UNIVERSIDADE DE SÃO PAULO CENTRO DE ENERGIA NUCLEAR NA AGRICULTURA

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Emission of greenhouse gases in the land-use change for sugarcane production in the Center-South region of Brazil

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To my parents and examples Vanilda and Antônio; To my fiancé Franz, With all my love!

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"The atmosphere is the key symbol of global interdependence. If we can't solve some of our problems in the face of threats to this global commons, then I can't be very optimistic about the future of the world."

Margaret Mead

ABSTRACT

DIAS, N. M. S. Emission of greenhouse gases in the land use change for sugarcane production in the Center-South region of Brazil. 2018. 82 p. Tese (Doutorado) – Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Piracicaba, 2018.

The Earth's atmosphere is warming due to a combination of natural effects and anthropic activities, which are directly related to the increment of greenhouse gas (GHG) emissions by burning fossil fuel. Brazil stands out in the world economic scenario as the main producer of ethanol, from sugar cane, considered a source of clean, renewable and economically viable energy. The expansion of this crop into pasture areas, in the Center-South region of Brazil, and the intensification in the production of this biofuel to supply the market have raised concerns about its sustainability. The agricultural is one of the main sectors responsible for the emission of GHG into the atmosphere, therefore, more studies are needed about how land use change (LUC) and production intensification, mainly due to the application of agricultural inputs rich in carbon and nitrogen, can affect GHG emissions. In the Center-South region of Brazil, the main LUC is composed of the succession native vegetation areas to pasture, and in sequence to sugarcane. Therefore, two studies were carried out aiming to determine soil GHG emissions under different land uses in the Center-South region of Brazil (Valparaíso-SP), as well as to characterize the emission factor of the main agricultural inputs in either sugarcane planting or ratoon areas. In the first study, three different land use areas were evaluated, composed of native vegetation, pasture and sugarcane. Among the land uses evaluated in this study, the soil under pasture exhibited the highest emission of carbon equivalents (CO_2 -eq), which was 41-fold higher than under native vegetation and 5.6-fold higher than under sugarcane. In the second study, two experiments were set up to determine the soil GHG emission fluxes after the application of sources of carbon and nitrogen during sugarcane cultivation. Experiment I: set up in a sugarcane planting area with application of ammonium nitrate, limestone and filter cake, in addition to a control treatment without application of any input. Experiment II: set up in a sugarcane ratoon area with application of vinasse and urea in the first year, and vinasse in the second year. In the first experiment, the soil tillage during the planting process produced a larger increase of soil GHG emissions when compared to the sugarcane ration area. Among the inputs applied to the cane plant, filter cake or ammonium nitrate produced the highest GHG emissions from the soil. On the other hand, in the area of sugarcane ration, the highest emissions were observed with the application of a combination of organic and mineral fertilizers (vinasse and urea), but with the application of only vinasse, the emission increment was less intense. The emission factors for C-CO₂ and N-N₂O reported by the IPCC are higher than those observed in this study, in the Center-South region of Brazil. The highest emission factor was observed for ammonium nitrate, with 0.13% for N-N₂O in the rainy season. Thus, the expansion of sugarcane planted areas plays an important role in GHG emission. New studies on this contribution to GHG emissions are urgently needed in different regions around the world, in order to define measures to limit emissions and aiming at maintaining the sustainability of this biofuel.

Keywords: Biofuel. Climate change. Sustainability

RESUMO

DIAS, N. M. S. Emissão de gases do efeito estufa na mudança de uso da terra para produção de cana-de-açúcar na região Centro-Sul do Brasil. 2018. 82 p. Tese (Doutorado) – Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Piracicaba, 2018.

O aquecimento da Terra decorrente de atividades antrópicas, está diretamente relacionado ao aumento das emissões de gases de efeito estufa (GEE) por queima de combustíveis fósseis. O Brasil se destaca no cenário econômico mundial como o principal produtor de etanol, de canade-açúcar, considerado uma fonte de energia limpa, renovável e economicamente viável. A expansão desta cultura sobre áreas de pastagem, na região Centro-Sul do Brasil, e a intensificação da produção deste biocombustível, necessárias para suprir o mercado têm levantado preocupações sobre a sua sustentabilidade. O setor agrícola é uma das principais fases relacionadas à emissão de GEE na atmosfera, sendo necessário maior entendimento sobre como as mudancas de uso da terra (MUT) e intensificação de produção podem afetar as emissões GEE, principalmente após a aplicação no solo de insumos agrícolas ricos em carbono e nitrogênio. Na região Centro-Sul do Brasil, a principal MUT é composta pela sucessão de áreas de vegetação nativa- pastagem- cana-de-acúcar. Foram realizados dois estudos com o objetivo de determinar as emissões de GEE do solo em diferentes usos da terra em Valparaíso-SP, bem como caracterizar o fator de emissão dos principais insumos agrícolas utilizados em áreas de cana planta e cana soca. No primeiro estudo, foram avaliadas três áreas de uso da terra, compostas por vegetação nativa, pastagem e cana-de-açúcar. Entre os sistemas de usos da terra avaliados neste estudo, a pastagem apresentou a maior emissão de carbono equivalente (CO₂-eq), no qual representou cerca de 41 vezes maior do que a vegetação nativa e 5,6 vezes maior do que a cana-de-açúcar. No segundo estudo, dois experimentos foram conduzidos simultaneamente para determinar os fluxos de emissões de gases do solo após a aplicação de fontes de carbono e nitrogênio durante diferentes fases do ciclo da cana-de-açúcar. Experimento I: realizado em uma área de plantio de cana-de-açúcar com aplicação de nitrato de amônio, calcário e torta de filtro, além de um tratamento controle sem aplicação de nenhum insumo. Experimento II: área de cana soca com aplicação de vinhaça e ureia no primeiro ano, e vinhaça no segundo ano. No primeiro experimento o revolvimento do solo no processo de plantio proporcionou as maiores emissões de GEE quando comparada a área de cana soca. Dentre os insumos aplicados na cana planta, a torta de filtro ou nitrato de amônio proporcionaram as maiores emissões de GEE do solo. Por outro lado, na área de cana soca, as maiores emissões foram verificadas quando houve a combinação de fertilizante orgânico e mineral (vinhaça e ureia), sendo que com a aplicação somente de vinhaça, o aumento das emissões foi menos intenso. Os fatores de emissão para C-CO₂ e N-N₂O relatados pelo IPCC ainda são maiores do que os observados neste estudo, realizado na região Centro-Sul do Brasil, no qual o maior fator de emissão foi observado para nitrato de amônio, com 0,13% para N-N₂O, na estação chuvosa. A expansão das áreas plantadas de cana de açúcar tem importante papel na emissão de GEE, sendo necessários novos estudos sobre essa contribuição em distintas regiões de produção em todo o mundo, na busca de medidas menos emissoras, visando a sustentabilidade deste biocombustível.

Palavras-chave: Biocombustíveis. Mudança climática. Sustentabilidade

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1. INTRODUCTION

The effects of global warming might affect human health and food production worldwide. According to the Human Impact Report (GLOBAL HUMANITARIAN FORUM, 2009), produced by the Global Humanitarian Forum, 300 million people are seriously affected by climate change that causes an economic loss of about 125 billion dollars per year. This report also predicts that by 2030 the number of deaths caused by this phenomenon will be 500,000 per year and that the number of people affected will rise to 600 million.

The Earth's atmosphere has been warming up due to a combination of natural effects and anthropic activities, and these warming effects could lead to significant climate change during this century (MILLER; SPOOLMAN, 2015). World climate change affects the ecosystem and can reduce biodiversity in areas of all continents (IPCC, 2007). Some sectors that may be especially vulnerable to the possible impacts of climate change, such as natural ecosystems, agroecosystems and socioeconomic systems (ARTAXO, 2008).

The reports generated by the Intergovernmental Panel on Climate Change (IPCC, 1996; 2001; 2007; 2014) confirm that the increase in global atmospheric concentrations of the three main GHGs: carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) are a consequence of human activities, mainly due to the use of fossil fuels and land use change. Fossil fuels are a rich source of carbon and are important sources of the emission of CO₂ into the atmosphere during burning. In addition, the conversion of native vegetation areas into agricultural use alters the physical and chemical characteristics of the soil, affecting the fluxes of GHGs between the soil and the atmosphere (BUSTAMANTE; KELLER; SILVA, 2009). In the last decades, the advancement of the agricultural frontiers to increase food production around the world has increased the pressure on natural resources, and led to a change of the natural vegetation. In many Brazilian regions, such as the Center-South region of the country, the livestock areas have been moved to substitute native vegetation areas once sugarcane has been taking place of old pasture areas. In this context, the conversion of native vegetation areas to farming practices alters the physic and chemical soil characteristics, in which affect the gas fluxes from the soil to the atmosphere. Furthermore, deforestation and burning of native vegetation in Brazil with the following conversion for LUC has been causing a significant increment in the GHG emissions, in which the country is in the fifth place among the countries with most emission of these gases. Livestock is an important source of GHG emission, mainly for CH₄ and N₂O, either by the LUC with the deforestation followed by the

burning of the biomass or by the animals that emit great amounts of GHGs from enteric fermentation and decomposition of cattle urine and feces deposited in the pasture (DINIZ, 2016).

The soil system exerts a key role in the biogeochemical cycles that transform, transport and renew sources of mineral nutrients. Soil has the ability to assimilate large amounts of organic waste into humus, convert the mineral nutrients in the waste into forms that can be used by plants and animals, and return the carbon to the atmosphere as CO_2 , which will become part of living organisms again through the plant photosynthetic process (MADIGAN et al., 2010; BRADY; WEIL, 2013).

Because soil is a key compartment in both processes, carbon emission and sequestration, an inadequate soil management can mineralize organic matter and transfer large amounts of GHG to the atmosphere (LAL, 2004). Methane emissions mainly come from burning biomass, ruminant farming, animal waste decomposition, cultivation of flooded areas, landfills, fossil fuels burning, enteric fermentation and the decomposition of waste under anaerobic conditions (LE MER; ROGER, 2001; PRIMAVESI, 2007). The sources of N_2O emission can be natural or anthropogenic, such as the use of nitrogen fertilizers, biological nitrogen fixation, fertilization with animal waste, incorporation of cultural residues and the burning of plant biomass (CERRI et al., 2009).

Agriculture production is responsible for 37% of the GHG emissions in Brazil (BRASIL, 2014). The recent 'boom' in ethanol production has gained international attention for the environmental impact of converting land to sugarcane monocultures (FARGIONE et al., 2008; MELILLO et al., 2009). When the land use is changed, its susceptibility to degradation and the agricultural practices adopted for the production of sugarcane determine the magnitude of the impact on the environmental quality at the local level (FISCHER et al., 2008; EFROYMSON et al., 2013). However, there is still a lack of information about GHG emission from the soil during LUC, normally from native vegetation through pasture to sugarcane cultivation in the Center-South region in Brazil, where this change has been occurring intensively over the last few years.

