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A spatially explicit assessment of sugarcane vinasse as a sustainable by-product

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HIGHLIGHTS
• Vinasse application in sugarcane crop is limited by local environmental laws.
• Biodigested vinasse replaces 30% of mineral nitrogen and 46% of phosphorous.
• GIS modeling is a powerful strategy to apply vinasse in safe environmental levels.
• Energy production and nutrient recycling from vinasse contribute to decarbonization.

GRAPHICAL ABSTRACT

ABSTRACT

This study evaluates the benefits of mineral fertilizers replacement for biodigested vinasse. Data from experimental anaerobic digestion (AD) of vinasse were applied to support the analysis. Based on previous experiments, this assessment assumed that vinasse production could reach 2.38 × 10⁷ m³/year generating around 66,585 MWh/year of electric energy from biogas burning in the Administrative Region of Campinas (ARC). This amount of energy could supply more than 103,000 inhabitants and avoid 35,892 tCO₂eq/year (from electric energy replacement). The biodigested vinasse might also reduce the total N, P, and K mineral fertilizers demand per hectare of sugarcane crop in 30%, 1%, and 46%, respectively, avoiding additional greenhouse gas emissions of 111,877 tCO₂eq/year. There is no biodigested vinasse surplus for a moderate fertigation rate of 100 m³/ha, complying with local environmental laws related to nutrients excess side effects in areas destined to sugarcane crop. Notwithstanding, a Geographic Information System analysis for a small adjacent area to ARC indicated nine different fertigation rates, ranging from 50 to 100 m³/ha. Even though the general analysis for ARC shows high NPK replacement levels, the fertigation practices should be subsidized for robust soil analysis and adequate to safe environmental levels. A management tool can be designed using the results here presented to subsidize investments for AD widespread adoption by the sugarcane industry to catch a reasonable practice from the economic and environmental perspectives.

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Abbreviations: AD, anaerobic digestion; APBR, anaerobic packed-bed reactors; ARC, Administrative Region of Campinas; CO₂, carbon dioxide; COD, chemical oxygen demand; GHG, greenhouse gas; GIS, Geographic Information System; GWP, Global Warming Potential; IPCC, Intergovernmental Panel on Climate Change; K, potassium; N, nitrogen; NO₂, nitrous oxide; P, phosphorous; SDGs, Sustainable Development Goals; UASB, Upflow Anaerobic Sludge Blanket; UNFCC, United Nations Framework Convention on Climate Change; VFA, volatile fatty acids.

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1. Introduction

Fossil-derived fuels have brought several environmental issues and oil price fluctuation (Moraes et al., 2014; Ranjan et al., 2013; Srirangan et al., 2012). Industrial and urban waste, and crop and agricultural by-products require long-term management strategies to properly manage and/or recycle (Palomar et al., 2019). In addition, residual biomass is an abundant source for developing a sustainable energy economy in the partial replacement of petroleum-based energy (Yamakawa et al., 2018). Still, bioenergy production costs must be reduced to be competitive and widespread (Bugge et al., 2016). Among the agro-industrial by-products, vinasse generated during the ethanol distillation process after the fermentation of sugarcane juice is especially interesting. Energy recovery from the anaerobic digestion (AD) of vinasse can reduce greenhouse gases (GHG) emissions and may produce positive impacts on socioeconomic regional, and local levels (Dias et al., 2013; Ekman et al., 2013; Moraes et al., 2014; Leme and Seabra, 2016; Fuess et al., 2018a; da Silva Neto et al., 2020).

Brazil is the worldwide leader in sugarcane ethanol production, and São Paulo State is the primary national producer. After the petroleum crisis in the 1970s, some countries developed programs to increase their energy autonomy (De Prettio et al., 2018; Soccol et al., 2005), and Brazil fostered the ProAlcool Program. Through it, the ethanol industry was supported by the development of automotive engines specially designed for this fuel and by the establishment of a successful first-generation sugarcane ethanol technology.

Vinasse is the main by-product of sugarcane ethanol, ranging from 12 to 20 L for 1 L of ethanol (Bonomi et al., 2012). The primary use of vinasse is so far as soil fertilizer (Fuess et al., 2018b; Moraes et al., 2014). However, there are limits for the soil’s vinasse disposal, which is regulated by the Environmental Protection Agency of São Paulo State, according to the organic compounds level presented (MAPA, 2009). Indiscriminate vinasse disposal may cause severe environmental side-effects such as soil salinization, metal ion, and sulfates saturation and, in general, nutrient leaching and percolation, among other undesirable damages (Fuess and Garcia, 2014; Christofoletti et al., 2013; Madejón et al., 2001). AD can largely reduce the vinasse chemical oxygen demand (COD), and the produced biogas can be converted into electric and thermal energy (i.e., biogas burning in stationary engines) or can be purified to biomethane (ANP, 2015; Leme and Seabra, 2016; Awe et al., 2017). Biogas can be included in the Brazilian energy matrix as a competitive alternative to natural gas for vehicle fuel, heating purposes, and cooking, contributing to air quality improvement and health promotion (Mulenga and Siziya, 2019).

