University of São Paulo
"Luiz de Queiroz" College of Agriculture

Sugarcane straw removal from the soil surface: effects on soil soluble products

Maria Regina Gmach

Thesis presented to obtain the degree of Doctor in Science. Area: Soil and Plant Nutrition

Piracicaba
2018

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versão revisada de acordo com a resolução CoPGr 6018 de 2011

Advisor:
Prof. Dr. **CARLOS EDUARDO PELLEGRINO CERRI**

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To my mother Cleci Faganello,

To my father Jacinto Gmach

To my sister Mariane Gmach

To my little sister and little brother Izadora and Mateus

I DEDICATE!

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“I have not failed.

I have successfully discovered ten thousand things that will not work.”

Thomas Edison

CONTENTS

RESUMO

Remoção da palha de cana-de-açúcar da superfície do solo: efeitos nos produtos solúveis do solo

O interesse no uso da palha de cana-de-açúcar como matéria-prima para a produção de bioenergia vem crescendo consideravelmente. No entanto, a remoção excessiva da palha pode afetar negativamente o funcionamento do solo. Portanto, o objetivo deste trabalho foi quantificar e caracterizar a solução ao longo do perfil sob níveis de remoção de palha da superfície do solo. Para isso, foi construído um sistema de lisímetros com colunas de 1, 20, 50 e 100 cm de solo, de textura franco argilo arenosa, proveniente de área comercial de cana-de-açúcar em Piracicaba-SP, Brasil. O experimento foi conduzido em área aberta, sujeito a precipitação e luz natural. Depois da estabilização do solo dentro dos tubos, foram adicionados os seguintes tratamentos: 0, 3, 6 e 12 Mg ha^{-1} de massa seca, representando 100 (solo nu), 75, 50 e 0% de intensidade de remoção de palha, respectivamente, sendo adicionados novamente após um ano. A solução percolada foi coletada e quantificada por 17 meses, a umidade do solo foi determinada por dois meses usando sensores. A concentração de carbono orgânico dissolvido (COD) foi mensurada com analisador automático. A solução do solo e solução da palha, feita por infusão em água, foram caracterizadas em HPLC para verificar a presença de compostos tóxicos. Posteriormente, as soluções da palha e solo foram usadas em testes de sementes de soja para avaliar os efeitos na germinação e crescimento inicial. Ao final do experimento, foram realizadas análises de densidade do solo e carbono orgânica do solo (COS). A palha remanescente foi pesada após um ano, anterior a nova adição, e pesada novamente ao final do experimento, para determinar a taxa de decomposição. O volume de solução percolado foi 30, 11 e 4% menor em 100, 75 e 50% do que em 0% de remoção, respectivamente. O solo descoberto armazenou menos água, indicando susceptibilidade à perda de água por evaporação. A simulação mostrou que 100 e 75% de remoção induzem longos períodos de restrição hídrica, que pode prejudicar o crescimento da planta. A produção de COD na camada superficial foi maior no solo sem remoção; a retenção foi maior de 1 a 20 cm em solo sem remoção, e maior em 20 a 50 cm em 50 e 75% de remoção. O solo descoberto liberou mais COD em de 20 cm do que em superfície, indicando perda de C. Abaixo de 100 cm, o COD lixiviado foi similar nos tratamentos, indicando grande retenção de C e pequenas perdas por lixiviação, mesmo em alta produção de COD. Mesmo com diferenças na retenção de COD, não foi identificado aumento no estoque de C abaixo de 5 cm. Foram encontrados compostos fenólicos na solução da palha, não encontrados na solução do solo, indicando que em condições naturais a palha não libera quantidades significativas de compostos tóxicos na solução do solo. O crescimento de plantas foi negativamente afetado pela solução da palha, mas não pela solução do solo. Nossos resultados sugerem que a manutenção de quantidade média de palha previne perdas e variação no conteúdo de água do solo. Maior quantidade de palha aumenta a produção de COD, que provavelmente altera sua composição, alterando a retenção no solo. O estoque de C não aumentou consideravelmente em subsuperfície, mas muito provavelmente aumentará em escala de tempo maior. Quanto maior a remoção de palha, proporcionalmente maior as taxas de C liberadas na forma de CO_2 e COD em subsuperfície, consequentemente, menor a retenção de C no solo. Maiores quantidades de palha na superfície liberam mais C para o solo, retido ou translocado com a água, podendo ser estocado em maiores profundidades do solo. Maior percolação de água no solo não significa maiores perdas de C por lixiviação em profundidade.

Palavras-chave: Armazenamento de água; Carbono orgânico; Carbono orgânico dissolvido; Compostos tóxicos; Crescimento de plantas

ABSTRACT

Sugarcane straw removal from the soil surface: effects on soil soluble products

The interest in using sugarcane straw as a feedstock for bioenergy production has been increased considerably. However, indiscriminate straw removal may negatively affect soil functioning. Therefore, this work aimed to quantify and characterize soil solution translocating along the profile, under straw removal rates from the soil surface. Lysimeter systems were built with 1, 20, 50, and 100 cm soil columns, with a sandy clay loam texture, from a commercial sugarcane field in Piracicaba-SP, southeastern Brazil. The experiment was conducted in open area, where the lysimeters were subjected to rainfall and sun radiation. After the soil stabilization within the lysimeters, the treatments were added, consisting of four straw amounts (0, 3, 6, and 12 Mg ha^{-1}), representing straw removal rates of 100 (bare soil), 75, 50, and 0%, respectively. After one year of the first straw addition, the same straw amounts were added again simulating the second harvest. Drained solution was collected and quantified by 17 months and soil moisture was determined over a period of two months using sensors. Dissolved organic carbon (DOC) concentration was measured in automatic analyzer. The soil solution and straw solution, made in water infusion, were characterized in High performance liquid chromatography (HPLC) to verify the presence of toxic compounds. After that, straw and soil solution were used in tests with soybean seed to evaluate the effects in plant germination and initial growth. At the end of the experiment, soil bulk density and soil organic carbon (SOC) analyses were performed. Remaining straw was weight before the new addition, and weight again at the end to determine the decomposition rates. The accumulated volume of solution drained was 30, 11 and 4% lower under 100, 75 and 50% removal rates compared to no removal. Bare soil stored less water, indicating susceptibility to lose water by evaporation. Simulation showed that 100% and 75% removal can induce longer periods of water restriction, which impair sugarcane growth. The DOC production on topsoil was higher in no straw removal; the retention was higher in 1 to 20 cm in no removal and higher in 20 to 50 cm in 50 and 75% removal rates. Bare soil released more DOC below 01 cm indicating a possible C loss. Below 100 cm DOC leachate was quite similar in all treatments, what shows a higher C retention and small C loss even in higher DOC production. Even with differences in DOC retention, increases in C stock below 5 cm were not noticed. We found many phenolic compounds in the straw solution, not found in the soil solution, indicating that in natural conditions straw does not release toxic compounds into soil solution. Plant growth was negatively affected by straw solution, but not by soil solution. Our findings suggest that the medium straw maintenance prevents variations and loss on soil water content. Higher straw amount increases DOC production, which likely alters its composition and subsequent retention in soil. Carbon stock did not increase in the soil subsurface, but probably will in the long-term. The higher straw removal, proportionally, the higher the C losses in the form of CO_2 and DOC, consequently the lower soil C retention. More straw on soil surface release more C amounts to the soil, retained or translocated with soil water, may be stored in deeper soil layers. Higher water percolation in the soil profile does not mean higher C losses by leaching in deeper soil. This study has the practical objective of finding an amount of straw to be maintained in the field that ensures the C storage and the better soil functioning, and also supply feedstock for bioenergy production.

Keywords: Water storage; Organic carbon; Dissolved organic carbon; Toxic compounds; Plant growth.

1. INTRODUCTION

Due to environmental issues, the demand for sources of bioenergy production has been increased. In this way, sugarcane production has become increasingly important due to the potential to produce sugar, ethanol and electricity. Sugarcane crop has great relevance in Brazilian agriculture, being the largest producer in the world with a planted area of 8.6 million hectares planned for 2018/19 crop. In this context, São Paulo state has great participation, being responsible for 51% of the total production (CONAB, 2018).

For environmental, agronomic, and economic issues, sugarcane harvest became mechanized in the region and the crop residues, called straw, remain on soil surface, producing on average of 10 to 18 Mg of dry mass per hectare per year (Leal et al. 2013). Due to bioenergy demand, there is a management practice that aims to remove part of the straw as feedstock for second-generation ethanol (E2G) and electricity production (Lisboa et al. 2017) because of its high heating value (Menandro et al. 2017). Consequently, there is growing interest within the sugarcane industry to remove straw from the field. However, the negative impacts which the straw removal management may cause is a threat to the soil functioning that may affect plant productivity.

Despite the increase in planted area and new technologies, in the last ten years there was no significant increase in the productivity in the region (CONAB, 2018) and problems with regrowth are occurring. This stagnation may be caused by water deficit periods and other many factors related to this new scenario of mechanized harvest jointly to the straw removal, as machinery use and soil compaction (Otto et al. 2001; Baquero et al. 2012; Souza et al. 2014, 2015; Cherubin et al. 2016). In this way, the straw layer prevents soil compaction (Braida et al. 2006; Satiro et al. 2017), increases soil water retention (Anjos et al. 2017), and reduces soil temperature and moisture ranges (Dourado-Neto et al. 1999). Thereby, the larger C input provided by the disposal of organic material, increases soil C stocks and nutrients cycling (Cerri et al. 2011; Satiro et al. 2017; Sousa Junior et al. 2018), and increases the production of active C fractions, such as dissolved organic carbon (DOC) (Högberg and Högberg, 2002; Michalzik et al. 2003) that can be translocated with soil water and retained in deeper soil layers. On the other hand, large sugarcane straw amount may release large amounts of allelopathic compounds, which can negatively impact plant growth (Sampietro et al. 2006, 2007).

The reasons affecting the sugarcane productivity and regrowth of ratoon are still unclear, may be caused by the large straw amount left on soil surface, or by the straw removal. Therefore, the hypothesis of this work is that total or high straw removal rates from soil surface reduces soil

moisture and water storage, affecting decomposition dynamics, which reduces the C input, reducing the production and translocation of DOC, also causing changes in its composition, which may, on the other hand, reduce the release of toxic compounds to the soil. To test the hypothesis, this work aimed to quantify and characterize the soluble products of sugarcane straw decomposition and its translocation in the soil profile, under different straw removal rates from the soil surface.

To accomplish the general objective, this thesis is organized into seven chapters. The **first** one is a brief general introduction about the research topics and the general experiment. The **second** one is a bibliographic review about DOC, punctuating the main processes that occur with this C fraction into soil, focusing tropical conditions. The **third** one addresses the impacts of sugarcane straw removal on soil water drainage and water storage, using a lysimeter system, simulating the impacts of straw removal on soil water storage over the whole sugarcane cultivation season. The **fourth** one evaluates the effects of sugarcane straw removal in DOC production and translocation in the soil profile, and verifies changes in C stock, pointing the environmental consequences, using the same lysimeter system. The **fifth** one verifies the presence of allelopathic compounds in sugarcane straw and throughout the soil solution, under different sugarcane straw removal intensities from the soil surface, and the impacts of these solutions in plant growth. The **sixth** one includes a C balance for each straw removal intensity from the soil surface, highlighting the importance of the C storage in reducing C losses. Finally, the **seventh** one provides the final considerations of this study.

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2. PROCESSES THAT INFLUENCE DISSOLVED ORGANIC MATTER ON THE SOIL: A REVIEW

Abstract

In tropical regions, the climate conditions favor fast soil organic matter (SOM) decomposition, releasing organic composts in solid, liquid, and gaseous forms with variable compositions to the soil. Dissolved organic matter (DOM), a complex mixture of thousands of organic compounds, is only a small fraction of the decomposition products, but it is highly mobile and reactive with the soil. Therefore, DOM has key soil functions related to soil aggregation (formation of organometallic complexes); the sources of energy of microorganisms; and the C storage, cycling, and provision of plant-available nutrients. The multifunctionality of DOM to sustain soil functions and important ecosystem services has raised the global scientific interest in studies focused on DOM fraction. However, previous studies were conducted predominantly under temperate soil conditions in natural ecosystems. Therefore, there is a paucity of information for tropical soil conditions under agricultural systems, in which the turnover of DOM is intensified by the adopted management practices. This review synthesized the available knowledge in the literature to identify and discuss the main sources, transformations, and fates of DOM in soils. In addition, the importance of this fraction in C cycling and other soil properties and processes was discussed, emphasizing agricultural systems in tropical soils. Thus, gaps and opportunities were identified to guide future researches about DOM in tropical soils.

Keywords: Dissolved organic carbon; Agricultural soils; Tropical soils; Brazil

2.1. Introduction

Dissolved Dissolved organic matter (DOM), mainly composed by dissolved organic carbon (DOC), is one of the most active and mobile C pools and has an important role in the global C cycle (Kalbitz et al., 2000). In addition, DOC affects soil negative electrical charges denitrification process; acid-basic reactions in the soil solution; retention and translocation of nutrients (cations); and the immobilization of heavy metals and xenobiotics (Zech et al., 1997). Soil DOM can be derived from different sources (inputs), such as atmospheric C dissolved in rainfall, litter and crop residues, manure, root exudates, and soil organic matter (SOM) decomposition (Figure 1). Regarding the soil, DOM availability depends on its interactions with mineral components (e.g., clays and Fe and Al oxides) modulated by adsorption and desorption processes (Saidy et al., 2015) and depends on the SOM fractions (e.g., stabilized organic molecules and microbial biomass) by mineralization and immobilization processes (Figure 1). Also, the intensity of these interactions changes according to soil inherent properties (Kaiser and Guggenberger, 2007), land use, and cropping management (Saidy et al., 2015).

During the decomposition of a given organic material, the majority of C is lost as CO_2 to the atmosphere by microbial oxidation. Depending on soil type and landscape slope, leaching and

runoff (Figure 1) are also important processes associated with soil DOM losses (Veum et al., 2009). In well-drained soils, leached DOC can reach the water table loading nutrients and pollutants that can contaminate groundwater (Thayalakumaran et al., 2015; Sparling et al., 2016), whereas runoff transports DOM and xenobiotics to other areas, rivers, and lakes.

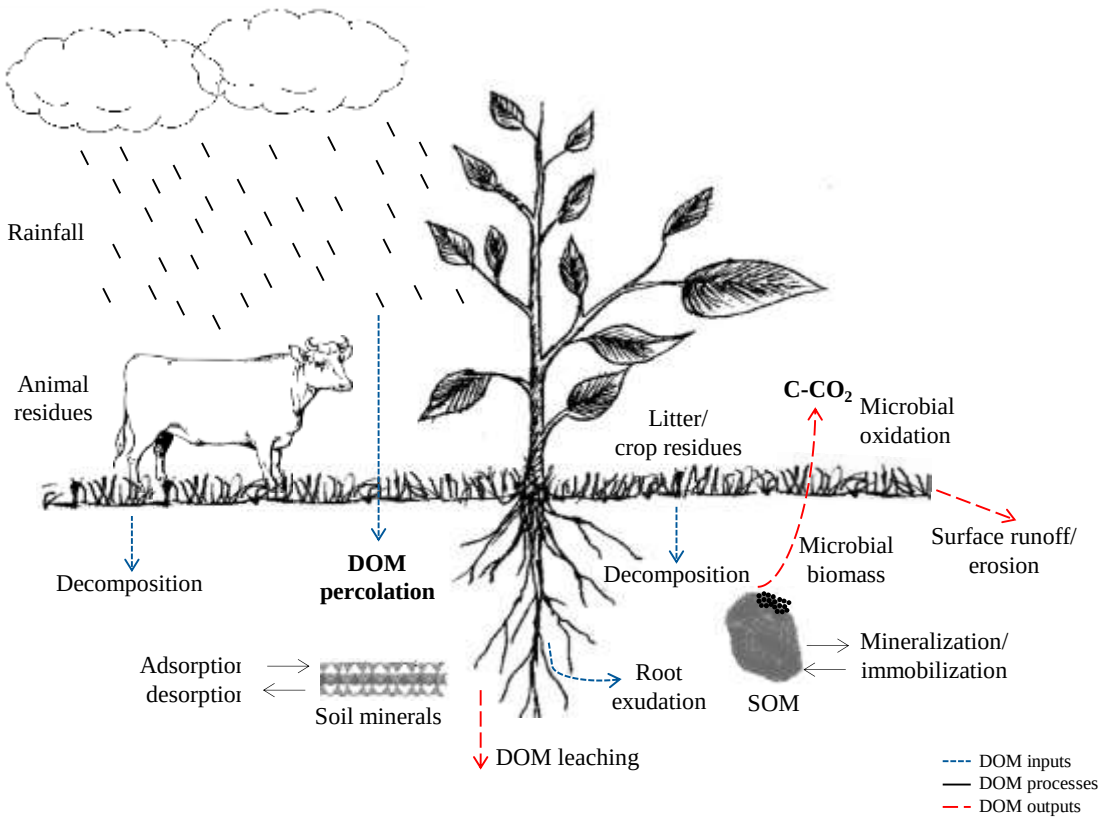

Figure 1 – Schematic representation of main inputs, transformation processes, and losses of DOM in soil system.

