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title: **Study of soil contaminated by vinasse applying leach test methods**

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INTRODUCTION

Vinasse is an effluent result from ethanol, buthanol and white rum production (Rezende, 1984). It is produced from sugar cane distillation and fermentation processes along the alcohol and sugar production.

Silva and Orlando Filho (1981) presents a range of vinasse composition (C, pH, N, P, K, Ca, Mg, S, Fe, Cu, Zn and Mn) based on samples collected from several Brazilian sugarcane industries (Table 1). High concentrations in macronutrients and micronutrients, and acidic pH are found in Brazilian vinasses.

Table 1. Range of vinasse composition based on samples from sugarcane industries in Brazil.

Elements	Range	Elements	Range
C	7.53–49.74 g/L	S	0.04–3.42
Macronutrients	g/L	pH	2.8–5.4
N	0.10–1.55	Micronutrients	mg/L
P	0.02–0.77	Fe	15–359
K	0.55–13.00	Cu	0.5–137
Ca	0.09–3.98	Zn	0.62–119
Mg	0.10–1.34	Mn	1.2–16

From: Silva and Orlando Filho (1981).

Thus, vinasse is extremely pollutant due to high values of organic material, low pH, high corrosivity and high rates of biochemical oxygen demand, despite the high temperature (Da Silva et al., 2007).

Brazil is the world largest producer of sugar cane, and the state of São Paulo is responsible for 75% of the national production (UNICA, 2009). In 2009 Brazil produced about 17 billion liters of ethanol. Cortez et al. (1998) reported that vinasse production varies from 10 to 15 liters of vinasse per liter of ethanol produced.

The focus of this work is to apply the leach test and nitric acid lixiviation methods to know different chemical signatures from the behavior of vinasse soil contamination in an old effluent lagoon without impermeable layer.

The study area is situated in Serra Azul municipality, 300 km from São Paulo city. In that area, the Guarani Aquifer System occurs and has from moderate to high indices of vulnerability for groundwater. The vinasse disposal in effluent lagoon happened since the 80's to 2004, where the main land use of the study area was sugar cane plantation. This plantation finished due to the agrarian reform, that originated Sepe Tiaraju rural settlement, the study area.

MATERIALS AND METHODS

A borehole was drilled into this old vinasse disposal lagoon, and 27 samples of soil were collected until 24 meter of depth. Eight samples were selected to analyze soil texture and consistence indexes in the following intervals of depth: 2–3, 6–7, 9.5–10, 12–13, 15–16, 18–19, 20–21 and 23–24 meters. Particle size distribution (ASTM, 1998) tests were carried out; however particle size distribution was also measured without using a soil dispersant so as to highlight some features of the tropical soil tested, as aggregation of the particles.

The percentage of ignition loss (Potts, 1992) was determined in 27 samples according to Potts (1992). The trace elements were determined using x-ray fluorescence spectrometry (XRF) in 27 samples.

Leach tests (Hageman 2007) were executed in 27 soils samples, and cations (Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}) and anions (SO_4^{2-}, NO_3^{-}, NO_2 and F^{-}) were analyzed by ion chromatography (IC). pH, Eh (mV) and electric conductivity (µS/cm) had also measured by portable equipments.

RESULTS AND DISCUSSION

Figure 1 shows granulometric curves of soil samples, with dispersant (WD) and without dispersant (ND) in the tests. These curves presented sand fractions in over than 50%, silt fractions from 16 to 29%, and clay fractions from 8 to 25 % of all depths, indicating that soil profile belongs to Botucatu Formation (a Guarani Aquifer System formation). It can be seen in Figure 1 that clay fractions decrease a long of the depth while the silt and sand fractions increase. From 15-16 m of depth, the curves, with and without dispersant, presented more differences between silt and clay fractions, due to aggregation of these fine particles. Average particle unit weight values were 27.9 kN/m^3.

