

Full Length Research Paper

## Effects of vinasse irrigation on effluent ionic concentration in Brazilian Oxisols

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The irrigation with vinasse can improve soil fertility. However, this use should take into account the characteristics of each soil because the vinasse has unbalanced amounts of mineral and organic elements which might lead to leach the ions, especially nitrate and potassium. The purpose of this study was to evaluate the impacts of vinasse irrigation on effluent ionic concentrations in Brazilian Ferralsols from two areas in Central Brazil: a sugarcane field, and a natural undisturbed savannah area. Soil samples from the two sites were placed into PVC columns with 120 cm height x 25 cm diameter with sugarcane. Undiluted vinasse was applied once on the surface of the soil columns at doses equivalent to 0, 300, 600 and 1200 m<sup>3</sup> ha<sup>-1</sup>. After 0, 60, 90 and 120 days of irrigation, samples of the effluent were collected and the concentrations of dissolved organic matter (DOM), Cl, Ca, Mg, Na, K, total Fe, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> as well as pH were determined. The ions concentration data were modeled in the chemical equilibrium model Visual Minteq v. 3.0. Results revealed vinasse's dose, days after irrigation and land use had a relevant effect on most nutrients effluent concentration. Contrasting pH values were observed for both soils and in the savannah soil was observed a decrease in pH at high vinasse doses. This paper thus revealed leaching of the DOM was strongly time dependent. High vinasse doses may lead to increase nutrient leaching and soil dispersion regardless the land use and time after irrigation.

**Key words:** Ion speciation, sugarcane, visual minteq, leaching, ethanol.

### INTRODUCTION

The total sugarcane world production is nearly 1.5 billion tons and is mostly located in tropical developing countries of Latin America, Africa, and Southeast Asia. Brazil is the world leader in the production of sugarcane with almost 9 million ha tilled area, processing approximately 681 million tons in the 2010/2011 harvest (IBGE, 2011). Primarily used for sugar production, in the last three decades the cane plant has become a new paradigm of clean and renewable energy. It decisively contributes to the sustainability of the planet against global warming

as currently the most efficient raw-material for ethanol production and bioelectricity are sugarcane juice and biomass, respectively (UNICA, 2008).

As ethanol production increases, the vinasse production increases as well. The vinasse is a nutrient-rich byproduct originated from sugarcane manufacture for producing ethanol. For each liter of ethanol, ten to eighteen liters of vinasse are produced (Freire and Cortez, 2000) with variable composition. The irrigation with vinasse can improve soil fertility (Silva, 2009).

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However, this use should take into account the characteristics of each soil because the vinasse has unbalanced amounts of mineral and organic elements which might lead to leach the ions, especially nitrate and potassium.

Interest in treated or composted organic wastes on Brazilian agriculture is based on high carbon levels from organic compounds (organic carbon) and nutrient on it, on cation exchange capacity enhancement (CEC) and acidity soil neutralization (Abreu Júnior et al., 2005). Rise carbon and soil nutrients levels can improve its physical and chemical properties, increasing plant yield and improving agricultural products quality, decreasing production costs. However, these wastes can present environmental pollution potential, that is, its soil or water addition can insert inorganic elements or toxic organic compounds or pathogens within the food chain (Abreu et al., 2005).

In addition to the water that percolates through the soil system, the application of a material which has large amount of potassium can affect the quantity of ions leaching into the soil profile, the concentration of solutes and the distribution of pore sizes, pH, cation exchange capacity, the reactions of dissolution/precipitation, and the ionic exchanges between nutrients in the liquid phase with those in the solid phase in depth during leaching (Ernani et al., 2003). The soil chemical balance is affected by several combinations of the above mechanisms after vinasse application.

The land use may influence the behavior of the ions in the soil after vinasse irrigation. In cultivated soils with many years of vinasse fertilization, apparently the ion exchange complex is saturated with chemical components from this byproduct and, in this case, intense leaching would be expected with consecutive irrigations. The objective of this study was to evaluate if increased vinasse rates can contribute to groundwater contamination through ion displacement from soil sites on sugarcane cultivated compared with savannah soil cropped with sugarcane a columns experiment.

## MATERIALS AND METHODS

### Study area and sampling procedure

The study used disturbed soil samples of a dystrophic Ferralsol (Nachtergaele, 2005) from two distinct sites with the same topographic condition, a cultivated field and a natural savannah area which was taken as control, located inside the Cerrado Biome. Both areas are located in the municipality of Goianesia, State of Goiás (15° 10' 00" S and 49° 15' 00" W). In the municipality the dominant climate is tropical wet-dry with an annual precipitation of 1,500 mm/yr and a rainy season from October to March (Figure 1).