Most studies have focused on understanding the soil DOM dynamics and its potential implications in water contamination in temperate forests and wetland areas, but results from agricultural sites remain scarce in the literature (Van Gaelen et al., 2014), especially in tropical conditions.

Therefore, this literature review aimed to verify the situations discussed in previous studies about DOM and determine the current interest of Brazil in this topic of research. Thus, available information in the literature is analyzed to describe the importance, source and production, transformation processes, and fates of DOM in the soil-atmosphere system, emphasizing agricultural soils in tropical conditions. Finally, gaps and opportunities were delineated to guide future researches towards a better understanding of the importance and implications of DOM changes in tropical soils.

2.2. Increase in scientific interest in DOC/DOM

Studies Since studies about soil DOC/DOM were introduced in the early 1980s, the interest on this topic in aquatic and terrestrial systems has grown at a linear rate. However, DOM studies in the soil systems and especially in agricultural soils are uncommon, especially in Brazil. To illustrate this contrast between global and the Brazilian number of DOM/DOC publications, a simplified bibliometric research in the Web of Science (WS) database was performed.

Initially, searching the terms "dissolved organic carbon" or "dissolved organic matter" as a "topic" from 1990 to 2017 provided totals of 14168 and 13054 publications, respectively. When the word "soil" was added in the searches, the totals of publications decreased to 4347 and 3163, respectively, during the same period. For comparison purposes, only the "DOC" topic was used to avoid an overlap of results. When the searches were restricted to studies conducted in Brazil, searching the terms "DOC" and "Brazil" found only 134 publications (Figure 2b), while searching "DOC" and "USA" found 593 publications for the same period. In addition, searching for "DOC" and "Europe" found 265 publications and searching for "DOC" and "Germany" found 217 publications, which is a large number for a relatively small country (territory 23 times smaller than Brazil).

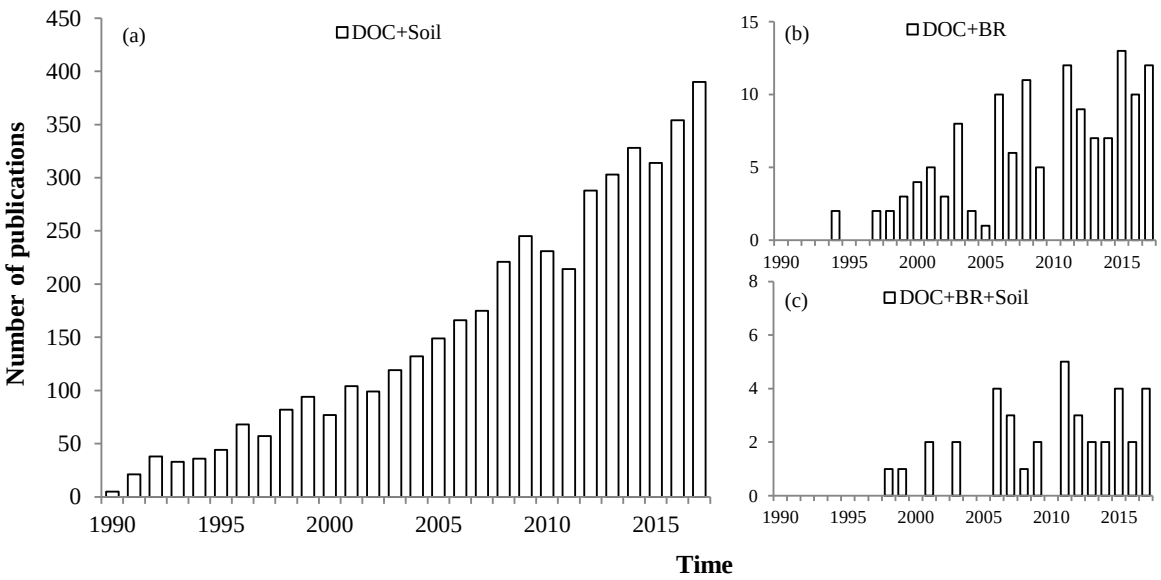

Figure 2 – Evolution in the number of publications in DOC research in the Web of Science database. a) globally, and; b and c) in Brazil. DOC+Soil: "dissolved organic carbon" AND "soil"; DOC+BR: "dissolved organic carbon" AND "Brazil"; DOC+BR+Soil: "dissolved organic carbon" AND "Brazil" AND "soil".

The number of publications decreased further when the word "soil" was added (i.e., "DOC" and "Brazil" and "soil"), resulting in 38 publications until 2017 (Figure 2c), but only 14 publications really showed results from the soil experiments, and only a few of these have DOC

fluxes as the main variables of study or evaluated DOM dynamics in the soil profile. Moreover, only one article evaluated DOC in the soil recently (2018) in Brazil.

Complementary to this search in Web of Science database, the same search was performed in the Scopus and Scielo databases (i.e., databases that comprise scientific papers published in Brazilian and some Latino-American journals). The results found in the Scopus database are very similar to those found in the Web of Science. In the Scielo database, the aim was also to find publications in Portuguese, but adding the terms "dissolved organic carbon" and "soil" only found 6 publications. In addition, terms such as "soluble carbon," "crop," and "carbon leaching" were also searched jointly with DOC or DOM and Brazil, but there were few results.

Based on these simple searches in the main scientific databases, the lack of the studies in Brazil involving this important C fraction was evident. Whereas the international scientific community is still concerned with understanding the implications of DOM in the functioning of natural and anthropic ecosystems, in Brazil, there is much to advance for understanding DOM dynamics, especially in agricultural systems with all the diversified management practices (e.g., no-till, cover crop, crop-livestock-forest integration, and green sugarcane harvesting).

2.3. Definition and main sources of DOM

Dissolved organic matter is considered a complex mixture of thousands of organic compounds with diversified chemical compositions and properties (Catalá et al., 2015; Flerus et al., 2012; Thurman, 1985). However, a small proportion of DOM can be chemically identified, mostly as low molecular weight substances such as organic acids, sugars, and amino acids (Herbert and Bertsch, 1995), making a complete chemical definition of DOM difficult (Silveira, 2005). The DOM is a source of energy and organic nutrient forms such as nitrogen (N) and phosphorus (P) readily accessible for soil microbiota (Burford and Bremner, 1975; McDowell et al., 2006). The origin, function, and fate of these compounds in terrestrial ecosystems are only partially understood (Wang et al., 2016), as well as the factors that control soil DOM in the soil profile (Zhou et al., 2015). The DOC is a minor fraction of soil organic carbon (SOC), although DOC is one of the most mobile and bioavailable portions (Ghani et al., 2013; Marschner and Kalbitz, 2003). The decomposition of DOM can indicate the processes that govern the accumulation and stabilization of SOM (Kaiser and Kalbitz, 2012).

The main inputs of DOM into the soil are the rainfall, plant residues, roots exudates, SOM, and microbial biomass (Kalbitz et al., 2000; Yano et al., 2005), and DOM can be produced mainly by recent plant residues/litter and from relatively stable SOM decomposition (McDowell

and Linkes, 1988; Michalzik et al., 2003). Some studies suggest that fresh C substrates, such as plant residues, roots, and exudates, and their secretions including organic acids, phenols, sugars, and amino acids are some of the most important DOM sources (Högberg and Högberg, 2002), (Wang et al., 2016). The DOC originating from fresh leaf litter may contribute to the formation of an A horizon, whereas DOC originating from root litter may explain the presence of SOC at depths in soil (Uselman et al., 2007).

In contrast, studies have showed that the decomposition of stable SOM is the most important source of DOM since more humified compounds predominate in DOM, suggesting that it originates from the large stock of native SOM than from recently added litter (Fröberg et al., 2003; Zsolnay, 1996) depending on the organic material. Thus, part of DOM is derived from the old SOM, indicating that the release of C from the plant to the soil solution is in steady state with its decomposition or that litter and young SOM can also be degraded by the microbiota without first going into solution (De Troyer et al., 2011). Therefore, mainly humified SOM and exchanges with aqueous phase may determine DOM chemical composition (Sanderman et al., 2008).

In general, recent litter and humified SOM constitute the two most important sources of DOM in soils (Kalbitz et al., 2000), varying DOM concentration according to the soil characteristics, soil use and tillage, and local climate. Thus, there are compounds that are specific to different functional soil or plant types, improving the capacity to use DOM as a soil quality indicator (Jones et al., 2014).

Furthermore, rainfall contributes to DOC content in the soil. A global study showed that the C present in rainfall is 80% in the organic form (DOC), corresponding to 430 x 10^{12} g C $year^{-1}$, and 20% in the inorganic form (DIC), corresponding to 80 x 10^{12} g C $year^{-1}$, totaling 510 x 10^{12} g C $year^{-1}$, in which 70% is deposited over land (Willey et al., 2000). These results show the importance of including rainfall in the global C balance. Besides containing C, rainfall also contributes with DOC movement and flux within the soil, and an increase in soil water flux may cause an increase in DOC content in soil solution (Chantigny, 2003).

2.3.1. Factors associated with production and inputs of DOM in the soil

The concentration of DOM in soil solution is controlled by several factors and processes, including the quantity and quality of the organic inputs, climate conditions, microbial activity (consumption and immobilization), soil texture and mineral adsorption and leaching (Chantigny, 2003; Filep and Rékási, 2011; McDowell, 2003).

2.3.1.1. Climate and soil type

Climate characteristics can modify DOM production and release. Warm and moist weather conditions, such as the tropical climate, increase the microbial activity and the release of DOM from decomposing materials (Kalbitz and Knappe, 1997). Rainfall coming after dry periods may release a higher concentration of DOM in the soil solution than in normal rainy periods probably because of the reduced rates of decomposition in dry soils that cause the accumulation of microbial products (Kalbitz et al., 2000). The rainfall intensity also may influence DOM sorption or leaching (Fröberg et al., 2007; Herbrich et al., 2017).

In general, high soil temperature and soil moisture were positively correlated to plant material decomposition rates, directly affecting DOM concentration in the surface soil layers (Zhou et al., 2015). Thus, DOC inputs and fluxes may be higher in tropical regions than temperate regions.

Moreover, soil characteristics affect DOM inputs to the soil, such as clay content, water holding capacity, porosity and infiltration rates, and mainly affect the sorption force governed by the concentration of clays and oxides in the soil (Saidy et al., 2013). The DOM concentration in the soil profile is a result of continuous sorption combined with microbial processing and subsequent desorption (Kaiser and Kalbitz, 2012). Aluminum (Al) and iron (Fe) oxides and hydroxides are some of the most important DOM adsorbents (Kaiser et al., 1996), especially in tropical soils.

2.3.1.2. Quantity and quality of organic residues

The role and dynamics of DOM in soils are related to the quantity and quality of organic residues, which depends largely on its sources (Kalbitz et al., 2000; McDowell and Likens, 1988). The lignin content in the residue regulates the litter decomposition rate and thus is important for the DOM production (Guggenberger, 1994; Kalbitz et al., 2006). There is a strong relationship between DOC flux and soil C:N ratio (Aitkenhead and McDowell, 2000), in which the decomposition of poor-N materials seems to result in the production of more soluble compounds, explaining the positive correlation between C:N ratio and DOC concentration (Kalbitz and Knappe, 1997). When the C:N ratio is less than 10, most of the C associated with SOM is consumed or re-assimilated by microbiota so that only a small portion of C remains in the soil as DOC (Kindler et al., 2011). Furthermore, declines in soil C:N could lead to significant declines in DOC flux, especially in soils with lower initial mean soil C:N such as grassland, savanna and others (Aitkenhead and McDowell, 2000).

Root exudates can also release different organic compounds, leading to intensive changes in the physical, biological, and chemical nature of soil (Jones et al., 2009). The dominant organic C compounds in roots reflect those key compounds to cell metabolisms, including sugars, amino acids, and organic acids (Kraffczyk et al., 1984).

2.3.1.3. Soil use and management

The labile DOC fraction is more sensitive to tillage disturbance than total SOC pool (Roper et al., 2010). Also, the potential of using DOM as an indicator for environmental changes and a tool for classifying ecosystems has been proposed in aquatic and marine sciences; consequently, using DOM in soil science seems desirable (Kaiser and Kalbitz, 2012). In the short-term, the relation between DOC and SOC concentration is not significant (Zhou et al., 2015), but the relationship is significant in the long-term perspective (Gregorich et al., 2000).

DOM production is sensitive to changes in land uses and management, such as the conversion of native forest to agriculture systems and the use of conventional tillage, i.e., activities which can increase microbial activity (Van Gaelen et al., 2014). Higher microbial activity increases DOM release for a short period (Brye et al., 2001; Leinweber et al., 2008) and induces faster turnover of the C fractions. In a study conducted in tropical soil from the Brazilian Amazon, an agroforestry system had a higher DOC concentration than native forest and pasture (Marques et al., 2012). Also, in the Brazilian savanna (Cerrado biome), Silva et al. (2007) found higher DOC flux in the soil under sugarcane crop than under forestation with eucalyptus and native forest areas. Unfortunately, little has been attempted to quantify factors that affect DOM production in tropical conditions (Wang et al., 2016).

The residues amendment from the soil surface and the resulting release of easily biodegradable DOM by the plant residues clearly induce microbial growth (De Troyer et al., 2011). The maintenance of crop residues in the soil surface is important to maintaining C inputs and subsequently maintaining SOC (Cherubin et al., 2018). Thus, soils under no cover can suffer significant C losses as DOC forms (Baldock and Skjemstad, 2000; Sousa Jr. et al., 2018).

In summary, a defined chemical composition of DOM is difficult, and the origins of DOM are still little understood. At the moment, it is known that the main sources of DOM are the plant residues/litter and the stable SOM, which varies mainly according to the organic material. Thus, the production and release of DOM depend on a range of factors, such as soil characteristics (e.g., quantity of clays and oxides), climate conditions (e.g., temperature and moisture), characteristics of the plant residues (e.g., C:N ratio, lignin content, roots length), and soil use and management practices. Through this information, it is possible to assume that DOM

production in the soil is higher in tropical conditions, under crop cultivation, and with plants with high C:N ratios and lignin content.

2.4. Soil DOM changes and their implications for the biogeochemical cycle

2.4.1. Adsorption/desorption of DOM in soil

The Sorption processes of organic C on mineral surfaces contribute to accumulation and stabilization of SOC on the environment (Feng et al., 2005; Saidy et al., 2015), and the free movement of DOM is mainly controlled by its adsorption to soil clay surfaces (Ussiri and Johnson, 2004). The sorption of OC to mineral surfaces is strong and only partially reversible, with only a small portion being extractable into fresh water, salt water, or organic solvents (Kahle et al., 2004; Kaiser and Guggenberger, 2007). Desorption varies according to the mineral, and while all DOC adsorbed by kaolinite are completely desorbed, only 28 to 35% of the adsorbed DOC are desorbed by Fe-oxides. These findings highlight the importance of the goethite and hematite on the adsorption of DOM in tropical soils (Benke et al., 1999). Moreover, there is a high correlation between DOM adsorption and specific surface area (SSA) of the clay fraction (Singh et al., 2016).

The biological stability of SOC sorbed to clay-oxide associations is influenced by the balance between the negative charge of the clays and the positive charge of the Fe-oxides (Saidy et al., 2015). Fe-oxides tend to be positively charged, especially in acids soils, and kaolinitic clays tend to carry less negative charges than other clays (Saidy et al., 2013). In this sense, oxides can interact with both clay minerals and organic compounds to form organic-mineral associations which may influence significantly the size of the organic matter fraction resistant to biodegradation (Schneider et al., 2010).

Polyvalent cations usually reduce DOM leaching and enhance DOM adsorption as a result of cation bridging and precipitation. Comparing cations adsorption, Singh et al. (2016) found that DOM adsorption was higher with increasing concentration of Ca^{2+} than of Na^{+}. In contrast, anions such as phosphate and sulfate compete with DOM for adsorption sites, increasing the DOM leaching (Kalbitz et al., 2000).

In general, soil with the predominance of clays with high SSA, higher cation exchange capacity, and especially the high content of Fe/Al oxides are more efficient to protect chemically and physically the C of microbial mineralization and other processes of losses (Kahle et al., 2003). Moreover, a high concentration of oxides reduces DOM concentration in the soil solution, reducing losses by leaching. Thus, oxidic soils are expected to retain DOM more effectively.

2.4.2. Effects of DOC in C sequestration

Soil organic carbon is the largest terrestrial SOM pool, contains about 1550 Pg of C, which is three times more than that found in the atmosphere or terrestrial vegetation (Lal, 2004). Therefore, the soil has a key function in C sequestration, mitigating global warming and climate changes. For its characteristics, DOM has an important role in the soil biogeochemical and is a crucial component of the net ecosystem C balance (Kindler et al., 2011). The DOM fraction is a potential source of the stabilized C occurring in subsoil by the C redistribution in deep layers (Fröberg et al., 2007; Kalbitz and Kaiser, 2008) leading to SOC accumulation (Schneider et al., 2010; Saidy et al., 2015), making it an important way to sequester C and decrease C lost in the CO_2 form (Lal, 2004; Smith, 2004).