AD technology allows the conversion of wastewater and solid residues with high organic matter into biofertilizer and biogas (composed of 50 to 70% methane and 30 to 50% carbon dioxide) (Pokhrel and Viraraghavan, 2004; Memon and Memon, 2020). Anoxic vertical bio-reactors, such as the Upflow Anaerobic Sludge Blanket (UASB), can be used for AD with the advantage of requiring a smaller area when compared to other technologies such as aerated and horizontal flow anaerobic lagoons. UASB can also work with high organic load and smaller sludge production than conventional aerobic biological treatments (Forster-Carneiro et al., 2012). New reactors arrangements aiming at better technical performance are, however, in constant evolution (Barros et al., 2017; Del Nery et al., 2018), as is the case of the Anaerobic Packed-Bed Reactors (APBR) (Fuess et al., 2017a; Fuess and Zaïat, 2018).

AD of vinasse is relevant from the economic, energetic, and environmental perspectives (Leme and Seabra, 2016; Parsaei et al., 2019; da Silva Neto et al., 2020). Biogas has high heat content from the energy side and can be used as fuel for electric energy generation or heat for boilers in production processes. In Brazil, the National Electric Energy Agency Resolution n.482 (ANEEL, 2015) allows decentralized energy production encouraging the use of biogas as a source of electricity. Moreover, increased dissemination of AD is expected after establishing the National Biofuels Policy (RenovaBio), an initiative of the Brazilian Ministry of Mines and Energy launched in December 2016 (MME, 2017) that supports the expansion of biofuel production based on environmental, economic, and social sustainability.

Environmentally, biodigested vinasse is more advantageous for crop fertilization than vinasse in natura because it contains nitrogen (N) in a chemical form more easily absorbed by the plant. During the AD process, the organic-N is converted into ammonia-N, which avoids such transformation in the soil. This conversion can be a source of greenhouse gas (GHG) emissions (Moraes et al., 2017). Nitrous oxide (N2O) has a Global Warming Potential (GWP) 265 higher than carbon dioxide (CO2) (IPCC, 2013). As a result of managed soils, N2O can be originated from direct N applications for soil fertilization and from indirect emissions related to soil organic matter contents associated to land-use change and priming effect, which also depends on tillage/non-tillage practices (Tubìello et al., 2015). Biodigested vinasse can supply more N for sugarcane crop reducing mineral applications and, consequently, N2O emissions. The proper vinasse fertigation rate, depending on soil chemistry and previous land-use (which determine Nitrogen, Phosphorus, and Potassium (NPK) requirements), ranges from 60 to 250 m3/ha (van Raij et al., 1996). Besides the issue related to N2O emissions, K’s particular excess in over-fertigated sugarcane soils requires attention. Although sugarcane presents high K requirement as a quality aspect related to its final sugar content, excess of K is directly related to leaching side-effects.

Despite there are various possibilities for different agro-industrial AD arrangements and specific project requirements (depending on climate and substrate characterization among other features), biogas versatility figures as a promising solution to the Brazilian biofuel industry (da Silva Neto et al., 2020). AD is efficient in reducing the organic load of vinasse, reaching more than 85% of reduction depending on the reactor technology (Moraes et al., 2014). It also optimizes bioenergy recovery from biogas, reaching over 30% of electric energy surplus, enhancing both the environmental and economic aspects (Fuess et al., 2018b). Moreover, AD technology might provide outstanding GHG mitigation, close to 48%, when biodigested vinasse is applied before its storage and transportation to soil disposal (Moraes et al., 2017), and as much as 27% when biomethane replaces diesel in a given scenario recently assessed by da Silva Neto et al. (2020).

Thorough AD, it is possible to generate electric energy from biogas burning, as well as to mitigate GHG from both the fertilizer replacement and the additional electric power, which can be inserted in the grid. This study also presents a mineral NPK replacement route with thermophilic biodigested vinasse, a biofertilizer that fulfills Brazilian sugarcane soil characteristics and its nutrients disposal limits. This proposal can, spatially explicitly, support the management of products that could cause pollution into solutions, at local and regional levels, to improve the environmental and health quality. The present research is connected to the Sustainable Development Goals (SDGs), which are intimately tied to a sustainable and inclusive future for humanity. The current Covid-19 crisis seriously exposed that time matters enormously to save lives, and the same is valid for the environment. A sustainable development strategy is mandatory worldwide to avoid unnecessary risks and fragilities related to the massive environmental destruction and its related decline in economic activity that accentuates the existing inequalities (Sachs et al., 2020), especially in developing countries.

