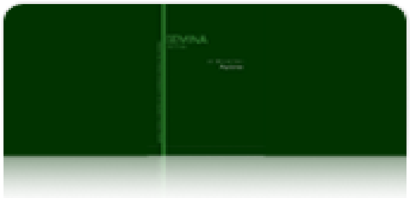

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Factors affecting clay dispersion in Oxisols treated with vinasse

Fatores afetando a dispersão de argila de Latossolos tratados com vinhaça

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Abstract

Vinasse is a potassium-rich waste generated in large amounts by the ethanol production that, applied in the soil, can promote changes in water dispersible clay and in its physical quality. The aim of this study was to evaluate the clay dispersion of Oxisols after vinasse application and correlate it with some chemical attributes. Samples were collected in two Oxisols (155 and 471 g of clay kg^{-1}), put in pots, received dosages of vinasse (0, 50, 100, 150 and 200 m^3 ha^{-1}) and remained incubated during 120 days. Phosphorous, organic carbon, pH H_2O, pH KCl, pH $CaCl_2$, Al^{3+}, $H+Al^{3+}$, Ca^{2+}, Mg^{2+}, K^+, Na^+, ΔpH and the proportion between monovalent and bivalent cations have been evaluated and correlated with the clay flocculation degree. Vinasse changed almost all chemical variables in both soils and increased the flocculation in the sandy soil, but did not change the clayey one. ΔpH, Mg^{2+} and K^+ significantly correlated with the flocculation degree in the sandy soil. It is possible to conclude that the dispersive effect of K^+ added by vinasse are irrelevant, considering the flocculant effect caused by the increment in Mg^{2+} and ΔpH after vinasse application.
Key words: Clay flocculation. Soil quality. Waste disposal.

Resumo

A vinhaça é um resíduo rico em potássio gerado em grandes quantidades pela produção de etanol que, aplicada ao solo, pode promover mudanças na dispersão de argila em água e em sua qualidade física. O objetivo desse estudo foi avaliar a dispersão de argila em Latossolos após a aplicação de vinhaça e correlacioná-la com alguns atributos químicos. Amostras foram coletadas em dois Latossolos (155 e 471 g de argila kg^{-1}), alocadas em vasos e permaneceram incubados por 120 dias após receberem doses de vinhaça (0, 50, 100, 150 e 200 m^3 ha^{-1}). O fósforo, carbono orgânico, pH H_2O, pH KCl, pH $CaCl_2$, Al^{3+}, $H+Al^{3+}$, Ca^{2+}, Mg^{2+}, K^+, Na^+, ΔpH e a proporção entre os cátions monovalentes e bivalentes foram avaliados e posteriormente correlacionados com o grau de floculação de argila. A vinhaça alterou quase todos as variáveis químicas em ambos os solos e aumentou a floculação no solo arenoso, mas não causou mudanças no argiloso. O ΔpH, Mg^{2+} e o K^+ se correlacionaram significativamente com o grau de floculação no solo arenoso. É possível concluir que o efeito dispersivo do K^+ adicionado pela vinhaça são irrelevantes, considerando o efeito floculante causado pelo incremento no conteúdo de Mg^{2+} e no ΔpH após a aplicação de vinhaça.
Palavras-chave: Floculação de argila. Qualidade do solo. Disposição de resíduo.

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Introduction

According to the survey conducted by the National Supply Company the 2016/17 production of sugar-cane will reach approximately 691,000,000 Kg (CONAB, 2016). Ethanol production is estimated in 30.3 billion litters. For each litter of ethanol produced, 13 litters of vinasse are generated (BARROS et al., 2010). Therefore, the generation of 393.9 billion liters of vinasse is estimated in Brazil for this period.

The major use of this residue is as a source of nutrients and organic matter for the soil by fertigation (CAMILOTTI et al., 2006). Some vinasse effects are well known, as pH changes, increment in organic carbon, cation exchange capacity, microbiological activity and improvement of some physical attributes (CHERUBIN et al., 2015; FUESS et al., 2014; RIBEIRO et al., 2011, 2012). Therefore, considering the variety of Brazilian soils, there is a lack of studies related to the behavior of this residue on the physical and electrochemical changes it can promote.

The water dispersible clay content is relatively sensitive to chemical changes and the determination of factors which affect dispersion is extremely useful for the guidance of management to be adopted, aiming to either increase or maintain the soil physical quality.