An important issue associated with the growth of sugarcane monoculture its impact on the attributes that reflect "soil health". Conversion of natural vegetation through extensive pastures (usually poorly managed) to sugarcane increases the risk of soil degradation (SPAROVEK; SCHNUG, 2001; POLITANO; PISSARRA, 2005; MARTINELLI; FILOSO, 2008). It has been suggested that the environmental impact on the soil is due to a combination of factors associated with this type of crop conversion and management system, which are reflected in its physical, chemical and biological attributes, such as changes in organic matter content, cation exchange capacity, pH, density, and changes in soil organism populations (PANKHURST et al., 2003).

The planned increase in ethanol production from sugarcane in Brazil, to supply growing domestic and international markets, has raised concerns about its sustainability (GOLDEMBERG et al., 2008). To meet this growing demand, there is a need to increase the sugarcane yield as well as expanding the area under cultivation. In order to reach the ethanol production targets in 2020, an additional 57,200 km² (5.72 million ha) would have to be planted with sugarcane (LAPOLA et al., 2010).

Goldemberg et al. (2008) point out that the expansion of sugarcane in Brazil is limited by soil quality, rainfall and logistics. In fact, the Brazilian region with the greatest potential for future expansion, which best provides the three conditions mentioned above, is the Center-South region of the country. In recent years, most of this expansion has occurred on land previously used for pasture (NASSAR et al., 2008) and about 88% of the expansion needed to meet the 2020 demand for ethanol will use areas previously used for pasture (LAPOLA et al., 2010).

The impact of ethanol production from sugarcane on the environment has been described through the use of indicators and criteria suggested in the main environmental sustainability assessment protocols, such as by Cramer et al. (2006), the Bonsucro Certification "Better Sugar Cane Initiative" (BONSUCRO, 2011), and the "Global Bioenergy Partnership" by FAO (GBEP, 2011). There are several indicators of environmental sustainability listed in each of these protocols. Bonsucro's indicators are related to GHG emissions, biodiversity and environmental services, soil and water quality, energy efficiency and the management of waste from the sugar and alcohol industry. On the other hand, Cramer et al. (2006) use GHG emissions, biodiversity, soil and water quality, and waste management as environmental indicators.

Assessments of environmental sustainability or studies that address the environmental consequences of human actions, have assumed increasing importance in contemporary society, being considered important mechanisms in the search and construction of sustainable development. Among various aspects of environmental sustainability, the soil is a key compartment. Emphasis should be given to quality, biodiversity, water and GHG related to the soil as indicators of environmental sustainability.

Currently, one of the greatest challenges facing humanity is climate change caused by anthropogenic activities, resulting in a change in the atmospheric gas composition. Science has advanced to understand the main causes of this change and the impacts of the increment of GHG levels on several sectors. These impacts have been the focus of discussion among authorities around the world at international events such as COP23 (2017), which aimed to define strategies to reduce GHG emissions. At that conference, Brazil presented new approaches to stop the Amazon deforestation and also the potential of the bioenergy generated by biofuels. Therefore, the constant increment of GHG levels in the atmosphere due to anthropogenic activities, and their effects on the climate, demands the creation of mathematical models that allow predicting the state of the future climate in time scales from weeks to centuries. This need arises from the practical irreversibility of changes at global level in the soil use and occupation, natural resources and their consequences for all live organisms on the planet (BRASIL, 2016).

1.1 Hypothesis and general objectives

In this study, it is hypothesized that land-use-change to sugarcane expansion increase the GHG emission, mainly due to the application of rich sources of carbon and nitrogen to the soil during planting and ratoon phases. Therefore, the aim was to quantify GHG emissions from the soil: *i*) during the conversion of native vegetation through pasture to sugarcane cultivation (Chapter 2) ; *ii*) and after different farming practices during different stages of sugarcane cultivation (Chapter 3); during both the dry and rainy season, to determine the specific emission factors for the Center-South region of Brazil.

This research is an integral part of the project "Integrating chemical, physical and biological attributes of soil to evaluate the environmental sustainability of land use with pasture and sugarcane", in which the main chemical, physical and biological attributes of the soil were evaluated to better understand the environmental sustainability of land use with pasture, sugarcane, and native vegetation (as a reference). The product of this proposal is to make possible the evaluation of the environmental sustainability of agricultural land use in three sugarcane expansion sites in the Center-South region of Brazil.

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2. GREENHOUSE GAS FLUXES AFFECTED BY THE LAND USE CHANGE SEQUENCE: NATIVE VEGETATION - PASTURE - SUGARCANE

Abstract

Land use changes directly affect the exchange of greenhouse gases (GHG) between soil and the atmosphere. In Brazil, there are many areas under changes from native vegetation to agricultural activities. The most common land use change is characterized by the succession of pastures taking the place of native vegetation, and sugarcane is moving into areas of old pasture. However, there is still a lack of information about the GHG emission fluxes from these different land uses and how agricultural management can affect the emissions of these gases in a region of Brazilian where land use change is occurring intensively. The aim of this study was to quantify the soil GHG emissions due to land use change, in the succession from native vegetation to pasture, and then to sugarcane, in the Center-South of Brazil. The experiment was carried out in Valparaíso (SP), in three closed areas containing native vegetation, pasture, and sugarcane. Whereas in the native vegetation the chambers recorded the natural emissions of GHGs from the soil, in the pasture area the treatments were composed of feces and cattle urine as well as the control, whilst for the sugarcane area the treatments were composed of the application of agricultural inputs routinely used during the sugarcane planting process (lime, filter cake, or ammonium nitrate). Greenhouse gases emission fluxes from the soil were sampled during the 36 to 30 days of two different climatic seasons (dry and rainy). Pasture areas exhibited the highest values of soil GHG emissions, mainly due to the high emission fluxes of N-N₂O and C-CH₄ compared to the others systems. The conversion of pasture areas to a more intensified production system, such as sugarcane in the Center-South region, reduced GHG emissions to the atmosphere. However, the sugarcane area emitted 7-fold higher CO_2 -eq than native vegetation. Therefore, despite the lower soil GHG emissions in the sugarcane area compared to pasture, studies are still necessary to identify the emission sources during all the stages of ethanol production, to develop GHG mitigation strategies for a more sustainable production of biofuels.

Key words: Land use expansion. N inputs. Animal wastes. Climatic change

2.1 Introduction

The concentrations of greenhouse gases (GHG) in the atmosphere have increased considerably, mainly after the anthropic activities has been intensified, in particular, those related to the burning of fossil fuels and changes in land use (LUC), due to the expansion of agriculture and livestock. However, the increment of GHG concentrations in the atmosphere compromises the climate security of future generations (BRASIL, 2016). In this context, global warming occurs due to the increase in the concentration of three main GHGs: carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), when they are continuously emitted into the atmosphere continuously. These GHGs are part of the global carbon and nitrogen cycle (RAICH; POTTER; BHAGAWATI, 2002).

With the expectation of the growth in the world population, 9.6 billion people in 2050 (UN, 2017), 240 million in Brazil alone in 2030 (IBGE, 2016), the world will demand 60% more food (FAO, 2016). The lack of food and the inadequate management of food production will probably contribute directly and indirectly to the increase the world hunger. One of the challenges of contemporary society is to increase the supply of food in the context of climate change, which interferes with the productive chain and restricts natural resources. It is not only necessary to increase production, but to increase it in a sustainable way in order to guarantee food security for further generations (BRASIL, 2016).

Soil degradation due to exacerbated use is one of the factors that reduce the maximum yield potential for food production, therefore, maintain a sustainable production, significant investments are necessary to recovery large areas around the world for food production (FAO, 2016). A study by the Food and Agriculture Organization of the United Nations (FAO, 2016) revealed that 33% of the world's soils are degraded as a result of several factors.

The impact of climate changes on the soil system, changes in atmospheric CO_2 concentrations, air temperature, precipitation volume and patterns may modify the soil-plant system and influence decomposition rates, affecting soil organic carbon levels (MOSIER, 1998). Organic carbon, in turn, has a significant influence on soil structure, soil fertility, microbial processes and soil populations, among other important properties (LAL, 2009).

Soil is one of three major production factors in classical economics, an essential input for housing and food production. Land use change, however, does not come without costs. Conversion of farmland and forests into urban development areas, reduces the amount of land available for food and timber production. Soil erosion, salinization, desertification, and other factors are associated with soil degradation during intensive agriculture and deforestation, reducing the quality of land resources and future agricultural productivity (LUBOWSKI et al., 2005).

Brazil stands out in the world for its intensive agriculture and livestock farming in large tracts of land. However, this sector has several GHG emitting processes and practices, such as burning of agricultural residues, application of nitrogen fertilizers, rice grown in flooded fields, animal waste management, enteric fermentation of ruminants, among others (BRASIL, 2016). In the current climate scenario, biofuels are entering the market with at least a dual function: to contribute to the reduction of GHG emissions and as an alternative fuel to substitute petrol-derived products (FAVRETTO et al., 2017).

The use of ethanol is gradually improving air quality in Brazilian cities (LANZOTTI, 2000), as well as the reduction in the emission of polluting gases to the atmosphere by up to 90% when compared to gasoline (UNICA, 2007). However, the rapid progress in ethanol production has attracted international attention to the environmental impact of the conversion of land to intensive cultivation and expansion of sugarcane (FARGIONE et al., 2008; MARTINELLI; FILOSO, 2008; FILOSO et al., 2015). In the last decade, sugarcane planted areas in the country have increased mainly at the expense of natural or degraded pastures (MARIN; NASSIF, 2013; OLIVEIRA et al., 2016; BORDONAL et al., 2017).

In this work is hypothesized that LUC sequence of native vegetation-pasturesugarcane increases the soil emission of GHG, in which sugarcane cropping will exhibit the highest emission fluxes, mainly by the intensification of the land use and by the application of rich sources of carbon and nitrogen. Therefore, the aim of this study was to quantify the soil GHG emissions due to land use change, in the succession from native vegetation –pasturesugarcane, in the Center-South of Brazil.

2.2 Material and Methods

A strategy for achieving the proposed objectives for a major succession of land use aimed at ethanol production, that is, the conversion of current pastures, areas originally under native vegetation, to the cultivation of sugarcane (Figure 1).



Figure 1 - The sequence of land use changes until the production of ethanol derived from sugarcane

2.2.1 Experimental location and design

Currently, the most intense expansion of sugarcane production onto pasture areas has occurred in the Center-South region of Brazil. Therefore, this model experiment for the conversion was carried out in Valparaíso (SP). The experiment was set up in three closed areas containing native vegetation (21°20'29"S, 50°56'32"O), pasture (21°20'31"S, 50°56'30"O) and sugarcane (21°20'33"S, 50°56'27"O) (Figure 2). The experimental area presents a tropical climate with a dry winter, annual precipitation of over 750 mm and an average temperature of the coldest month >18 °C). An initial physic-chemical characterization of the soils was performed in the 0-10 cm layer (Table 1). The sugarcane area was cultivated with the CV7870 variety, whereas the pasture area was planted with *Brachiaria brizantha*. The soil was classified as Dystrophic Red Oxisol (EMBRAPA, 2013).