This article provides a critical analysis of vinasse disposal and energy/nutrients recycling, mainly to subsidize the current fertigation practices to support safe environmental vinasse management in the field. The article is structured as follows: (i) experimental sugarcane vinasse thermophilic anaerobic digestion, (ii) biogas and biodigested further applications, (iii) GHG mitigation from electric energy generation, (iv) sugarcane agronomic nutritional requirements and calculation of fertigation rates, (v) sugarcane soil NPK replacement, (vi) GHG mitigation from soil emissions for in natura and biodigested vinasse, and (vii) GIS modeling to assess NPK replacement and additional requirements for a typical ARC sugarcane soil.
2. Materials and methods

The research methodology used in this paper is summarized in Fig. 1.

2.1. Experimental reactor configuration

A lab-scale semi-continuous reactor (capacity of 4.3 L) was kept in continuous operation for 58 days. The reactor was initially fed with 1.93 L of vinasse. Then, 50 mL of diluted vinasse sample (containing 65% of pure vinasse) was added every three days. Vinasse and inoculum used for the experimental trial were obtained from an ethanol-producing plant located at the Administrative Region of Campinas (ARC) in the State of São Paulo, Brazil. Physicochemical analysis of the substrates was done according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1999): pH (4500-H+ B); total alkalinity (2320B); total solids (2540B); total volatile solids (2540E); ammonium nitrogen (4500-0NH3-C) using a digester block (Mark Marconi, model MA 4025), and chemical oxygen demand (4520D). Total Kjeldahl Nitrogen was determined according to method 978.02 from the Official Methods of Analysis (AOAC, 1997). Biogas samples were collected in duplicates directly from the reactor and analyzed in a gas chromatograph (GC 2014, Shimadzu Corporation, Japan), equipped with a thermal conductivity detector and a packed column for compound separation (Shin Carbon ST 50/80 mesh). The biogas composition was determined under the following conditions: drag gas nitrogen (35 mL/min, 5 bars), 200 °C, thermal conductivity detector at 200 °C, and sample injected volume of 0.5 mL.

2.2. Biogas production and potential of electric energy generation

The experimental biogas volume and its methane content were used to estimate the biogas potential for electric energy generation in a stationary engine, according to Eq. (1) (Campello et al., 2020):

\[
EG = (Q_{\text{biogas}} \times LCV_{\text{CH}_4} \times C_m \times \eta_e \times CMW) / C_0 / C_1
\]

where \( EG \) is the potential of electricity generation (MWh/m³ of vinasse); \( Q_{\text{biogas}} \) is the volume of biogas (Nm³ of biogas/m³ of vinasse fed to the reactor) according to the experimental data; \( LCV_{\text{CH}_4} \) is the lower calorific value of methane (8500 kcal/Nm³); \( C_m \) is the percentage of methane in biogas (%) according to the experimental data; \( \eta_e \) is the engine efficiency (%), assumed as 38%; and \( CMW \) corresponds to kcal conversion to MWh.

2.3. Environmental impact assessment

Two scenarios were designed for the environmental impact assessment. The first one evaluated the climate change impacts of electric energy generation from biodigested vinasse, and the second, the use of the biofertilizer compared to the vinasse in natura. Impacts related to the transportation of the vinasse were not considered since, for both scenarios, it was assumed the use of the same irrigation equipment for transport and distribution, and the same distance and land cover.

2.3.1. GHG mitigation from electric energy generation

The mitigation of GHG emissions/m³ of vinasse due to the avoidance of electricity consumption from the grid (due to the additional electricity generated from biogas burning) was estimated from Eq. (2) using the average CO₂ emission factor for the electricity dispatch to the grid from January 2018 to December 2018 (12 months) of 0.539 tCO₂eq/MWh (MCTIC, 2018). Refer to Supplementary material for additional information on monthly emission factors.

\[
\text{GHG emissions} = 0.539 \times \frac{\text{tCO}_2\text{eq}}{\text{MWh}} \times EG
\]
2.3.2. NPK replacement and direct and indirect GHG emissions from soil

To calculate the total volume of vinasse produced in the study area, a production mix of 56% of sugar and 44% of ethanol was obtained from data reported for 2015 for the 21 sugarcane mills located in ARC (PROCANA, 2015). For soil emissions from vinasse application, the whole area destined to sugarcane cultivation in ARC, São Paulo, Brazil, was considered (see Fig. 2B), which comprehends 21 sugarcane mills. In the 2017/2018 harvest season, the whole sugarcane crop area corresponded to 513,123.30 ha for productivity of 82.60 t/ha (IEA, 2019).

Sugarcane agronomic nutritional requirements were obtained from the fertilizer and liming recommendations for the State of São Paulo (van Raij et al., 1996). They vary according to the expected productivity, local soil chemistry, and macronutrient contents. The nutritional requirements change during the sugarcane growth cycle (plant cane and ratoon) depending on soil P and K levels, according to Table 1.