Two trench 120 cm depth were opened, one in the savannah and another within commercial sugarcane area, for samples collection. The samples were collected by 20 cm layers tick up to 120 cm depth in the soil profile and separately stored in bags. Then, these samples were transported to Federal University of Goiás/Agronomy Campus EA/UFG and stored in the lab. The soil was collected in



Figure 1. Location of experimental sampling site (Abreu, 2006).

both areas, in 2005.

A chemical soil analysis is shown on Table 1. In the cultivated area, which has been cultivated since 1984 with sugarcane and was limed in 1998, there was irrigation with vinasse instead water use, which corresponded to 700 m<sup>3</sup> ha<sup>-1</sup> year<sup>-1</sup>, in aspersion systems form. Soil from the savannah area, near the sugarcane cultivated, located at same soil type and topographic conditions was sampled.

The field samples were placed, without sieve, into PVC columns with 120 cm high by 25 cm in diameter which was internally coated with raffia bags to reduce preferential flow in the columns wall. A sugarcane thole of the variety 72,454 RB with sprouts of approximately 20 cm was planted in each column. The columns were equipped with a drain at the bottom that was attached to a 600 mL plastic bottle to sample the effluent.

One year before sampling the columns effluent, additional fertilization was performed in the soil columns with monoammonium phosphate to attend the plant needs. The fertilization, which was the same for all treatments except the control, was calculated as recommended by Raji et al. (1997) to sugarcane plants. The soil columns were incubated and cultivated for a year before vinasse irrigation just to allow the sedimentation and aggregation of soil particles improved by sugarcane root system cultivated inside these columns.

Undiluted vinasse was applied at the surface of the soil columns at different doses (0, 300, 600 and 1200 m<sup>3</sup> ha<sup>-1</sup>) and the effluent was collected after 0, 60, 90 and 120 days of irrigation. The procedure was the same for the soils from the cultivated and control areas. The experiment was performed in triplicate for each soil and vinasse dose.

The amount of water used for irrigation during the experiment corresponded to the annual rainfall in the region of Goianesia municipality, turned into daily rainfall, which resulted in approximately 3.20 L column<sup>-1</sup> applied once a week during the evaluation period. The effluent samples were collected one day after irrigation, just in those predetermined four times, and the excess volumes during interval between sampling were discarded.

**Table 1.** Original soil analysis. Goianésia, GO, Brazil.

Treatment	Clay	Silt	Sand	pH	P(Mehl)	K	S available	Ca <sup>2+</sup>	Mg <sup>2+</sup>	H+Al	Al <sup>3+</sup>	CEC*	SOM
	-----%-----			CaCl <sub>2</sub>	-----mg dm <sup>-3</sup> -----			-----cmol <sub>c</sub> dm <sup>-3</sup> -----				%	
<b>0 - 25 cm</b>													
Cultivated	48.0	14.0	38.0	5.3	5.2	471.3	36.3	2.0	1.0	2.5	0.0	6.6	1.1
Savannah	52.0	17.0	31.0	4.3	1.0	45.5	6.9	1.1	0.5	6.1	0.5	7.8	2.6
<b>25 - 50 cm</b>													
Cultivated	48.0	14.0	38.0	4.9	1.1	319.5	38.9	0.9	0.6	2.7	0.0	5.0	0.6
Savannah	52.0	17.0	31.0	4.2	0.4	19.5	5.9	0.3	0.2	5.2	0.6	5.7	1.4
<b>50 - 75 cm</b>													
Cultivated	48.0	14.0	38.0	5.0	0.3	201.0	44.0	0.9	0.6	2.5	0.0	4.5	1.2
Savannah	52.0	17.0	31.0	4.3	1.3	10.2	4.9	0.2	0.1	3.8	0.4	4.2	1.0
<b>75 - 100 cm</b>													
Cultivated	48.0	14.0	38.0	5.1	0.3	148.3	35.1	0.8	0.5	2.4	0.0	4.0	0.6
Savannah	52.0	17.0	31.0	4.3	0.1	12.8	6.9	0.2	0.1	3.5	0.2	3.9	0.8

CEC\* Cation exchange capacity; SOM: Soil Organic Matter. (Source: Oliveira, 2006).

