figures 1, 2, 3 and 4) can also be related to differences in water retention between the soils. With the occupation of all the negative electrical charges of the soil by the cations, the surplus of K that remains in the solution suffers greater influence of mobility in relation to the volumetric content of water in the soil

(wetting front) (Barber, 1962; Ribeiro et al., 2014), causing higher or lower leaching rates. It is worth mentioning that this phenomenon is accentuated when the main form of K displacement by the soil in the solution is through mass flow.

Given that Cerrado soils are highly weathered, especially the Oxisols, they have a predominance of aluminosilicate minerals measuring the same as particles in the clay fraction with negative charge (Raij, 1986). Therefore, they have great affinity with soil bases (K, Na, Ca, and Mg), especially in soils with medium to clayey texture. This justifies our detection of the highest values of both CEC and nutrients in LVdf.

In the LVdf profile, organic matter (OM) increased at increasing depth to a maximum of 57.85 g dm^{-3} at 0.07 m depth and decreased to a minimum concentration of 45.25 g dm^{-3} at 0.18 m depth, while pH increased from 4.13 at 0.01 m depth to 4.62 at 0.18 m depth (Figures 5 and 6).

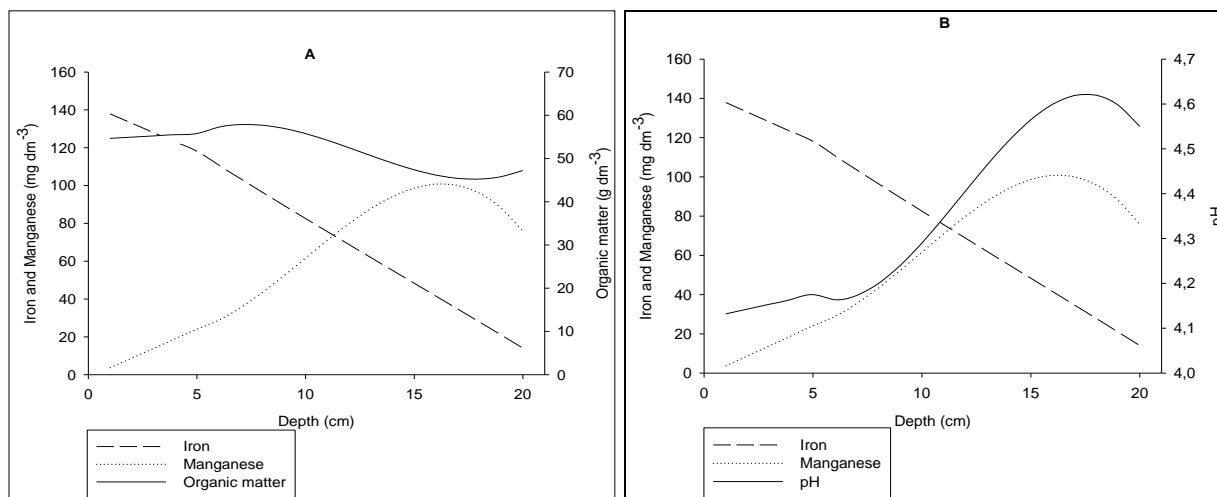


Figure 5. Concentrations of iron (A and B), manganese (A and B), organic matter (A) and pH (B) in the Rhodic Hapludox (LVdf) after application of vinasse

The iron ion (Fe) had a 89.85% concentration decrease with increasing depth and pH, from 137.87 mg dm⁻³ at a depth of 0.01 m to 14.00 mg dm⁻³ at a depth of 0.2 m, showing the influence of pH on the Fe concentration, while OM remained more stable and was not influenced so much by the retention of Fe ion. According to Schmitz et al. (2017) pH is one of the factors that most influences the solubility of metals, and its increase causes the reduction of their solubility, due to the formation of precipitates.

The manganese ion (Mn) increased with increasing depth and pH of soil, starting from a minimum concentration of 3.7 mg dm⁻³ at a depth of 0.01 m and reaching a maximum concentration of 100.82 mg dm⁻³ at a depth of 0.16 m.

The copper ion (Cu) concentration (Figure 6) decreased 13.95% along the entire profile, starting from a concentration of 3.87 mg dm⁻³ at of 0.01 m depth to 3.33 mg dm⁻³ at a depth of 0.2 m, showing a greater interaction of Cu with OM but not showing an influence of increased pH on Cu retention in this LVdf profile.