In the study area, the sugarcane soil is predominantly a ferralsol (Fig. 2A), with intermediary P_resin level from 7 to 15 mg/dm³ and K⁺ ranging from 1.6 to 3.0 mmolc/dm³ (Fig. 3A, field data for 517 soil samples in an ARC adjacent area). The whole NPK requirement was calculated since the study area, and adjacent regions were predominantly similar to this typical soil chemistry (Fig. 3B) (ferralsol). Finally, the replacement level for mineral fertilizers was evaluated (refer to Supplementary material).

Considering the United Nations Framework Convention on Climate Change (UNFCCC) methodologies for National Greenhouse Gas Inventories, the direct and indirect emissions were calculated according to the Intergovernmental Panel on Climate Change (IPCC) Guidelines. The

![Fig. 2. Administrative Region of Campinas' typical soil (A), sugarcane plantation areas and sugar mills location (B).](image_url)

Table 1: Nutritional needs for sugarcane growth cycles: plant cane and ratoon.

| Cycle   | Expected productivity | N  | P_resin (mg/dm³) |
|---------|-----------------------|----|-----------------|
|         |                       | 0-6| 7-15 | 16-40 | >40 |
| Plant cane | <100                  | 30 | 180  | 100   | 60  | 40   |
|          | 100-150               | 30 | 180  | 120   | 80  | 60   |
|          | >150                   | 30 | 140  | 100   | 80  | 60   |
| Ratoon   | 0-0.7                 | 100| 80   | 40    | 40  | 0    |
|          | 0.8-1.5               | 150| 120  | 80    | 60  | 0    |
|          | >1.5                  | 200| 160  | 120   | 80  | 0    |

| Cycle   | Expected productivity | N  | P_resin (mg/dm³) | K⁺ (mmolc/dm³) |
|---------|-----------------------|----|-----------------|---------------|
|         |                       | 0-15| >15 | 0-1.5 | 1.6-3.0 |
| Plant cane | <60                   | 60 | 30   | 0    | 90   | 60   |
|          | 60-80                 | 80 | 30   | 0    | 110  | 80   |
|          | 80-100                | 100| 30   | 0    | 130  | 100  |
|          | >100                  | 120| 30   | 0    | 150  | 120  |
methods and models (Tier 1) were selected from Chapter 11 - Volume 4: Agriculture, Forestry, and Other Land Use (IPCC, 2006).

Direct emissions of N$_2$O followed Eq. (3) (IPCC, 2006):

$$N_2O_{Direct} - N = N_2O - N_{N inputs} + N_2O - N_{OS} + N_2O - N_{PRP}$$

(3)

where $N_2O_{Direct} - N$ = annual direct N$_2$O-N emissions from managed soils, t N$_2$O-N year$^{-1}$; $N_2O - N_{N inputs}$ = annual direct N$_2$O-N emissions from N Inputs managed soils, t N$_2$O-N year$^{-1}$; $N_2O - N_{OS}$ = annual direct N$_2$O-N emissions from managed organic soils, t N$_2$O-N year$^{-1}$; $N_2O - N_{PRP}$ = annual direct N$_2$O-N emissions from urine and dung inputs to grazed soils, t N$_2$O-N year$^{-1}$.

Due to the specific characteristics of Brazilian cultivations, it is not common to have pasture and sugarcane. Thus, $N_2O_{Direct} - N_{PRP}$ is neglected in the face of livestock which emit CO$_2$ and N$_2$O. Furthermore, sugarcane is a very traditional crop in the São Paulo state, dating to the beginning of colonization, explaining why there is no emission from the organic matter natural to the soil and N$_2$O - N$_{PRP}$ is considered null. The conversion of N$_2$O-N emissions to N$_2$O emissions for reporting purposes was performed by using Eq. (4).

$$N_2O = N_2O - N_{N inputs}/28$$

(4)

The conversion to GHG emissions was obtained by multiplying the emissions of N$_2$O for its GWP (265 kg CO$_2$eq/kg N$_2$O), as presented in Eq. (5).

$$\text{GHG emissions} = N2O \times \text{GWP}_{N2O}$$

(5)

The indirect emissions of N$_2$O are: fossil fuel combustion-related to the agricultural process, and the N$_2$O produced through the leakage of NO$_3$ in the underground (thus, subsequent transformation into N$_2$O). The indirect N$_2$O emissions from atmospheric deposition of N volatilized from managed soils, N$_2$O emissions from N leaching/runoff from managed soils were disregarded in the present assessment.

$$N_2O_{(ATD)} - N = (\{F_{SN} \cdot \text{frac}_C\} + \{F_{SN} + F_{PRP} \cdot \text{frac}_C\}) \cdot EF$$