**Table 2.** Vinasse composition. Goianésia, GO, Brazil.

pH		4.02	
CE	mS cm <sup>-1</sup>	12,100.00	
Fe	mg L <sup>-1</sup>	27.00	
Cloretos		2,400.00	
SST		37,450.00	
NT		405.00	
NH <sub>3</sub>		107.00	
SO <sub>4</sub> <sup>2-</sup>		943.00	
Na		18.50	
Cr		0.04	
Cd Total		0.06	
Pb		0.27	
Ni		0.15	
Cu		0.28	
Cr total		0.04	
Ca		823.00	
Mg		295.00	
K		3,920.00	
Mn		0.35	
Zn		0.23	
DBO		mg L <sup>-1</sup> O <sub>2</sub>	11,133.33
DQO			31,000.00

#### Analytical methods

The effluent samples were immediately transferred to the Soil and Foliar Analysis Laboratory of the Federal University of Goiás (LASF/UFG), and stored in the fridge under 5°C, until further analysis.

The measured variables on undiluted vinasse were determined according to Greenberg et al. (1992) (Table 2). The following measured variables were determined for the effluent samples: dissolved organic matter (DOM) by Walkley-Black wet combustion without heating (Nelson and Sommers, 1996), Fe, Ca and Mg were determined by atomic spectroscopy (Wright and Stuczynski, 1996), Na and K were determined by flame emission spectrometry (Wright and Stuczynski, 1996), NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were determined by steam-distillation method using MgO and Devarda's alloy (Mulvaney, 1996), S-SO<sub>4</sub><sup>2-</sup> was determined by turbidimetry using BaCl<sub>2</sub> (Faithfull, 2002) and pH was measured using electrode method (Thomas, 1996). The determination of chlorine (Cl<sup>-</sup>) was made using a selective electrode performed according to Abreu et al. (2001).

#### Statistical analysis and ion speciation data modeling

The nutrients data were submitted to analysis of variance by the F test (Table 3). The relationships between vinasse doses and time after irrigation within each land use and its influence on the soil solution chemical parameters were obtained through multiple regression tests by general linear model (GLM), using the SAS software (2000). The Visual Minteq v. 3.0 chemical speciation model (Gustafsson, 2007) was used for ion speciation of soil effluent. The modeling took all solution phase measured variables, the Davies equation to calculate the activity coefficients, the Gaussian model of complex for the speciation of the organic matter, and the ionic strength was calculated by the program.

## RESULTS AND DISCUSSION

The analysis of variance (Table 3) indicated there were no significant differences just for the element NO<sub>3</sub><sup>-</sup> in any of the sources of variation assessed. Significant differences in pH and nutrients concentration were observed according to the vinasse doses, DAI, and

**Table 3.** Summary of analysis of variance for the measurable variables on soil solution.

Variation sources	pH	DOM	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	K <sup>+</sup>	Na <sup>+</sup>	Fe <sup>3+</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
	CaCl <sub>2</sub>	mg dm <sup>-3</sup>									
	P > F										
T	*	*	*	*	ns	*	*	*	*	*	*
S	*	ns	ns	*	ns	*	*	*	*	*	*
D	*	ns	*	ns	ns	*	*	*	*	*	*
S × D	*	ns	ns	ns	ns	*	*	*	*	*	*
T × S	*	*	*	*	ns	*	*	*	ns	ns	*
T × D	ns	ns	*	ns	ns	*	*	ns	*	*	*
R <sup>2</sup>	0.72	0.57	0.89	0.38	0.25	0.85	0.90	0.72	0.75	0.92	0.90
CV	5.41	94.33	47.53	9.88	21.18	97.84	31.54	136.29	160.55	61.92	88.92

T: days after application (0, 60, 90, 120 days); S: soil source (savannah; cultivated: crop with 21 years of application); D: doses (0, 300, 600, 1200 m<sup>3</sup> ha<sup>-1</sup>); \*: probability < 0.05; F: test F. DOM: Dissolved organic matter.

land use.

The surface application of vinasse on dystrophic Ferralsols leads to significant changes in the soil solution chemistry and in the percolate, in most cases regardless of the land use and time after vinasse application. On the other hand, the effects of land use and days after irrigation were noticed when the nutrients analysis were done individually. In this case, the responses of the savannah soil were distinct from that of the cultivated soil for most nutrients as discussed below.