In long-term studies, De Troyer et al. (2011), Fröberg et al. (2003), and Hagedorn et al. (2004) found that organic matter from plant residues do not accumulate in the DOC pool; instead, organic matter is mostly released as CO_2. However, Uselman et al. (2007) found that during high rainfall and at low temperature, a larger fraction of the ^{14}C from plant litter is lost as DOC, translocated or leached, than released as CO_2, likely by favoring more leaching than microbial metabolism. These results indicate that the proportion of C released as a CO_2 form or as a DOC form is closely related with local climate characteristics.

Recently, Deng et al. (2017) showed that DOC leaching from the litter layer to the topsoil in a subtropical forest was the major cause of rain-induced soil CO_2 pulse; consequently, there is a great concern about the contribution of DOC in increasing CO_2 release in tropical soils due to increase in DOC fluxes by accelerated microbial activity. Nevertheless, correlations between DOC fluxes and CO_2 release in tropical soils still needs to be further verified.

2.4.3. Effects of DOM on soil properties

The DOC can be considered an alternative tool for monitoring adverse impacts on soil quality for being a sensitive fraction (Silveira, 2005). Due to its high mobility, the movement of DOM is significant to the cycling and distribution of nutrients such as N and P (Veum et al., 2009) and Fe and Al complexes (Fujii et al., 2009) in ecosystems.

Soluble organic acids that compound DOM have functional groups, especially carboxylic and phenolic, that participate in many chemical reactions in soil, such as organic metal complexation, and increase the rate of ion adsorption, and metal detoxification (Franchini et al., 2003; Roberts, 2006). These acids complex exchangeable Al in the soil solution, becoming it nontoxic to plants (Amaral et al., 2004; Franchini et al., 1999). Therefore, in tropical soils, these organic acids can compete with other ions such as phosphate ions for the adsorption sites,

increasing P availability to plants (Andrade et al., 2003; Jones, 1998). The organic acids can also form stable organometallic complexes with Fe and Al in a wide pH range (Sposito, 1989). In addition, greater soil structural quality (e.g., higher aggregate stability, soil porosity, and water retention) is positively associated with DOM movement in the soil profile (Marques et al., 2012) since its movement and sorption are related to the water fluxes (Herbrich et al., 2017).

The metal detoxification activity depends on the origin of DOM since DOM originating from plant residues does not contribute significantly to the transport of organic pollutants and metals (Amery et al., 2007) because this DOM is easily degradable and quickly decomposed rather than leached through deeper soil horizons. However, DOM derived from SOM can be used to predict the movement of both organic and inorganic pollutants in soil (Amery et al., 2008).

The soil pH can affect DOM mobility; however, the effects are still uncertain. Nonetheless, Tipping and Woof (1990) reported reduced adsorption capacity at high pH values thus DOM mobilization is enhanced. Consequently, small increases in soil pH would lead to increases in the amounts of mobilized SOM.

In summary, DOM dynamics and processes are mainly affected by adsorption in the soil mineral phase and more strongly adsorbed by Fe and Al oxides, higher SSA clays, and polyvalent cations. Moreover, DOM is important in nutrient cycling and distribution in the profile, in phosphate availability, and in the complexation of Al, heavy metals, and pollutants. In subsoil, DOC is an important source of the stabilized SOC and is a potential C reservoir in deep soils, having an important role in C cycling and sequestration in the soil. Based on the aspects discussed, in tropical condition, DOM can be assumed to be strongly adsorbed by the Fe and Al oxides; however, the fast production and changes of DOC can be an impulse of CO_2 emission. Considering the great influence and benefits, direct and indirectly of DOM in multiple soil chemical, physical, and biological properties and the lack of information in tropical soils, this topic needs to be further explored in those conditions.

2.5. DOM outputs and losses

Terrestrial Terrestrial hydrological pathways of C flow include rainfall, surface runoff, and drainage or leaching. The DOC fraction is more linked with leaching, while the particulate C fraction is more linked with superficial runoff (Edwards et al., 2008). Then, the process of DOM percolation from the soil surface transfers C and nutrients to the deeper layers through soil solution (Fröberg et al., 2007). Thus, DOM can undergo sorption and be stored or lead to

aquifers, moving from the terrestrial to the aquatic system (Sparling et al., 2016). In this way, DOM leaching may be an important pathway of continuous soil C and nutrient losses (Kindler et al., 2011).

The main source of DOM leaching is from SOM because DOM from fresh plant residues is largely retained or consumed on the topsoil, while only a small fraction is moved through the soil profile (Fröberg et al., 2007, 2009). Some microorganisms can also contribute with DOM leaching, such as mycorrhizal symbionts that contribute to C flow, mainly through their structures, resulting in the release of a range of exudates into the mycorrhizosphere (Jones et al., 2009).

Carbon losses by superficial runoff can be avoided with soil conservationist management, and continuous vegetal cover can provide a significant reduction in runoff, preventing potential contamination of waters by DOM (Veum et al., 2009). The DOC mobilization in runoff water is resultant of the antecedent soil moisture, as more DOC is released from drier soils (Van Gaelen et al., 2014). Then, the monitoring of C losses by runoff and leaching to the deep soil is required in agricultural soils to estimate C balances (Nachimuthu and Hulugalle, 2016).

The DOM leaching is also controlled by the magnitude and direction of the drainage water fluxes. During intensive and frequent rainfalls, elevated DOC concentration was found in groundwater from a sugarcane crop in Australia and was supplied via water flow (Thayalakumaran et al., 2015). Fast water movement, such as strong rains, might decrease DOM sorption in the soil, as well as microbial processing, resulting in fresh residues-derived DOM transported deeper into the soil (Fröberg et al., 2007). On the other hand, less time is available for desorption of SOM which may cause lower DOC concentration in the soil solution compared to a slower water percolation (Herbrich et al., 2017). Consequently, with more water volume in the soil, more DOM is probably derived from fresh residues than from SOM desorption.

Leaching of DOM is considered a continuous form of C and nutrient losses from the soil and becomes a pollutant as it reaches aquifers. In contrast, DOM may be a large reservoir of C in deep soils when it is adsorbed and stored in deep layers. Carbon losses by soil surface are generally linked with soil management system; however, a C loss by leaching depends on many factors, such as soil characteristics, soil management, and rainfall intensity. In the case of tropical conditions, in which most areas contain deep soil, DOM fraction may be labeled as an important reservoir of C in depth. To verify this hypothesis, more studies with DOM production and leaching must be done in tropical soils to estimate a complete C balance.

2.6. Final remarks and future perspectives

The The DOM concentration in soil solution is highly variable and depends on site-specific soil, climate, and land management conditions (Sparling et al., 2016). The vast majority of studies with DOM have been performed under temperate soils, predominating shallow soils. In contrast, little is known about tropical soils, which are highly weathered, deeper, and contain large amounts of Al and Fe oxides and hydroxides, leading to large adsorption.

The DOM fraction is an important active and bioavailable C source for microbial biomass, besides to sequester and store C in deep layers. Despite its benefits, DOM dynamics has been preferentially evaluated in forests and peat soil, whereas only a few studies have been conducted in agricultural soils (Wang et al., 2016), and while land use and management practices directly affect the C fractions into the soil, there is little experimental data involving DOM mechanisms and processes.

Future studies are essential to determining the potential of best management practices (e.g., no-till, cover crop, crop rotation) to increase soil DOM, how crop residue removal to feed animals or produce bioenergy can affect DOM dynamics in the soils, and whether is it possible to avoid DOM leaching in agricultural soils. Our research shows that little importance has been given to this topic in Brazilian agricultural soils, revealing a gap of information about DOM that should be addressed by future studies.

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3. SUGARCANE STRAW REMOVAL EFFECTS ON SOIL WATER STORAGE AND DRAINAGE

Abstract

To enhance global bioenergy production, the Brazilian industry's interest in using sugarcane straw as a feedstock for electricity and cellulosic ethanol production has increased recently. However, indiscriminate straw removal may negatively affect key soil functions related to water infiltration, retention, and availability to plants. Therefore, a lysimeter system with a 0.2-m soil column was built to evaluate the effects of straw removal rates on water drainage and water storage in a sandy clay loam soil from a commercial sugarcane field in Piracicaba-SP, Southeastern Brazil. The experiment was conducted in an open area where the lysimeter system was subjected to rainfall. After soil stabilization, the treatments consisting of four straw amounts of 0, 3, 6, and 12 Mg ha^{-1} were applied, representing straw removal rates of 100, 75, 50, and 0%, respectively. The water drainage was quantified and collected for 17 months, and the soil water storage was measured over a two-month period. The soil water holding capacity was determined by an inverse modeling approach minimizing the differences between soil water storage measured in the field and simulated by a water balance model. Our results reveal that the accumulated drained reduced 30, 11, and 4% under bare soil, 75%, and 50% straw removal rates when compared to no removal management, respectively. Bare soil presented the lowest water storage over most of the days, indicating a greater susceptibility to losing water through evaporation and drying. The long-term simulation for early, mid, and late sugarcane harvest seasons suggests longer periods of water restriction under higher straw removal rates (i.e., 100 and 75%), potentially impairing sugarcane growth and thus yield. Also, the findings suggest that partial residue maintenance, such as 6 Mg ha^{-1} of straw on the soil surface, seems to be sufficient to prevent excessive water losses and daily variations on soil water content, sustaining soil water storage rates above the critical point to suitable sugarcane growth.

Keywords: Crop residues; Water resources; Agricultural management; Mulching; Bioenergy

3.1. Introduction

Water deficit is one of the main reasons for declining crop yields, especially in Brazilian tropical regions (Ferreira et al. 2017; Sentelhas et al. 2015). In the largest sugarcane-producing region (southeastern region) of Brazil, the average yields have been relatively stable in the last decade, varying between 70 and 86 Mg ha^{-1} (Conab 2017), although more advanced and sustainable technologies (e.g., green harvesting system) were widely adopted across the region. The low yields in recent years are mainly a result of water shortages combined with other factors, such as soil compaction due to mechanized harvesting (Otto et al. 2011) and recent straw removal management from the soil surface.

Several studies have shown that intensive machinery traffic in fields degrades the soil structure, primarily bare soil, leading to increased bulk density (Baquero et al. 2012; Hunke et al. 2015b; Souza et al. 2014). Machinery traffic also reduces porosity, aeration, water infiltration, and water availability (Castro et al. 2013; Cherubin et al. 2016a; Franco et al. 2015; Hunke et al.

2015a), creating an imbalance between air and water in the pore space (Cherubin et al. 2016b) and increasing the risk of runoff and soil erosion.

Straw maintenance on the soil surface is a key to sustaining numerous soil properties and functions directly and indirectly related to water use efficiency (Carvalho et al. 2017; Cherubin et al. 2018; Leal et al. 2013). The thick layer of straw considerably suppresses soil water evaporation and therefore helps conserve soil water (Denmead et al. 1997), increasing soil water retention (dos Anjos et al. 2017) and minimizing damage caused by rainwater (Marin et al. 2014; Olivier and Singels 2012). Besides reducing soil temperature and moisture ranges (Dourado-Neto et al. 1999), straw maintenance increases soil C stocks (Cerri et al. 2011; Satiro et al. 2017; Sousa Junior et al. 2018), prevents soil compaction (Braida et al. 2006; Satiro et al. 2017), reduces surface sealing (Goddard et al. 2008), increases infiltration rates (Karami et al. 2012), and may increase drought resistance (Liao et al. 2014).

Straw removal for energetic purposes is a recent activity in Brazil, and this growing interest in bioenergy production by means of sugarcane residues has become a threat to soil physical quality and thus to soil water storage and its availability to the plants. Therefore, this work hypothesizes that indiscriminate straw removal from the soil surface decreases the physical quality of the soil and changes water dynamics, causing a reduction in water infiltration and drainage, thus increasing water evaporation and reducing soil water retention. To adequately improve water use efficiency, it is essential to understand the factors and mechanisms affecting water balance partitioning in agricultural areas. Consequently, this research establishes a new drainage lysimeter system to evaluate the effects of sugarcane straw removal management on soil water storage and drainage. In addition, the results are extrapolated using a simulation modeling to predict the impacts of sugarcane straw removal on soil water storage over the whole sugarcane cultivation season.

3.2. Material and methods

3.2.1. System description and experimental design

To estimate the soil water balance under different sugarcane straw amounts removed from the soil surface, a 5 mm thick wall PVC drainage lysimeters tubes with a diameter of 0.2 m and a length of 0.2 m were built. The drainage lysimeters were placed 1.5 m above ground level and suspended by an iron structure frame. The soil column of 0.2 m deep, representing a volume of ~ 0.0063 m^3, was used since it represents the most important layer related to water and nutrients uptake by roots. Moreover, the soil column is where the water evaporation occurs. At

the bottom of the lysimeters, perforated stainless-steel plates 2 mm thick and a 125-µm sieve mesh were placed to hold the soil column preventing soil losses. Furthermore, a funnel was attached beneath with a rubber ring to ensure tight fitting and connected to glass bottle by a hose to collect soil solution draining from the lysimeters to the glass (Fig. 1).

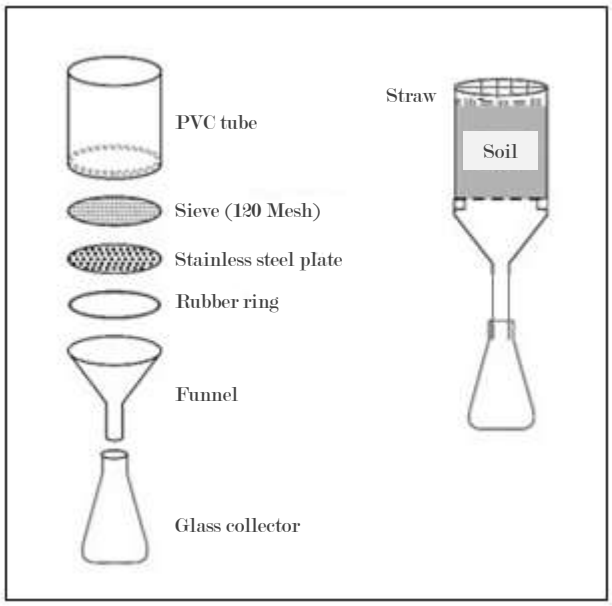

Figure 1 – Lysimeter tube system design developed to evaluate rain water drained.

Soil from commercial sugarcane field, classified as Rhodic Kandiudox (Soil Survey Staff 2014), with a sandy clay loam texture (600, 70, 330 g kg^{-1} of sand, silt, and clay, respectively) was used to fill the lysimeters. Soil installation was performed via a destructive method by repacking layers with a rubber hammer on the outer side of the tubes to recover the field soil bulk density of 1.32 and 1.37 Mg m^{-3} in 0-0.1 and 0.1-0.2 m layers, respectively.

After soil assemblage, the lysimeters were placed in an open field area at the University of São Paulo campus in Piracicaba-SP, far from shading or interferences with the rainwater intake throughout the experiment period, i.e., from January 2016 to May 2017. For soil stabilization, the lysimeters were exposed for some rainfall events along two weeks. In addition, in soils with 33% clay, soil shrinkage can occur with drying by reducing the soil volume and leaving an empty space between the soil and the lysimeter wall, causing preferential flow. Therefore, special attention was given to the soil shrinkage throughout the experiment period and especially in the dry period preceded by rainfall.

The climate type in the study area is classified as subtropical with dry winters and hot summers (Cwa – Köppen's classification) with an average annual rainfall of 1,300 mm. The mean air temperature is 23 °C, with temperatures above 35 °C in the summer and temperatures of 10 °C in the winter.

A completely randomized experimental design with four treatments and four replications was used, and the treatments comprised three sugarcane straw (cv. SP80-3280) disposal amounts on the soil surface, i.e., 3, 6, and 12 Mg DM ha^{-1}, representing the field straw removal rates of 75, 50, and 0%, respectively. In addition, a control treatment consisting of bare soil, representing 100% straw removal, was used. Chopped sugarcane straw from a mechanical harvester (green and dry leaves) was collected in the field and brought to the laboratory for drying of small aliquots to determine the humidity and subsequent weighing according to the selected treatment. Next, the straw mulch blanked was placed on the open top of the lysimeter tube system in contact with the total area and stuck with a metal grid. After eleven months, the remaining straw dry mass was determined and a new portion of chopped straw mass based on the treatment selected was placed on the previous straw mass.

3.2.2. Sample collection, modelling, and data analysis

Throughout the experimental period, drainage was collected and quantified using a graduated test tube. Depending on the rainfall intensity, the water collections were extended for up to four days, ending when the percolation completely ceased.