Organic compounds, charges in mineral particles and adsorbed cations can affect the stability of a clay suspension, changing the stability of aggregates, which are important for the maintenance of soil physical quality (RIBEIRO et al., 2013; SILVA et al., 2006; VICENTE et al., 2012). Clay flocculation is the initial process of soil aggregation and is mainly affected by electrostatic forces (CARDOSO et al., 2013; CHOROM; RENGASAMY, 1995). Organic matter also influences flocculation, or by the formation of bridges between particles, favoring their union or increasing the density of negative charges, favoring repulsion in electronegative soils and reducing its structural stability (LEE et al., 2015; PLAZA et al., 2015).

The hypothesis is that vinasse will affect clay dispersion due to variations in chemicals attributes. So, the aim of this study was to evaluate the clay dispersion of Oxisols after vinasse application and correlate it with some chemical attributes.

Material and Methods

Soil samples were collected on the superficial layer (0.00 – 0.20 m), 0.40 m from sugar-cane planting line in two areas of Oxisol with distinct texture (Table 1). In both areas, 400 kg ha^{-1} of 25–00–25 (N–P_2O_5–K_2O) fertilizer was applied in the ratoon.

Table 1. Physical and chemical attributes of Oxisols samples collected before the experiment.

Soil	Clay	C	Fe_2O_3 ^{A}	pH	Al^{3+}	Ca^{2+}	Mg^{2+}	K^+	P	ΔpH
	------- (g kg^{-1}) -------			H_2O	------ (cmol$_c$ kg^{-1}) ------				(mg kg^{-1})	
Sandy	155.00	6.95	22.08	5.75	0.02	1.39	0.66	0.10	9.71	-1.16
Clayey	471.00	12.18	106.16	6.49	0.00	5.66	1.98	0.15	3.22	-0.80

Analysis according to EMBRAPA (1997) $^A Fe_2O_3$: grams of iron oxide in clay fraction per kilogram of soil. Iron oxides dissolved by sodium dithionite-citrate-bicarbonate. ΔpH = pH KCl – pH H_2O.

The used vinasse was collected in the outlet pipe of the distillery to the distribution pond, in a sugar-cane mill located in Maracaí, São Paulo, Brazil. Its chemical composition is situated in Table 2.

The experiment was performed in plastic pots with 1 kg of soil. The treatments consisted of vinasse dosages: 0, 50, 100, 150 and 200 m^3 ha^{-1} with 6 repetitions in a completely randomized design. Pots were irrigated until the limit field capacity and remained incubated for 120 days.

Table 2. Physical and chemical attributes of Oxisols samples collected before the experiment[a].

pH	N	OM	P_2O_5	CaO	MgO	S	K_2O
H_2O	----------	----------	----------	($kg\ m^{-3}$)	----------	----------	----------
4.00	0.70	8.76	0.11	1.61	0.92	0.62	2.86

After incubation, samples were collected for clay dispersion and chemical analysis according to EMBRAPA (1997). Water dispersible clay was quantified after 1-hour agitation at 200 RPM in horizontal orbital shaker according to Stokes' Law (BARRAL et al., 1998; MELO et al., 2015). The flocculation degree (FD) was calculated as indicated in Eq. 1. Total clay was obtained by shaking 20 g of soil with 100 mL of 0.1 mol L^{-1} NaOH solution during 16 h at 200 RPM. Organic carbon was determined after being oxidized by potassium dichromate and titrated with $FeSO_4$; phosphorous, K^+ and Na^+ were extracted with MEHLICH-1 (1:10) and determined in spectrophotometer for phosphorous and photometer for K^+ and Na^+; pHs determined in 1:2.5 soil: solutions ratio of H_2O (distilled water), $CaCl_2$ 0.01 M and KCl 1 M; Al^{3+}, Ca^{2+} and Mg^{2+} were extracted with KCl 1 M (1:10) and determined by titration with NaOH 0.01 M for Al^{3+} and EDTA 0.025 M for Ca^{2+} and Mg^{2+}. ΔpH was calculated according to Mekaru and Uehara (1979) (Eq. 2).

$$FD\ (g\ kg^{-1}) = \frac{(WDC - TC)}{TC} \qquad (1)$$

Where: WDC – water dispersible clay, TC – total clay.

$$\Delta pH = pH\ KCl - pH\ H_2O \qquad (2)$$

The data was tested for residues normality by Shapiro-Wilk test and for homogeneity of variances by Levene test. Box-Cox transformation was used for variables that did not met the ANOVA assumptions and, in case of transformation ineffectiveness, the Kruskal-Wallis test was performed.