(6)

where $N_2O_{(ATD)} - N$ = annual amount of N$_2$O-N produced from atmospheric deposition of N volatilized from managed soils, t N$_2$O-N year$^{-1}$; $F_{SN}$ = annual amount of synthetic fertilizer N applied to soils, t N year$^{-1}$; $F_{PRP}$ = annual amount of urine and dung N deposited by grazing animals on pasture, range and paddock, t N year$^{-1}$; $\text{frac}_C$ = fraction of applied organic N fertilizer materials (FON) and of urine and dung N deposited by grazing animals (FPRP) that volatilizes as NH$_3$ and NOx, kg N volatilized (t of N applied$^{-1}$); $F_{SN}$ = fraction of synthetic fertilizer N that volatilizes as NH$_3$ and NOx, kg N volatilized (t of N applied$^{-1}$); $F_{PRP}$ = fraction of applied organic N fertilizer materials (FON) and of urine and dung N deposited by grazing animals (FPRP) that volatilizes as NH$_3$ and NOx, kg N volatilized (t of N applied$^{-1}$); $EF$ = emission factor for N$_2$O emissions from atmospheric deposition of N on soils and water surfaces, kg N$_2$O-N (kg N$_2$O-N + NOx, N$_2$O-N volatilized$^{-1}$).

Adding urea to soils for fertilization can lead to loss of the CO$_2$ fixed during the industrial process. Urea (CO(NH$_2$)$_2$) is converted into NH$_3$, OH$^-$, and HCO$_3^-$ in the presence of water and urease enzymes. Eq. (7) (IPCC, 2006) was used to calculate the carbon emitted from urea fertilization.

$$\text{CO}_2 - \text{C}_{\text{Emmission}} = M \cdot EF$$

(7)

where $\text{CO}_2 - \text{C}_{\text{Emmission}}$ = annual C emissions from urea application, t C year$^{-1}$; $M$ = annual amount of urea fertilization, t/year$^{-1}$; $EF$ = emission factor, t of C (t of urea)$^{-1}$.

2.4. Fertilization rates and NPK replacement study case

The ARC adjacent area selected to show the fertilization rates map and NPK replacement level (Fig. 4) considered 112 soil data collected in 2017 in field experiments. From a Geographic Information System (GIS), a geostatistical interpolation method was used, which is essentially a method of estimation by local weighted averaging (Oliver, 1990), represented in Eq. (8):

$$Z(S_i) = \sum_{i=1}^{N} \lambda_i Z(S_i)$$

(8)

where $Z(S_i)$ is the measured value at the ith location; $\lambda_i$ is a weight factor for the measured value at the ith location; $S_i$ is the prediction location; and $N$ is the number of measured values.

The kriging method assumes that at least some of the spatial variation observed in natural phenomena can be modeled by random processes with spatial autocorrelation, as well as requires that the spatial autocorrelation be explicitly modeled (Burrough, 1986; Heine, 1986; McBratney and Webster, 1986; Press et al., 1988). This method defines which of the input points will be used to interpolate the value for each cell in the output raster, and is often used in soil science and geology.

3. Results and discussion

3.1. Vinasse AD chemical and analytical parameters

Table 2 presents the characterization of in natura and biodigested vinasse. All the physicochemical parameters from the initial characterization agree with the results reported in the literature (Fuess et al., 2018a). In general, vinasse has a high organic matter concentration, represented by chemical compounds such as residual sugars, organic acids, and glycerol. The reactor mixture (vinasse and inoculum) had a pH of 8.36 and an alkalinity of 727.1 mg/L after 58 days of operation. These conditions are considered favorable for the growth of methanogenic archaeas. Additionally, after this period, the variations in ammonia reached 344.93 mg/L, the C:N dropped to 2.84, the Volatile Suspended Solids/Total Suspended Solids ratio (VSS:TSS) was 0.83 and COD 8407.1 mgO$_2$/L. These results were similar to those presented by Cruz-Salomón et al. (2017) for AD of vinasse in UASB reactor with a final COD of 6500 mgO$_2$/L and by Ferraz Júnior et al. (2016) where the pH was 8.3, and COD remained from 5700 to 8400 mgO$_2$/L after 180 days of the experiment.