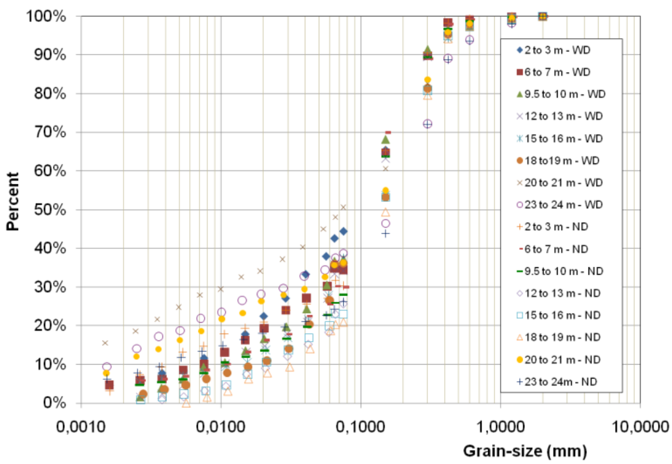

Figure 1. Particle distribution curves obtained using a dispersant (labeled WD) and without using a dispersant (labeled ND).

The results of x-ray fluorescence spectrometry in the soil samples indicate that the percentage of SiO_2 and K_2O is higher in the deepest samples, while the percentage of TiO_2, Al_2O_3, Fe_2O_3, MnO and CaO is higher in the superficial samples. Analyses results also indicated higher concentrations of Zn, V, Zr and Ga in lower depths, decreasing in concentration in deeper profile, and concentrations of Ba, Sr and Pb increasing in concentration along the profile.

Others analyzed elements had presented distribution not related directly to depth. However, all the substances had high concentrations in soil samples, and their excessive amounts could be related to vinasse disposal for years. Detailed studies have been elaborated.

Table 1 presents average, median values of parameters determined by XRF in soils samples.

Table 1. Average, Median, Maximum and Minimum values for elements determined by XRF in soils samples (27 samples collected from 0 to 27 meters depth).

Element/Substance	Average	Median	Max	Min	Element/Substance	Average	Median	Max	Min
SiO_2 (%)	53.97	52.10	70.10	40.60	Ga(μg/g)	17.55	18.50	21.30	10.70
TiO_2(%)	2.96	3.12	3.84	1.73	Mo(μg/g)	3.45	3.30	4.30	2.40
Al_2O_3(%)	23.88	24.40	29.30	17.80	Nb(μg/g)	33.13	33.00	37.00	25.00
Fe_2O_3(%)	11.04	11.70	15.00	5.20	Ni(μg/g)	8.93	9.00	12.00	5.80
MnO(%)	0.05	0.06	0.06	0.03	Pb(μg/g)	13.92	14.10	18.20	8.30
MgO(%)	0.06	0.06	0.07	0.04	Rb(μg/g)	4.65	4.15	7.30	2.10
CaO(%)	0.08	0.08	0.15	0.05	*S(μg/g)	173.04	122.00	365.00	61.00
Na_2O(%)	0.06	0.06	0.06	0.05	Sn(μg/g)	4.97	4.00	6.90	4.00
K_2O(%)	0.08	0.10	0.12	0.02	Sr(μg/g)	42.16	40.00	63.00	23.80
P_2O_5(%)	0.16	0.15	0.24	0.13	Th(μg/g)	12.56	12.40	15.10	8.80
%Loss Ignition	6.74	6.98	9.52	4.29	V(μg/g)	200.19	203.00	264.00	139.00
As(μg/g)	5.24	5.40	5.80	2.50	Y(μg/g)	7.75	7.60	11.40	5.40
Ba(μg/g)	76.05	75.00	120.00	26.30	Zn(μg/g)	35.08	34.00	50.00	22.90
Cr(μg/g)	46.81	46.00	63.00	37.00	Zr(μg/g)	563.96	563.00	637.00	495.00
Cu(μg/g)	35.91	38.00	46.00	19.10					

*S – amount informed

The percentage of loss on ignition indicates the quantity of volatile elements in the sample, mostly CO_2 and water. It could be related to some volatilization of alkaline metals, fluoride and sulfur dioxide. The quantity of volatile elements in the superficial samples is higher than the amount in the deepest samples. The values of ignition loss indicated a percentage decrease along the profile (from 15% to 11%) (Fig. 2).