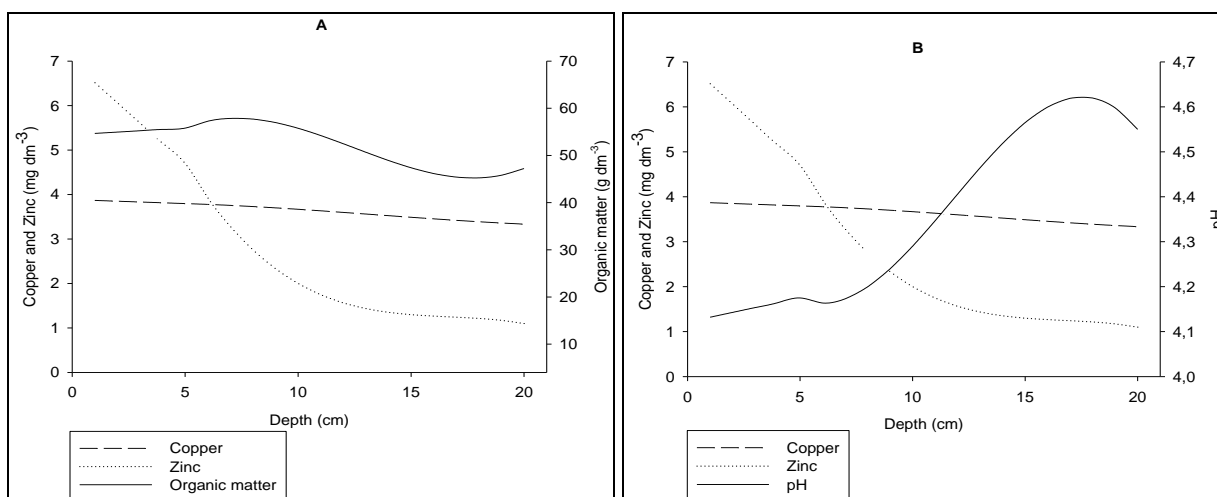


Figure 6. Concentrations of copper (A and B), zinc (A and B), organic matter (A) and pH (B) in the Rhodic Hapludox (LVdf) after vinasse application

The zinc ion (Zn) decreased 83.13% along the LVdf profile, starting from a concentration of 6.52 mg dm⁻³ at a depth of 0.01 m to a concentration of 1.10 mg dm⁻³ at

a depth of 0.2 m. Thus, Fe presented the strongest relationship to pH in the profile, with an increase in pH corresponding to a decrease in Zn concentration. The pH

increase causes an increase in the cation exchange process of metals in the soil due to reduced availability of H^+ ions that interact with negative charges (EPA, 2007).

In agreement with the results expressed in Figures 5 and 6, Dias (2018) observed that after the application of pig manure in Oxisol, the highest concentrations of Cu and Zn remained in the first 0.05 m of soil, showing a lower eminent risk of groundwater

contamination due to the lower transport of these ions to the deeper layers of soil.

OM increased with depth in the LVd profile to a maximum of 17.23 g dm^{-3} at a depth of 0.2 m, with an 10.45% increase when compared to the concentration of 15.43 g dm^{-3} at a depth of 0.01 m, while pH remained stable at a mean of 4.23 along the soil profile (Figures 7 and 8).

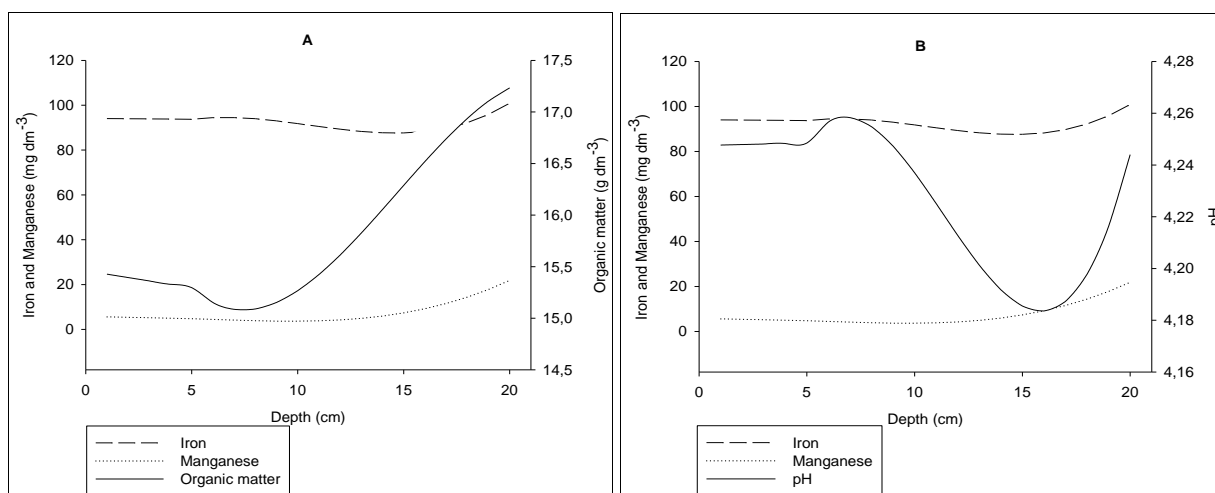


Figure 7. Concentrations of iron (A and B), manganese (A and B), organic matter (A) and pH (B) in the Oxisol-Typic Hapludox (LVd) after vinasse application

Fe decreased along the LVd profile to a minimum concentration of 87.6 mg dm^{-3} at a depth of 0.15 m, differing from the dynamics in LVdf (Figures 5A and 5B), while Mn remained stable up to a depth of 0.14 m, where it had a concentration of 5.99 mg dm^{-3} . From this depth down, Fe had a considerable

concentration increase up to a depth of 0.2 m, where it had a concentration of 21.90 mg dm^{-3} , representing a 265.61% increase.