Figure 2 - Experimental areas used for soil GHG sampling, considering different land uses (native vegetation, pasture and sugarcane) in the central-southern region of Brazil (Valparaíso-SP; GoogleMaps[®], 2017)



Table 1 - Physico-chemical analysis of the soils (0-10 cm layer) from the soil under native vegetation, pasture and sugarcane before greenhouse gas sampling, located in Valparaiso (SP)

		Native vegetation	Pasture	Sugarcane
pН	(CaCl ₂)	4.6	4.0	5.0
Organic matter	$g dm^{-3}$	36.3	27.7	13.3
Humidity	%	13.6	18.5	16.2
Р	$mg \ dm^{-3}$	10.0	7.0	21.3
S	$mg \ dm^{-3}$	6.3	6.0	6.7
K	$mmol_c dm^{-3}$	2.1	1.6	3.3
Ca	$mmol_c dm^{-3}$	22.3	3.0	8.0
Mg	$mmol_c dm^{-3}$	10.3	2.7	5.3
H+A1	$mmol_c dm^{-3}$	17.7	27.3	16.0
SB	$mmol_c dm^{-3}$	34.8	7.3	16.7
CEC	$mmol_c dm^{-3}$	52.5	34.6	32.7
BS	%	65.3	21.3	47.3
AS	%	3.0	34.7	7.0
В	$mg \ dm^{-3}$	0.48	0.25	0.18
Cu	$mg \ dm^{-3}$	0.47	0.63	1.03
Fe	$mg \ dm^{-3}$	63.3	119.0	53.0
Mn	$mg \ dm^{-3}$	18.2	15.2	6.3
Zn	$mg \ dm^{-3}$	1.8	2.07	1.1
С	%	2.2	1.83	0.71
Ν	%	0.15	0.08	0.03
C/N ratio		22.3	22.6	14.7

Legend: S - sulfur; P - phosphorus; K - potassium; Ca - calcium; Mg - magnesium, H+Al - acidity potential; SB - sum of bases; CEC - cations exchange capacity; BS - base saturation; AS – aluminion saturation; B - boron; Cu-copper; Fe - iron; Mn - manganese; Zn - zinc; OM - organic matter; C - carbon; N - nitrogen; C/N – carbon/nitrogen ratio.

GHG sampling from the soil in both experimental areas were performed during 36 days in the dry season (August to September of 2014) and during 30 days in the rainy season (from December of 2014 to January of 2015). In order to obtain significant data, the experiments were set up and sampled in two seasons, *i*) dry season - characterized by lower air temperature and precipitation; *ii*) rainy season – characterized by high air temperatures and precipitation.

Air temperature and rainfall data during the GHG sampling period were obtained from the InMet Automatic Meteorological Station (National Meteorological Institute), located at the experimental station of the "Universidade Federal de São Carlos (UFSCar)" in Valparaiso, near to the experimental areas (Figure 3). Means of air temperatures and the sum of rainfall precipitation during the GHG sampling periods were, respectively: 26.4 °C and 31 mm in the dry season, and 25.8 °C and 172 mm in the rainy season. In addition, soil temperatures varied between the dry and rainy seasons, as well as among the land use areas (Figure 4). The mean values of soil temperature (at 2 cm depth) were in the dry and rainy seasons, respectively: 22.8 °C and 25.9 °C for native vegetation, 25.6 °C and 27.6 °C for pasture, and 26.7 °C and 23.4 °C for sugarcane.



Figure 3 - Air temperature and rainfall in Valparaíso-SP during the experiment period during the dry and rainy seasons
Figure 4 - Temperature inside (IN) and outside (OUT) the sampling chamber and the soil temperatures at different soil depths (2 cm, 5 cm and 10 cm) under native vegetation, pasture and sugarcane during the GHG sampling over the two climatic periods



2.2.2 Experimental design and treatments

Experiments were carried out in a completely randomized design. Five static chambers for the collection of GHG were installed for each treatment. In the native vegetation area, without the application of treatments, the chambers recorded the natural emissions of GHG from the soil. In the pasture area, the treatments were feces and cattle urine and controls; (I) pasture without application of waste and (II) water. The treatment with water was used as a comparison to the urine treatment to verify the influence of the humidity in the emission. The amount of feces and urine applied was based on the values observed in extensive cattle breeding systems, where the daily average is approximately 1 kg of feces and 1 L of urine per dejection (DINIZ, 2016; GONZÁLEZ-AVALOS; RUIZ-SUÁREZ, 2001; ORR et al., 2012). Sugarcane area was composed with the application of lime (2.0 t ha⁻¹), filter cake (30 t ha⁻¹) and ammonium nitrate (60 kg ha⁻¹), in which represent the main sources of carbon and nitrogen during sugarcane planting process.

According to Instituto Forestal (2005), cited by Diniz (2016), the predominant natural vegetation in the region is classified as semideciduous seasonal forest, with trees that regulate their water balance and their leaves fall in periods of low rainfall incidence. This experiment covers the stretches of Atlantic Forest found in the interior of the state of São Paulo.

The pastures were formed mainly by *Brachiaria brizantha*, where the farm produces Nelore beef cattle, raised in an extensive system, with nutritional supplementation of protein salt throughout the year. The urine and feces used in the experiment were collected from a group of 12 dairy cattle, with an average weight of 400 kg and two-years-old. The application of these wastes inside and around the static GHG chamber, fixed to the soil was done immediately after the collection, simulating the animal waste, thus enabling measurements closer to reality. These animals were raised in the pasture for one year and in confinement for 90 days, with feed supplemented composed of maize, citrus pulp, soybean meal, cottonseed and cane silage.

2.2.3 Water filled pore space of the soil

Soil density determination was performed in 10 mini-trenches using the volumetric ring method (BLAKE; HARTAGE, 1986) and used to calculate the percentage of water filled pore space (%WFPS), assuming soil particle density of 2.65 mg m⁻³ according to Bielders et al. (1990) and Fageria and Stone (2006). The mean percentages of WFPS were in the dry and rainy seasons, respectively: 30.3% and 32.7% for native vegetation, 49.7% and 73.1% for pasture, and 73.1% for sugarcane.

2.2.4 Soil greenhouse gases fluxes

The collection of GHG samples from the soil was performed as described in Steudler et al. (1991), in which static chambers were set up and inserted 5.0 cm into the soil (ROCHETTE et al., 2008). The chambers were composed of base, with dimensions of 45 cm x 70 cm width and 30 cm height, with removable-lid (45 cm x 70 cm width and 7 cm height), noting that the base was fixed in the soil, avoiding disturbance of the soil and facilitating various collections during the experimental period. The volume of each chamber was measured by three-point heights from the soil surface to the lid. Soil GHG emission samples were collected daily (between 10h:00 and 14h:00) for 15 days after the treatment was initiated. Subsequently, the collections were performed on interspersed days, and terminated on the fortieth day.

To determine the GHG fluxes inside the chambers, during an incubation period of 30 min samples were taken at 10-min intervals, (*i.e.*, T0, T10, T20 and T30 min) using a BD 50 ml nylon syringes. At the same time, soil temperatures were measured at 2, 5 and 10 cm deep, in addition to the temperatures at the surface, inside and outside the chamber. Air temperature and rainfall were also recorded for later correlation with the emissions (Figure 3).

The concentrations of C-CO₂, C-CH₄ and N-N₂O were determined in each sample by gas chromatography (SRI 8610C, Torrance, CA, USA), maintained at 81 °C to separate molecular gases. Determination of CH₄, CO₂ with flame ionization detector (FID) and N₂O electron capture detector (ECD), using nitrogen as gas flow, was performed by gas chromatography (SRI 8610C Model, Torrance, CA, USA). This chromatograph has two HayeSep-N packaged columns and uses nitrogen (5.0) as the entrainment gas at 25 mL min⁻¹. In the FID, the samples were submitted to combustion by hydrogen (5.0) and flame of synthetic air. The flux of each GHG was calculated using the linear change in the concentrations as a function of the incubation time within the chamber according to Equation 1. The daily emission of C-CO₂, C-CH₄ as N-N₂O was calculated based on the mean hourly flux obtained from the five replicates (chambers) for each treatment (OLIVEIRA et al., 2013).

$$Flow = (d[gas]/dt) \times (Vh/A) \times ((1-e/P)/VM)$$
(1)

Where: (d[gas]/dt) - change in the gas concentration as a function of time (mol gas mol⁻¹ s⁻¹); Vh - volume of the chamber used for GHG sampling (m³); A - chamber surface area (m²); e/P - water pressure/atmospheric pressure in the chamber (kPa kPa⁻¹); VM - molar volume of the chamber (m³ mol⁻¹).

The emission of GHG that accumulated over the total experimental period was determined by integrating the data points and the total GHG emission is the sum of the C-CO₂, N-N₂O and C-CH₄ fluxes. From the accumulated emissions of N-N₂O the emission factor of this GHG was calculated in relation to the amount of N added through the mix of inputs (filter cake and nitrogen fertilizer). Nitrous oxide and CH₄ fluxes were converted to CO_2 -*eq* according to their global warming potential (GWP) of 298 and 25 times that of CO₂, respectively (IPCC, 2006; OLIVEIRA et al., 2013) (Equations 2, 3 and 4).

$$CO_2 - eq(CO_2) = CO_2 \times (12/44)$$
 (2)

$$CO_2$$
-eq $(N_2O) = N_2O \times (44/28) \times 298$ (3)

$$CO_2 - eq(CH_4) = CH_4 \times (16/12) \times 25$$
 (4)

Where: $CO_2 - CO_2$ flow; $N_2O - N_2O$ flow; $CH_4 - CH_4$ flow; (12/44) - relationship between the molecular weight of carbon and CO_2 ; (44/28) - relation between the molecular weight of N_2O

and nitrogen; (16/12) - relation between the molecular weight of CH₄ and carbon; 298 - global warming potential of N₂O over CO₂; 25 - global warming potential CH₄ over CO₂.

The amount of GHG emitted from the soil was a sum of the emissions of the treatments in the pasture area (Control + Feaces + Urine; DINIZ, 2016) and in the sugarcane area (Control + Lime + Filter Cake + Ammonium nitrate).

2.2.5 Statistical analysis

Descriptive analysis was used for the daily GHG flux data, whereas the accumulated GHG and CO₂-*eq* data were analyzed using ANOVA and, when significant, Tukey test with a significance level of 5% was used (SAS version 9.2, SAS Institute, Cary, NC).

2.3 Results

2.3.1 Emission fluxes of greenhouse gases from the soil

Peak daily emissions of C-CO₂, C-CH₄ and N-N₂O, under the three land uses, occurred during the first five days after the beginning of the experiments (Figure 5). The same emission peak pattern was observed during the dry and rainy seasons, in the two-year evaluation period. Considering the entire experimental period, the lowest emission of C-CO₂ was observed under native vegetation at 30.7 mg C-CO₂ m⁻² h⁻¹, during the dry season, whereas the highest emission was verified under pasture at 1561.7 mg C-CO₂ m⁻² h⁻¹ during the rainy season (Figure 5). The lowest emission of N-N₂O m⁻² h⁻¹ was observed under native vegetation (38.2 µg N-N₂O m⁻² h⁻¹) and the highest emission was observed under sugarcane (3483 µg N-N₂O m⁻² h⁻¹), both cases during the dry season. In the case of C-CH₄, the lowest daily emissions occurred under native vegetation (-93.8 µg C-CH₄ m⁻² h⁻¹), whilst the highest was observed under pasture (17625.4 µg C-CH₄ m⁻² h⁻¹), again, both in the dry season (Figure 5).