The evolution of biogas composition, ammoniacal and total nitrogen, methane yield, and COD can be seen in Fig. 5. From day 28, methane production increased steadily to reach a composition of 49% on day 58 (Fig. 5A). These results are consistent with other sugarcane vinasse treatment findings in an anaerobic fluidized bed reactor (dos Reis et al., 2015). It is noticeable the increase from 126 mg/L to 345 mg/L (Fig. 5B), which can be attributed to the microbial activity on sugarcane vinasse proteins and melanoidins. The dead bacteria proteins can be subsequently used as a source of nitrogen through endogenous metabolism. The quick solubilization of ammonia in water can also explain the high levels in the final solution. The wide range of inhibiting ammonia concentrations is probably due to the differences in substrates and inoculum composition, environmental conditions, temperature, and pH (Rajagopal et al., 2013). Chen et al. (2008) found that ammonia tolerance for AD processes in levels up to 4000 mg/L could cause an apparent inhibition of the methanogenic phase. The lower initial pH does not favor methanogenic bacterial community growth. As a consequence, the gradual build-up of volatile fatty acids (VFAs) inhibits methane synthesis. Besides, VFAs production and consumption, and the ammonia presence may cause, to some extent, the generation of sulfuric acid by the action of some sulfur-reducing bacteria, which could be present in anaerobic gel immobilized sludge at UASB reactors startup (Del Nery et al., 2018; Whitman et al., 2014). On days 14, 28 and 39; 6 N NaOH was added to keep the pH above 8.0 to favor the AD process. In terms of vinasse alkalization, to favor the methanogenic phase in APBR reactor, Fuess (2017) used NaOH and NaHCO$_3$ throughout the first 50 days of the operational period. The increase in methane content may be related to the pH increase from 8.0.
Fig. 3. (A) Soil typical P and K levels in the study area, (B) pedological map in the study region.
(Source: Adapted from Rossi [2017].)
to 8.5, which is more suitable for the growth of thermophilic methano- 
genic archaeas. During the methane yield increments along the 60 days, it is worth observing that COD dropped from 10,584 mgO₂/L to 8407 mgO₂/L, corresponding to 20.5% organic load reduction (Fig. 5C). The theoretical COD values for some compounds in AD steps, obtained by stoichiometric analysis of each compound’s complete combustion reaction in equivalent COD (gO₂/mol), are glucose 192.77; hydrogen 16.0; acetic acid 32.0; propanoic acid 111.85; butyric acid 160.0.

The analysis of acidogenic reactions and their effects over the initial parameters of vinasse (Fig. 5, Table 2) shows that the initial values did not change. So, propanoic acid synthesis from glucose (C₆H₁₂O₆ + 2H₂ → 2CH₃CH₂COOH + 2H₂O) could be the predominant reaction accounting for the increasing COD in the reaction mixture. Accordingly, hydrogen, mainly insoluble in an aqueous medium, is quickly consumed by the hydrogen trophic, an essential electron carrier in several reduction reactions (Fang and Zhang, 2015; Prakash et al., 2018; Stams et al., 2003; Whitman et al., 2014). Therefore, the biodigested from anaerobic fermentation could be assumed as a valuable fertilizer due to its increased nitrogen availability for a better short-term soil fertilization action.

3.2. Biogas production and electricity generation potentials

From the methane yield of 3800 ml for a total 2547.50 ml of vinasse fed to the experimental reactor, the theoretical electric energy generation in a stationary engine burning biogas (see Eq. (1)), with an efficiency of 38%, reaches 0.0028 MWh/m³ of vinasse. This value is 20% lower than that obtained by Silva dos Santos et al. (2018), and equal to the result reported by Moraes et al. (2014). Vinasse production from the ethanol production process, estimated as 15 L per each liter of ethanol produced, for the sugarcane crop area in ARC, São Paulo, Brazil (513,123.30 ha for 2017/18 harvest season), accounted for 2.38 × 10⁷ m³/year, for the assumption yield of 85 L of ethanol per ton of milled sugarcane. Further, assuming the AD of the whole vinasse potential production, the electric energy generation for the referred harvest season could reach 66,585 MWh/year.

In Brazil, ethanol sugarcane refineries usually sell their electric energy surplus, contributing to a more renewable energy matrix. Thereby, the additional electricity generated could represent a socially positive impact. According to the National Energy Balance, the average electricity consumption was 0.646 MWh/person in 2018 (EPE, 2018),
corresponding to an estimation of more than 103,000 inhabitants who could be ‘locally’ supplied by the energy yield here reported.

3.3. Environmental impact assessment

3.3.1. GHG emissions mitigated from electric energy generation

From the potential electric energy estimated from vinasse AD in the comprehended area, it would be possible to dispatch to the energy grid a total amount of 66,585 MWh/year for the 2017/18 harvest season. The avoided GHG emissions from the input of the locally renewable energy in the grid could reach 35,893 t CO2eq per year, corresponding to 0.00085 t CO2eq/ton sugarcane milled. It represents 14% of the avoided emissions of the Bagasse Cogeneration Project at “Usina Alta Mogiana S/A”, a Brazilian sugarcane mill certified for a Clean Development Mechanism (UNFCCC, 2005a) that aims at the reduction of 11,183.57 t CO2eq/year for 1.8 × 106 m3/year, the local crop’s fertigation rate was estimated in 100.

