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BIOTECHNOLOGY

Influence of sugarcane variety and management on the mineral composition of vinasse from alembic cachaça

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ABSTRACT. Vinasse is the main waste of the productive activity of fermentative processes for ethanol and cachaça production due to the large volume generated, but little is known about the composition of vinasse from alembic cachaça. The present study evaluated the influence of the sugarcane variety (RB867515, RB966928 and RB855453) and management (conventional and organic) on the mineral composition of vinasse from alembic cachaça in a randomized block design with four parcels. Vinasse samples were evaluated for pH and concentrations of carbon, nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, copper, manganese and zinc and carbon/ntrogen ratio. There was a significant effect of management only on three elements of the vinasse composition, C, K and Mg. Regarding the variety, there was a significant effect only on Ca and Mg concentrations in the varieties RB867515 and RB855453. The sugarcane variety and management had little influence on the composition of vinasse from alembic cachaça. The average concentration of macro- and micronutrients of the vinasse samples indicates that it can be used in fertigation due to the rich composition in macro- and micronutrients when compared to the cachaça or ethanol vinasse compositions reported in literature, especially N, P, K, Ca, Mg, S, Fe and Cu.

Keywords: organic management; conventional management; macronutrients; micronutrients.

Influência do manejo e da variedade de cana-de-açúcar sobre a composição mineral da vinhaça de cachaça de alambique

RESUMO. A vinhaça é o principal resíduo da atividade produtiva dos processos fermentativos para a produção de etanol e cachaça devido ao volume gerado, no entanto pouco se conhece sobre a composição da vinhaça de cachaça de alambique. O presente trabalho avaliou a influência do manejo (convencional e orgânico) e da variedade (RB867515, RB966928 e RB855453) sobre a composição mineral da vinhaça de cachaça de alambique em experimento com blocos ao acaso com quatro parcelas. As amostras de vinhaça foram avaliadas quanto ao pH e concentrações de carbono, nitrogênio, fósforo, potássio, cálcio, magnésio, enxofre, ferro, cobre, manganês e zinco, e relação C/N. Houve efeito significativo do manejo somente sobre a concentração de três nutrientes da composição da vinhaça: C, K e Mg. Em relação à variedade, houve efeito significativo somente nos teores de Ca e Mg nas variedades RB867515 e RB855453. O manejo da cana e a variedade tiveram pouco efeito sobre a composição da vinhaça de cachaça de alambique. A concentração média de macro e micronutrientes das amostras de vinhaça de cachaça de alambique a torna fortemente recomendável para uso em fertirrigação devido à composição rica em macro e micronutrientes quando comparada à composição da vinhaça de cachaça ou de bioetanol relatada na literatura, destacando-se N, P, K, Ca, Mg, S, Fe e Cu.

Palavras-chave: manejo orgânico; manejo convencional; macronutrientes; micronutrientes.

Introduction

Among the sugarcane products, the cachaça production features as a promising activity with a high value aggregation. The cachaça-producing unities are commonly located in rural areas because they demand relevant area for cultivation. A large volume of water is required for this activity, what justifies its installation near water courses. This proximity may aggravate the environmental problems due to the effluent disposal (Rosa & Martins, 2013).

The sugarcane juice extracted after milling sugarcane stalks is fermented by native or selected yeasts of the species *Saccharomyces cerevisiae*. Natural ferment, when the fermentation is initiated by autochthonous yeasts from the sugarcane juice, is a common practice to produce artisanal cachaça

(Gabriel et al., 2012). The fermented must is then distilled to obtain a beverage denominated cachaça, a term exclusively utilized for the beverage derived from Brazilian sugarcane (Brasil, 2005).