Statistical analyses were performed in R software. The package "car" was used for Levene test; the package "MASS" for Box-Cox transformation; "ExpDes.pr" was used for ANOVA and polynomial regression; and "Agricolae" for the Kruskal-Wallis test and for the Spearman's correlation.

Results and Discussion

The results and the statistical differences are show in Table 3.

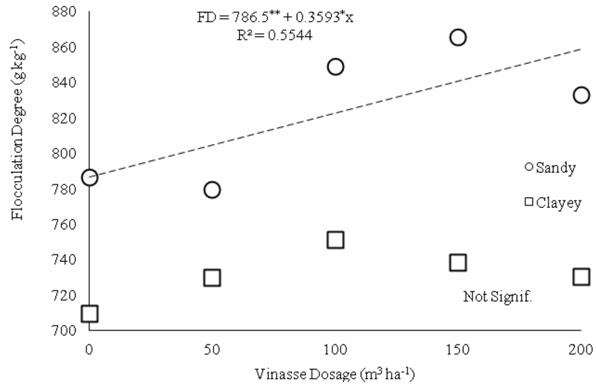
Almost all variables from sandy soil changed, except for organic carbon. In clayey soil, less variables were affected by vinasse application. The Flocculation degree was incremented in sandy soil and statistically did not change in the clayey one (Table 3 and Figure 1).

Table 3. Results and statistical differences for the evaluated variables in function of vinasse dosages in to Oxisols.

Soil	Dosage	FD	P	C	pH			Al^{3+}	$H+Al^{3+}$	Ca^{2+}	Mg^{2+}	K^+	Na^+	1+/2+	ΔpH
					$CaCl_2$	H_2O	KCl								
	($m^3\ ha^{-1}$)	------- ($g\ kg^{-1}$) -------						----------------- ($cmol_c\ kg^{-1}$) -----------------							
Sandy	0	786.0 BC	8.45 A	6.93 A	4.98 D^B	5.83 C^A	4.67 C^B	0.02	3.38 A^B	1.18 C	0.54 D	0.11 E^B	0.00 C^B	0.06 C	-1.17 C^A
	50	779.3 C	6.33 B	7.48 A	5.87 C	6.28 B	5.83 B	0.00	2.67 B	2.32 B	0.65 C	0.40 D	10.00 B	3.50 B	-0.45 B
	100	848.8 AB	6.40 B	7.82 A	6.00 B	6.33 AB	6.00 AB	0.00	2.54 C	2.56 A	0.82 B	0.73 C	10.00 B	3.18 B	-0.33 A
	150	865.2 A	5.98 B	7.32 A	6.08 AB	6.38 AB	6.07 A	0.00	2.51 C	2.48 AB	0.88 AB	1.14 B	10.00 B	3.36 B	-0.32 A
	200	832.9 ABC	6.22 B	7.26 A	6.10 A	6.40 A	6.10 A	0.00	2.54 C	2.46 AB	0.97 A	1.25 A	18.33 A	5.67 A	-0.30 A
	CV (%)	6.49	13.35	7.46	1.24	23.69	2.61	NaN	3.30	7.51	9.73	8.17	18.89	15.74	35.92
Clayey	0	709.3 A	3.34 A	12.24 A	5.92 E^B	6.50 A	5.70 B^B	0.00	3.42 A^B	5.71 A	1.72 D	0.18 E^B	0.00 C^B	0.02 C	-0.80 BC^B
	50	729.3 A	3.33 A	11.22 B	6.10 D	6.52 A	5.83 B	0.00	3.25 B	5.53 A	1.76 CD	0.37 D	10.00 B	1.43 B	-0.68 B
	100	750.8 A	3.43 A	10.91 B	6.18 C	6.53 A	5.67 B	0.00	3.17 BC	5.76 A	1.87 BC	0.68 C	10.00 B	1.41 B	-0.87 C
	150	738.1 A	3.73 A	10.75 B	6.25 B	6.57 A	6.03 A	0.00	3.10 C	5.91 A	1.99 AB	1.00 B	10.00 B	1.40 B	-0.53 A
	200	729.9 A	4.12 A	10.51 B	6.33 A	6.60 A	6.13 A	0.00	3.10 C	5.84 A	2.01 A	1.13 A	20.00 A	2.70 A	-0.47 A
	CV (%)	3.81	16.06	5.45	0.69	0.94	2.53	NaN	3.08	6.16	5.64	7.97	15.12	6.99	18.12

CV: Coefficient of Variation. FD: flocculation degree, P: phosphorous-MEHLICH-1, C: organic carbon. 1+/2+: ratio between monovalent and bivalent catios ($K^+ + Na^+$) / ($Ca^{2+} + Mg^{2+}$). [A] evaluated by ANOVA using transformed variables. [B] evaluated by Kruskal-Wallis test. NaN: not analyzed.