The accumulated emissions of C-CO₂ and N-N₂O during the dry season were higher under sugarcane when compared to pasture and native vegetation (Figure 6). However, during the rainy season, under pasture, the soil exhibited the highest emissions of C-CO₂ and N-N₂O (p<0.05; Figure 6). Furthermore, the accumulated emission of C-CH₄ was higher under pasture when compared to sugarcane and native vegetation, in both the dry and rainy seasons (Figure 6). Despite exhibiting the lowest emissions of GHGs during the different climatic periods, the soil under native vegetation showed a variation in GHG emission due to the seasonality of the climate, where the emission during the rainy season was three times higher than that during the dry season (Figure 6).

Figure 5 - Daily emissions of C-CO₂, N-N₂O and C-CH₄ from the soil under native vegetation, pasture and sugarcane during the dry and rainy seasons, in Valparaíso (SP). The error bars show the standard error of the mean (n = 20)







2.3.2 The conversion of N₂O and CH₄ emission flows into CO₂ equivalents (CO₂-eq)

The values of the accumulated GHG flows (N₂O and CH₄), regardless of the CO₂ values, were used to calculate their CO₂-*eq*. The total value emitted under native vegetation in this study was 237 kg CO₂-*eq* ha⁻¹ yr⁻¹ (Figure 7). This value was used as the reference for the comparison of the treatments used.

After converting the N-N₂O and C-CH₄ flows to CO_2 -*eq* for all the GHG sources sampled, the result for pasture was 9728 kg CO_2 -*eq* ha⁻¹ yr⁻¹, which was approximately 41-fold higher than that observed under native vegetation. Under sugarcane, the CO_2 -*eq* emission was 1710 kg CO_2 -*eq* ha⁻¹ yr⁻¹, 7-fold higher when compared to the emission verified under native vegetation. Furthermore, the annual CO_2 -*eq* emission under pasture was 5.6-fold greater than that observed under sugarcane. Figure 7 - Calculated carbon dioxide equivalent (CO_2 -*eq*) emissions of N_2O and CH_4 from the soil under native vegetation, pasture and sugarcane during the dry and rainy seasons, in Valparaíso (SP). The error bars show the standard error of the mean



2.4 Discussion

Brazil is one of the largest ethanol producers and in an important producer and exporter of meat (FAO, 2017). Although Brazil still has a great amount of land that could be converted to agricultural practices, there is concern about how LUC could affect soil GHG emissions, once the physic-chemical characteristics of the soil changes affecting the exchange of gases between the soil and atmosphere. The fluxes of soil GHG emissions under different land uses are dependent on the environmental conditions and the regions where they occur. However, previous studies have confirmed opposite conclusions about LUC in different Brazilian regions, such as the Cerrado (SIQUEIRA NETO et al., 2011) and the Amazon (FERNANDES et al., 2002). In the present study, we bring new insight about the way LUC effects GHG emissions from the soil in the Center-South region of Brazil, which is currently characterized by intense LUC from native vegetation to pastures, and sequentially to sugarcane.

The initial hypothesis of this study was partially rejected. Despite LUC increasing the soil GHG emissions, in this study we verified that under pasture the soil exhibited higher GHG emissions when compared to sugarcane and native vegetation. During a year, the soil under pasture emitted a CO₂-eq approximately 41-fold higher than under native vegetation and 5-fold higher than under sugarcane (Figure 7). In addition, the sugarcane area emission was 7-fold higher than under native vegetation. The conversion of native vegetation to pasture areas can result in changes to soil physical and water properties, the quantity and quality of

organic matter, nutrient dynamics, species composition, microclimate and biogeochemical processes (KELLER et al., 1992).

The high CO₂-eq in the pasture area occurred due to higher emissions of N-N₂O during the rainy season and C-CH₄ for both seasons (Figures 5 and 6). Among the total emissions of CO₂-eq in the pasture area, only 6.2% was derived from the Braquiaria Brizantha without any C or N source input, whereas 78% and 15.8% occurred due to the deposition of urine and feces, respectively (DINIZ, 2016). Some authors suggest that the addition of organic material to the soil stimulates soil microbiota activity, which, in addition to consuming all carbon added, might also accelerate the degradation of soil organic matter (MOREIRA; SIQUEIRA, 2006). The addition of cattle urine may increase the solubility of carbon present in the soil, leading to an increase in the decomposition of this carbon and thus leading to a potential increase in CO₂ emissions (UCHIDA et al, 2011; LAMBIE et al., 2013).

Soil emission of C-CO₂ was higher under pasture when compared to the other systems in the rainy season (Figure 6). In fact, the main soil GHG emission under pasture is associated with feces decomposition, due to the rich sources of C and N (DINIZ, 2016). In the rainy season, the urine and feces decomposition were boosted by the higher soil humidity due to the rainfall, when compared to the dry season (Figure 3). Oxygenation and humidity of the soil are important factors that influence several soil-processes; the denitrification reaction is favored in environments with high water saturation (DE KLEIN; VAN LOGTESTIJN, 1994; LUO; WANG; SUN, 2010). According to Siqueira Neto et al. (2002), pasture areas exhibited higher emission of N-N₂O when compared to native vegetation in the Cerrado. On the other hand, higher N₂O emission was observed under the native vegetation in relation to the pasture in the Amazon (VERCHOT et al., 1999; GARCIA-MONTIEL et al., 2001). When no other limiting factor is present in the system, the combination of the high availability of mineral N and high water saturation can be considered a stimulus for the induction of soil N₂O fluxes (SMITH et al., 2003; BENTO et al., 2018).

In the conversion of native vegetation to pasture, the soil ceases to be a drain and becomes a source of CH_4 , mainly in the dry season (Figure 6). This is possibly related to soil compaction, which affects soil permeability and favors the creation of anaerobic micro-sites, where CH_4 production occurs (BALL et al., 1999). In addition, in this work we only assessed the soil emission of GHG to the atmosphere, in which pasture areas already exhibited higher emissions when compared to sugarcane and native vegetation areas. However, GHG emissions from the pasture could still be higher when the emission due to cattle eructation, where amounts of up to 720 kg head-1 yr-1 C-CH₄ can be recorded (LIMA et al., 2010).

Although the sugarcane area did not show values higher than those for GHG emission under pasture, mainly in the rainy season (Figure 6), this agricultural system was shown to be an important source of GHG emission from the soil, mainly after the application of mineral or organic sources of nutrients. The main contribution of the sugarcane area was due to the emission of CO₂ and N₂O, but he CH₄ soil emission levels under sugarcane were similar those under native vegetation, which is a sink of this GHG (Figure 6). The main contribution to the CO_2 -eq emission under sugarcane was the emission of N-N₂O (Figure 7). Among the agricultural practices that composed the sugarcane area in this study, soil tillage during the sugarcane planting process was responsible for 64.2% of the total CO₂-eq emitted. In addition, the application of organic or mineral sources of nutrients contributed 14.5%, 12.1% and 9.2% when ammonium nitrate, filter cake and lime were applied, respectively.

The emission of CO_2 from the soil under sugarcane to atmosphere occurs mainly as a result of biological processes, degradation of organic residues, such as filter cake application, by microbial activity and roots respiration (LAL, 2009; BORDONAL et al., 2015; 2017). Despite the production of CO_2 by these several soil reactions, the emission of this GHG also occurs due to the transport of the gas through the pore-spaces towards the soil surface (BALL et al; 1999; KANG et al., 2000).

According to IPCC (2006), emission estimates are associated with the direct and indirect emissions of CO₂, N₂O and CH₄, for example, the GHG emissions from diesel consumption by machinery are important contributors to the total emission of farming practices. The contribution of diesel to total the emissions from the sugarcane planting process is 750.2 kg CO₂-eq ha⁻¹ yr⁻¹(BORDONAL et al., 2013). Even if we include the emissions from fuel burning during the sugarcane planting in this study, the total emission under sugarcane would still be 4-fold lower than those observed under pasture.

The soil C-CH₄ emissions under sugarcane and native vegetation were negative (Figures 5 and 6), indicating that the predominant process in the soil was consumption of this GHG. This may be related to the fact that in well-drained soils, such as the soils of this study (Table 1), the oxidation of CH₄ by methanotrophic organisms is generally the dominant process. However, in environments with very low redox potential, typical of very humid or flooded areas, methane production is favored (MOSIER et al., 1991; STRIEGL et al., 1992; LE MER; ROGER, 2001). The increase in precipitation during the rainy season influenced the gas emissions, reducing the consumption of this GHG. This is related to the fact that the increase in humidity reduced the oxidation capacity of CH₄ by the soil organisms. In Brazil,

this behavior was also observed in Cerrado (POTH et al., 1995; SIQUEIRA NETO et al., 2011) and in Amazonian forests (VERCHOT et al., 2000; FERNANDES et al. 2002).

The native vegetation exhibited the lowest GHG emissions among the LUC. In addition, the GHG emissions varied in response to the climatic seasons (Figures 5 and 6). The changes of CO₂ between the soil and the atmosphere were strongly controlled by soil temperature and humidity, the emission increasing as these factors increase (BOWDEN; NEWKIRK; RULLO, 1998). In Cerrado areas, whose soils are typically acidic and porous, with rapid drainage and good aeration, there was no significant variation in GHG fluxes between the dry and rainy periods (CASTALDI et al., 2006). Furthermore, the vegetation is an important factor that influences the GHG fluxes, because the large amount of organic matter in the forest soils increases the nutrient content and improves soil structure, favoring water retention and mineralization of soil organic matter. Furthermore, the low N₂O fluxes observed in both seasons in native vegetation is likely due to the inadequate soil humidity, insufficient to stimulate the production of N₂O, even when the water content in the soil increased during the rainy season, favoring the nitrification process over denitrification (FIRESTONE; DAVIDSON, 1989; BATEMAN; BAGGS, 2005). This event could be explained by the fact that the experimental soil is sandy, where water drainage occurs rapidly, even during the rainy season, making water retention difficult (CASTALDI; ERMICE; STRUMIA, 2006). In other Brazilian regions, N₂O emission fluxes under native vegetation did not vary with the climatic season in the Cerrado (VARELLA et al., 2004), but there was an increment in emission during the rainy season in the Amazon (VERCHOT et al., 2000; MELILLO et al., 2001) and Cerradão (SIQUEIRA NETO et al., 2011).