Vinasse rates and time showed significant effects over pH on cultivated soil and savannah soil (control), and an interaction effect between these two variables over pH in cultivated areas has been observed (Table 4). However, on cultivated soil with passing of time, an increase on solution pH was observed. This apparently contrasting pH effects observed for the cultivated and savannah soils can be related to soil microorganism's action, which leads to increased pH (Rossetto, 1987; Silva and Ribeiro, 1998). Thus, although the vinasse has acidic character, after a given period of soil reaction along with biological reactions the pH can increase due to microorganism's action. This pH increase was observed for both land uses however at different vinasse doses. As a consequence, the changes in pH may strongly influence the solubility and retention of the ions (Camargo, 1991).

The absence of significant differences in the DOM concentrations for the vinasse doses (Table 3) in both soils may be due to stable binding between clay minerals and organic particles (Bartoli et al., 1992) which would prevent the leaching of organic compounds through the soil column regardless of the amount of applied vinasse. Different DOM retention mechanisms may have influenced the observed changes in DOM through time of incubation. However, it is unclear why the DOM concentration decreased in the savannah soil after 90 days of incubation for all vinasse doses whereas in the cultivated soil there was continuum increase in the DOM concentration (Table 4).

The sugarcane crops demand a high amount of potassium, an element present in several compounds, mostly proteins, and that is part of the chlorophyll, organic acids, and vegetal hormones (Santiago and Rossetto, 2005). Thus, the plant gives a fast response to K application (Rossetto et al., 2004). Rossetto et al. (2004) suggest a critical level of 82.11 mg dm<sup>-3</sup> of potassium in the soil. In this study, the concentration of K in the cultivated soil was 471.12 mg dm<sup>-3</sup> before the application of vinasse treatments, whereas it was 44.85 mg dm<sup>-3</sup> in the savannah soil at 0 to 25 cm depth (Table 1). Thus, the K concentration in the cultivated soil was above the critical level whereas in the savannah soil, initially, it was below that level. This indicates an excess of K in the cultivated soil since the beginning of the experiment and that may have facilitated K leaching. The observed free form of K in the effluent (Figure 2d) may be due to the large concentration of counter ions provided by the vinasse, combined with the pre-existing amount in the soil occupying its charges. It is important to mention that the ion K<sup>+</sup>, found in high concentration in the fresh vinasse (Table 2: 3920 mg dm<sup>-3</sup>), is the element required in great amount by this sugarcane plants and is considered the major environmental problem concerning the byproduct in the ethanol industry (CETESB, 2006). Potassium leaching increased as vinasse application doses and time after application increased, thus suggesting saturation of exchange sites with free K passing through soil profile (Table 4). This result disagrees with Lyra et al. (2003) and Madejón et al. (2001) who worked with a Spodosol, Entisol and Inceptisol, respectively, and found no increase in K leaching after vinasse application. It indicates that the type of tropical soil may influence K leaching after vinasse application.

Although, the vinasse had significant Mg and Ca concentrations (Table 2: 295 mg dm<sup>-3</sup> and 824 mg dm<sup>-3</sup>, respectively) the concentration values observed in the effluent of the cultivated soil were higher than that of

**Table 4.** Regression equations for days after irrigation (T) and vinasse rates (V) for measurable variables on columns effluent on cultivated soil and control (savannah soil).