At the beginning of the experiment, a moisture sensor (Decagon EC-5, Pullman, USA) previously calibrated to the soil type used in this experiment was installed with three replicates in the middle of the lysimeter, i.e., at 0.10 m depth. The soil moisture data were obtained at 30-minute intervals, and the daily average was assumed to be uniform for the entire soil column. This assumption was used to simplify the soil moisture storage estimation in response to the sugarcane straw amounts remaining on the soil surface along the assessment period (February and March), which these times were chosen due to the history of heavy rain spaced with days of high evapotranspiration demands (ESALQ 2018). Thus, the soil water storage (h, mm) was calculated using the daily average of soil moisture content measured by the moisture sensors (θ, $m^3\ m^{-3}$) considering the soil depth (Z, m) based on Equation 1:

$$h = \int_0^L \theta(Z)dz \qquad (1)$$

The maximum amount of water retained in the soil matrix as soon as the drainage ceases is defined as the soil water holding capacity (SWHC, mm), which represents the main input parameter for the water balance estimation. Moreover, the critical water potential that represents the amount of energy in which water is readily available for plants was established as -150 kPa for sugarcane (Allen et al., 1998), resulting in θ_{cr} = 0.172 $m^3\ m^{-3}$, and was converted to a critical water storage (h critical) of 34.4 mm through a Pedotransfer function (Tomasella et al., 2000).

The daily soil water storage variation (Δh, mm) throughout these two months was also estimated by Equation 2:

$$\Delta h = Z(\theta_i - \theta_{i-1}), \qquad (2)$$

where θ_i is the soil moisture content ($m^3\ m^{-3}$) on day i and θ_{i-1} is the soil moisture content ($m^3\ m^{-3}$) of the previous day (i-1). On sunny days, negative Δh values were considered as the amount of water lost through evaporation, i.e., the daily soil evaporation (mm); while on rainy days, this value was considered to be 0.

The daily sequential water balance model (Thornthwaite and Mather, 1955) that accounts for the water budget resulting from the application of the principle of mass conservation in a given soil volume was used. The estimations were performed via the Microsoft Excel spreadsheet developed by Rolim and Sentelhas (2006) using the daily rainfall records (mm) and daily soil evaporation (mm) as the main input. For SWHC estimation, the model's output and soil water storage (h, mm) were compared against the measurement values determined by moisture sensors from field observations. This approach is usually known as inverse modeling and minimizes the difference between model output and observed values, in this case, soil water storage (Fig. 2).

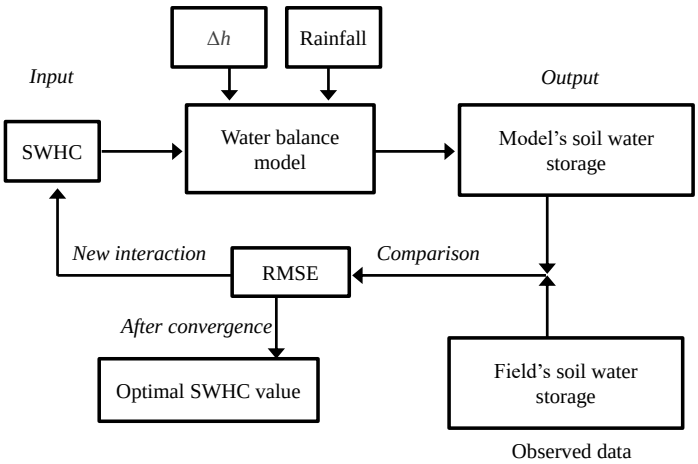

Figure 2 – Inverse modeling scheme for soil water holding capacity (SWHC) estimation under different amounts of straw on the soil surface.

The least root mean square error (RMSE) procedure between soil water storage (h, mm) measured by soil moisture sensors and the simulated values of h (mm) obtained from the water balance model was used as a statistical indicator. The RMSE of a model prediction with respect to the estimated variable X_{model} is defined as Equation 3:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}\left(h_{obs,i}-h_{model,i}\right)^2}{n}} \quad , \qquad (3)$$

where h_{obs} is the storage water value measured in the lysimeter, h_{model} is the simulated water storage value at time/place i, and n is the total number of observations. The RMSE measures accuracy, such that when the observed and the estimated data are similar, RMSE is close to zero. Therefore, the SWHC for each treatment was determined by the lower RMSE value of the daily soil water storage h (mm) (Fig. 3), resulting in 48, 46, 57, and 60 mm under 100, 75, 50, and 0% removal rates, respectively.

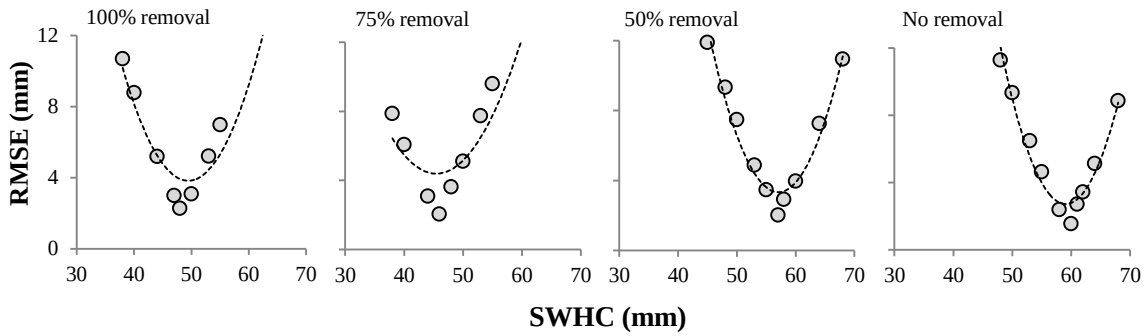

Figure 3 – Root Mean Square Error (RMSE) analysis of soil water storage in soils with different sugarcane straw removal rates.

After SWHC optimization, the soil water storage data (simulated vs. measured) was compared via the following statistical tests, as suggested by Smith et al. (1997): sample correlation coefficient (r), modeling efficiency (EF), coefficient of determination (CD), and mean difference (M). Water drainage was then compared using the F-test of variance analysis, and the means were compared according to the Tukey test (p <0.05).

To predict the best management in terms of sugarcane straw removal rate to enhance soil water storage, a daily sequential water balance model with 30-year climatological records was used for the Piracicaba region. In this region, the sugarcane harvest season may range from April to November based on the sugarcane variety (early, mid or late season) and local weather conditions; hence, plants may be subject to seasonal changes in water availability. Therefore, three harvest periods were considered for the evaluation in our analysis.

3.3. Results

3.3.1. Drainage

Drainage differed between the different straw removal rates throughout the experimental period (Fig. 4). Under higher rainfall levels (e.g., February 19, 2016; November 4, 2016), the

mean drainage values were similar regardless of the amount of straw left on the soil surface, overcoming the maximum water holding capacity of this soil. However, at lower rainfall levels (e.g., October 18, 2016; March 3, 2017), the straw mulch significantly affected drainage, with highest drainage volumes being observed under thicker mulch treatment (i.e., under lower removal rates). The accumulated drainage also indicates differences among treatments (Fig. 4).

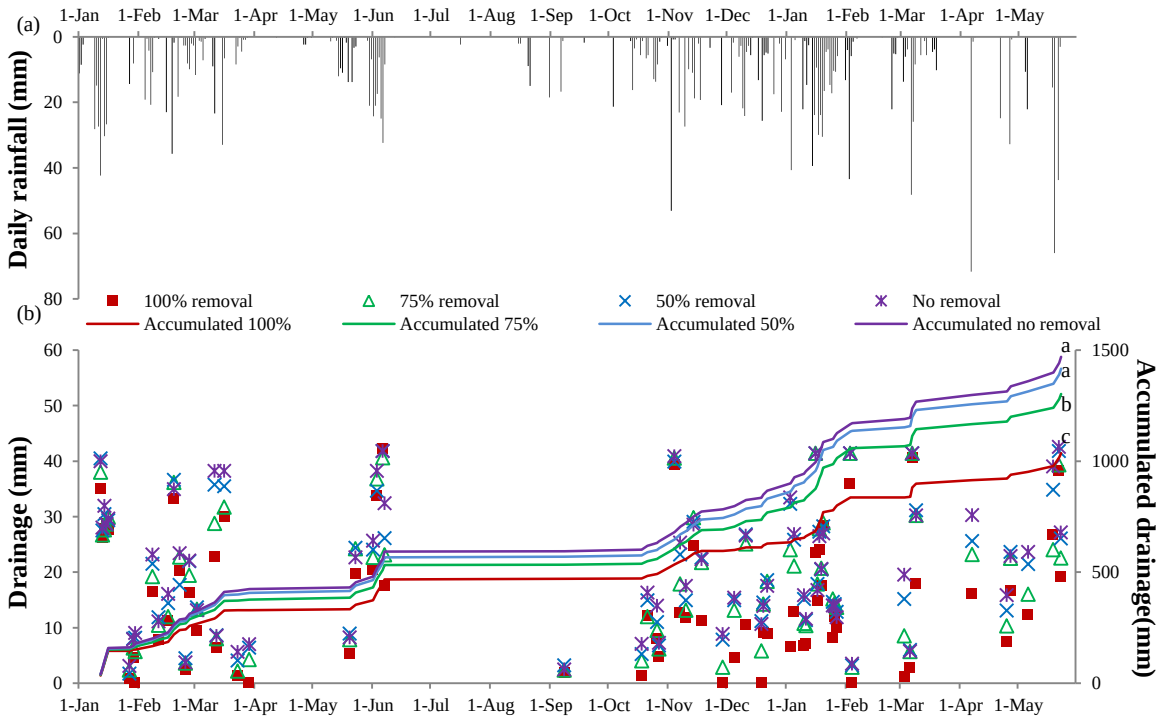

Figure 4 – Daily rainfall (water inputs) (a) and volume of water drained and accumulated drainage (water output) (b) in the 0.2-m soil layer under different sugarcane straw removal rates. Mean values followed by the same letter do not significantly differ in terms of total accumulated water drainage at the end of the experimental period (Tukey´s test; $p < 0.05$).

The lowest water infiltration capacity under bare soil may be associated with the structural degradation of the surface layer. In fact, the impact of raindrops directly on the soil surface under the total straw removal induced the splash erosion that promotes the detachment and short-distance transport of soil particles (Fernández-Raga et al. 2017). These detached particles block soil pores and result in soil surface sealing, as observed visually, reducing water infiltration rate and creating a water blade that is susceptible to evaporation and possible surface runoff.

3.3.2. Soil water storage and water balance modeling

Under Under 0 and 50% removal rates, the highest daily water storage (*h*, mm) was achieved. In contrast, under 75 and 100% removal, lower water storage was observed and

reached based on the critical moisture points (Fig. 5a', b', c' and d'). These results agree with the observed drainage in the lysimeters in which a higher drainage volume was achieved under 0 and 50% removal rates.

Daily water storage and drainage values were also simulated by the water balance model under different straw removal rates (Fig. 5a, b, c, d). The SWHC optimization provided better models results, in this case, by the small difference between the measured and the simulated of water storage values. In treatments with 100 and 75% removal rates, smaller differences between SWHC and *h* critical was observed, i.e., in the readily available water, characterizing lower water storage margin before water deficit imposition. However, daily water drainage was considerably different between measured and simulated data (Fig. 5a, b, c, d), mainly under 100% or 75% straw removal. In addition, lower straw removal rates (i.e., 0 and 50%) induced higher accumulated water drainage over the period of two months (145 and 139 mm, respectively) compared to 75 and 100% straw removal rates (129 and 98 mm, respectively), as was also observed over the entire experimental period (Figure 5).

The model accurately estimated SWHC according to linear regression and several statistical parameters (Fig. 6), indicating that the model was efficiently calibrated. The CD effectively measures the proportion of the total variance of observed data and is explained by the simulated data (Smith et al. 1997). In our case, all CD rates were close to 1, meaning that there were only small differences between the variance in measured and simulated values, while CD values greater than 1 (100, 75, and 50% removal) indicate that the deviation of the predictions from the simulated mean is smaller than that from the measured means. When CD values are below 1 (indicating no removal), the deviation is higher in the simulated prediction, as shown in Figure 6. The mean difference (M) values were close to zero, indicating that our results contain no bias or consistent errors. The EF ranged from 0.67 (100% removal) to 0.88 (no removal), while the correlation coefficients (r) were > 0.84, showing a positive correlation between measured and simulated data.

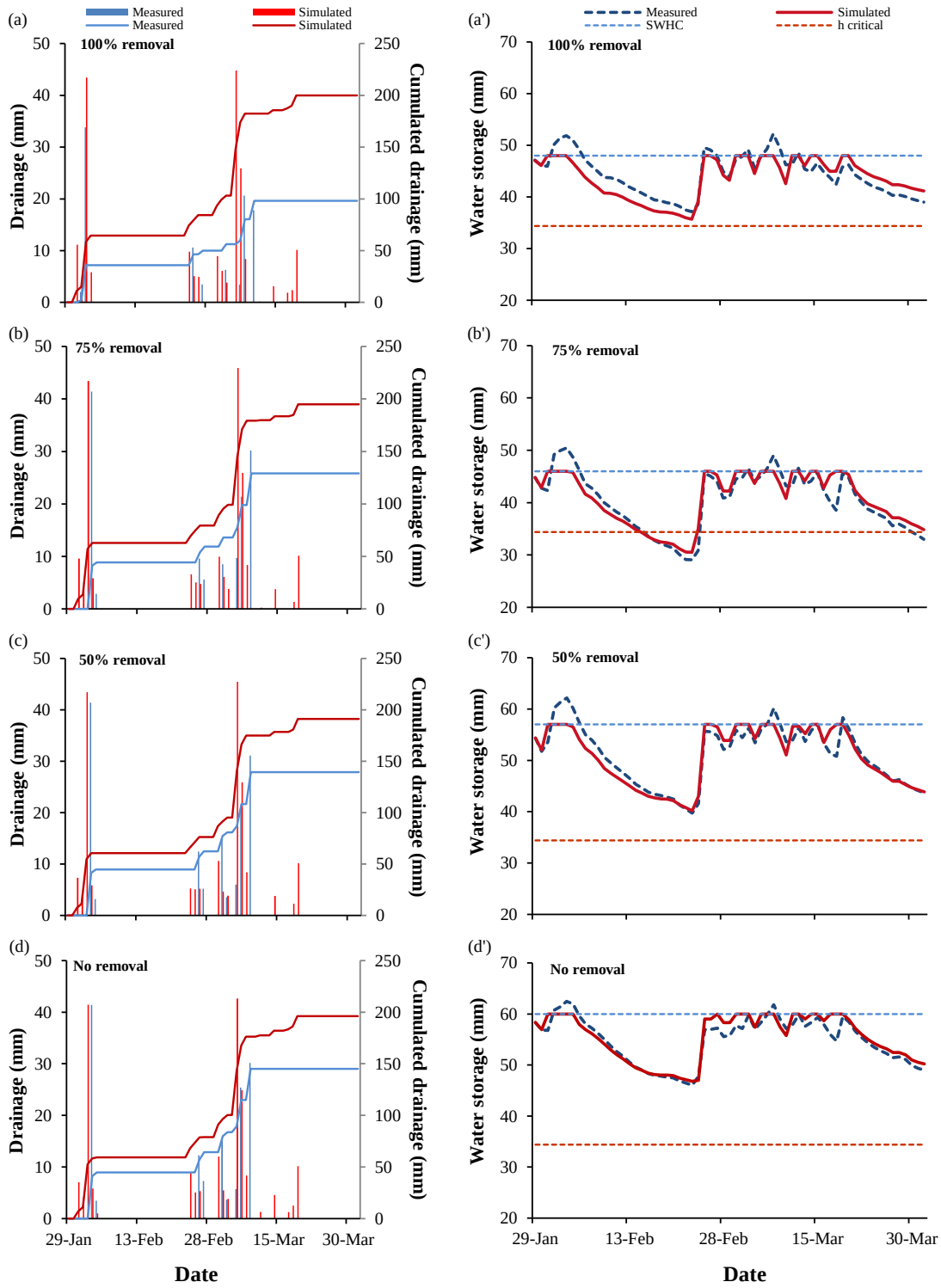

Figure 5 – Daily drainage (bars) and accumulated drainage (line) – left side; and soil water storage (*h*, mm) measured by lysimeters and simulated by the water balance model under different straw removal rates – right side. SWHC is the soil water holding capacity found by RMSE; *h* critical is the critical water storage for plants found by a PTF function.

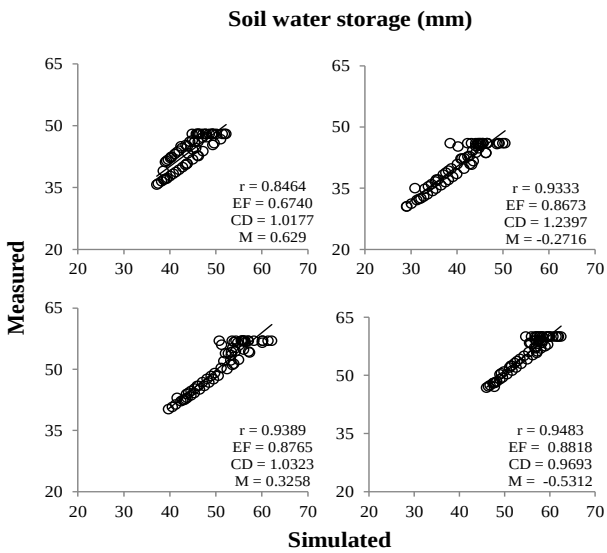

Figure 6 – Linear regression between measured and simulated soil water storage values (mm). r: sample correlation coefficient; EF: modeling efficiency; CD: coefficient of determination; M: mean difference; RMSE: root mean square error.