Cu concentration (Figure 8) decreased 56.04% along the entire profile, starting from a concentration of 0.91 mg dm^{-3} at a 0.01 m depth to 0.4 mg dm^{-3} at 0.2 m depth.

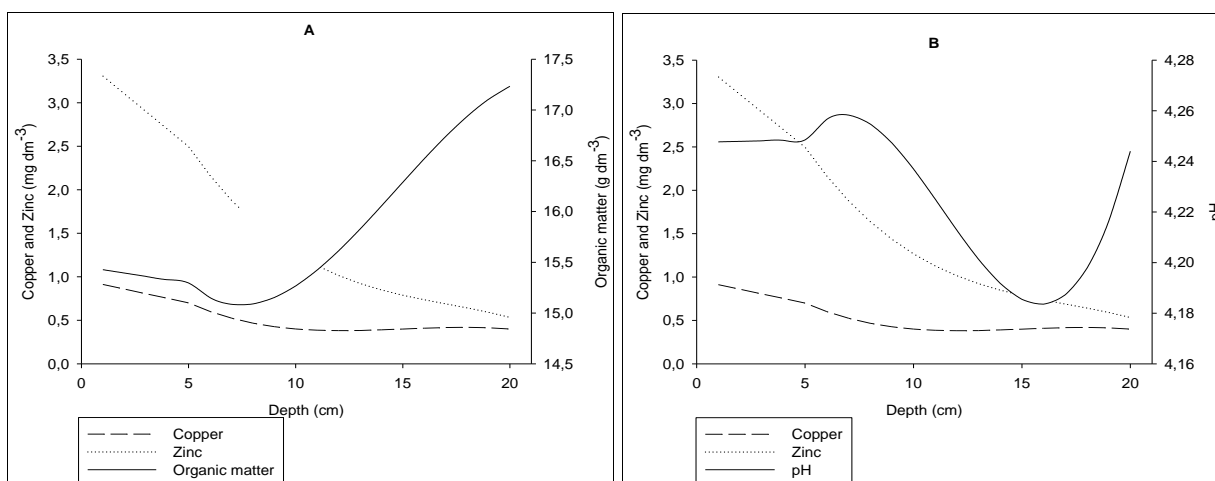


Figure 8. Concentrations of copper (A and B), zinc (A and B), organic matter (A), and pH (B) in the Oxisol-Typic Hapludox (LVd) after application of vinasse in the elution column

Zn decreased 83.94% along the LVd profile, from a concentration of 3.30 mg dm^{-3} at a depth of 0.01 m to a concentration of 0.53 mg dm^{-3} at a depth of 0.2 m.

Organic matter played a fundamental role in the retention capacity of Cu and Zn in LVd, in which the added organic content may have promoted chelation of these metals, reducing their leaching (Schmitz et al., 2017). This shows that pH stability did not alter the solubility of the metals along the soil profile (Figures 7 and 8).

According to Oliveira and Matitiazzo (2001) and Smanhotto et al. (2010), high organic matter concentrations decrease the presence of Zn and easily leachable forms in the solution because of the potential for forming precipitates with Fe and Mg oxides and complexation with the organic matter.

LVdf had higher concentrations of Fe, Mn, Cu, and Zn ions and OM than LVd, showing the greater interaction of ions and MO with the clayey texture. It was also observed that, except for Zn ion, the behavior of ions, pH, and OM was different in LVd when compared to LVdf, showing the influence of texture and potential CEC on ion and OM retention. This suggests that a different management should be applied when fertigating to these soils to avoid soil and groundwater contamination by heavy metals, especially when working on sandy soils.

Mn had the greatest mobility for LVdf and LVd deeper layers among all metallic ions.

CONCLUSIONS

Vinasse application increases the bases contents in the soil at all the evaluated depths, with greater intensity in LVdf soil. K concentration in both soils decreased with depth but with higher leaching in LVd soil. K concentrations increase after vinasse application promotes ion transport, mainly of Ca and Mg, to deeper layers in both studied soils. Ca and Mg contents are inversely proportional to combined depth and K concentrations in LVdf and LVd after vinasse application. The decrease in K concentrations, as a function of soil depth, decreases Na contents and CEC values in

LVdf and LVd, with greater intensity in the most superficial layer (0.00-0.05 m) in LVdf soil. In general, metallic ions had greater mobility in the sandy soil, resulting in higher concentrations of leached contents in the 0.15-0.20 m layer. Interactions between pH/organic matter and ions also were observed.

ACKNOWLEDGEMENTS

The authors thank the National Council for Scientific and Technological Development (CNPq); the Coordination for the Improvement for Higher Level Personnel (CAPES); the Research Support Foundation of the State of Goiás (FAPEG); the Ministry of Science, Technology, Innovation, and Communications (MCTIC); and the Federal Institute of Education, Science, and Technology Goiano (IFGoiano) - Campus Rio Verde, for the financial and structural support to conduct this study.

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