2.5 Conclusion

The conversion sequence native vegetation-pasture-sugarcane increased GHG emissions from the soil. However, the conversion of pasture areas into a more intensified production system, such as sugarcane, did not result in higher emissions as was initially hypothesized in this work. In the sugarcane system, there was a reduction of 8.0 t CO_2 -eq ha⁻¹ yr⁻¹ emitted from the soil, when compared to the pasture system. Despite these lower soil emissions in the sugarcane area, it is still necessary to increase the environmental sustainability of biofuels (ethanol), so it is important to study the emission sources in order to delineate GHG mitigation strategies.

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3. SOIL GREENHOUSE GAS FLUXES DERIVED FROM THE MAIN INPUTS APLLIED TO THE SUGARCANE FIELD

Abstract

There is an international focus on climate change due to the increased emission of greenhouse gases (GHG) and the consequent increase in the average temperature of Earth's surface. Although ethanol emits lower amounts of GHG when compared to fossil fuel, the major concerns about GHG emissions are those coming from farming practices. In this context, the aim of this study was to quantify the GHG emissions from the soil as a result of the main farming practices adopted for sugarcane production in the Central-South of Brazil. Two experiments were set up in Valparaíso (SP), the first experiment was carried out in a sugarcane planting area with the application of ammonium nitrate (60 kg ha⁻¹ N), or lime (2 t ha⁻¹), or filter cake (30 t ha⁻¹), and a control treatment with zero application. The second experiment was carried out in a sugarcane ration area with the application of vinasse (200 m^3 ha⁻¹) and urea (100 kg ha⁻¹ N) in the first year, and vinasse (200 m³ ha⁻¹) or water (200 m³ ha⁻¹) ¹) in the second year. In both experiments, the application of the treatments and the sampling of the GHG fluxes from the soil were carried out for approximately 40 days during the dry and rainy seasons, in two consecutive years. The emission fluxes of C-CO₂, C-CH₄ and N-N₂O were analyzed. Our results demonstrated that the main GHG emission from the soil under sugarcane cultivation occurred from the soil tillage after sugarcane planting. The application of carbon and nitrogen sources to the soil, such as mineral or organic fertilizers, enhanced the GHG emission fluxes from the soil, mainly in the first days after application in either areas, sugarcane planting or ratoon. Among the inputs applied to the cane plant, filter cake or ammonium nitrate produced the highest GHG emissions from the soil. On the other hand, in the area of sugarcane ratoon, the highest emissions were observed when a combination of organic and mineral fertilizers was applied (vinasse and urea). The application of only vinasse produced a less intense increment in emissions. However, the emission factors for CO₂ and N₂O reported by the IPCC, are still higher than those observed in this study performed in the Center-South region of Brazil. The highest emission was observed for ammonium nitrate, with 0.13% for N-N₂O, in the rainy season. However, because of the expansion in sugarcane planted areas there could be an increment of GHG emissions. Therefore, new studies are necessary understand the process and reduce GHG emissions during sugarcane production in ethanol production regions around the world.

Key-words: Ethanol. Global warming. Climate change. GHG emission.

3.1 Introduction

Brazil is the second largest producer of ethanol derived from plant biomass and leader in the production of ethanol from sugarcane (UNICA, 2018). Ethanol from sugarcane is consolidated as an indispensable product in the Brazilian fuel supply system, even with large price swings, a reduction in the ethanol production has occurred due to the international economic recession, climatic problems and gasoline exemptions (MANOCHIO et al., 2017). According to the Environmental Protection Agency (USEPA, 2010), by using ethanol the greenhouse gas (GHG) emissions can be reduced by up to 61% when compared to petrolderived fuels, such as gasoline. Such a substitution further reinforces the need for assessments of all GHG emissions in the ethanol production chain, starting with the sugarcane cultivation in the field. The three main GHGs are methane (CH₄), nitrous oxide (N₂O) and carbon dioxide (CO₂). Biomass-derived fuels play an important role in this scenario (FOLEY et al., 2005).

Among biofuels, ethanol stands out due for the competitiveness of its production chain in the market, as well as its environmental sustainability. The impact of the production of sugarcane ethanol on the environment has been described using indicators and criteria suggested in the main environmental sustainability assessment protocols. The FAO Global Bioenergy Partnership (GBEP, 2011) lists eight indicators, including GHG emissions in the product life cycle. The criteria for the Bonsucro "Better Sugarcane Initiative" certification (2011) are also related to GHG emissions. Most of the GHG emitted from sugarcane, to produce ethanol, results from the agricultural phase (GARCIA; SPELING, 2010).

In Brazil, the agricultural sector is responsible for 37% of the national GHG emissions. The sources of the GHG emission such as lime application, synthetic nitrogencontaining fertilizers, and land use change are some of the items included in the calculations of the Brazilian GHG inventory (BRASIL, 2014). In the LUC, soil tillage and others management system may be important sources or sinks of GEE (BERNOUX et al., 2005).

In addition to the use of nitrogen fertilizers and limestone for the sugarcane cultivation, during the sugar and ethanol production there are a range of by-products derived from the industry, such as vinasse and filter cake. Vinasse is considered the main residue from the sugarcane industry, which is rich in nutrients and has a high load of organic material (SILVA et al., 2007), and for this reason is commonly applied via fertigation to the soil. It is estimated that around 10 to 18 L of vinasse is produced for each 1 L of ethanol, depending on the operating conditions and the production system used (KUMAR et al., 1998).

Filter cake is also applied to the sugarcane crop, acting as an organic fertilizer, minimizing application costs due to the increase in nutrient concentration of the soil and consequent reduction in the use of inorganic fertilizers. The production of filter cake varies from 35 to 45 kg ton⁻¹ of processed sugarcane (LUZ; VITTI, 2012). The use of these two residues in agriculture generates several benefits for plant growth and reduces the accumulation of waste material. However, there is growing concern about environmental sustainability and GHG emissions (CARMO et al, 2012; OLIVEIRA et al., 2013; SIQUEIRA NETO et al., 2015).

In this study we hypothesized that the main soil GHG emissions during the cane-plant phase are derived from tillage, whereas during the ratoon phase the application of mineral N fertilizers results in higher GHG emission when compared to organic sources of nutrients. The aim of this study was to quantify soil GHG emissions, the contribution of the soil tillage and the main inputs of C and N (e.g., N-fertilizer, limestone and coproducts from ethanol production: vinasse and filter cake), applied to sugarcane fields.

3.2 Material and methods

3.2.1. Study sites

Two experiments were carried out in the experimental area of the Univalem/Raízen Factory, in Valparaíso-SP (21°20'33"S, 50°56'27"O), which is the main area in the Center-South region in Brazil with sugarcane expansion program into pasture areas. The climate is classified as tropical with dry winter, annual rainfall greater than 750 mm and an average temperature of the coldest month of >18 °C according to the Köppen classification. For the initial characterization of the physical-chemical properties of the soil (Tables 1 and 2), soil was sampled from the 0-10 cm layer. The experimental areas selected were cultivated with sugarcane, variety CV7870. The experiments were set up during the winter (dry season) and during the summer (rainy season).

		Dry season		Rainy season	
		Sugarcane after planting	Sugarcane ratoon	Sugarcane after planting	Sugarcane ratoon
pН	(in CaCl ₂)	4.7	4.7	5.0	4.8
S	$mg \ dm^{-3}$	10.6	6.8	6.7	7.3
P (resin)	$mg \ dm^{-3}$	11.0	10.6	15.0	15.0
K	$mmol_c dm^{-3}$	2.3	1.7	3.3	1.9
Ca	$mmol_c dm^{-3}$	8.2	6.0	8.0	5.7
Mg	$mmol_c dm^{-3}$	3.2	3.2	5.3	3.0
H+A1	$mmol_c dm^{-3}$	16.2	15.4	16.0	15.0
SB	$mmol_c dm^{-3}$	13.7	10.5	16.6	10.6
CEC	$mmol_c dm^{-3}$	29.9	25.9	32.7	25.6
BS	%	45.8	40.4	47.3	41.3
В	$mg \ dm^{-3}$	0.14	0.15	0.18	0.14
Cu	$mg \ dm^{-3}$	0.4	0.4	1.0	0.4
Fe	$mg \ dm^{-3}$	21.8	23.0	53.0	35.3
Mn	$mg \ dm^{-3}$	9.1	8.9	6.3	7.2
Zn	$mg \ dm^{-3}$	0.7	0.7	1.1	0.8
ОМ	$g dm^{-3}$	9.8	12.8	13.3	11.7
Sand	$g kg^{-1}$	878	873	869	873
Silt	$g kg^{-1}$	17	21	23	31
Clay	$g kg^{-1}$	105	105	108	96

Table 1 - Soil physico-chemical characteristics (0-10 cm layer) at the beginning of the dry and the rainy seasons, before the application of the treatments in the first year of the experiment

Legend: S - sulfur; P - phosphorus; K - potassium; Ca - calcium; Mg - magnesium, H+Al - acidity potential; SB - sum of bases; CEC - cations exchange capacity; BS - base saturation; B - boron; Cu-copper; Fe - iron; Mn - manganese; Zn - zinc; OM - organic matter; C - carbon; N - nitrogen; C/N - carbon/nitrogen ratio.

•

		Dry season		Rainy season	
		Sugarcane after planting	Sugarcane ratoon	Sugarcane after planting	Sugarcane ratoon
pН	(in CaCl ₂)	5.2	5.8	4.8	5,8
S	$mg \ dm^{-3}$	7.0	7.0	10.0	10.0
P (resin)	$mg \ dm^{-3}$	26.0	9.0	58.0	31.0
K	$mmol_c dm^{-3}$	2.4	2.4	3.2	3.3
Ca	$mmol_c dm^{-3}$	20.0	23.0	11.0	71.0
Mg	$mmol_c dm^{-3}$	11.0	11.0	5.0	51.0
H+A1	$mmol_c dm^{-3}$	13.0	12.0	18.0	11.0
SB	$mmol_c dm^{-3}$	33.4	36.4	19.2	125.3
CEC	$mmol_c dm^{-3}$	46.4	48.4	37.2	136.3
BS	%	72.0	75.0	52.0	92.0
В	$mg \ dm^{-3}$	0.23	< 0.2	0.22	0.24
Cu	$mg \ dm^{-3}$	0.5	0.5	0.5	0.4
Fe	$mg \ dm^{-3}$	23.0	22.0	52.0	33.0
Mn	$mg \ dm^{-3}$	4.6	4.4	8.0	4.0
Zn	mg dm ⁻³	0.3	0.2	0.3	0.7
ОМ	$g dm^{-3}$	10.0	9.0	9.0	23.0
Sand	$g k g^{-1}$	834	859	842	809
Silt	$g kg^{-1}$	41	40	59	65
Clay	$g kg^{-1}$	125	100	100	126

Table 2 - Soil physico-chemical characteristics (0-10 cm layer) at the beginning of the dry and the rainy seasons, before the application of the treatments in the second year of the experiment

Legend: S - sulfur; P - phosphorus; K - potassium; Ca - calcium; Mg - magnesium, H+Al - acidity potential; SB - sum of bases; CEC - cations exchange capacity; BS - base saturation; B - boron; Cu-copper; Fe - iron; Mn - manganese; Zn - zinc; OM - organic matter; C - carbon; N - nitrogen; C/N - carbon/nitrogen ratio.