In In terms of daily water storage variation (Δ*h*, mm), greater differences were found between high and medium removal rates (75 and 50%). In the bare soil, low variation was observed, except during rainy days (Fig. 7). Moreover, the control treatment resulted in the lowest water storage over a high number of days, indicating a greater trend of the soil to lose water through evaporation and drying, apart from the fact that water is absorbed only by the soil matrix due to the lack of a straw layer. Also, the straw layer maintenance on the soil surface induced lower variations of water storage on most days.

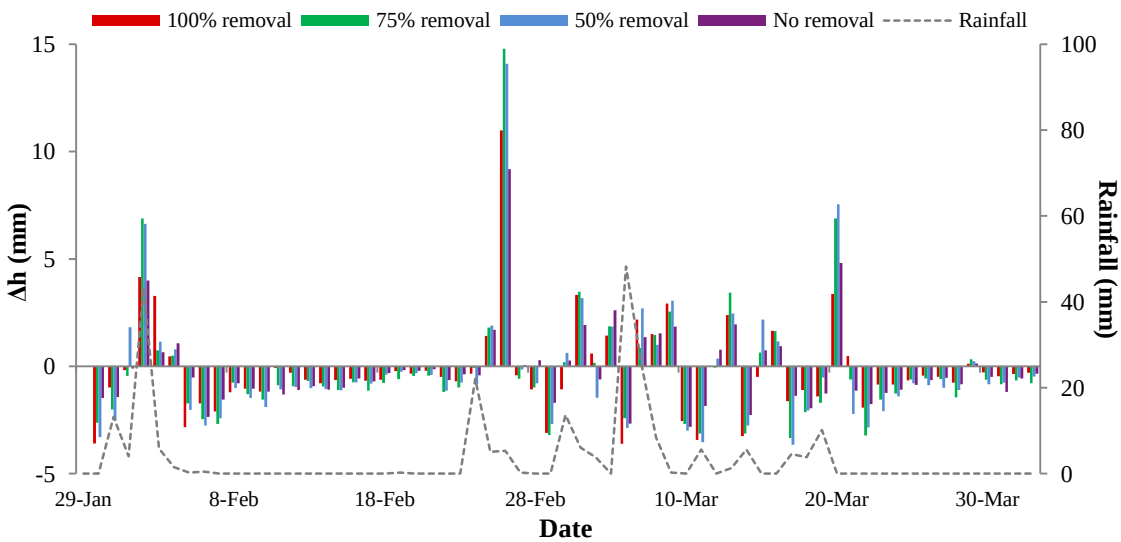

Figure 7 – Daily water storage variation (Δh, mm) and daily rainfall records (mm) for two months (February and March 2017).

Sugarcane straw removal may greatly affect the daily soil water storage over the course of the year. Considering the daily climatological normal series for the Piracicaba region (Fig. 8) and the SWHC values determined via inverse modeling (Figs. 2 and 3), the simulation showed a significant soil water storage variation throughout the year due to different rainy seasons, strongly affecting the plant development.

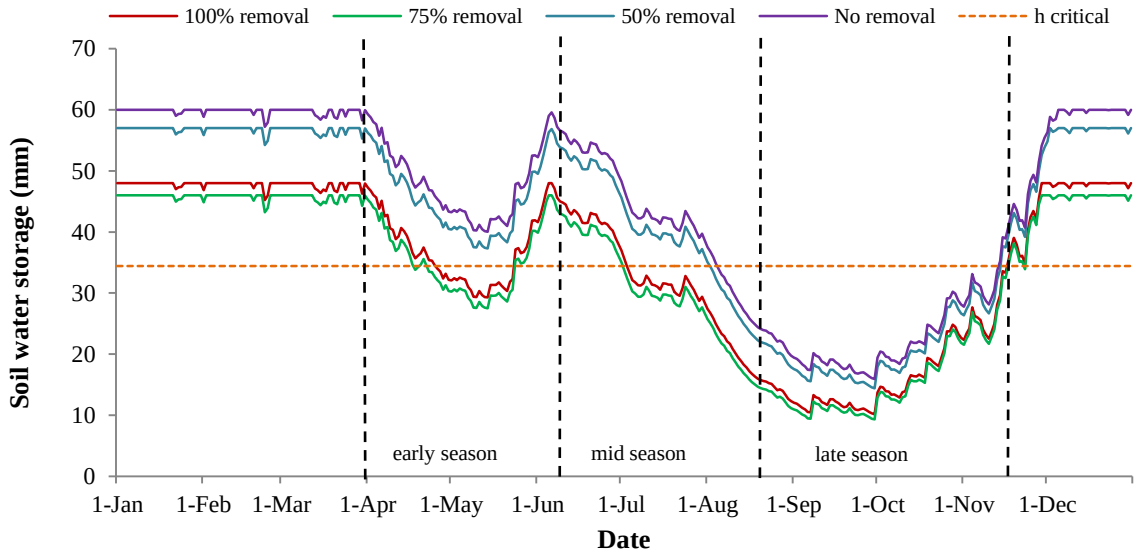

Figure 8 – Daily soil water storage simulated by the water balance model under different sugarcane straw removal rates. The horizontal dashed line indicates the critical level of water storage for plants, found by a PTF function. The vertical dashed lines indicate the main harvest periods in Piracicaba, SP region.

Over the year, more intensive straw removal rates (100 and 75%) were associated with lower soil water storage relative to less intensive removal rates (50 and 0%). Soils under 100 and 75% removal rates reached the critical level earlier, at the beginning of July, than soils under 50 and 0% removal rates. During the dry period (Jul-Nov), water storage levels were below the critical point, leading to water stress, especially under higher straw removal values (Fig. 8).

3.4. Discussion

3.4.1. Sugarcane straw effects on soil water conservation

The findings of this study confirm that straw mulch management considerably affects soil water dynamics (soil water storage and drainage). Therefore, straw mulch management has effects on the water partitioning at the land surface by affecting hydrologic processes such as evapotranspiration, drainage (groundwater recharge), and runoff (Scanlon et al. 2005); at least until canopy closure. The drainage assessment in the soil provides an important indicator of soil conservation since deficient drainage increases water lost by surface runoff and soil degradation

by erosion. The results show that 50% straw removal is sufficient for maintaining adequate drainage levels for deeper soil layers, with probably less adverse effects of the runoff. Crop residues can improve soil water storage by increasing infiltration rates and decreasing runoff losses and by reducing evaporation and fluctuations in the soil surface temperature, increasing soil water retention capacity (Blanco-Canqui and Lal 2009; Liu et al. 2014).

In terms of drainage, the results agree with other studies that show bare soils or soils under high removal rates exhibit lower moisture levels (Awe et al. 2015; Dourado-Neto et al. 1999). Hence, for drier soils, more water is necessary to bring the soil back to field capacity or above the critical point for supplying water to plants and provide subsequent drainage to deeper soil layers (Oliveira et al. 2010). The largest amount of water flow is likely associated with a hydraulic conductivity that describes the ease a fluid can move through pore spaces or fractures, which is a function of soil moisture $K(\theta)$ (mm d^{-1}), allowing water percolation to deep soil layers. Thus, water infiltration to deeper soil layers is higher with increasing amounts of sugarcane straw left on the soil surface. The lower drainage may be also partly due to surface sealing and increased bulk density levels (Hunke et al. 2015b; Lal 2009; Souza et al. 2015, 2014). Soil aggregates exposed at the soil surface are most vulnerable to destructive forces. The surface aggregates that collapse and slake down during wetting may form a layer of dispersed soil particles that are typically several millimeters thick. These disperse particles block the macropores of the top layer and thus tend to inhibit the infiltration of water into the soil (Hillel 1998). These particles can reduce water infiltration rates by 10-fold compared with no sealing soil (Benyamini and Unger 1984).

The straw mulch protects the soil from water losses, increasing the soil water retention period and minimizing the damages caused by raindrops (Marin et al. 2014; Olivier and Singels 2012). Valim et al. (2016) compared soil under different straw amounts on the soil surface and found that bare soil presented an infiltration rate about 15 and 20 mm h^{-1} lower than soil with 8 and 12 Mg ha^{-1} of straw, respectively.

The SWHC values differed between the treatments and were considerably higher in soils without straw removal, indicating that straw removal from the soil surface decreased soil water storage capacity. It likely is associated with higher water evaporation under bare soils (Denmead et al. 1997) because crop residues act as a barrier to prevent oscillations in daily water storage levels, thereby avoiding abrupt changes in soil moisture content (dos Anjos et al. 2017). Thus, the oscillation in daily water storage in bare soil is more evident than that of covered soils (Ruiz-Corrêa et al. 2017). The water balance model used adequately reflects the actual data.

3.4.2. Impacts of straw removal rates on available soil water to sugarcane growth

Sugarcane growth is usually divided into four development phases of germination/emergence, tillering, stalk growth, and maturation (Cock 2003; Silva et al. 2011). The tillering phase starts about 40-60 days after planting or ratoon development, and in the tillering and growth phases, the plants require high amounts of water (Singh et al. 2007), resulting in increased partitioning in biomass to the stalks (Baracat-Neto et al. 2017; Lisboa et al. 2018; Silva et al. 2011).

Therefore, it is important to manage the initial development phase during a period of high soil water availability (Scarpare et al. 2015). However, as mentioned, the harvest period (the beginning of the ratoon cycle) in this region may cover eight or more months. Thus, straw management can minimize the adverse drought effects mainly in the tillering and stalk growth.

According to the long-term water balance simulation, a straw maintenance of 50% (6 Mg ha^{-1}) was sufficient for maintaining the water storage levels above the critical point. Water shortage prevention may significantly reduce the need for salvage irrigation for plants to survive. In addition, plants growing under favorable soil water conditions rapidly develop their canopy, thereby protecting the soil surface from the direct incidence of solar radiation and, hence, water losses by evaporation. The shading effect on soil evaporation caused by the canopy closure is important after three or four months of plant development (Ruiz-Corrêa et al. 2017), minimizing the straw effects.

The simulation results show that intensive straw removal performed in sugarcane harvested in April/May (i.e., early harvest season) can more negatively affect the tillering and initial growth phase because the rainfall significantly decreases in this period, drastically reducing the soil water content, especially for bare soils. Therefore, the data suggests maintaining at least 50% (6 Mg ha^{-1}) of the straw on the soil surface to minimize the water stress to plants. Sugarcane harvested in July/August (i.e., the middle harvest season) may suffer in the initial sprouting phase and in the tillering phase because of low soil water content. In this period, the difference in soil water storage was almost 10 mm between bare soil and soil with a straw removal rate of 50%; however, in this phase, soils usually show a water deficit, but recover afterward. Sugarcane harvested in October/November (i.e., late harvest season) is less prone to water stress in the sprouting phase; in contrast, the plant growth can be negatively affected by soil hypoxic conditions due to rain excess.

At the end of the growth phase in July, the plants are prone to suffer from water deficit, possibly damaging plant development, although all soils reached critical levels from August onwards. However, greater stress increases the complexity of the water uptake by the plants

(Bastidas-Obando et al. 2017). Furthermore, in June, straw maintenance delays water deficits, even in relatively dry periods. In fact, keeping the entire amount of straw on the field or only 50% did not result in considerable differences, implying that straw amounts in the range of 6 Mg ha^{-1} (50% removal) may be sufficient to maintaining soil moisture and water retention for plant growth. Also, the need to maintain large amounts of sugarcane straw on the soil surface varies throughout the sugarcane cycle due to seasonal rainfall pattern. In general, in three sugarcane harvest periods and subsequent regrowth, the water deficit in some seasons tends to impede plant development. However, these effects may be mitigated with medium straw rates, such as 6 Mg ha^{-1} or more, because in several stages, this amount of straw kept the soil water storage above the critical level. In addition, low removal rates may reduce the need for salvage irrigation at certain times throughout the crop cycle.

Regarding soil water storage, although not all water held in the soil matrix is readily available for plants, it is an important aspect of plant development, especially at the beginning of the plant development cycle. Considering that in sugarcane, at the beginning of the cycle, evapotranspiration is about 2 mm day^{-1}, the number of days it takes for the plants to enter the critical level (34 mm storage) in the mid-season, from the 1st of June, was estimated according to the simulated water storage. Comparing the 50% removal and bare soil treatments, at 50% removal, it took 20 more days for the plant to enter the critical level, indicating almost one more month of adequate soil water supply for plants.

Although the method was efficient in the soil water drainage and storage evaluation, and this pioneering simulation information is extremely valuable, it is fundamental to validate these results in the field by monitoring soil moisture during the year in sugarcane straw removal experiments.

3.5. Conclusions

This study focused on establishing better management strategies in terms of sugarcane straw removal rate to enhance soil water storage. The built drainage lysimeter system efficiently allowed the soil water balance to be assessed. The findings indicate that straw maintenance on the soil surface favors soil water storage and water infiltration to deep layers and reduces daily soil water storage variations, especially after more intense rainfalls, compared to intensive straw removal management.

Due to seasonal rainfall distribution in the largest sugarcane-producing region of Brazil, the straw maintenance on soil surface has the potential to mitigate drought effects on plant

growth. Our simulation revealed that for moderate straw removal (50%), keeping 6 Mg ha^{-1} of straw on soil surface could be performed, since the remaining straw is enough to maintain suitable soil water availability to plant growth and suitable soil structure to ensure sufficient drainage.

According to the long-term water balance simulation, in the early season, it is not recommended to remove 50% straw or more. However, in the late season, it might be acceptable to remove more than 50% of the straw for bioenergy production considering soil moisture, as it is generally high during this time. However, with straw removal, many others chemical, physical, and biological soil properties are also affected; thus, more studies in all these topics are necessary.

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4. DISSOLVED ORGANIC CARBON RESPONSES FOR SUGARCANE STRAW REMOVAL IN BRAZILIAN OXISOL

Abstract

The increasing demand for using feedstock for bioenergy production has increased the interest in crop residues (e.g., sugarcane straw) over the past few years. The removal of sugarcane straw reduces organic carbon inputs to the soil and may change the production and translocation of dissolved organic carbon (DOC), and subsequent soil C storage. This study assesses the effect of straw removal on DOC production and translocation and C storage using a lysimeter system consisting of four soil columns with lengths of 1, 20, 50 and 100 cm. The soil was Rhodic Kandiudox with a sandy clay loam texture, coming from a commercial sugarcane field in the municipality of Piracicaba (São Paulo State, Brazil). The straw amounts (treatments) added on the soil surface were 0, 3, 6, and 12 Mg ha^{-1} (dry mass), representing total straw removal (TR – bare soil), high removal (HR), medium removal (MR) and no removal (NR). The straw addition was then repeated after one year. Afterward, the lysimeters were subjected to natural rainfall, and the soil solution was collected for 17 months. The DOC production at 1 cm was 606, 500, 441, and 157 kg ha^{-1} in NR, MR, HR, and TR, respectively. Most of the DOC produced at the NR was retained within the soil layer between 1 and 20 cm and had an increase of C stock in the upper soil (0-5 cm), while for MR and HR, the retention was strongest in the soil layer between 20 and 50 cm. The small DOC production (at 1 cm) in bare soil showed that no organic material inputs over time may result in soil C loss as DOC from the topsoil to the deeper soil. The DOC leaching to the deeper soil (i.e., > 100 cm) differed little between TR and soils with straw, suggesting that the high DOC retention by the soil (rich in clays and Fe oxides) did not allow high DOC leaching. Considering the large area of sugarcane production in Brazil, these findings show that the long-term straw removal can considerably limit C inputs to the soil, reducing DOC production and translocation into the soil, reducing the C storage.

Keywords: Crop residues; Dissolved organic matter; Carbon stock; Agricultural management

4.1. Introduction

Bioenergy production has been increased around the world, as a way to mitigate greenhouse gas emission and effects of global warming (IPCC, 2007). Cellulosic materials are considered as promising potential feedstock for producing so-called second generation ethanol (E2G), which is considered as the biofuel having the largest potential to replace fossil-derived fuels at the lowest environmental impact (Ojeda et al., 2011). Sugarcane stands out due to its large biomass production and the rich lignocellulosic leaves and tops, which after harvest is left on the field (crop residues - straw), consequently, sugarcane straw is now increasingly removed from the field for E2G production (Menandro et al., 2017). The increased removal of straw from the soil surface is considered a threat to sustainability of sugarcane production since potentially affecting soil functions (Blanco-Canqui and Lal, 2009; Carvalho et al., 2017; Cherubin et al., 2018).

The crop residues removal decreases the amount of decomposable organic material, consequently reduces the organic carbon (OC) inputs into soil. Crop residues are the major source for the production of dissolved organic carbon (DOC). Any change in litter input, therefore, will change in the DOC inputs into the soil. Dissolved organic carbon is considered the most mobile and bioavailable fraction of soil organic carbon (SOC) (Ghani et al., 2013; Marschner and Kalbitz, 2003), and is significant to the cycling and distribution of nutrients (Veum et al., 2009), organic acid-metal complexation (Franchini et al., 2003), and energy source to the microbial activity (De Troyer et al., 2011). In addition, it plays an important role in the redistribution of C within the soil profile (Fröberg et al., 2007; Kalbitz and Kaiser, 2008; Uselman et al., 2007). Some studies suggest that fresh C materials, such as roots and litter, are the most important DOC sources (Högberg and Högberg, 2002; Michalzik et al., 2003). Other studies show that the decomposition of stable SOM is the most important source of DOC, since humified compounds predominate in dissolved organic matter (Fröberg et al., 2003; Zsolnay, 1996).