Although the historical, cultural and economic context of cachaça, its production is related to several environmental problems especially related to effluents and residues (Menezes, Alves, Valeriano, & Guimarães, 2013; Rosa & Martins, 2013). Vinasse, the main residue originated from distillation, is produced in concentrations ranging from 8 to 10 liters per liter of product (Oliveira, Andrade, Faria, Evangelista, & Morais, 2009), characterized as an acidic suspension, with high chemical oxygen demand, dark brown color and unpleasant odors (Jiang et al., 2012; Christofoletti, Escher, Correia, Marinho & Fontanetti, 2013). It has been considered for several uses as yeast and energy production, recycling for utilization in fermentation, substrate for hydroponics, concentration by evaporation and fertigation (Christofoletti et al., 2013; Santos et al., 2013), which is the most common use due to the rich composition in micro- and macronutrients. An adequate use of vinasse in soils replaces nutrients, increases the agricultural productivity, raises the soil pH, increases the soil water retention, favors the microbial growth and improves the soil structure (Rosa & Martins, 2013). Doses of 300 m^3 ha^{-1} have resulted in higher sugarcane productivity (Aquino, Medina, Brito & Fonseca, 2015). Although the use of vinasse in fertigation is highly recommended for sugarcane crop, its application may result in imbalance in nutrient and cation-exchange capacity, causing changes in soil chemical reactions with leaching of its constituents into groundwater (Aquino et al., 2015). Varying patterns of N_2O emissions by bacteria from vinasse during fertigation were observed by Cassman, Lourenço, Carmo, Cantarella & Kuramae (2018) as well as increase in the emission of greenhouse gases (Moran-Salazar et al., 2016).

The major constituents of vinasse are water, organic matter and potassium, an important plant nutrient. Other elements such as N, P, Ca, Mg, S, Na and Cl are also found in vinasse at lower concentrations (Doelsch, Masion, Cazevieille, & Condom, 2009). The composition of vinasse is quite diverse and varies according to the raw material composition, type of fermentative process, conduction of alcoholic fermentation, yeast strain, type of equipment and distillation process (España-Gamboa et al., 2011).

Vinasse from alembic cachaça contains high concentrations of organic matter, potassium, iron and small portions of other macro- and micronutrients. Studies have demonstrated that the application of vinasse from alembic cachaça with and without nitrogen supplementation results in higher yield of stalks when compared to sugarcane without vinasse application (Oliveira et al., 2009). The small-scale cachaça production is not harmful to the environment regarding the vinasse production and the amount produced can be used for fertigation, animal feed or biogas production (Christofoletti et al., 2013; Bernal, Santos, Silva, Barros, & Ribeiro, 2017).

Vinasse originated from ethanol-producing industries is much better known in its composition due to the widespread use in fertigation. Vinasse from cachaça production has received attention in the last years due to the expansion of the cachaça business, however the content of macro- and micronutrients should be better examined in order to evaluate its potential use in fertigation. In this context, the aim of this study was to evaluate the influence of sugarcane variety and management on the composition of the vinasse obtained after the fermentation process for alembic cachaça production. Our aim was also to discuss its suitability for fertigation by comparing its composition to the vinasses already reported for ethanol and cachaça production.

Material and methods

Experimental area and treatments

The experiment was conducted in an area belonging to the *Centro de Ciências Agrárias, Universidade Federal de São Carlos* - Campus Araras, State of São Paulo, Brazil. Sugarcane was planted in April 2014 in a total area of 3,200 m^2 using a randomized block design with nine treatments (3 sugarcane varieties – RB 867515, RB966928 and RB855453; 3 sugarcane managements – control, organic and conventional) and four replicates (36 parcels). Each parcel consisted of an area of 37.5 m^2, with 5 rows and a spacing of 1.5 per 5.0 m length.

Regarding the management, the following procedures were applied: Control – only the control of spontaneous herbs by manual weeding; Organic – organic fertilizer Visafértil® (81.67 kg $parcel^{-1}$), limestone (PNRT 70, 11.25 kg $parcel^{-1}$) and manual weeding; Conventional – chemical fertilization (22.5 kg 6-30-20, 2.5 kg potassium chloride), limestone (PNRT 70, 11.25 kg $parcel^{-1}$) and control of spontaneous herbs by application of Demolidor® BR (300 mL in 20 L water).