3.2.2 Experimental design and treatments

The experiments were carried out using a completely randomized design, in selected areas with sugarcane cultivation in the dry season and rainy season of two years. The dry seasons extended from August to September of 2014 and from September to October of 2016, whereas the rainy seasons was from December of 2014 to January of 2015 and from January to February of 2017.

In both experiments, the treatments consisted of the application of nutrients as mineral fertilizers or as by-products from ethanol production, as these are the main inputs at the sugarcane planting and ration stages.

The first experiment was set up in a sugarcane area after planting and the soil application of ammonium nitrate (60 kg ha⁻¹ N), lime (2 t ha⁻¹) or filter cake (30 t ha⁻¹). The chemical characteristics are shown in Table 3. The second experiment was set up in a sugarcane ratoon area (after the third cut) with the application of vinasse (200 m³ ha⁻¹; the chemical characteristics are shown in Table 4) and urea (100 kg ha⁻¹) as a topdressing in the first year of experiment and vinasse (200 m³ ha⁻¹) or water (200 m³ ha⁻¹) in the second year. However, during the rainy season in the second year (Jan/Feb of 2017), no vinasse treatment was performed due to the lack of availability of this residue at the local sugarcane industry. In both experiments, five static chambers were set up for each treatment for the collection of GHG from the soil.

		First year		Second year	
	_	Dry season	Rainy season	Dry season	Rainy season
OM	%	58.4	67.7	31.1	33.9
Organic-C	%	30.5	35.7	14.3	14.8
Total MR	%	38.3	29.1	57.2	64.2
Soluble MR	%	11.0	11.2	6.9	8.9
Insoluble MR	%	27.3	17.9	60.3	55.2
Ν	%	2.4	2.4	1.38	1.53
$P(P_2O_5)$	%	1.8	1.7	0.87	1.20
K (K ₂ O)	%	-	-	0.16	0.18
Ca	%	3.38	3.19	0.87	1.03
Mg	%	0.28	0.29	0.16	0.15
S	%	0.07	0.05	0.02	0.03
Cu	$mg kg^{-1}$	30.0	32.0	11.0	20.0
Mn	$mg kg^{-1}$	600	641	266	393
Zn	$mg kg^{-1}$	92	100	60	103
Fe	$mg kg^{-1}$	-	-	9357	12008
В	$mg kg^{-1}$	-	-	2.0	3.0

Table 3 - Filter Cake chemical characteristics applied to the sugarcane ration experiment during the dry and rainy seasons in the two-year experiment

Legend: Chemical analysis with dried sample at 65 °C; OM – organic matter; C - carbon; N - nitrogen; MR – mineral residue; S - sulfur; P - phosphorus; K - potassium; Ca - calcium; Mg - magnesium, Cu-copper; Fe - iron; Mn - manganese; Zn – zinc.

Air temperature and rainfall data were obtained from the InMet Automatic Meteorological Station (National Meteorological Institute), located at the experimental station of the "Universidade Federal de São Carlos (UFSCar)" in Valparaiso, near to the experimental areas (Figure 3). Means of temperatures of air and soil (2 cm), and the sum of rainfall the precipitation during the period of GHG sampling from the soil were, respectively: 26.4 °C, 26.7 °C and 31 mm for the dry season of the first year; 25.8 °C, 22.8 °C and 172 mm for the rainy season of the first year; 20.9 °C, 23 °C and 176mm for the dry season of the second year; and 27.6 °C, 27.8 °C and 88 mm for the rainy season of the second year (Figures 1 and 2).

		First year		Second year	
	-	Dry season	Rainy season	Dry season	
pН		5.5	4.4	4.9	
Density	$g m L^{-1}$	0.96	0.94	0.95	
OM	$g L^{-1}$	17.8	8.3	10.9	
C/N ratio		23.3	27.9	6.8	
Total-C	$g L^{-1}$	6.3	9.5	5.0	
Total MR	$g L^{-1}$	9.8	7.4	6.1	
Insoluble MR	$g L^{-1}$	0.2	0.1	5.2	
Soluble MR	$g L^{-1}$	9.6	7.3	0.18	
Ν	$g L^{-1}$	0.27	0.34	0.74	
$P(P_2O_5)$	$g L^{-1}$	0.12	0.15	0.14	
K (K ₂ O)	$g L^{-1}$	3.60	3.85	2.24	
Ca	$g L^{-1}$	0.86	1.05	0.75	
Mg	$g L^{-1}$	0.33	0.35	0.16	
S	$g L^{-1}$	0.69	0.89	0.26	
Cu	$mg L^{-1}$	1.0	1.0	< 0.01	
Mn	$mg L^{-1}$	6.0	9.0	3.0	
Zn	$mg L^{-1}$	1.0	11.0	1.0	
Fe	$mg L^{-1}$	18.0	26.0	24.0	

Table 4 - Vinasse chemical characteristics applied in the sugarcane ration experiment during the dry and rainy seasons in the two-year experiment

Legend: OM – organic matter; C - carbon; N - nitrogen; MR - mineral residue; S - sulfur; P - phosphorus; K - potassium; Ca - calcium; Mg - magnesium, Cu-copper; Fe - iron; Mn - manganese; Zn – zinc.

Figure 1 - Air temperature and rainfall in Valparaíso-SP during the dry and rainy seasons when the greenhouse gases were sampled from the soil



Figure 2 - Temperature inside (IN) and outside (OUT) of the greenhouse gas (GHG) sampling chamber and the soil temperature at different soil layer depths (2 cm, 5 cm and 10 cm) in the sugarcane area at the sampling times



3.2.3 Water filled pore space of the soil in the sugarcane areas

Soil density determination was performed in 10 mini-trenches using the volumetric ring method (BLAKE; HARTAGE, 1986) and used to calculate the percentage of water filled pore space (%WFPS), assuming soil particle density of 2.65 mg m⁻³ according to Bielders et al. (1990) and Fageria and Stone (2006). The mean percentages of WFPS for the sugarcane planting were 79.1% and 59.2% in the dry seasons, and 70.7% and 63.6% in the rainy seasons, both in the first and second year, respectively. In the sugarcane ratoon area, the mean percentages of WFPS were 80% and 41% in the dry seasons, and 70.8% and 44.0% in the rainy seasons, both in the first and second year, respectively.

3.2.4 Soil greenhouse gases fluxes

The GHG sampling from the soil was performed as described by Steudler et al. (1991), in which the static chambers were inserted 5.0 cm into the soil surface (ROCHETTE et al., 2008). The chambers were composed of a base, with dimensions of 45 cm x 70 cm width and 30 cm height with a removable-lid (45 cm x 70 cm width and 7 cm height), noting that the base was fixed to the soil, to avoid disturbance of the soil and facilitating multiple collections during the experimental period. The volume of each chamber was measured by three-point heights from the soil surface to the lid. Soil GHG emission samples were collected daily (between 10h:00 and 14h:00) for 15 days after the initiation of the treatments. Subsequently, the collections were performed on interspersed days, and were finalized between the 30^{th} and 40^{th} day.

To determine the GHG fluxes inside of the chambers, a 30-minute incubation was performed, taking samples at 10-min intervals, (*e.g.* T0, T10, T20 and T30 min) with BD 50 ml nylon syringes. At the same time, soil temperatures were measured at a depth of 2, 5 and 10 cm, as well as the temperatures of the soil surface, inside and outside the chamber. Air temperature and rainfall were also recorded for later correlation with emissions.

Determination of CH₄, CO₂ with flame ionization detector (FID) and N₂O electron capture detector (ECD), using nitrogen as gas flow, was performed by gas chromatography (SRI 8610C Model, Torrance, CA, USA). The flux of each GHG was calculated using the linear change in the concentrations as a function of the incubation time within the chamber according to Equation 1. The daily emission of C-CO₂, N-N₂O and C-CH₄ (g m⁻² day⁻¹) was calculated based on the hourly fluxes obtained in the five replicates (chambers) of each treatment (OLIVEIRA et al., 2013).

$$Flow = (d[gas]/dt) \times (Vh/A) \times ((1-e/P)/VM)$$
(1)

Where: (d[gas]/dt) - change in gas concentration as a function of time (mol gas mol⁻¹ s⁻¹); Vh - volume of the chamber used in the GHG sampling (m³); A - chamber surface area (m²); e/P - water pressure/atmospheric pressure in the chamber (kPa kPa⁻¹); VM - molar volume of the chamber (m³ mol⁻¹). The emission of GHG accumulated over the total period was determined by integrating the data points and the total GHG emission, the result of the sum of the fluxes of C-CO₂, N-N₂O and C-CH₄. From the accumulated emissions of N-N₂O the emission factor of this GHG was calculated in relation to the amount of N added through the mix of inputs (filter cake and nitrogen fertilizer). Nitrous oxide and CH₄ fluxes were converted to CO₂-*eq* according to their global warming potential (GWP) of 298 and 25 times that of CO₂, respectively (IPCC, 2007; OLIVEIRA et al., 2013) (Equations 2, 3 and 4).

$$CO_2 - eq(CO_2) = CO_2 \times (12/44)$$
 (2)

$$CO_2 - eq(N_2O) = N_2O \times (44/28) \times 298$$
 (3)

$$CO_2 - eq(CH_4) = CH_4 \times (16/12) \times 25$$
 (4)

Where: $CO_2 - CO_2$ flow; $N_2O - N_2O$ flow; $CH_4 - CH_4$ flow; (12/44) - relationship between the molecular weight of carbon and CO_2 ; (44/28) - relationship between the molecular weight of N_2O and nitrogen; (16/12) - relationship between the molecular weight of CH_4 and carbon; 298 - global warming potential of N_2O over CO_2 ; 25 - global warming potential CH_4 over CO_2 .

The emission factor for the $C-CO_2$ and $N-N_2O$ were calculated according to the equation 5.

$$EF = \left(\frac{\Sigma GHG - \Sigma control}{N - C input}\right) \times 100 \tag{5}$$

Where: $\sum GHG$ – emission of nitrogen or carbon source treatment; $\sum control$ – emission of the control treatment; *N-C input* – amount of nitrogen or carbon applied to the soil, via filter cake, vinasse or ammonium nitrate.

3.2.5 Statistical analysis

Descriptive analysis was used for daily GHG flux data, whereas the accumulated GHG data were analyzed using ANOVA and, when significant, Tukey test with a significance level of 5% was used (SAS version 9.2, SAS Institute, Cary, NC).

3.3 Results

3.3.1 Emission of the greenhouse gases from the soil in the sugarcane planting area

The daily emissions of C-CO₂ under sugarcane after the application of the treatments exhibited peaks during the first 6 days of GHG sampling, during the dry season in the first year and during the rainy season of the two years of experimental evaluation (Figure 3). During the dry season of the second year, emission peaks were already observed during the first 3 days after the application of the treatment. The control treatment with zero input of any nutrient source exhibited the lowest emission (5.7 mg C-CO₂ m² h⁻¹), while the highest recorded emission occurred after the application of filter cake (771 mg C-CO₂ m⁻² h⁻¹; Figure 3).