The DOC production in terrestrial system varies according to soil type, climate (Kalbitz and Knappe, 1997), quantity and quality of residues (Kalbitz et al., 2000), land use system and soil management (Brye et al., 2001; Gregorich et al., 2000; Leinweber et al., 2008; Vinther et al., 2006). Typically, the DOC concentrations are elevated in surface soils (Gregorich et al., 2000; Hassan et al., 2016) and decrease with increasing soil depth (McDowell and Likens, 1988) due to adsorption by soil mineral phases, such as Fe and Al oxides (Kaiser et al., 1996; Kalbitz et al., 2000). The DOC translocations in soil profile can be the source of C in deeper soils (Fröberg et al., 2007; Sparling et al., 2016). It is considered a substantial component of the net C balance of the ecosystem (Kindler et al., 2011) but may be exported into aquatic systems (Sparling et al., 2016), representing a small but continuous C flux from the terrestrial system into aquatic systems.

Crop residues removal for bioenergy purposes is a new scenario in world agriculture. Brazil has a great potential to produce bioenergy through sugarcane straw. The literature does not reveal any study addressing the effects of the sugarcane straw removal management on DOC production, retention, and losses and on C storage into the soil profile, considering oxidic soils rich in oxides. This study tested changing DOC production and retention in the soil, as well as on C stocks, specifically due to the management of sugarcane straw removal. The guiding of the hypothesis was that high removal levels of sugarcane straw from the soil surface strongly reduce the production and translocation of DOC within the soil profile, reducing DOC retention and C storage.

4.2. Material and methods

4.2.1. Study installation and environmental conditions

To measure the DOC flux at different soil depths, a set of free-draining lysimeters representing 1, 20, 50, and 100 cm soil depth were built from PVC tubes with a diameter of 0.2 m. The small soil layer of 1 cm was adopted to allow the interaction between straw and soil microorganisms, and had the intention of assessing DOC production from straw. Perforated stainless-steel plates with a thickness of 2 mm and a 125-μm sieve mesh were placed at the bottoms of the lysimeters to prevent soil loss. A funnel was attached beneath with a rubber ring to ensure tight fitting and was connected to a glass bottle by a hose to collect the soil solution draining from the lysimeters (Fig. 1).

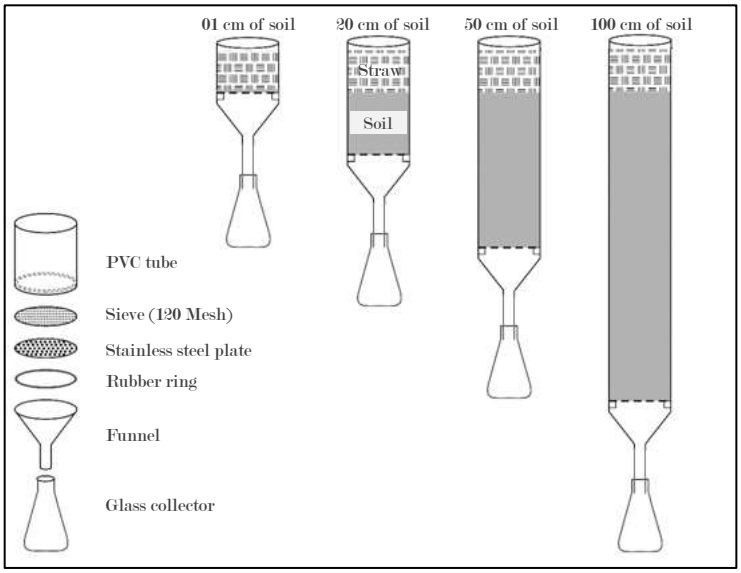

Figure 1 – Scheme of lysimeter tube system design developed to evaluate soil solution drainage in four different soil depths.

Soil used within the lysimeters was taken from a commercial sugarcane field. The soil was classified as Rhodic Kandiudox (Soil Survey Staff, 2014) with a sandy clay loam texture (600, 70, 330 g kg^{-1} of sand, silt, and clay, respectively). This soil represents a common soil type used for sugarcane cultivation in the region, and the average soil properties in the 0-30 cm layer were the following: CEC of 6.5 $cmol_c$ kg^{-1}, pH_{water} of 5.0 and base saturation of 53%. In addition, the soil bulk densities were 1.32, 1.37, and 1.38 Mg m^{-3} and the soil C stock was 16.2, 14.8, and 13.2 Mg ha^{-1} in 0-10, 10-20, and 20-30 cm layers, respectively. The soil presents kaolinitic and hypoferric character, with dominance of kaolinite ($Al_2Si_2O_5(OH)_4$), and the main mineral composition of the soils at the horizons BA, BW1 and BW2, respectively, are: quartz (SiO_2), 15, 13, and 13%; Fe-

oxide (Fe_2O_3) 2.1, 2.1, and 2.1; Al-oxide (Al_2O_3) 13, 14, and 13.3; and titanium oxide (TiO_2) 1.1, 1, and 1. The Ki index was 1.85, 1.6, and 1.2.

The lysimeter system was in a field in Piracicaba-SP and run for a period of 17 months, comprising two summer periods, simulating two harvest periods. The climate in the area is classified as subtropical with dry winters and hot summers (Cwa – Köppen's classification). The average annual rainfall of 1,300 mm and the mean air temperature is 23°C, with temperatures above 35°C in the summer and a minimum of 10°C in the winter.

4.2.2. Experimental design and treatments

A completely randomized experimental design with four treatments and four replications was used. The lysimeter system was in an open area far from shading or possible interferences with the rainwater input. Then, the treatments, corresponding to chopped sugarcane straw (cultivar SP80-3280) from a mechanical harvest, were added to the open top of the lysimeter system. The treatments corresponded to the following straw additions on the soil surface: 12, 6, and 3 Mg ha^{-1} of dry mass, which represent the removal rates: no removal (NR), medium removal (MR, 50% of removal), and high removal (HR, 75% of removal) of straw, respectively. Also, a bare soil representing total removal (TR, 100% of removal) was evaluated. After eleven months, equally large portions of straw were added to simulate the second harvest. Before that, the straw remaining from the previous application was weighted, and the small portions were dried to determine the remaining dry mass. Notice the lysimeters were kept free of plants to evaluate the isolated effects of straw on soil organic C; thus, the water drainage through the lysimeters is likely a bit larger than under natural conditions due to the lack of transpiration.

4.2.3. Sample collection and analyzed parameter

Over the entire experimental period, the soil solution percolated was collected and quantified. Depending on the rainfall intensity, the water collections were extended to up to four days, ending when the percolation completely ceased. Thereafter, the solution was passed through 0.45-μm membrane filter Sartorius® and analyzed for DOC using an automatic analyzer Shimadzu® TOC-VCPN® (Kyoto, Japan). The DOC flux values were calculated by the multiplication of DOC concentration and the volume of percolated solution, as performed by Sparling et al. (2016). Then, the DOC retention between layers was calculated by subtracting the DOC flux of the layer above by the layer below (e.g., DOC retention in 1-20 cm = DOC flux at 1 cm - DOC flux at 20 cm).

At the end of the experiment, the soil was sampled at different depth increments (0-5, 5-10, 10-20, 20-30, 30-40, 40-50, 50-60, 60-70, 70-80, 80-90, and 90-100 cm). Soil bulk density was

determined for all layers using a volumetric ring. Then, samples were ground to fine powders prior to the organic C determination by dry mass oxidation, in four replications, using a LECO CN-2000 (St. Joseph, USA). The C stocks (Mg ha^{-1}) were calculated according to Equation 1.

$$C\ stock = C\ x\ BD\ x\ D \qquad \text{Eq (1)}$$

where C is the concentration of C (%), BD is the soil bulk density (Mg m^{-3}), and D is the soil depth in the evaluated layer (cm).

Also, at the end of the experiment all remaining straw was weighted and dried to estimate the decomposition rates. The dry matter results were corrected for ash content to exclude contamination by soil. Straw ashes were then measured for each site by calcining 1 g of straw dry matter aliquot in a muffle furnace at 550°C for 2 h.

4.2.4. Data analysis

Analysis of variance (ANOVA) was performed after checking the normality of the results. The means of cumulative DOC flux, and soil C stock were compared according to Tukey´s test ($p < 0.05$). The statistical analyses were carried out using the "R" Foundation for Statistical Computing v.3.5 software.

4.3. Results

4.3.1. Water conditions

During the 17 months of experimental period 149 days with precipitation were recorded, totaling 2,127 mm, in which 1,005 mm occurred in the first year and 1,122 mm in the second year. Both the 2016 and 2017 summer seasons (November to March) were rather rainy and warm, with more than 50 mm of precipitation occurring in single days. However, the first four months of 2017 were less warm and rainy than 2016. During the winter period (from June to September) precipitation is usually low, although in June 2016 an untypically strong rainfall occurred.

The total amount of drained water over the entire experimental period was higher in soils with lower straw removal, e.g., 1,035, 1,302, 1,416, and 1,468 mm to 20 cm depth and 1,077, 1,244, 1,278, and 1,329 mm to 100 cm depth for the TR, HR, MR, and NR, respectively.

4.3.2. DOC production and release on topsoil

The DOC production seen at 1 cm layer was generally small at the beginning of the experiment, and the concentration almost not differing among soils with and without straw

addition during the first two months (Fig. 1; $p > 0.05$). The DOC production increased over time, mainly after the second straw addition (Fig. 1a), and the increase was proportional to the amount of straw added. In more intense rainfall events, the DOC concentration in the soil solution tended to be small, except for after heavy rains following dry periods, during which the C concentrations were large (see June 2016 and March 2017; Fig. 1).

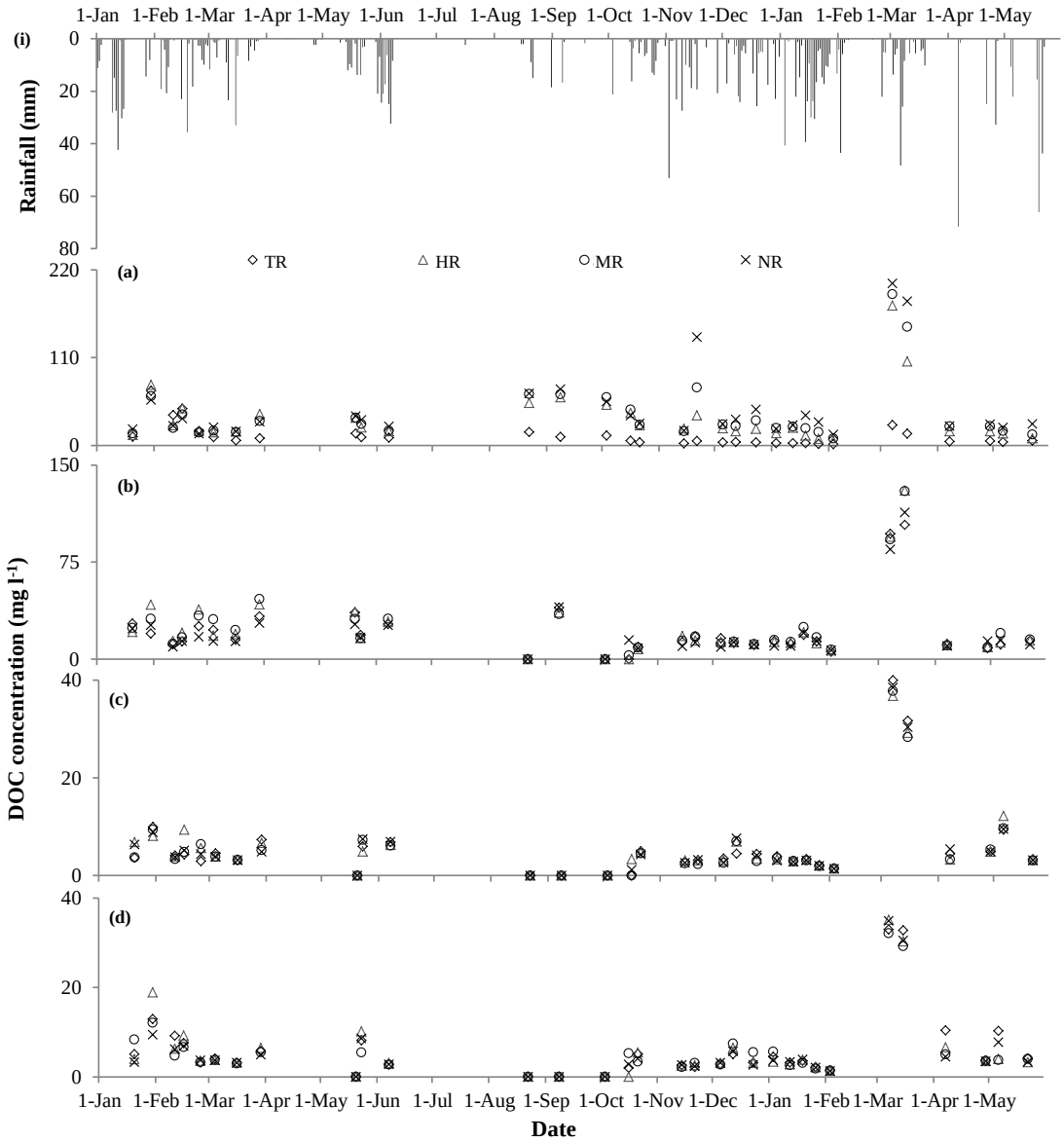

Figure 2 – Daily DOC concentration (mg l^{-1}) under different management systems of sugarcane straw removal from the soil surface after two-year straw application. (i) represents daily precipitation (mm); a) DOC concentration at 1 cm soil depth; b) DOC concentration at 20 cm soil depth; c) DOC concentration at 50 cm soil depth; d) DOC concentration at 100 cm soil depth. TR: total straw removal; HR: high straw removal; MR: medium straw removal; NR: no straw removal.

The total DOC produced was not totally proportional to the straw amount on the soil surface since the MR and HR treatments produced only 17 and 27% less (106 and 165 kg ha^{-1} less) of cumulated DOC than the NR (606 kg C ha^{-1}; Table 1; $p < 0.05$), respectively. Also, the

DOC production in the bare soil occurred only in the first year, and it was 284, 343, and 449 kg ha^{-1} smaller than produced at HR, MR, and NR, respectively. A high DOC production occurred right after the second straw addition (mid-November 2016), and it was especially higher for the largest straw addition (NR) ($p < 0.05$).

4.3.3. DOC translocation

The DOC concentrations in the soil solution decreased with increasing soil depth, however, this did not occur in the bare soil, in which the DOC concentration was higher at 20 cm than the topsoil (Figs. 1 and 2). At 1 cm, DOC concentrations were higher with decreasing straw removal, but at 20 cm the DOC concentrations did not follow this pattern (Fig. 2). The high DOC concentration after the second straw addition was not seen at 20 cm or deeper (Fig. 1). At 20 cm, the differences among treatments become less distinct, but the DOC concentrations for the MR and HR were still high during most rain events (Fig. 1), and both these soils presented the largest cumulative DOC fluxes at 20 cm (Table 1; $p < .05$); in contrast, despite the larger DOC production in NR, the DOC flux at 20 cm was smaller.

The DOC flux in the upper soil was higher with decreasing straw removal (e.g., no straw removal), but not at 20 cm (Table 1; $p < 0.05$). The DOC retention in the 1-20 cm soil layer was remarkably strong, mainly for the NR, corresponding to 29, 30, and 51% of the total DOC produced for the HR, MR, and NR. The DOC retention in this soil is fast when the DOC concentration in the soil solution is high, e.g., the retention after the second straw addition at 1-20 cm was 12 and 27 kg ha^{-1} for the MR and NR, respectively.

At 50 cm soil depth, the decrease in DOC concentrations was higher (Fig. 1c), and the differences among treatments became even more indistinct. The retention caused rather similar DOC concentration and fluxes, differing only from the bare soil ($p < 0.05$). Thus, the retention between 20 and 50 cm depth represents 53, 54 and 34% of the total DOC produced, for the HR, MR, and NR, respectively. For bare soil also there was retention of the DOC produced, observed at 20 cm.

The differences in DOC concentrations among the treatments are lower at 100 cm depth (Fig. 1d; $p > 0.05$). The DOC fluxes at 100 cm compared to at 50 cm were little lower, showing the small retention at 50-100 cm soil layer, which represents 1.5, 2, and 1.8% of the total DOC produced for the HR, MR, and NR, respectively. The total retention of the produced DOC, during the passage of the following 99 cm of soil was about 370, 430, and 530 kg ha^{-1} for the HR, MR, and NR. Consequently, 84, 86, and 87% of the total DOC at 1 cm was retained by the soil. The bare soil retained 47% of the total DOC produced by the soil, at 20 cm depth.