Leach tests results showed that lower values of electric conductivity (11 μS/cm) in leached solution were found in shallower and deeper samples (0–2 and 22 to 24 m, respectively), and higher values from 2 to 22 meters depth (varying from 18 to 37 μS/cm) (Fig. 2).

Regard to physical-chemical parameters from leached solutions, pH results indicated acidity in the surface (average pH 5.2) and neutral to slightly alkaline in deeper soils (average pH 7.0).

The acidity in soils samples (pH 4.0–4.5) had close association with vinasse disposal (pH 2.8–5.4) (Fig. 3). Eh results (from +105 to -45 mV) indicated oxidant environment in surface samples becoming reduced in deeper samples (Fig. 3).

Higher concentrations of SO_4^{2-} (Fig. 4), NO_3^- (Fig. 5), Ca^{2+} (Fig. 6), Na^+ and Mg^+ (Fig. 7) were found in lower depths (mainly the interval 6 to 9 meter), in oxidant environment, and they decreased in concentration in deeper profile (reduced environment). Fluorine concentrations

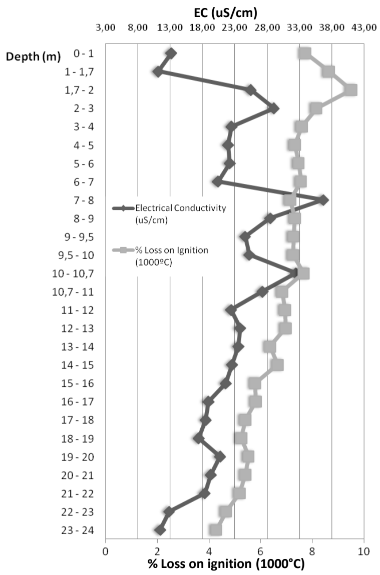

Figure 2. Electric Conductivity (μS/cm) and % Loss on ignition results — leached solutions in depth intervals (m).

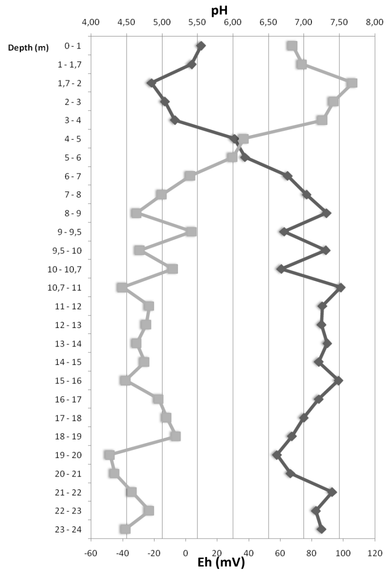

Figure 3. pH and Eh (mV) results — leached solutions in depth intervals (m).

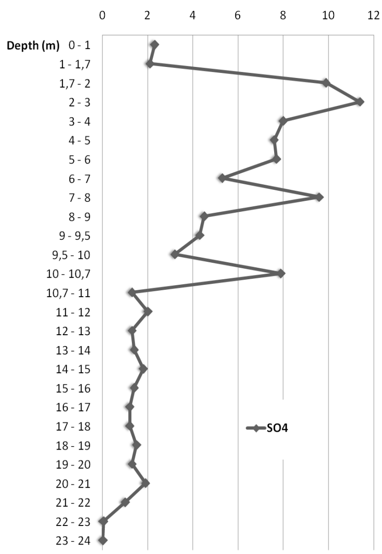

Figure 4. Sulfate concentration distribution — leached solution in depth intervals (m).