Fermentation

Sugarcane was harvested in August 2015. The stalks were cut manually, separately from each treatment, the straw and the top were removed. The sugarcane juice was extracted by milling, which was cleaned with water, detergent and 70% alcohol before and after each parcel processing. The sugarcane juice was passed through a decanter to take impurities and piths out.

The fermentations were carried out in four 1000-L tanks (250 to 350-L working volume), one for each parcel, each treatment at a time. The fresh baking yeast Itaiquara®, in the proportion of 10 g L^{-1}, was hydrated in warm water before inoculation in the tank. The fermentation was carried out at room temperature (30-35°C) for approximately 48 hours. The initial cell concentration was 10^7-10^8 cells mL^{-1}. After completing the fermentation, the must was distilled in 300 L copper alembics with pre-heater and cooler, discarding the 'head' and 'tail' fractions (around 10% of the initial and final distillate, respectively).

The vinasse was transferred to the storage tank after collecting the samples. Vinasse samples (50 mL) were maintained in plastic bottles at -5°C until analysis.

Sugarcane preparation, fermentation and distillation were carried out at the *Laboratório de Agricultura Orgânica, Centro de Ciências Agrárias, Universidade Federal de São Carlos* - Campus Araras, State of São Paulo, Brazil.

Vinasse analysis

For the analysis of N, P (P_2O_5), K (K_2O), Ca (CaO), Mg (MgO), S (SO_4), Cu, Fe, Mn and Zn, the samples were initially solubilized with concentrated acids. Samples were digested and the following methodologies were utilized to determine the concentration of each nutrient: N, by using the Kjeldahl method; P, by molecular absorption spectroscopy; K, by atomic emission spectroscopy; Ca, Mg, Cu, Zn, Fe and Mn, by atomic absorption spectroscopy; and S, by turbidimetry. C was determined by the colorimetric method with sodium dichromate. pH was measured by potentiometry. Analyses were carried out at the *Laboratório de Química e Fertilidade do Solo, Centro de Ciências Agrárias, Universidade Federal de São Carlos* - Campus Araras, State of São Paulo, Brazil.

Statistical analysis

The results were tested by analysis of variance to check for the effect of the varieties and management on the vinasse composition. When the means differed significantly at 5% of significance, Tukey's test was applied to compare the means. The software *Assistat* 7.6 (Silva, 2016) was used for statistical analysis. The results were transformed as follows: C, to Arcsen $\sqrt{x/100}$; N, to X + 5; Fe, Cu and C/N, to log X; P, to X + 1; K, to X + 5; Ca, Mn and S, to $\sqrt{X}$; Mg, to Sen X; Zn, to $1/\sqrt{X}$.

Results and discussion

There was effect of sugarcane management only on six nutrients of the vinasse: C, K, Ca, Mg, S and Mn, Tables 1 and 2. Comparing only between organic and conventional managements, higher concentrations were observed in the conventional management for C, Mg and K (Figure 1). Concerning the sugarcane variety, there was a significant effect only regarding Ca and Mg, featuring the varieties RB867515 and RB855453 (Table 1, Figure 2).

Sugarcane management had little impact on the vinasse composition. Conventional management resulted in significantly higher concentrations of some nutrients than organic management probably because of the fast and ready availability of nutrients to the plants, which enriched the vinasse composition. A long-term experiment may have showed better results for the organic management due to the incorporation of organic matter to the soil.

Table 1. Summary of analysis of variance for the concentrations of macronutrients determined in vinasse samples from cachaça produced with distinct sugarcane varieties under different managements.