The main emissions of N-N₂O observed under sugarcane occurred during the first 5 days after the application of the treatment (Figure 4). The highest emission of N-N₂O (216.4 μ g N-N₂O m⁻² h⁻¹) was observed one-day after filter cake application during the dry season of the second year (Figure 5). On the other hand, no differences in N-N₂O emission were observed between the treatments applied to the soil under sugarcane (Figure 5).

Figure 4 - Daily emissions of N-N₂O from the soil after sugarcane planting and with the application of ammonium nitrate (NH₄NO₃; 60 kg ha⁻¹), lime (2.0 t ha⁻¹) or filter cake (30 t ha⁻¹) during the dry and rainy seasons, in Valparaíso (SP). Error bars show the standard error of the mean (n = 20)



The daily emissions flows of C-CH₄ from the soil varied positively and negatively for all treatments under sugarcane and no difference in the emission patterns was observed for any of the treatments between the dry and rainy seasons (Figure 5). Nevertheless, the lowest emission of C-CH₄ was observed 19-d after liming during the rainy season of the first year (-95.8 μ g C-CH₄ m⁻² h⁻¹), whereas the highest emission for this GHG occurred almost 30-d after filter cake application during the dry season (94.7 μ g C-CH₄ m⁻² h⁻¹; Figure 5).

Figure 5 - Daily emissions of C-CH₄ from the soil after sugarcane planting and with the application of ammonium nitrate (NH₄NO₃; 60 kg ha⁻¹), lime (2.0 t ha⁻¹) or filter cake (30 t ha⁻¹) during the dry and rainy seasons, in Valparaíso (SP). Error bars show the standard error of the mean (n=20)



The accumulated emissions of C-CO₂, N-N₂O and C-CH₄ from the soil under sugarcane after the input of ammonium nitrate, lime or filter cake in the different seasons are described in the Figure 6. In this study, the emissions of C-CO₂ were higher when filter cake was applied in the dry season of the first year and in the rainy seasons of both evaluated years (Figure 6).

No differences in the soil emission patterns were observed for N-N₂O among the treatments or between the seasons (Figure 6). Nonetheless, liming produced the lowest emission of N-N₂O during the dry season of the first year and the rainy season of the second year (Figure 6). On the other hand, the application of the ammonium nitrate and filter cake exhibited higher N-N₂O emissions than those for lime application to the soil during the dry season of the first year. Ammonium nitrate also presented a higher emission for this GHG when compared to lime application during the rainy season of the second year (Figure 6).

During the dry season of the first year, the control treatment and lime application exhibited lower emissions for soil C-CH₄ when compared to ammonium nitrate application to the soil (Figure 6). During the rainy season of the second year, control treatments and filter cake application exhibited lower accumulated C-CH₄ emissions from the soil than those of the ammonium nitrate and lime treatments (Figure 6).

Figure 6 - Accumulated emissions of C-CO₂, N-N₂O and C-CH₄ from the soil after sugarcane planting and with the application of ammonium nitrate (AN; 60 kg ha⁻¹), lime (2.0 t ha⁻¹) or filter cake (FC; 30 t ha⁻¹) during the dry and rainy season, in Valparaíso (SP). Error bars show the standard error of the mean



3.3.2 Emission of the greenhouse gases from the soil in the sugarcane ratoon area

In the first year of evaluation of the sugarcane ration experiment, vinasse supplemented with urea was applied and the GHG soil emissions were compared to those from the control treatment. In this study, the application of vinasse and urea increased soil C-CO₂ emissions during both seasons whereas, N-N₂O emissions increased only during the rainy season (Figure 7). The highest C-CO₂ and N-N₂O emissions were observed during the rainy season, reaching peaks of 906 mg C-CO₂ m⁻² h⁻¹ and 1417 μ g N-N₂O m⁻² h⁻¹, respectively, after vinasse and urea application to the soil (Figure 7). On the other hand, no difference was observed for soil C-CH₄ emissions after vinasse + urea application, regardless of the season (Figure 7).

Figure 7 - Daily emissions of C-CO₂, N-N₂O and C-CH₄ from the soil in the sugarcane ration experiment after the topdressing application of vinasse (200 m³ ha⁻¹) and urea (100 kg ha⁻¹) during the dry and rainy seasons of the first year of the experiment, in Valparaíso (SP). Error bars show the standard error of the mean (n = 20)



In the second year of the sugarcane ration experiment, vinasse application increased soil C-CO₂ and N-N₂O emissions during the dry season (Figure 8). On the other hand, similar to that observed in the first year of the experiment, vinasse application did not affect soil C-CH₄ emissions (Figure 8). During the rainy season, there was no vinasse available from the sugarcane industry to apply to the soil. However, GHG emissions from the soil in the sugarcane ration experiment with zero input was evaluated. The emission flux of C-CO₂ increased whereas C-CH₄ decreased at the 27^{th} day of evaluation after the treatment start (Figure 8).

Figure 8 - Daily emissions of C-CO₂, N-N₂O and C-CH₄ from the soil in the sugarcane ration experiment after the application of vinasse (200 m³ ha⁻¹) or water (200 m³ ha⁻¹) during the dry and rainy seasons of the second year of the experiment, in Valparaíso (SP). Error bars show the standard error of the mean (n = 20)



Taking into account the accumulated GHG emissions from the soil during the initial stages of sugarcane ration experiment, the application of vinasse and urea produced higher C-CO₂ and N-N₂O emissions when compared to the control treatment during all the seasons evaluated (Figure 9). The main differences in C-CO₂ and N-N₂O emissions were observed in the rainy season, where the application of vinasse and urea produced emissions 1.7 and 4.0-fold higher than the control treatment, for C-CO₂ and N-N₂O, respectively (Figure 9). On the other hand, no differences were observed in soil C-CH₄ emissions after the application of any of the treatments (Figure 9).

Figure 9 - Accumulated emissions (both dry and rainy seasons) of C-CO₂, N-N₂O and C-CH₄ from the soil in the sugarcane ration experiment after the application of vinasse (200 m³ ha⁻¹) and urea (100 kg ha⁻¹) in the first year and vinasse (200 m³ ha⁻¹) or water (200 m³ ha⁻¹) in the second year, in Valparaíso (SP). Error bars show the standard error of the mean



3.3.3 Conversion of N₂O and CH₄ fluxes into CO₂ equivalent (CO₂-eq)

When the CO_2 -*eq* was calculated by the conversion of N-N₂O and C-CH₄ emissions from the sugarcane ration experiment, the application of lime produced the lowest CO_2 -*eq* emission in comparison with the other treatments during the dry season of the first year (Figure 10). During the rainy season of the first year, no differences in CO_2 -*eq* emission were observed (Figure 10).

In the second year, the application of filter cake (38.5 kg CO_2 -*eq* ha⁻¹) produced a higher CO_2 -*eq* emission than the control treatment (3.7 kg CO_2 -*eq* ha⁻¹) during the dry season. The application of ammonium nitrate (46.7 kg CO_2 -*eq* ha⁻¹) produced a higher CO_2 -*eq* emission than the lime application (16.1 kg CO_2 -*eq* ha⁻¹) and the control treatment (21.9 kg CO_2 -*eq* ha⁻¹; Figure 11) during the same period.

Figure 10 - Calculated carbon dioxide equivalent (CO₂-*eq*) from the emissions of N₂O and CH₄ from the soil after sugarcane planting and with the application of ammonium nitrate (AN; 60 kg ha⁻¹ N), lime (2.0 t ha⁻¹) or filter cake (FC; 30 t ha⁻¹) during the dry and rainy season of the first year of experiment, in Valparaíso (SP). Error bars show the standard error of the mean



Figure 11 - Calculated carbon dioxide equivalent (CO₂-*eq*) from the emissions of N₂O and CH₄ from the soil after sugarcane planting and with the application of ammonium nitrate (AN; 60 kg ha⁻¹ N), lime (2.0 t ha⁻¹) or filter cake (FC; 30 t ha⁻¹) during the dry and rainy season of the second year of experiment, in Valparaíso (SP). Error bars show the standard error of the mean



In the sugarcane ration experiment, the application of vinasse and urea produced higher CO_2 -eq emission than the control treatment during the dry and rainy seasons of the first year of evaluation (Figure 12). Furthermore, the CO_2 -eq emission was higher during the rainy season than the dry one, mainly when vinasse and urea were applied (4.0-fold higher than CO_2 -eq emission in the control treatment, Figure 12). However, in the second year, vinasse application did not differ from water application, but both produced higher CO_2 -eq emissions than the control (Figure 13).

Figure 12 - Calculated carbon dioxide equivalent (CO_2-eq) from the emissions of N₂O and CH₄ from the soil in the sugarcane ration experiment after the application of vinasse (200 m³ ha⁻¹) and urea (100 kg ha⁻¹ N) in the dry and rainy season in the first year of experiment, in Valparaíso (SP). Error bars show the standard error of the mean



Figure 13 - Calculated carbon dioxide equivalent (CO₂-*eq*) from the emissions of N₂O and CH₄ from the soil in the sugarcane ration experiment after the application vinasse (200 m³ ha⁻¹) or water (200 m³ ha⁻¹), during the dry and rainy season in the second year of the experiment, in Valparaíso (SP). Error bars show the standard error of the mean


3.3.4 Emission factor for C-CO₂ and N-N₂O from agricultural inputs during sugarcane cultivation

The emission factor is evaluated using from the amount of C-CO₂ and N-N₂O emitted from the soil as a function of the amount of C and N applied thought the inputs to the soil. In this study, the emission factors were calculated for the treatments with the soil application of filter cake, ammonium nitrate and vinasse for the different seasons. The emission factor values for C-CO₂ when filter cake was applied were 14.0% and 5.0 % during the dry seasons of the first and second year, respectively, and 0.2% and 1.3% during the rainy seasons of the first and second year, respectively. However, values for N-N₂O were 0.001% and 0.003% during the dry seasons of the first and second year, respectively, and 0.04% and 0.01% during the rainy seasons of the first and second year, respectively. For vinasse application, the emission factor was 0.49% for C-CO₂ and 0.02% for N-N₂O, during the dry season of the second year. Moreover, the emission factors for N-N₂O when ammonium nitrate was applied were 0.018% and 0.13% during the dry seasons of the first and second year, respectively, and 0.07% and 0.09% during the rainy seasons of the first and second year, respectively.

3.4. Discussion

GHG soil emissions in sugarcane areas was assessed in this work after the soil applications of C and N sources for plant growth, during planting and ratoon stages, in the Center-South region of Brazil. The majority of soil GHG emissions occurred due to soil management in the sugarcane planting process, confirmed by the higher values observed in the control treatment when compared to those observed in the sugarcane ratoon control (p<0.05; Figures 6 and 9). According to the initial hypothesis of this study, the main soil GHG emissions during the sugarcane planting phase occurred due to the soil tillage. However, in the cane-ratoon phase the application of mineral N fertilizers did not resulted in higher GHG emission when compared to the organic sources of the same nutrients.