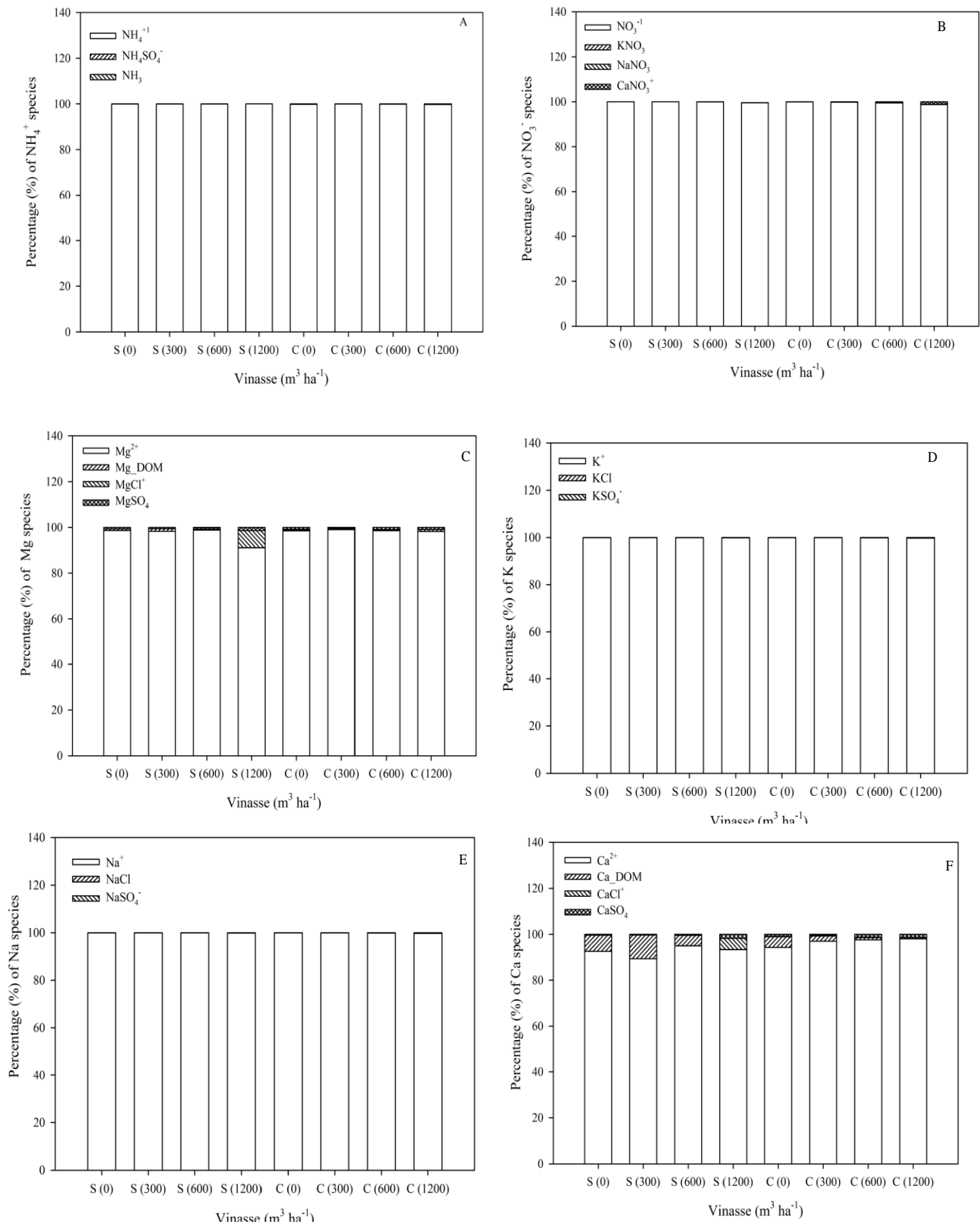
		Equation	R <sup>2</sup>	F	P
pH	Control	6.36-0.01T*+0.001V*+0.00007T <sup>2</sup> *-0.000001V <sup>2</sup> *+0.000002TV	0.61	13.05	0.0001
	Cultivated	6.49+0.009T*-0.002V*-0.0001T <sup>2</sup> *+0.000001V <sup>2</sup> *+0.000006TV*	0.59	11.30	0.0001
Cl <sup>-</sup>	Control	5.74-0.14T*-0.0007V+0.0008T <sup>2</sup> *+0.000002V <sup>2</sup> *-0.000004TV	0.90	69.03	0.0001
	Cultivated	3.09-0.08T*+0.0002V+0.0005T <sup>2</sup> *+0.000001V <sup>2</sup> +0.000005TV	0.67	14.05	0.0001
DOM	Control	0.004+0.0004T*-0.00001V-0.000003T <sup>2</sup> *+0.000000008V <sup>2</sup> -0.00000002TV	0.51	8.81	0.0001
	Cultivated	-0.0001-0.00004T+0.000002V+0.000001T <sup>2</sup> *-0.000000002V <sup>2</sup> +0.00000004TV	0.53	7.78	0.0001
Mg <sup>2+</sup>	Control	2.11+0.11T-0.04V-0.001T <sup>2</sup> +0.00006V <sup>2</sup> *+0.0001TV	0.56	10.26	0.0001
	Cultivated	46.07-1.04T-0.23V*+0.005T <sup>2</sup> +0.0002V <sup>2</sup> *+0.002TV*	0.73	19.58	0.0001
K <sup>+</sup>	Control	-2.92+0.32T*-0.02V+0.002T <sup>2</sup> *+0.00006V <sup>2</sup> *-0.0001TV	0.79	30.01	0.0001
	Cultivated	-15.38+0.47T+0.05V-0.001T <sup>2</sup> +0.00009V <sup>2</sup> *-0.001TV*	0.77	17.30	0.0001
Na <sup>+</sup>	Control	4.39-0.007T-0.002V-0.000004T <sup>2</sup> +0.000005V <sup>2</sup> *+0.00006TV*	0.72	21.62	0.0001