Figure 1. Flocculation degree in two Oxisols in function of vinasse dosages.



*Significant at 5%, ** Significant at 1%.

Excess of surface charges is one of the major factors affecting clay dispersion (CHOROM; RENGASAMY, 1995). When the pH gets closer to the isoelectric point of particles, the charge excess is reduced. The lower number of negative charges demands less amounts of cations to balance them, resulting in a thinner electric double layer (MAHANTA et al., 2014). Therefore, repulsive forces between particles are suppressed, favoring flocculation. ΔpH measures charges excess and was the variable that better correlated with the flocculation degree of the sandy soil (Table 4).

The surface charge variation in sandy soil was considerably higher than in clayey soil probably due to its smaller buffering capacity, caused by the granulometric difference (Figure 2, Table 1). ΔpH tended to zero in both soils.

Iron oxides are known flocculant agents and their higher content may also have contributed to the absence of response in clayey soil (Table 1) (RIBEIRO et al., 2013). It is known in the pH $CaCl_2$ range of this experiment (4.98 – 6.33) that iron oxides have net positive charge and the presence of particles of opposed charges favors flocculation, because there is no electrostatic barrier between them to keep the system dispersed (TREFALT et al., 2014).

Mg^{2+} and K^{+} also correlated with the flocculation degree in sandy soil. Mg^{2+} is a flocculant ion due to its relatively high capacity to compress the electric double layer, explaining the positive coefficient (Table 4) (ARIENZO et al., 2012; MAHANTA et al., 2012; RENGASAMY; MARCHUK, 2011).

K^{+} is a dispersant ion and the positive correlation with flocculation degree was not expected (MARCHUK et al., 2012; MARCHUK; RENGASAMY, 2012). This probably happened due to the impossibility to isolate the factors affecting clay flocculation when vinasse is applied. The correlations between the explanatory variables are shown in Table 5.

The high correlation between the explanatory variables was advantageous because it allowed the observation of which effect is predominant when the ΔpH, Mg^{2+} and K^{+} are increased. The increase in K^{+} was not enough to reduce the flocculation of the clays when the ΔpH and Mg^{2+} are also increased by applying vinasse.

Table 4. Spearman correlation coefficient (Rs) between flocculation degree and the evaluated chemical variables.

Soil	Statistic	Phosp.	C	pH CaCl2	pH H2O	pH KCl	Al^{3+}	$H+Al^{3+}$	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	1+/2+	ΔpH
Sandy	Rs	-0.1376	-0.0098	0.3088	0.0007	0.2958	-0.0275	-0.2421	0.2637	0.3968	0.3757	0.2846	0.2063	0.5096
	p-value	0.4684	0.9590	0.0968	0.9970	0.1124	0.8852	0.1974	0.1591	**0.0299***	**0.0408***	0.1275	0.2741	**0.0040****
Clayey	Rs	0.1791	-0.1520	0.2039	0.1238	0.1234	NaN	-0.2733	0.1896	0.2409	0.2076	0.1949	0.0598	0.1374
	p-value	0.3438	0.4225	0.2799	0.5147	0.5158	NaN	0.1439	0.3157	0.1997	0.2709	0.3021	0.7534	0.4692

Phosp: phosphorous-MEHLICH-1, C: total organic carbon, 1+/2+: ratio between monovalent and bivalent catios (K^{+} + Na^{+}) / (Ca^{2+} + Mg^{2+}). *, ** Significant at 5% and 1%, respectively.

Table 5. Spearman correlation coefficient (Rs) between the explanatory variables that correlated with flocculation degree in sandy soil.

Variable	Statistic	ΔpH	Mg^{2+}
Mg^{2+}	Rs	0.7818	-----------
	p-value	$<0.001^{***}$	-----------
K^{+}	Rs	0.8094	0.9309
	p-value	$<0.001^{***}$	$<0.001^{***}$

** Significant at 0.1%.

Conclusions

Only the sandy soil was responsive to the application of vinasse and the ΔpH, Mg^{2+}, K^{+} correlated with the flocculation degree. The high dependence of these variables allows us to infer that the dispersive effect expected by the increase in K^{+} was overlapped by the flocculant effect arising from changes in ΔpH and Mg^{+}. Thus, vinasse increased flocculation, even increasing the levels of K^{+} in the sandy soil.

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