OTC (mg/L) 6955.50 3528.16 2802.40
C/N 16.78 4.21 2.84
P (mg P2O5/L) 17.00 1400.00
K (mg K2O/L) 1400.00

a Not detected.

b Data for phosphorus (P) and potassium (K) were obtained from Salomon (2007).

The two usual growth cycles of harvesting, ratoon, and plant cane were considered to evaluate the whole harvest season’s nutritional requirements. Refer to Supplementary material for detailed gathered information regarding soil condition, NPK, and the limiting requirements for both growth cycles. Overall, liming, a practice to reduce soil acidity aiming to improve plant growth, is applied depending on the soil base balance of Ca2+ and Mg2+ ions. Urea addition, the less expensive N soil fertilizer (Worldbank, 2019), produces CO2 emissions derived from the fixed amount in its industrial production process (Tubbioli et al., 2015). In the presence of water and urease enzymes, urea is converted into ammonium (NH4+), OH− and bicarbonate (HCO3−), the latter evolves into CO2. P application is intimately related to soil classification, and its presence is not associated with GHG emissions. On the other hand, P excess is directly associated with soil eutrophication and water bodies leaching. For K excessive application, apart from leaching risks, another side effect is the plant’s lower Ca absorption, which compromises its growth.

Taking into account the vinasse production from sugarcane ethanol, 2.38 × 107 m3/year, the local crop’s fertigation rate was estimated in 100 m3/ha, which agrees with previous studies and current practices in the study area (Moraes et al., 2014). However, this rate is slightly lower than that reported by Fues et al. (2018a). They assessed the biodigested vinasse application rates for 210 harvesting days (for the 2014/15 São Paulo State harvest period), and the seasonal characterization of vinasse for two different AD arrangements (fixed bed reactors in single and in two-phase). For the fertigation rate here reported, there is no vinasse surplus to be destined to a sugarcane region outside the study area. The reduction in NPK mineral fertilizer requirements from biodigested vinasse compared with in natura vinasse is 65%, 1%, and 100% per hectare of sugarcane crop fertilized. The net reduction of NPK accounts for 30%, 1%, and 46%, respectively. For the vinasse production and fertigation rate obtained in the present study, 46% of the total sugarcane area (based on K requirements) can be adequately fertilized according to both plant cane and ratoon’s nutritional needs.

Considering that all the potential vinasse production for the studied area was treated in anaerobic reactors and the generated electric energy might be enough to supply 8% of the total inhabitants of the study area (ARC). Currently, in the State of São Paulo, the sugarcane industry is already providing energy from bagasse burning to the energy grid. The energy surplus obtained from biogas burning could represent a competitive advantage for the whole sugar and ethanol sector associated with using of an alternative biofertilizer instead of mineral fertilizers.
of the simple vinasse disposal in sugarcane crop. Theoretically, UASB reactors produce around 10 Nm$^3$ of biogas/m$^3$ of vinasse, which is almost 10-fold higher than the experimental yield. Previous studies (Fuess, 2017; Fuess et al., 2017b) indicate that APBR reactors are efficient for vinasse treatment when considering the associated costs such as operational stability, organic matter removal, and methane (CH$_4$) production; despite UASB reactors being efficient and slightly less expensive than APBR reactors.

Fig. 5. (A) Evolution of biogas composition, (B) ammoniacal nitrogen and CH$_4$ percentage, (C) chemical oxygen demand (COD) and CH$_4$ concentration with time of reactor operation.
Fig. 6. Maps presenting the potential of harnessing biogas production related to nutrient recycling: (A) for vinasse in natura, and (B) for biodigested vinasse.
Although the cleaning and purification of biogas into biomethane is a bottleneck (Leme and Seabra, 2016; Awe et al., 2017), previous studies have shown that the end-use of biomethane in heavy vehicles presents the best environmental performance (Ferreira et al., 2019). Moreover, biomethane is compatible with natural gas. The existing infrastructures and technologies could be employed to boost fossil fuels’ direct substitution in transport, reducing CO₂ emissions by 50% (Pääkkönen et al., 2019). Hence, the use of biomethane for the agricultural fleet is also an outcome of a better vinasse treatment and management. Still, a better biomethane destination, for the energy grid, city buses fleet, or truck supply requires further assessment and substantial investments to support a national biogas strategy to ensure considerable access for affordable and clean energy to the country’s totality population.

Another critical aspect to be highlighted for the Brazilian scenario is the RenovaBio governmental Law. This state policy aims to recognize all able and clean energy to the country’s totality population.