	Cultivated	6.55-0.06T-0.01V+0.0003T <sup>2</sup> +0.00001V <sup>2</sup> *+0.0002TV*	0.58	9.28	0.0001
Ca <sup>2+</sup>	Control	-1.61+0.55T-0.06V-0.005T <sup>2</sup> +0.0001V <sup>2</sup> *-0.00006TV	0.64	14.16	0.0001
	Cultivated	39.03-1.08T-0.12V+0.006T <sup>2</sup> +0.0002V <sup>2</sup> *+0.002TV*	0.88	49.45	0.0001
Fe <sup>3+</sup>	Control	-12.82+45.04T*-4.33V*-0.41T <sup>2</sup> *+0.008V <sup>2</sup> *-0.002TV	0.76	24.57	0.0001
	Cultivated	561.25-6.31T-1.59V*+0.008T <sup>2</sup> +0.001V <sup>2</sup> *+0.02TV*	0.61	10.46	0.0001
SO <sub>4</sub> <sup>2-</sup>	Control	-1.32-0.08T+0.01V+0.001T <sup>2</sup> *+0.000009V <sup>2</sup> -0.0002TV*	0.59	11.30	0.0001
	Cultivated	-4.25+0.05T+0.008V+0.0004T <sup>2</sup> +0.00003V <sup>2</sup> *-0.0002TV	0.65	10.43	0.0001
NH <sub>4</sub> <sup>+</sup>	Control	23.06-0.04T+0.0005V+0.0001T <sup>2</sup> -0.0000005V <sup>2</sup> +0.000002TV	0.30	0.84	0.5500
	Cultivated	21.04-0.07T+0.003V+0.0003T <sup>2</sup> -0.000001V <sup>2</sup> +0.000002TV	0.67	3.67	0.0400
NO <sub>3</sub> <sup>-</sup>	Control	1.48-0.005T-0.00006V+0.00001T <sup>2</sup> -0.0000001V <sup>2</sup> +0.000003TV	0.29	0.82	0.5600
	Cultivated	1.23+0.001T-0.0003V-0.000004T <sup>2</sup> +0.0000003V <sup>2</sup> -0.000001TV	0.29	0.74	0.6100

