



Digested bioenergy byproduct with low concentration of nutrients increased greenhouse gas emissions from soil



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ABSTRACT

This research measured greenhouse gas emissions (GHG) from well-drained soil after using two forms of vinasse (*in natura* and digested) as fertilizer and the interaction of both with urea. Although carbon (C) and nitrogen (N) content in digested vinasse was two times less than in the normal vinasse (part of the N was lost during filtration and used by cellular synthesis of reactor biomass), N₂O emissions were four-fold higher in the treatment with digested vinasse plus urea (302.8 mg N-N₂O m⁻²) than in the treatment with normal vinasse amended with urea (70.9 mg N-N₂O m⁻²). Differently from all the other treatments, digested vinasse alone resulted in positive emissions of CH₄. CO₂ emissions follow vinasse *in natura* > vinasse *in natura* + urea > digested vinasse + urea > urea > control > digested vinasse, contradicting again the paradigm of C availability and N₂O emissions. Many efforts have been made to describe models with an input of nutrients, their availability and N₂O release. It can be concluded that the amount of nutrients is not sufficient and microbiological factors may contribute to improve GHG emission estimates.

1. Introduction

Considering the growing demand for alternatives to fossil fuels, biomass ones are increasingly important in the global economy. According to estimates from the Organisation for Economic Co-operation and Development (OECD), Brazil will increase its ethanol production of sugarcane from 2013 to 2023 to reach 49.7 million m³, corresponding to over 31% of the world's production (158 million m³).

Sugarcane production systems are known for their ability to reduce greenhouse gas (GHG) emissions by replacing gasoline with produced ethanol and energy cogeneration with burning bagasse (Cerri et al., 2010). However, with the expected increase in production in the coming years, there are concerns about the environmental sustainability of the ethanol supply chain (Goldemberg et al., 2008).

The main problems that can be caused by increased ethanol production, according to Goldemberg et al. (2008) are: land-use change, an increase in using inputs and the destination of by-products. Among them, the latter is not least important because for every litre of ethanol produced, approximately 11.3 L of vinasse is generated (Moraes et al., 2014). In other words, in the 2013–2014 harvest, over 305 million m³ of vinasse were generated. Due to its characteristics, the most common use of this by-product is as a fertilizer for sugarcane plantations.

However, the high volume used can cause various environmental impacts (Fuess and Garcia, 2014). Since 2014, the largest sugarcane producers in Brazil have adopted vinasse concentration followed by blending it with minerals and other organic by-products from the food industry. This organic mineral blend can be used at a rate of 5–7 m³ ha⁻¹ and meets the nutritional requirements of sugarcane. This practice may reduce the environmental impacts of vinasse by reducing the area of application and fossil fuel consumption during mineral fertilization and vinasse application.

Among the negative implications of using this by-product in soil, the capacity of GHG emissions was shown by Carmo et al. (2013). In particular, nitrous oxide emissions were observed due to the high content of organic matter, which interacts with the nitrogen added by the by-product itself (Oliveira et al., 2013) or with forms added by mineral fertilizers (Carmo et al., 2013; Siqueira Neto et al., 2016). Pitombo et al. (2016) showed the importance of micro-organisms added to soil and vinasse to produce high GHG emissions.

To reduce GHG emissions produced by the interaction of this by-product with soil, anaerobic treatment of vinasse is an appealing practice as this technology is based on converting its organic load into biogas, thus reducing its potential in relation to GHG emissions and nutrient leaching (Moraes et al., 2014). As vinasse is mainly a source of

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K for sugarcane and this nutrient is not removed through anaerobic digestion, although there are no field experiments which have tested the sugarcane yield, it is assumed that there is no influence on the vinasse fertilization potential after anaerobic digestion (Wilkie et al., 2000).

Studies carried out using residues from other sources show that, in some cases, anaerobic treatments may be an important factor to reduce GHG emissions (Cayuela et al., 2010) because when treated, the residue used in soil adds carbon in a more stable way and is less available for microbial consumption and consequent production of CO₂ and N₂O.

However, there are no quantitative data for these gas emissions measured directly from the soil after vinasse application digested anaerobically in the soil. Thus, as a contribution to the study of GHG emissions by vinasse application in soil, the study described in this article was carried out. Currently, the tools developed to predict the GHG emissions from a system consider the nutrient availability in the media (Ding et al., 2016). Therefore, the hypothesis to be evaluated is that reducing the amount of organic material readily available for microorganisms, by anaerobic digestion, presents a negative effect on microbial activities resulting in lower carbon dioxide and nitrous oxide emissions, leading to a better GHG balance.

2. Material and methods

2.1. Soil

Soil from a 0 to 20 cm layer of Red Latosol (Hapludox), located in the region of São Carlos (São Paulo State), under Cwa climate conditions (humid tropical climate with a rainy summer and dry winter) according to the Köppen Climate Classification was collected. This soil has been in a commercial sugarcane plantation for over 15 years, with a bulk density (BD) of $1.165 \pm 0.07 \text{ g cm}^{-3}$ ($n = 3$), 163, 270 and 568 g kg⁻¹ of sand, silt and clay, respectively; pH (CaCl₂) of 5.2, 13 g kg⁻¹ of organic carbon and 1.4 g kg⁻¹ of total nitrogen. The collected material was dried at 50 °C for five days, and then sieved using a mesh (4 mm).