Romero et al. (2019) assessed the bioenergetics potential using agricultural residues (sugarcane straw and eucalyptus residues) as raw material to produce bioethanol and bioelectricity, to diversify the energy matrix and replacement of fossil fuels of ARC. Besides the fossil energy replacement in ARC, a GIS study case, like the one here presented, contributes to a better environmental management and the development of new policies to address the sugarcane residues. Although vinasse and biogas conversion into electricity and biomethane are not standard practices in Brazil, the AD technology presents an outstanding potential to improve the environmental and energetic sugarcane chain operation (da Silva Neto et al., 2020). Furthermore, other industries and countries present successful experiences with AD commercial technologies to support a broad adoption of vinasse AD, biogas use and biodigested application in the sugarcane Brazilian production chain.

4. Conclusions

This study shows that in natura vinasse substitution by biodigested vinasse is a suitable strategy for N fertilization in sugarcane crops. Biogas burning may also provide electric energy surplus to the grid, so important for green economic development in Brazil and other countries. Besides, it would be possible to expand the Brazilian sugar and ethanol industry’s competitive advantage, which is already in an outstanding strategic level since the 1970s. AD potential still needs further studies to

![Fig. 7. Soil GHG emissions for in natura and biodigested vinasse and the potential mitigation obtained from the last.](image)

Table 3
Direct and indirect GHG emissions (without LUC).

| Equation | Parametersa | In natura vinasse (N input = 45,440.15 t year−1)b | Biodigested vinasse (N input = 16,032.02 t year−1)c |
|----------|-------------|-------------------------------------------------|-------------------------------------------------|
| Eq. (3)  | N₂O − N₅₀input (t year−1) | 454.40 | 160.32 |
|          | N₂O − N₅₀(t year−1) | 0 | 0 |
|          | N₂O − N₅₀ (t year−1) | 0 | 0 |
|          | N₂Oneutral − N (t year−1) | 454.40 | 160.32 |
|          | N₂Oneutral (t CO₂eq year−1) | 120,549.71 | 42,484.85 |
| Eq. (6)  | Fₛₐₕ | 45,440.15 | 16,032.02 |
|          | Fₛₐₕ – GASF | 0.1 | 0.1 |
|          | Fₛₐₕ | 0 | 0 |
|          | Fₛₐₕ | 0 | 0 |
|          | Fₛₐₕ – GASM | 0 | 0 |
|          | EFₚ | 0.01 | 0.01 |
|          | N₂O − ATD − N (N₂O−N year−1) | 71.45 | 25.19 |
|          | N₂Oneutral (t CO₂eq year−1) | 18,922.58 | 6676.19 |
| Eq. (7)  | M | 45,440.15 | 16,032.02 |
|          | EF | 0.20 | 0.20 |
|          | CO₂ from urea (t CO₂eq year−1) | 33,322.78 | 11,756.81 |
|          | Total direct GHG emissions (t CO₂eq year−1) | 153,872.49 | 54,241.67 |
|          | Total indirect GHG emissions (t CO₂eq year−1) | 18,922.58 | 6676.19 |
|          | Total GHG emissions (t CO₂eq year−1) | 172,795.07 | 60,917.86 |

a Parameters from IPCC (2006) default values – Tier 1.

b According to sugarcane crop N requirement and in natura vinasse characterization for a fertigation rate of 99 m³ ha⁻¹.

c According to sugarcane crop N requirement and biodigested vinasse characterization for a fertigation rate of 100 m³ ha⁻¹.
explore its full potential. Governmental subsidies to research and expand its adoption among ethanol and sugar producers may advance a renewable energy grid in Brazil. Fostering a low-carbon energy grid will contribute to sustaining new business models benefiting all stakeholders and, consequently, sustainable cities. Supply chains need to be based on circular economy principles as land-use strategies need to promote urban-rural integration. A management tool may be designed using this study’s results to subsidize investments for the sugarcane industry to adopt AD. Additionally, the GIS analysis shows different fertilization rates, varying by soil chemical characteristics, in a smaller area of São Paulo State. The fertilization rate from 50 to 110 m³/ha suggests that vinasse application should be better implemented with advanced tools, such as Precision Agriculture and Spatial Analysis. These tools also allow precise management to comply with environmental laws and avoid side-effects from the widespread fertilization in sugarcane crops.

Beyond the environmental benefits, our findings also suggest a method that, once applied, can exploit vinasse embodied energy and nutrients available within the sugarcane production chain. The approach integrating GIS and UNFCC-IPCC models may support to reach at least two of the seventeen UN Sustainable Development Goals: affordable and clean energy and climate action.

CRediT authorship contribution statement

Luz Selene Buller: Conceptualization, Methodology, Writing - original draft preparation, Writing - review & editing. Cristhly Willy da Silva Romero: methodology, data curation, validation, writing - original draft preparation. Rubens Augusto Camargo Lamparelli: Methodology, Formal analysis, Data curation, Validation, Resources, Funding acquisition. Samuele Fontenelle Ferreira: Experimental investigation. Ana Paula Bortoleto: Writing - review & editing. Valdineide Solange I. Mussatto: Methodology, Formal analysis, Data curation, Validation, Resources, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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