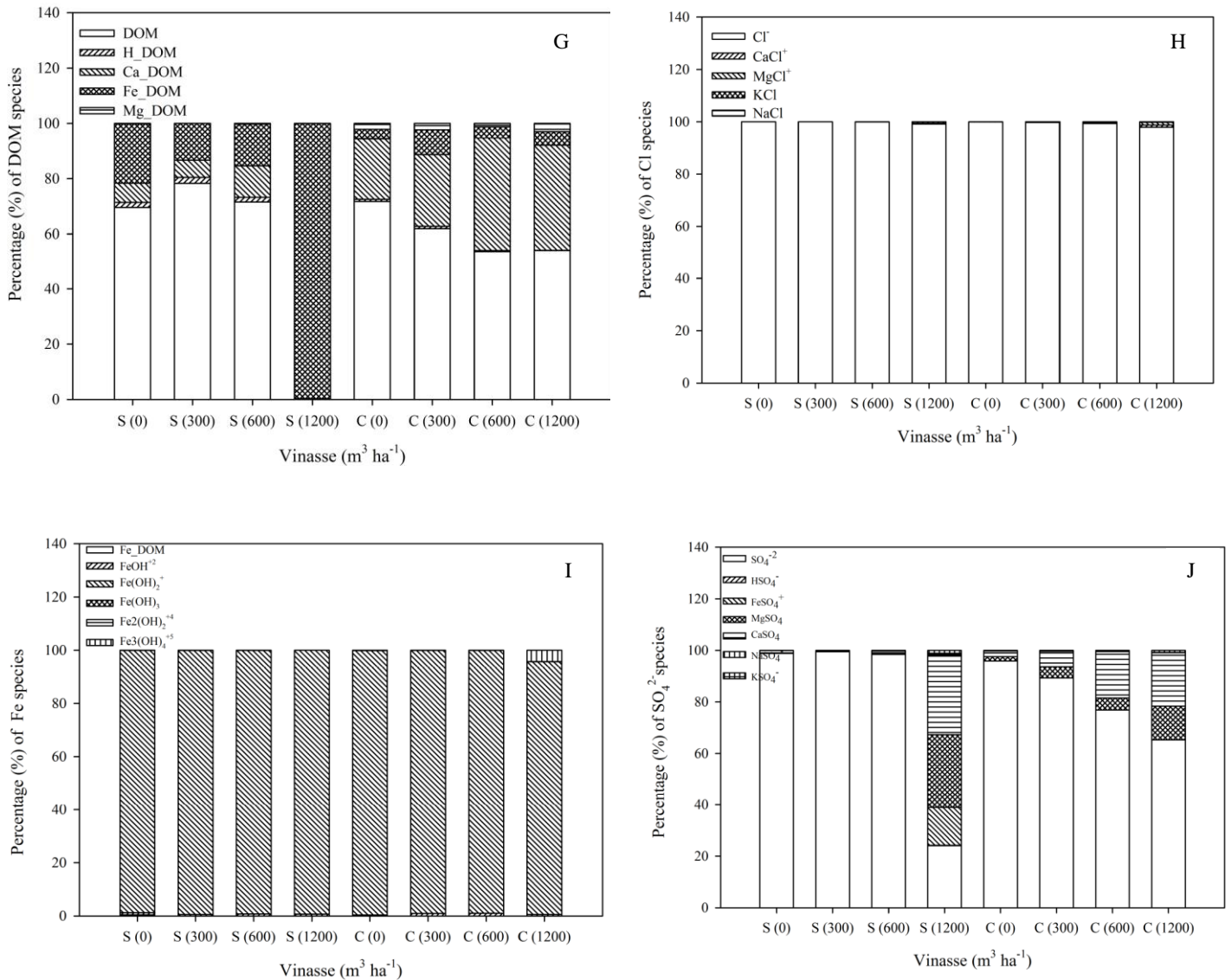
the vinasse (Table 4). We hypothesized that high Mg and Ca concentrations in the effluent may be due to ion displacement from soil exchange sites by the K ions after the application of high doses of vinasse. This result agrees with Gloaguen et al. (2007) who worked with ions leaching from sewage effluent application on a Brazilian dystrophic Ferralsol and found a similar increase in Mg and Ca in the soil effluent. Magnesium is an essential macroelement for the proper development and productivity of the sugarcane crop, and its critical level is of 48.62 mg dm<sup>-3</sup> in the soil (Benedini et al., 2008). The suitable levels of Mg for plant needs, also influences the sugarcane response to the additions of lime and potassium (Rossetto et al., 2004; Silveira et al., 1980). In this study, the savannah soil was the only soil in need for magnesium. In the cultivated soil, as expected, the concentration of magnesium in the soil was around 121 mg dm<sup>-3</sup>. After the fertigation with vinasse, there was an increase in Mg concentrations in the effluent, as the vinasse doses increased. This supports the hypothesis that increase in Mg leaching as free ion was due to the saturation of the ionic exchange complex (475.89, 1416.37, 2404.37 and 19,895.34 mg dm<sup>-3</sup> of Mg in the cultivated soil at doses of 0, 300, 600, and 1200 m<sup>3</sup> ha<sup>-1</sup> of vinasse, respectively). The initial concentration of calcium in the soil did not show problems in terms of