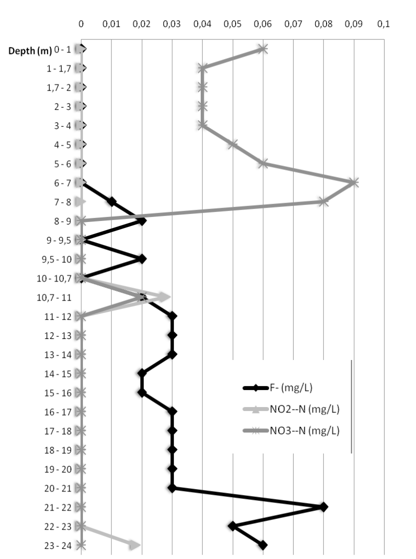

Figure 5. Fluorine, Nitrite and Nitrate concentration distribution in leached solution in depth intervals (m).

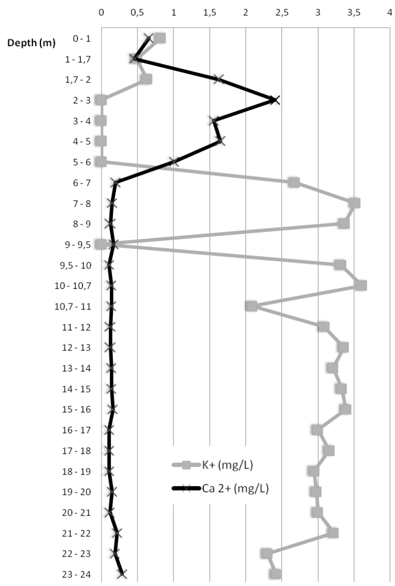

Figure 6. Concentrations of potassium and calcium — leached solutions in depth intervals (m).

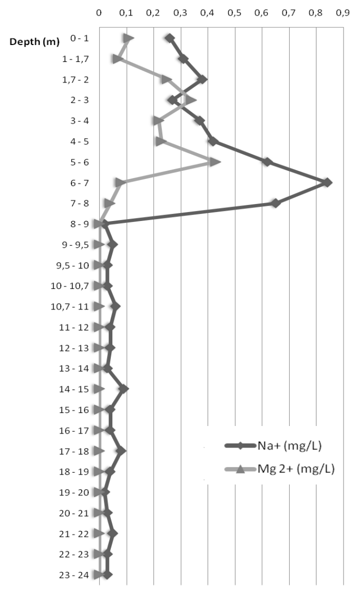

Figure 7. Concentrations of sodium and magnesium — leached solutions in depth intervals (m).

The occurrence of high concentrations of Ca^{2+} (Fig.6), Na^{+} and Mg^{2+} (Fig. 7), from 1.7 to 9.5 m, could indicate the mass of vinasse in soil releasing theses ions to percolation solutions. Concentrations in soils (determined by XRF analysis) had similar distribution in depth

K^{+} distribution had augmentation in deeper samples (Fig. 6). Analysis results by XRF indicated that potassium concentration also increase in deeper samples. According to Da Silva et al. (2007), mineral and organics elements, mainly potassium and nitrate, could be leached when disposed vinasse volume is higher than the soil capacity of ion retention. Bebe et al. (2009) reported that potassium had increased in all soils depth when they were fertirrigated by vinasse, regardless periods and time of applications.

CONCLUSION

The behavior of solutions leached from soil samples indicated that the soil had been presented vinasse (or its altered product) along the profile (24 meters depth). Silty-clayey sands were defined for all depth and were weathering material from Guarani Aquifer sandstones.

The high concentrations of all elements analyzed in soils by XRF indicated vinasse presence in all depth of the borehole studied.

The leach test method showed elements distribution tendencies along the profile. This method defined two distinct oxi-reduction zones: one oxidized zone from 0–7 meters, acid pH and positive Eh leached solutions, grading to reduced zone (from 8 to 24 meters), with neutral pH and negative Eh leached solutions. $SO_4^{\ 2-}$ presence in shallower depth and others oxidized elements could be reduced in deeper profile and then, its concentrations decreased. Na^{+}, Mg^{2+} and Ca^{2+} in shallow depth could indicate presence of specific clays or organic material, which hold theses ions in first meters of depth, or presence of vinasse.

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