Analysis	Sources of variation				Variation Range[1]	CV (%)
	Management (M)	Variety (V)	Interaction (M x V)	Blocks		
DF	2	2	4	3	-	-
pH	1.3045 ns	0.3506 ns	1.8027 ns	0.9766 ns	3.68 - 4.30	11.18
C (kg m^{-3})	5.8221**	2.8417 ns	1.9663 ns	2.0927 ns	8.53 - 19.95	16.99
N (kg m^{-3})	1.3077 ns	0.1109 ns	0.5995 ns	0.3157 ns	0.48 - 1.35	10.68
C/N	2.2854 ns	0.2811 ns	0.8199 ns	0.8055 ns	12.58 - 36.42	25.39
P (kg m^{-3})	1.7565 ns	2.8757 ns	1.0179 ns	0.3229 ns	0.09 - 0.47	16.56
K (kg m^{-3})	3.4509*	0.4985 ns	2.3253 ns	10.8817**	0.94 - 2.43	10.56
Ca (kg m^{-3})	4.0171*	4.2795*	0.6029 ns	0.6829 ns	1.17 - 3.42	27.68
Mg (kg m^{-3})	3.7491*	7.4244**	0.7137 ns	1.0106 ns	1.84 - 3.64	26.86
S (kg m^{-3})	3.5158*	2.0393 ns	1.7275 ns	4.6510*	0.55 - 1.51	19.01

[1]The lowest and the highest mean value among the vinasse samples regardless the management and variety; DF: Degrees of freedom; CV: Coefficient of variation; *Significant at 0.05 probability level by F-test; **Significant at 0.01 probability level by F-test; ns: non-significant.

Table 2. Summary of analysis of variance for the concentrations of micronutrients determined in the vinasse samples from cachaça produced with distinct sugarcane varieties under different managements.

Analysis	Sources of variation				Variation Range[1]	CV (%)
	Management (M)	Variety (V)	Interaction (M x V)	Blocks		
DF	2	2	4	3	-	-
Fe (ppm)	0.6683 ns	0.2100 ns	1.1768 ns	1.7976 ns	31.03 – 93.52	17.66
Cu (ppm)	1.9039 ns	1.7089 ns	0.9270 ns	13.3789**	25.46 – 100.21	14.76
Mn (ppm)	4.2128*	2.1271 ns	0.5566 ns	1.5474 ns	1.30 – 4.72	29.84
Zn (ppm)	1.1342 ns	0.0807 ns	0.4119 ns	4.0190*	2.79 – 6.70	29.18

[1]The lowest and the highest mean value among the vinasse samples regardless the management and variety; DF: Degrees of freedom; CV: Coefficient of variation; *Significant at 0.05 probability level by F-test; **Significant at 0.01 probability level by F-test; ns: non-significant.

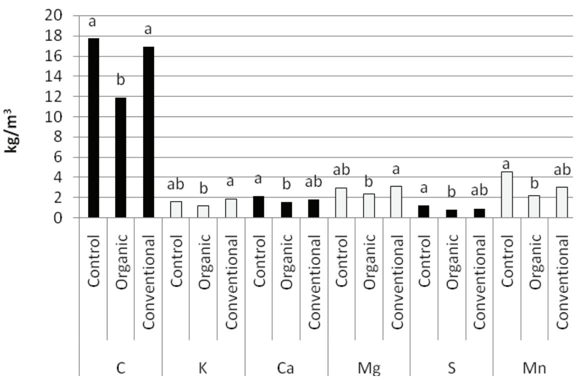

Figure 1. Average concentrations of C, K, Ca, Mg, S and Mn in vinasses obtained under distinct sugarcane managements. Means followed by different letters, for each nutrient, are significantly different by Tukey's test at 0.05 probability level.

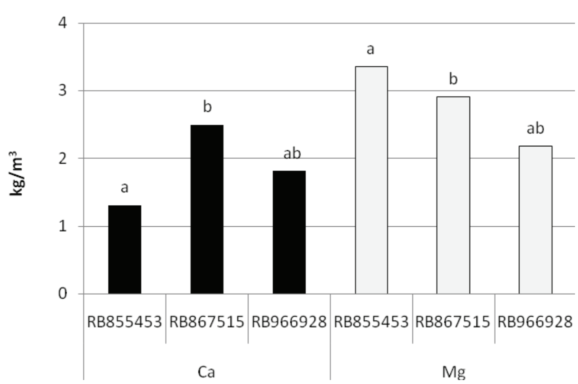

Figure 2. Average concentrations of Ca and Mg in vinasses obtained under distinct sugarcane varieties. Means followed by different letters, for each nutrient, are significantly different by Tukey's test at 0.05 probability level.