deficiency, since the critical level for the sugarcane crop is between 160.32 and 200.40 mg dm<sup>-3</sup> (Azeredo et al., 1981; Benedini et al., 2008) and that was high for both soils (Table 1). However, the vinasse provided a large amount of this element to the effluent of the columns and there were concentrations well beyond those necessary for the development of the plant. Thus the excess of Ca was leached mainly in the free form (Figure 2d). Also, the high vinasse doses led to the formation of complex ion-organic carbon, such as the observed association Ca-DOM and that may have influenced the fate of DOM molecules.

In agreement with Gloaguen et al. (2007), the increased Na concentration in the leaching with the increase in the vinasse dose may be due to the opening of exchange complex caused by high monovalent ions concentration, Na and K in the vinasse (Table 4). The excess Na was leached after the saturation of soil exchange sites. Through the process of saturation of the soil exchange sites by Na, it is likely that other ions were replaced and released to the soil solution.

According to Klar (1987), the amount of sodium in irrigation water that would not harm the soil in terms of soil sodification, should be less than 69 mg dm<sup>-3</sup>. This element at high concentrations, along with boron, bicarbonate, and chlorine, causes physiological disorders





**Figure 2.** Concentration of ions and organic matter in the soil solution under different uses and vinasse rates ((S): Savannah soil; (C): Cultivated soil). Data from Minteq speciation analysis.

to the plants (Batista et al., 2002). Due to the frequent input of sodium from the use of the vinasse, the concentration of this element in the effluent showed a considerable enhancement as the vinasse doses increased. This behavior indicates that there may be a tendency to soil sodification after vinasse application. In this study, a concentration up to 20.50 mg dm<sup>-3</sup> of Na in the effluent of columns exceeding almost 2 mg dm<sup>-3</sup> that quantity on vinasse (Table 2) was observed, suggesting sodification due to the passage of Na through the 1.20 m of soil profile.

Chlorine concentrations on soil solution were extremely dependent on time (Table 4) and its quantity was higher in the beginning decreasing with time. Vinasse rates had presented a quadratic effect just on control. This behavior

of the chlorine co-ion may be due to the greater counter ion availability in the soil when higher doses of vinasse were used which enabled the formation of molecules thus reducing its concentration in the ionic form and influencing its retention in the soil charges (Figure 2b).

An interesting finding of this study was the high concentration of Fe on solution at the 1200 m<sup>3</sup> ha<sup>-1</sup> vinasse dose, especially on control, where there was observed a quadratic effect of time and vinasse rates on Fe concentration (Table 4). On cultivated soil, an interaction effect between days after irrigation and vinasse rates occurred (Table 4). It was found that the Fe concentration in the vinasse was 27 mg dm<sup>-3</sup> whereas in the effluent from the savannah soil the Fe concentration was about 10,000 mg dm<sup>-3</sup>. Effluent solutions of orange

color and large amounts of Fe deposited (crusts) on the surface of the sampling bottles were observed for the treatments with vinasse doses of 1200 m<sup>3</sup> ha<sup>-1</sup>, regardless of the land use, and this can be explained by iron solubility.

We hypothesize that high vinasse doses could have disrupted soil structure thus solubilizing iron from Fe-oxide minerals in both types of use from this Ferralsol. As a consequence, iron solubility may have caused soil dispersion and that could promote soil structural problems, as reported by Amézketa (1999).

The high SO<sub>4</sub><sup>2-</sup> leaching found at 0 day for cultivated soil was likely because of the replacement of the pre-existing soil solution by fresh effluent, in agreement with Gloaguen et al. (2007). During the first 60 days after irrigation, significant increase in sulfate leaching was observed when the 1200 m<sup>3</sup> ha<sup>-1</sup> vinasse dose was applied probably because of the replacement on mineral particles net charge and sulfates ions free mobility (negative charge ion) in this soil type, which often presents negative charge (Table 4). On cultivated soil with 600 m<sup>3</sup> ha<sup>-1</sup> and on savannah soil with 1200 m<sup>3</sup> ha<sup>-1</sup> was observed an enhancing on calcium sulfate forms (Figure 2f) which can be explained by high free Ca<sup>2+</sup> concentration on effluent from soils treated with high vinasse rates.

Generally, the ions Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were found in the free ionic form in the effluent, regardless of the amount of applied vinasse and land use (Figure 2). The other measured nutrients were bound to other ions in the solution phase. The other ions measured showed a decrease in their percentages of the free form as the vinasse doses increased resulting in a bond increment between other ions of soil solution phase.

## Conclusions

The continuous use of vinasse in the soil may saturate the soil exchange capacity favoring the leaching of ions. The use of vinasse doses at 1200 m<sup>3</sup> ha<sup>-1</sup> leads to significant increases in the levels of calcium and magnesium in the soil thus favoring the formation of complexes with sulfate and chlorine co-ions and with the dissolved organic matter. The leaching of these ions is facilitated by the formation of ionic pairs. Potassium leaching increased as vinasse application doses increased thus suggesting saturation of exchange sites with free K passing through soil profile. Large amounts of vinasse applied to the soil may favor soil dispersion, as evidenced in this study by the substantial increase in iron concentration in the effluent of the columns.

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