The dry soil was weighed and, according to its field BD, 4115 kg of soil was used to form the 0 to 20 cm layer in a PVC column (25 cm height × 15 cm diameter) with 2 mm holes spread on the bottom to avoid anaerobic zone formation. The mesocosms were kept in a greenhouse.

The soil column presented a field capacity of $0.3799 \text{ mm}^3 \text{ mm}^{-3}$, measured using a pressure of 0.1 bar. After having been allocated, water was added to reach the soil field capacity and it dried naturally until 53% of its field capacity. The soil was kept for 15 days until treatments were added when the humidity was 60% of its field capacity. Soil moisture was maintained for the 90-day experiment by weighing and sprinkling water daily. Water was added at least 12 h prior to gas sampling to avoid the influence of this event on the gas fluxes.

2.2. Vinasse *in natura* and digested

The vinasse *in natura* was collected from the inlet of a storage pond in an ethanol mill in the region of São Carlos (São Paulo State) 5 h before the fertirrigation operation. The digested vinasse was collected from a pilot-scale up flow anaerobic sludge blanket (UASB) reactor with a capacity of 60 L reaction volume, fed with the same vinasse *in natura* used to fertirrigate the experiment after filtration pre-treatment (3 μm), a volumetric organic load of 17.5 kg Chemical Oxygen Demand (COD) m⁻³ day⁻¹ and a Hydraulic Retention Time (HRT) of 24 h, with a recirculation of 400% and a COD removal capacity ranging between 80% and 90%. Both vinasse *in natura* and digested were chemically and physically characterized (Table 1). Considering the experimental procedure used in this, and in similar research, it was expected to find different nitrogen concentration depending on the treatment to which

Table 1
Characterisation of vinasses used as fertilizer in the experiment.

Vinasses	pH	C-total	N-total	P (P ₂ O ₅)	K (K ₂ O)	Ca	Mg	S	C:N
g·L ⁻¹									
<i>In natura</i>	3.8	6.38	0.31	0.1	1.39	0.47	0.24	0.22	21
Digested	7.7	2.79	0.18	0.07	1.27	0.42	0.22	0.06	15

the vinasse was submitted. Some nitrogen is found in the solid portion of the vinasse, thus filtration removes part of the nitrogen. Filtration of the vinasse may be necessary in some experiments to avoid sedimentation and sludge bed clogging in experimental UASBs. During anaerobic digestion, part of the nitrogen is used for cellular synthesis of the microorganisms of the anaerobic granules.

2.3. Experimental design

The soil columns were numbered from 1 to 24, resulting in four replicates per treatment distributed in a completely randomized design along a bench in a greenhouse.

There were six treatments combining organic and inorganic fertilizers as follows: control; vinasse *in natura*; digested vinasse; urea; vinasse *in natura* plus urea; and digested vinasse plus urea. In the control treatment, there was no fertilizer application. In treatments where there was only vinasse application, the dosage was equivalent to the maximum recommended without splitting by CETESB (150 m³ ha⁻¹); where urea was added, the dosage was 100 kg N ha⁻¹; where nitrogen was added by mineral fertilizers or by blending the vinasse with urea. In treatments where there was no addition of liquid effluent, the same volume of water was added so that the soil moisture was not different between treatments. The vinasse *in natura* and digested vinasse added to the soil an amount of 47 kg N ha⁻¹ and 957 kg C ha⁻¹, 27 kg N ha⁻¹ and 419 kg C ha⁻¹, respectively, urea added 100 kg N ha⁻¹, vinasse *in natura* and digested were supplemented with 53 kg N ha⁻¹ and 73 kg N ha⁻¹ from urea, respectively to complete the 100 kg N ha⁻¹.

2.4. Gas sampling

During the first 60 days, the soil columns were closed once every two days for 30 min from 9 am to 10 am for sampling (Savage et al., 2014) using the static chamber method (Varner, 2003). The atmospheric pressure, headspace volume and air temperature were measured during the collection to calculate the air chamber volume. The gases were sampled using 60 mL plastic syringes at 0, 15 and 30 min, which were transferred to 20 mL tight vials closed with a gas impermeable septa (Belco Glass, Inc.). After this initial period, samples were collected every three days in the following 30 days, making a total of 2880 analysed gas samples.

The concentrations of N₂O, CO₂ and CH₄ were determined by gas chromatography in Shimadzu GC-2014® equipment. The N₂O was detected using an Electron Capture Detector (ECD) and CH₄ and CO₂ using a Flame Induced Detector (FID).

In order to obtain the accumulated emission values, linear interpolation calculations were used to obtain the gas fluxes on the days where there was no collection (Allen et al., 2010). The emission factors of each treatment were obtained according to Carmo et al. (2013). Conversion of GHG emission into CO₂ equivalent considered 28 and 265 the global warming power (GWP) of CH₄ and N₂O, respectively (Myhre et al., 2013). CO₂ was not considered as a greenhouse gas in this case because it came from a biogenic source (IPCC, 2006).

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