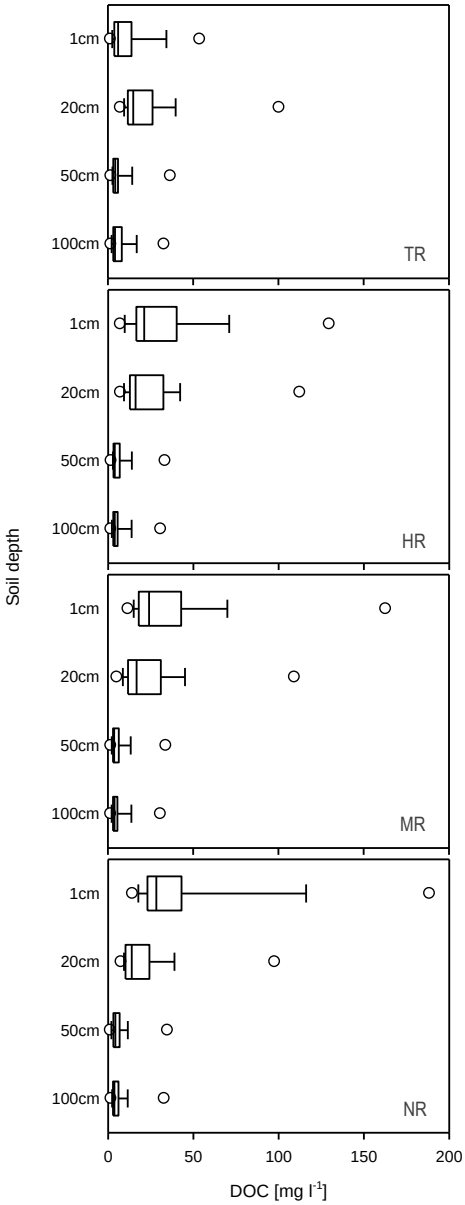

Figure 3 – Depth distribution of average dissolved organic carbon (DOC) concentration (mg l^{-1}) in soil solution under different management system of straw removal from the soil surface after two-year straw application. The extents of the box indicate 25th and 75th percentiles, the lines inside the box the 50th percentile. Whiskers represent 10th and 90th percentiles and outliers are given as open symbols. TR: total straw removal; HR: high straw removal; MR: medium straw removal; NR: no straw removal.

In turn, only 13 to 16% of the total DOC produced from soils with straw addition was transported below the 100 cm depth. The difference in the DOC leaching at 100 cm between bare soil and soil without straw removal was 12 kg ha^{-1}, during the whole experimental period.

Table 1 – Cumulative DOC fluxes (kg ha^{-1}) at different soil depths and DOC retention between soil layers, of different management systems of sugarcane straw removal from the soil surface after two-year straw application.

Soil depth cm	Straw removal intensities			
	TR	HR	MR	NR
	DOC flux, kg ha^{-1}			
1	157 c*	441 b	500 b	606 a
20	221 c	314 ab	351 a	294 b
50	67 b	80 a	81 a	88 a
100	65 b	73 a	70 ab	77 a
	DOC retention, kg ha^{-1}			
1-20	-64	127	149	312
20-50	154	235	269	206
50-100	2	7	11	11
1-100	104	368	429	529

* Mean values followed by the same letter within each soil depth did not differ from each other according to Tukey's test ($p < 0.05$).

4.3.4. Carbon production and storage

Straw decomposition rate was rather different among the straw additions in the first year, being faster at the larger straw application (Table 2). However, after the second straw addition the decomposition rates were similar for the three straw amounts.

Table 2 –Straw decomposition and DOC production of different management system of straw removal from the soil surface after two-year straw application.

Straw removal	First year			Second year			Total		
	C straw applied[a]	C remaining[b]	C lost[c]	C straw applied[a]	Total C straw[d]	C remaining[e]	Total C lost[f]	DOC net[g]	DOC:CL[h]
	--	--	--	--	g m^{-2}		--	--	
HR	126	41	85 (67%)	126	167	76	176 (70%)	28	0.16
MR	252	57	195 (77%)	252	309	118	386 (76%)	34	0.09
NR	504	85	419 (83%)	504	589	270	738 (73%)	45	0.06

[a] Straw intensity * 420 g C kg^{-1} of straw.
[b] Straw intensity remaining at the first year.
[c] Straw C lost (a – b) at the first year.
[d] Total C straw, considering the straw remaining at the first year and the second straw application (a + b).
[e] Straw intensity remaining, considering the two years.
[f] Total C straw lost at the two years (a + a – e)
[g] Net straw DOC flux (DOC in treatments with straw – DOC in bare soil)
[h] DOC produced at 0-1 cm and carbon lost (CL) ratio (g : f)

The contribution of the DOC to the total C decomposed from straw was 16, 9, and 6% for the HR, MR, and NR, respectively (Table 2). Thus, only 6% of the C was recovered as DOC

at 1 cm at the largest straw addition, while 16% of the C was recovered at the smallest straw addition.

Furthermore, soil C stocks were different among the treatments only for the 0-5 cm layer (Table 3; $p < 0.05$). The NR showed the largest C stock, while TR showed the smallest C stock ($p < 0.05$). In addition, all the others deeper layers did not show significant changes in soil C stocks.

Table 3 – Soil carbon stocks (Mg ha^{-1}) under different management systems of sugarcane straw removal from the soil surface after two-year straw addition, at the soil profile.

Carbon stock, Mg ha^{-1}				
Depth cm	Straw removal intensities			
	TR	HR	MR	NR
0-5	8.6 b*	9.2 ab	9.3 ab	9.9 a
5-10	8.0	8.2	8.3	8.4
10-20	14.7	14.9	15.6	15.6
20-30	12.2	12.3	12.5	13.3
30-40	10.3	10.3	10.3	10.6
40-50	9.5	9.5	9.2	8.9
50-60	8.7	8.8	8.9	8.3
60-70	8.5	8.2	8.3	8.2
70-80	8.2	8.0	7.9	8.3
80-90	8.2	8.2	8.3	8.5
90-100	8.1	8.7	8.2	8.2

* Mean values followed by the same letter within each soil depth did not differ from each other according to Tukey's test ($p < 0.05$). Soil depth without letters did not present significant difference among the treatments.

4.4. Discussion

4.4.1. DOC production

There were large differences in DOC production in the 0-1 cm soil layer for the different surface straw additions. Thus, DOC seems rather responsive to residue management changes, with its production dropping with straw removal from the soil surface.

The difference in DOC production between bare soil and the different straw amounts indicate that most DOC produced was from straw; however, it is not possible to exclude partial retention of straw-derived DOC within the 0-1 cm soil layer. In turn, part of the DOC collected at 1 cm soil may have been released within the topsoil. Also, the DOC production from the bare soil underlines the possible DOC production within the 0-1 cm soil layer.

In addition, the large DOC concentrations during some heavy rainfall after long dry periods likely result from the accumulation of degradation products and or microbial necromass over the dry period, becoming dissolved by the percolating water (Kalbitz et al., 2000). During dry periods, DOC concentrations were generally higher, but fluxes were small due to little percolating water. In contrast, in periods with frequent rainfall, DOC concentrations were generally small. Also, due to larger volumes of percolating water, DOC fluxes were larger during wetter periods than during dry periods. Furthermore, the DOC concentrations at 1 cm increased with decreasing straw removal (Fig. 2). Consequently, having more straw on the soil surface produces more DOC in the soil and in the topsoil.

4.4.2. DOC translocation within the soil profile

The differences in DOC translocating along the soil profile was caused by the DOC produced from straw and topsoil and the volume of percolated water. The smallest water infiltration in the bare soil is likely due to exposing the soil surface to rainfall. The impact of raindrops directly on the soil surface causes breakdown of soil structure and subsequent clogging of pores (Fernández-Raga et al., 2017). Then, the resulting sealing of the soil surface reduces the water infiltration rate, thereby reducing DOC flux throughout the soil profile.

For all treatments with straw, the DOC concentrations were largest in the topsoil and decreased with soil depth, which agrees with previous observations (Gregorich et al., 2000; Hassan et al., 2016). Nevertheless, part of the surface-derived DOC seems to be transported to deeper layers with the percolating surface soil water (Fröberg et al., 2007).

The reduction in DOC along the soil profile can be attributed to adsorption of the DOC to the surfaces of soil minerals, such as clays and Fe and Al oxides (Fujii et al., 2013; Kaiser et al., 1996). The latter of predominate in oxide-rich soils, such as Oxisols. Thus, right after adding the straw, the large DOC production from fresh straw observed in the 0-1 cm layer did not result in increased DOC at 20 cm, indicating strong retention. Similar observations on the strong retention of readily soluble material from litter have been reported by Fröberg et al. (2009).

The DOC concentrations in the topsoil increased with decreasing straw removal, but the results showed the opposite trend at 20 cm (see Figure 2). Consequently, having more straw on the soil surface produced more DOC; however, the retention in the 1-20 cm soil layer increased. The increase in retention with more DOC entering the 1-20 cm layer suggests that there was also a change in the composition of the dissolved organic matter produced.

Differences in DOC composition also may explain the differences in DOC retention by the soil among treatments. For NR, the DOC retention was strongest between the 1 and 20 cm

layer, equaling 51% of the total DOC produced in the 0-1 cm layer. Then, for MR and HR, the strongest DOC retention occurred between the 20 and 50 cm layers, being 54% of the total DOC produced in the 0-1 cm layer in both treatments. Seemingly, the DOC produced from the different straw amounts differed in reactivity, which suggests differences in the straw decomposition, and thus, differing in production of soluble breakdown products and metabolites.

In bare soil, the upper soil produced DOC, underlining that also OC stored in the mineral soil can become a source of DOC (Fröberg et al., 2009, 2007). The DOC released in the 1-20 cm layer, however, was mostly retained within the 20-50 cm layer, indicating the translocation of C with percolating water within the soil profile, which agrees with ideas presented by Kaiser and Kalbitz (2012).

The DOC produced from straw and in the 0-1 cm soil layer was mostly retained within the first 50 cm of soil, and the DOC retention was approximately 85% for the three treatments with straw. In contrast, the retention observed in the 50-100 cm layer was small; it retained less than 2% of the DOC produced from straw and upper soil. Since the deeper soil had less organic carbon than the overlying layers, it had a large sorption capacity for DOC. The small retention is likely because most of the sorptive DOC was already retained in the upper soil, and the DOC entering the subsoil was hardly capable of interacting with the soil mineral surfaces.

The DOC fluxes at a depth of 100 cm differed little between straw removal levels (~12 kg ha^{-1}), which is similar to the results in a study by Janeau et al. (2014) studying no-tillage and other management systems. The results indicate that more than 80% of the total DOC produced in the 0-1 cm soil layer was retained during the percolation of the soil water down to a depth of 100 cm. The DOC passing the entire 100 cm of soil represented between 13 to 16% of the DOC produced from straw and topsoil; thus, the DOC might become lost from the soil and reach the groundwater (Sparling et al., 2016). Also, elevated DOC concentrations can reach the groundwater in periods of high rainfall (Thayalakumaran et al., 2015).

4.4.3. Organic carbon production and storage

Regarding the C loss during straw decomposition, the contribution of DOC was proportionally smaller to the smaller straw removal (see Table 2). Thus, in NR, the contribution of DOC to total C losses from added straw was smaller, but the DOC production was larger. The results indicate that the proportion of DOC production is not linked to the absolute input of fresh straw, but they relate much to the extent and intensity of the decomposition rates. Also, the small contribution of DOC to the overall C loss from the added straw suggests that a large part

of C from straw was lost as CO_2 due to microbial activity (Vasconcelos et al., 2018) or as storage in the soil (Satiro et al., 2017).

The DOC production in the 0-1 cm layer showed a strong positive correlation with the straw C loss at the soil surface, meaning that larger decompositions contribute to larger DOC productions ($r = 0.904$; $p < 0.05$). Since the decomposition of added straw increased with the straw amount, the removal of straw translates directly into smaller DOC production.

When comparing C stocks in the soil profiles at the end of the experiment, only the upper soil layer showed changes, suggesting strong retention of DOC produced from straw or direct incorporation of straw C during microbial processing or by straw debris entering the upper soil layer. Because the results did not show other soil layers having increased C stock while showing considerable retention of DOC within the entire soil profile in the treatments with straw, the total DOC fluxes were too small in relation to the large C stocks to cause detectable changes. Thus, most likely, the experimental period was too short to determine the effect of DOC on soil organic C storage in greater depths (Zhou et al., 2015), but the effect might become significant at longer time scales (Gregorich et al., 2000).

4.5. Conclusion

The study assessed possible changes in DOC and C storage in soil subjected to straw removal from the soil surface. The results show that straw removal considerably reduces the DOC production and subsequently reduces the C inputs into the soil, supporting the initial hypothesis.

The DOC percolation through the soil profile indicated differences in DOC retention with differing straw amounts. For example, the soil under no straw removal had higher DOC retention in the first 20 cm and had an increase of C stock in the upper soil than soil with straw removal, but there were no differences in C stocks below 5 cm. Also, the bare soil produced DOC from soil and transported to the deeper soil. Thus, no organic material inputs over a long time may cause C losses from topsoil to the deeper soil.

The overall DOC leaching to greater soil depths (i.e., at 100 cm) differed little between bare soil and soils with straw despite the difference in DOC production, suggesting that the high DOC retention by the soil (an Oxisol rich in clays and oxides) was strong enough to avoid DOC losses by leaching. In soils with smaller contents of reactive mineral phases, the effects on fluxes and on C stocks may be rather different.

Considering the large area of sugarcane production in Brazil covering a wide range of soil types and characteristics (i.e., highly clayey to highly sandy), more studies in contrasting regions are necessary to better evaluate the effects of straw removal on DOC and C storage.

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5. SUGARCANE STRAW LEACHATES: CHARACTERIZATION AND EFFECTS ON SOYBEAN INITIAL GROWTH

Abstract

Sugarcane harvest in the last years have been replaced by mechanized harvesting, leaving a large amount of crop residues (straw) on the soil surface. This high layer of straw is causing damages to plant growth and even to sugarcane regrowth, which may be linked with organic compounds released by sugarcane straw. Therefore, we verified the biochemical characterization of straw and soil solution under different amounts of straw left on the surface, and evaluated the effects of these solutions in soybean initial growth. For this, we made three experiments: i) we made a straw infusion solution, in the proportions 30, 60, and 120 g straw L^{-1} for 4 h, equivalent to 3, 6, and 12 Mg ha^{-1} of straw in four litters of water (I3, I6, and I12, respectively), and characterized in HPLC analyzer; ii) we built lysimeters of 1 and 20 cm depth and collected soil solution under 0, 3, 6, and 12 Mg ha^{-1} of straw on soil surface (SC, S3, S6, and S12), and also characterized in HPLC; iii) we used the straw and soil solution acquired in the experiments i and ii and to wet soybean seeds in the germination and vigor test, besides using a water control (WC). The results showed that straw solution in high intensity (I12) contain several phenolic compounds which can be damage to plants growth, as well as ferulic, vanilic, sringic, and coumaric acids. However, soil solution collected in both depths did not showed any of these compounds, in any straw intensity. The soybean germination was higher in all treatments wet with soil solution than with straw solution. Root and hypocotyl length were not affected by any soil solution, but were affected by the straw solution, being smaller in I12 solution. These results show that sugarcane straw contains phenolic compounds and may release them during the decomposition process. But in natural conditions of weather and soil, in oxidic soils, these compounds are not present in soil solution or are in rather low concentration, not affecting soybean initial growth.

Keywords: Phenolic compounds; Organic acids; Allelopathy; Decomposition products

5.1. Introduction

Sugarcane production is an important activity in Brazilian agriculture, currently the largest world producer. In the past, sugarcane harvest included burning of straw. Due to environmental and economic issues burnt management has been replaced by mechanized harvesting (i.e., green unburnt harvesting). Unburnt sugarcane harvesting left a large amount of straw on soil surface, approximately 10 to 20 Mg ha^{-1} of dry mass per year (Leal et al. 2013).

High amounts of sugarcane straw kept on soil surface showed negative effect on ratoon development which led to low tiller biomass and productivity (Ball Coelho et al. 1993; Villegas et al. 2007), mainly if harvest is made in the rainy period. The reasons why these have been occurring are already unclear, may be one of them is related to the presence of toxic compounds in sugarcane straw that are released during decomposition process.

Crop residues release biochemical products which may have allelopathic effects, being toxic to themselves and other plants, besides being toxic to microorganisms and fauna (Cherubin et al.

2018). An allelopathic agent is a group of secreted substances by leaves, roots exudates, microbial activity, material in decomposition and others, that inhibits plants development, even in plants of the same species, defined as auto toxicity (Inderjit and Dakshini 1995; Lorenzi, 1983; Muller, 1996; Putnam, 1985; Viator et al. 2006).