The sugarcane variety RB966928 here studied has been one of the most planted cultivar in the last years in Brazil. It is an early to medium maturing sugarcane cultivar (Daros et al., 2010) as well as RB855453 (Leite, Crusciol, Silva, Venturini Filho, & Suriano, 2009). From our results, only a punctual effect of the sugarcane variety on Ca and Mg concentrations in vinasse has been observed. No previous report has been found associating sugarcane variety or management with vinasse composition, which certainly has been demanded in order to assess the contributions of these variables to the by-product composition in the cachaça industry.

The main chemical components of vinasse are K, N, Ca and Mg, but K is the most important nutrient as this residue is considered for agricultural use. The Brazilian laws require a K balance to assess the amount of vinasse to be applied in sugarcane fields. The application of vinasse is controlled by the amount of K_2O applied, and the measure of K_2O in the soil before the application is required (Rein, 2011). Estimated doses of 142 - 174 m^3 of vinasse per hectare with potassium levels of 0.73 - 0.88 kg m^{-3} increased the stalk yield of sugarcane (Oliveira et al., 2009). In our study, a range of 0.94 to 2.43 kg m^{-3} was observed regardless of sugarcane variety and management (Table 1). Therefore, the potassium requirements of sugarcane can be supplied by adequate vinasse application (Rein, 2011), and considering the alembic cachaça vinasse here studied, the highest concentration of K was found under conventional sugarcane management (Figure 1). It is also noteworthy that K concentration in our vinasse samples is higher than K concentration obtained by Margarido et al. (2010) and Oliveira et al. (2009) for alembic cachaça vinasse (0.46; 0.73-0.88 kg m^{-3}, respectively).

Sugarcane vinasse is reported to be deficient in nitrogen in comparison to vinasse derived from sugar beet (Parnaudeau, Condom, Oliver, Cazevieille, & Recous, 2008). The concentration of N in our vinasse samples varied from 0.48 to 1.35 kg m^{-3} (Table 1), which is much higher than the concentrations reported for alembic vinasse by Margarido et al. (2010) and Oliveira et al. (2009), 0.28 and 0.23-0.33 kg m^{-3}, respectively. Regarding vinasse from bioethanol production, the concentration of N obtained in the present study is similar to that of vinasse from molasses (Rocha, Lora & Venturini, 2008) but higher than the vinasse from sugarcane juice (Rocha et al., 2008; Oliveira et al., 2009).

Other nutrients that featured in our alembic vinasse samples compared to results in the literature for alembic vinasse (Oliveira et al., 2009; Margarido et al., 2010) and bioethanol vinasse (Rocha et al., 2008; Mariano, Crivelaro, Angelis & Bonotto, 2009; Silva, Bono & Pereira, 2014) were P, Ca, Mg, S, Fe and Cu. Fuess, Rodrigues, & Garcia (2017) observed both priority pollutants (Cu, Cr, Ni, Pb and Zn), and phytotoxic elements (Al and Fe) in bioethanol vinasse. For the other nutrients, the concentrations in the alembic vinasse were comparable.

The concentrations of Fe and Cu in the present work reached very high values (31.03-93.52 ppm, 25.46-100.21 ppm, respectively) probably due to the alembic material (copper distiller and iron pipes). The result for Fe was only comparable to Mariano et al. (2009), which indicated a concentration as high as 97.50 ppm for bioethanol vinasse. A more detailed evaluation is required to verify how these concentrations of micronutrients can affect the development of sugarcane in case of using vinasse for fertigation.

Conclusion

The sugarcane variety and management do not significantly alter the mineral composition of vinasse from alembic cachaça. The average concentration of macro- and micronutrients of the vinasse samples indicates that it can be used in fertigation due to the rich composition in macro- and micronutrients when compared to the cachaça or ethanol vinasse compositions reported in literature, especially N, P, K, Ca, Mg, S, Fe and Cu.

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