Soil tillage influenced GHG emissions during the renovation of sugarcane planting. Comparing emissions sources, in equivalent annual emissions, this practice accounted for 64.2% of emissions at this stage of sugarcane cultivation. The rotation of the soil increases aeration, making the environment favorable for oxidation processes, such as the oxidation of organic compounds (C) resulting in an increment of CO₂ emissions (SIX et al., 1999; RYAN; LAW, 2005), oxidation of CH₄ to CO₂ by methanotrophic organisms (WANG; INESON, 2003; CERRI, et al., 2010) and the oxidation of ammonium and nitrites by the nitrification process (SCHMIDT, 1982; KHALIL et al., 2004; BATEMAN; BAGGS, 2005; COSTA et al., 2008). All these reactions increase GHG emissions from soil to the atmosphere.

In the present work, the GHG emissions associated with the application of N fertilizers to the soil under sugarcane were lower than those reported for other countries or for the application of others N-containing sources (CARMO et al., 2013, BUTTERBACH-BAHL, 2013; FILOSO et al., 2015;). However, Brazil is considered a major contributor to worldwide GHG emissions due to the large area devoted to agricultural production. Therefore, it is crucial that emissions due to the expansion of the sugarcane areas and other agricultural activities in Brazil, is controlled to help climate change mitigation (BENTO et al., 2018)

In the sugarcane planting area, soil C-CO₂ emission was higher after application of the filter cake (Figures 4, 5 and 6), mainly in the dry season. Soil reactions might be boosted by the application of filter cake mainly in the dry season, since its humidity can reach 80%. In this case, the humidity of the filter cake would not cause anaerobiosis, but increase microbial activity that could lead to an increase in oxidation reactions (LA SCALA et al., 2005; SILVA-OLAYA et al., 2013). It is worth mentioning that the emission peaks observed for C-CO₂ may be a result of the so-called 'priming' effect that stimulates the mineralization of organic matter after the input of C and N as organic residues (KUZYAKOV et al., 2000) and consequently increases microbial activity (MOREIRA; SIQUEIRA, 2006; DIAS, 2013). This effect is directly dependent on the type of soil and the organic substrate added.

Similarly as observed for C-CO₂, the emissions of N-N₂O were higher after the soil application of either ammonium nitrate or filter cake (Figure 6). The addition of N-containing fertilizers to soils accelerates the N cycle, boosting processes that produce N-N₂O, such as nitrification and denitrification (PITOMBO et al., 2016). In this context, soil moisture also controls the rates of nitrification and denitrification in soils (FARQUHARSON; BALDOCK, 2008), which would explain the effect observed after filter cake application in the dry season (Figures 4 and 6).

Peaks of N-emission can also be related to the so-called "hot spot" and "hot moment", these spatiotemporal variations are the result of the dynamic and variable character of N_2O (BUTTERBACH-BAHL; DANNENMANN, 2011; GROFFMAN et al., 2009). Although more robust analysis tools were used, there is a need for a better understanding of soil N processes and their relationship to microbial diversity when we refer to the magnitude and spatio-temporal dynamics of soil N-N₂O fluxes (BUTTERBACH-BAHL et al., 2013).

The C-CH₄ showed an ample variation, oscillating between a GHG source and a drain, along the evaluation period. However, the flux was negative throughout the dry season, and

might be related to the fact that the absorption of CH_4 by soil is a result of the action of methanotrophic bacteria, which are obligate aerobes (MOSIER et al., 2004). During the rainy season when the treatments were applied to the cane plants, more of this GHG was emitted probably due to the action of prokaryotic microorganisms, the methanogenic Archaea. Under anaerobiosis these microorganisms have the capacity to catabolize acetate and carbon compounds into CH_4 (LEIGH et al., 2011).

In sugarcane ration, the application of vinasse and urea in the first year or only vinasse in the second year, increased C-CO2 and N-N2O emissions from the soil when compared to control treatments (Figures 7 and 8). However, the main increments of C-CO₂ and N-N₂O emissions from the soil occurred in the first days after the application of the vinasse and/or urea, which could be the result of the 'priming' effect (KUZYAKOV et al., 2000), similar to that observed in the sugarcane planting area after filter cake application (Figures 3 and 6). Furthermore, the N-N₂O emissions just after the application could not be explained by the chemical reactions related to N in the soil, but probably due to the vinasse filling the soil pore spaces (DENMEAD et al., 2009). However, the soil in the present study is classified as a sandy soil, with up to 125 g kg⁻¹ of clay (Table 2). In this case, the large part of the vinasse could be easily have drained into deeper soil layers, mainly in the rainy season after rainfall precipitation. After the application of vinasse and urea in the first year, soil CO₂eq emission exhibited different emission fluxes between the climatic seasons (Figures 7 and 8), the rainy season CO_2 -eq emission from the soil was six times higher than during the dry season (Figure 12). Such results may be associated with the vinasse application, N supply and anaerobic soil, since the main contribution to the increment of the CO_2 -eq was due to the increase in N-N₂O emissions after vinasse and urea application (Figure 9). According to Oliveira et al (2013), vinasse is an easily decomposable source of organic matter, resulting in higher GHG emissions.

When only vinasse was applied in the second year, this treatment did not differ from the water application with respect to the soil N-N₂O emissions (Figure 9). In a previous study, vinasse application to a clay soil also increased the soil emission fluxes of N-N₂O in the first days after the application (DIAS, 2013), but the emissions were not considered high when compared to other authors (CARMO et al., 2012). In this case, the low emissions of N-N₂O were related to the increment in the soil bacterial community, particularly nosZ activity (DIAS et al., 2013), a gene related to the reduction of N₂O to N₂ (HENRI et al., 2005; SINGH et al., 2011). In fact, many other soil organisms are related to the release of N₂O and might be affected by the input of N and C from the vinasse application. Pitombo et al. (2016) showed that vinasse application affected Firmicutes-type bacteria and some fermenters, where the vinasse was considered the main source of these organisms.

On the other hand, vinasse application to the soil did not increase C-CH₄ emissions (Figures 7, 8 and 9), indicating that the C loading via this organic product did not interfere with the fluxes of this GHG. Carmo et al. (2012) and Oliveira et al. (2013) observed the same effect. In contrast to the results described by Weier et al. (1999), Denmead et al. (2009), Carmo et al. (2012) and Oliveira et al. (2013), the C-CH₄ fluxes in this study demonstrated the ability of the soil to serve as a source and sink for this GHG and not just a methane sink.

The calculated emission factors for the soil application of filter cake, ammonium nitrate and vinasse for the different seasons were lower than those proposed by the IPCC (IPCC, 2007). The emission factor is based on the amount of N-N₂O emitted, as a function of the N dose applied to the soil, via N-containing fertilizers (BOUWMAN, 1996), vinasse (OLIVEIRA et al., 2013; CARMO et al., 2012) and filter cake (IPCC, 2007). This factor is used in the preparation of GHG inventories (IPCC, 2007). There are several studies of the estimates of direct N₂O emission factors, and most of them report that the value proposed by the IPCC does not represent the real values observed under field conditions (ABBASIB; ADAMS, 2000; JANTALIA et al., 2008; SMEETS et al., 2009; CARMO et al., 2012; SIQUEIRA NETO et al., 2015). Clearly, more information is needed to fully understand the impact of biofuel production on the environment and on its sustainable development (BENTO et al., 2018).

In this work, we evaluated the soil emission of GHG in sugarcane areas, during the sugarcane planting and ratoon stages, and after the applications of commonly used C and N sources for plant growth. The hypothesis of this study was partially confirmed, since the main emissions came from the soil management techniques routinely used in sugarcane cultivation during planting. Despite the increase in GHG emissions after N-fertilizer application, it was not the predominate contribution when considering emissions of the other N sources, such as filter cake (Figures 3, 4 and 5). However, mitigating actions should include the use of alternative sources of fertilizers in a program of sustainable ethanol production.

3.5. Conclusions

The main GHG emission from the soil comes from the soil tillage after sugarcane planting phase. Inputs of carbon and nitrogen to the soil can be important sources of GHG emission during sugarcane planting or the ratoon phase, when applied via mineral or organic fertilizers. Despite the increase in GHG emission from the soil the application of nitrogencontaining sources (vinasse and urea) as a topdressing on the sugarcane ratoon area, the inputs that cause the most significant GHG emissions from the soil occur during sugarcane planting after the application of either filter cake or ammonium nitrate. However, the emission factors for CO_2 and N_2O reported by the IPCC are higher than those observed in this study, which was performed in the Center-South region of Brazil. The expansion in the area planted with sugarcane can cause an increase in GHG emissions during sugarcane production in the ethanol production regions around the world. Thus, the search for practices and alternative nitrogen and carbon sources that lead lower GHG emissions during biofuels production is of extreme importance.

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4. FINAL CONSIDERATIONS

The land-use-change succession native vegetation-pasture-sugarcane, as well as the farming practices during sugarcane cultivation, enhance greenhouse gas (GHG) fluxes from the soil to atmosphere.

Figure 1 - Soil CO_2 -eq emission values for the main systems in land-use-change in the Center-South region of Brazil: native vegetation-pasture-sugarcane



Different land uses for agriculture purposes result in different rates emissions of CO_2 , N_2O and CH_4 from the soil. Integrating soil GHG fluxes and carbon equivalents during land use change demonstrate that the soil under pasture emits larger amounts of GHGs into the atmosphere when compared to soil under native vegetation or sugarcane. In addition to the emissions caused by the changes in soil characteristics caused by the land use change, those caused by manure/urine represented an important participation in the total emissions observed for the pasture system. Although sugarcane cultivation exhibited lower soil emissions of GHG when compared to pasture, the farming practices, such as soil tillage during sugarcane planting process, were shown to be important promoters of soil GHG emissions. The application of filter cake and nitrogen-containing fertilizers during sugarcane planting were

the most significant sources of GHG emissions, mainly for CO_2 and N_2O . In the sugarcane ration area, the combined application of mineral and organic fertilizers (urea and vinasse) were responsible for the main increment in soil GHG emissions. However, the emission factors observed for the inputs used in sugarcane production in the Center-South region of Brazil are still lower than those proposed by the IPCC. In this context, this study shows that the mean values of GHG emission factors reported by the IPCC might not adequately represent the real values in some agricultural regions in Brazil, such as we verified for Center-South region, and this is probably due to variations in the climate and size of the planted areas. Further studies should be performed in the different Brazilian agricultural regions to determine the specific emission factors for each region.

One of the greatest challenges facing humanity nowadays is to limit climate change caused by human interference, which changes in the gas composition of the planet's atmosphere. Such changes have been the focus of discussions, among authorities around the world, at international events such as COP23 (2017) that aimed to define strategies to reduce GHG emissions. What could be done to slow down the predicted climate change? GHG emissions and wasted energy must be reduced with more emphasis on cleaner renewable energy resources, such as ethanol instead of gasoline. The threat of climate disruption drives us to seek preventive solutions such as reducing the use of fossil fuels and adopting more sustainable agriculture. We must develop and implement a strategy, however hard it may seem that will lead us to environmental, economic and social benefits.