Sugarcane straw releases damage substances to some weeds, which showed growth inhibition in presence of sugarcane solution due to organic acids production, as vanilic, ferulic, coumaric, and siringic acids (Sampietro et al. 2006). The same organic acids were identified in corn residues (Chou and Patrick 1976). Phenolic compounds found in sugarcane leachates can also cause decreases in root length in plants (Sampietro and Vattuone 2006a; Sampietro et al. 2007), and in sugarcane regrowth (Villegas et al. 2007). Phenolic compounds, that include these organic acids, are present in lignin labeled in the aromatic ring (Long et al. 2015). Lignin is a heterogeneous polymer of phenolic compounds (Aquino-bolaños and Mercado-silva 2004), which represents 25% of the sugarcane straw composition (Gomez et al. 2010; Menandro et al. 2017). Yong-zhi et al. (2015) identified that 25% of the chromatography peaks in maize straw were organic acids, considered allelopathics in high concentration (Chou and Patrick 1976; Rice, 1984).

The intensity of microorganisms in soil is a factor that can strongly influence the availability of phenolic compounds (Inderjit and Weiner 2001), because microorganisms metabolize other carbon sources faster, becoming more toxics (Sampietro and Vattuone 2006b). These interactions explain why residues with similar phenolic content can have different inhibitory activities in plant growth (Blum 1996).

Sugarcane mechanized harvest is a relatively recent activity in Brazilian scenario, and it is known that high amounts of straw on soil surface can impair the sugarcane regrowth and the initial growth of successor plants. Thus, the hypothesis of this work is that higher amounts of sugarcane straw on soil surface release high concentration of organic compounds to the soil that are toxic to plants, causing damage to soybean initial growth. To verify this, we performed three experiments: Experiment 1 related to the characterization of sugarcane straw solution to verify the presence of organic compounds; Experiment 2 deal with the characterization of soil solution with different straw intensities on the surface, to verify the presence of toxic compounds; and Experiment 3 related to the soybean seed analysis test to evaluate its initial growth in the presence of these solutions.

5.2. Material and methods

5.2.1. Experiment 1

5.2.1.1. Sampling and treatments

To verify the presence of toxic compounds in sugarcane straw, a straw infusion solution (IS) was made. The treatments corresponded to three straw amounts of the sugarcane cultivar SP80-3280, were as follows: 3 Mg ha^{-1} (I3); 6 Mg ha^{-1} (I6) and; 12 Mg ha^{-1} (I12), following the methodology suggested by (Sampietro and Vattuone 2006a), in which fresh straw was previously dry at 60°C for 48 h, and different amounts of dry sugarcane straw were soaked with Mili-Q water, in the proportions 30, 60, and 120 g straw L^{-1} for 4 h. The obtained solutions were sterilized by passing through sterile filter membrane Millipore 0.22 μm Sartorius® (Goettingen, Germany), with a vacuum pump.

5.2.1.2. Solution characterization

The biochemical characterization of straw solution was performed using a High-Performance Liquid Chromatography (HPLC) system (series 20A Shimadzu) coupled with a hybrid quadrupole/time-of-flight mass spectrometer (Microtof-QII from Bruker Daltonics) was used as detector. Previously, the samples containing 50 ml of solution were lyophilized at -45°C until complete water elimination. Afterward, the solids were placed in a vial, diluted with 1.5 ml of acetonitrile HPLC grade, shaken for 30 minutes, centrifuged at 5000 rpm for 10 minutes and replaced in another vial to measurement. The chromatographic separation was performed using a HILIC Ascentis Express Column (100 mm x 2.1 mm, 2.7 μm, from Sigma-aldrich,). The mobile phase was composed by water plus 20 mM of ammonium acetate (solvent A) and acetonitrile (solvent B). Isocratic elution mode (95 %B:5 %A, v/v) was used in a flow-rate of 0,25 mL min^{-1}. The column was maintained in a temperature of 40 °C and 5 μL of each analyzed sample was injected in the column by using an autosampler. The samples reaching the ionization source of mass spectrometer were ionized by ESI operating in negative mode, where the following conditions were applied: capillary voltage: 4 kV; nebulizer gas pressure (N_2): 4 bar; drying gas flow-rate (N_2): 8 $Lmin^{-1}$. Full scan mode in a range from 50 to 2200 Da was used for monitoring the compounds and a 1 Hz was the acquisition rate of the instrument. The compounds were identified by their exact mass values with mass errors lesser than 5 ppm.

5.2.2. Experiment 2

5.2.2.1. Study site and system description

To verify the presence of the allelopathic compounds derived from sugarcane straw in the soil we evaluated soil solution (SS) under different amounts of sugarcane straw left on the soil surface. For this, a drainage lysimeter in a suspended system with PVC tubes with 0.2 m of diameter was built, with 1 and 20 cm of soil column.

Soil samples used to fill the lysimeters were from a commercial sugarcane field. The soil was classified as Rhodic Kandiudox (Soil Survey Staff, 2014) and had a sandy clay loam texture (600, 70, 330 g kg^{-1} of sand, silt, and clay, respectively). It represents a common soil type used for sugarcane cultivation in the region. Perforated stainless-steel plates with a thickness of 2 mm and a 125-µm sieve mesh were placed at the bottoms of the lysimeters to prevent soil loss. A funnel was attached beneath with a rubber ring to ensure tight fitting, and was connected to glass bottle by a hose to collect soil solution draining from the lysimeter.

After the assemblage, the lysimeter system was placed in a field in an open area far from shading or interferences with the rainwater intake, in Piracicaba-SP, at 550 m above sea level, a traditional sugarcane region in Brazil, from January 2016 to May 2017. The climate in the area is subtropical (Cwa), with dry winters and hot summers, with an average annual rainfall of 1,300 mm. The lysimeters were kept opened without any treatment over two weeks that contributed to stabilize the soil in the system before applying the straw amounts (treatments).

5.2.2.2. Treatments and solution collection

The treatments used were the same straw amounts as in Experiment 1: 3 Mg ha^{-1}; 6 Mg ha^{-1} and; 12 Mg ha^{-1}, below 1 cm soil layer ($S3_1$, $S6_1$ and $S12_1$, respectively) and below 20 cm soil depth ($S3_{20}$, $S6_{20}$ and $S12_{20}$), using the same sugarcane straw, and the control treatment consisted of bare soil (SC). A completely randomized experimental design with four treatments and four replications was used, in both soil columns. Over the entire experimental period, soil solution was collected and quantified.

The biochemical characterization was made following the same methodology used in Experiment 1, in HPLC. Soil solution was characterized in four periods: solution collected in February 2016 (beginning); September 2016 (end of the first year); November 2016, after the second straw addition (beginning); and March 2017 (middle of the second year), in which the C concentration in the solution were high. The sampling were made in different experimental periods due to phenolic acids content change in different seasons of the year, being the result of

increased microbial activity due to high soil temperature and soil association with organic matter (Kuiters and Denmmaw, 1987).

5.2.3. Experiment 3

To assess possible toxic effects of sugarcane compounds, two seed analysis tests were made in soybean seeds cv. ANTA 82 RR with superprecoce cycle of 108 to 120 days and semi-determined habit, with a high germination index (90%). Soybean was chosen for two reasons: soybean seed is one of the most used in tests due to its high and fast response to changes; and because soybean is a crop widely used as a sugarcane successor in the canevial reform process, may suffer from the presence of toxic compounds from sugarcane straw. The first test was a germination test made following the standard procedure suggested by RAS Manual (2009), in which 50 seeds per repetition were placed on two Germitest sheets and one above covering the seeds. To moisten the paper were used the solution in a proportion of 2.5 times the sheets weight, being used eight different solutions: straw infusion solution I3, I6, and I12, soil solution SC, S3, S6, and S12 below 1 cm soil layer; and one water control (WC), in four replicates. The germination rolls were placed in germinators with 25°C. The germination assessment was performed four and seven days after assembly.

The second test was the seedling length test, in which the rolls assembly was similar to the germination test, but only using 20 seeds arranged side by side for the correct vertical root growth. The seeds remained in the germinator for three days and the evaluation was made using the Seed Vigor Automated Analysis System "Vigor-S" software (Castan et al., 2018), which assess the root length, hypocotyl length, total length, seed vigor, and others.

5.3. Results

5.3.1. Biochemical characterization of straw and soil solution

Sugarcane straw released organic compounds that are considered toxic to plants, mainly phenolic acids. However, these compounds were found in the straw infusion solution with higher straw intensity (I12) (Fig 1). The infusion with medium (I6) and low (I3) straw intensity did not present the compounds.

These compounds found in straw infusion were also not found in the soil solution in any sampling period, both the soil solution collected on topsoil and the collected at 20 cm depth (Fig 1). The comparison between straw infusion at the highest concentration (I12) and soil solution under higher straw intensity at the first sampling period, collected on topsoil ($S12_1$) and in

subsurface ($S12_{20}$) showed that soil solution did not present significant peaks of organic compounds as the straw solution (Fig 1).

Some of the organic acids sought in the solution could be identified through peaks pointing to the exact molar mass value of the compound. The organic acids identified in the I12 solution were: coumaric acid, ferulic acid, vanillic acid, syringic acid, and piperonylic acid (Fig. 2). Moreover, were found other common compounds in sugarcane infusion and soil solution, such as glucose, xylitol, mannitol, and anti-oxidants. Nevertheless, none of these compounds was found as a defined peak in the soil solution, at any sampling period, which shows that soil solutions did not contain even low intensities of these organic acids. A different peak was found in $S12_1$ (Fig 1a), identified as phthalate, a manmade chemical widely used in industrial applications, as plasticizers in the manufacture of flexible vinyl plastic, used in PVC (EPA, 2012; Hauser and Calafat, 2005).

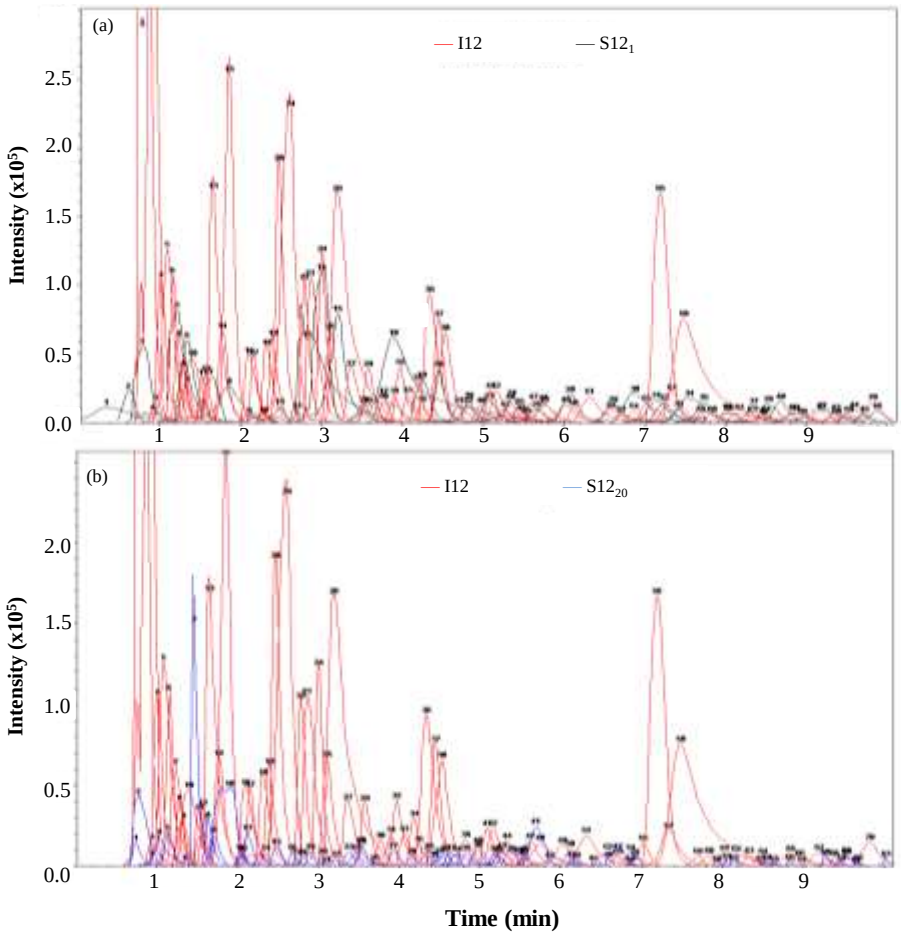

Figure 1 – Organic compounds in soil and straw solution evaluated via HPLC, comparing the compounds found in the straw infusion with 12 Mg ha^{-1} of straw (I12) and soil solution under 12 Mg ha^{-1} of straw: a) at 1 cm soil layer ($S12_1$); and b) at 20 cm soil layer ($S12_{20}$).

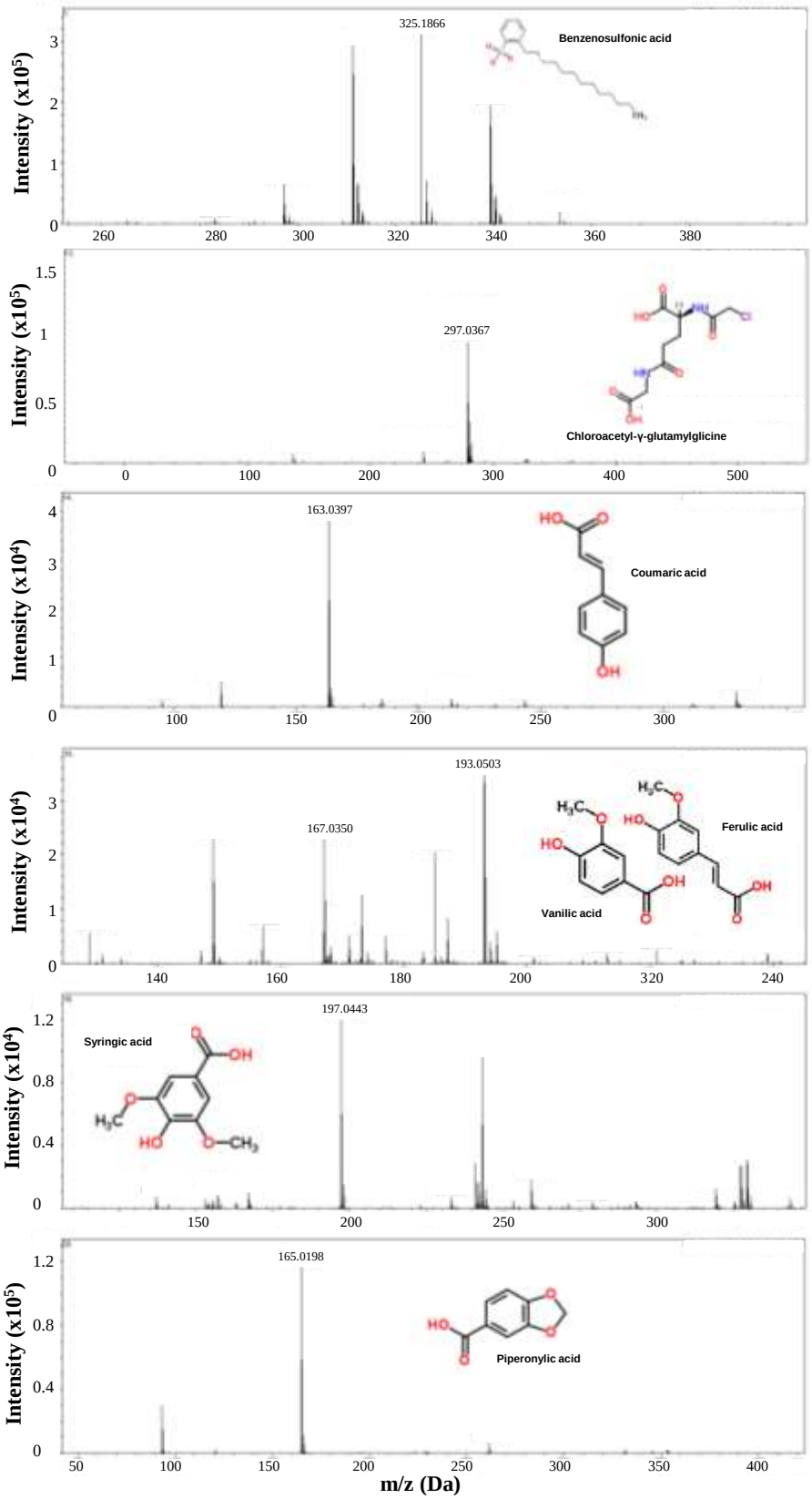

Figure 2 – Organic compounds found via HPLC in straw infusion solution with 12 Mg ha^{-1} of straw (I12). The peaks represent the compounds, with their respective molar mass right above.

5.3.2. Effects on plant development

The result in the soybean seeds germination shows difference among treatments from soil solution, in which the highest germination rate was using solution from bare soil (SC) (Fig. 3a). Among straw infusion solution there was no difference in the seeds germination rate. Comparing the seed germination rates under soil solution and straw infusion, at the same straw intensities, seeds wet with straw infusion showed lower germination rates than seeds wet with soil solution, in all straw intensities.

The initial soybean growth was affected by the different solution. There were differences in initial root length, hypocotyl, and in total length among the treatments wet with straw solution. The highest total length in straw solution was in WC and I3, and the lowest was in I12 with 9.07 cm, as well as the lowest root and hypocotyl length (Fig. 3b). Seeds wet with soil solution did not present differences in the seedling length, both in the root and the hypocotyl, among the treatments. In general, total seedling was higher in seeds wet with soil solution.

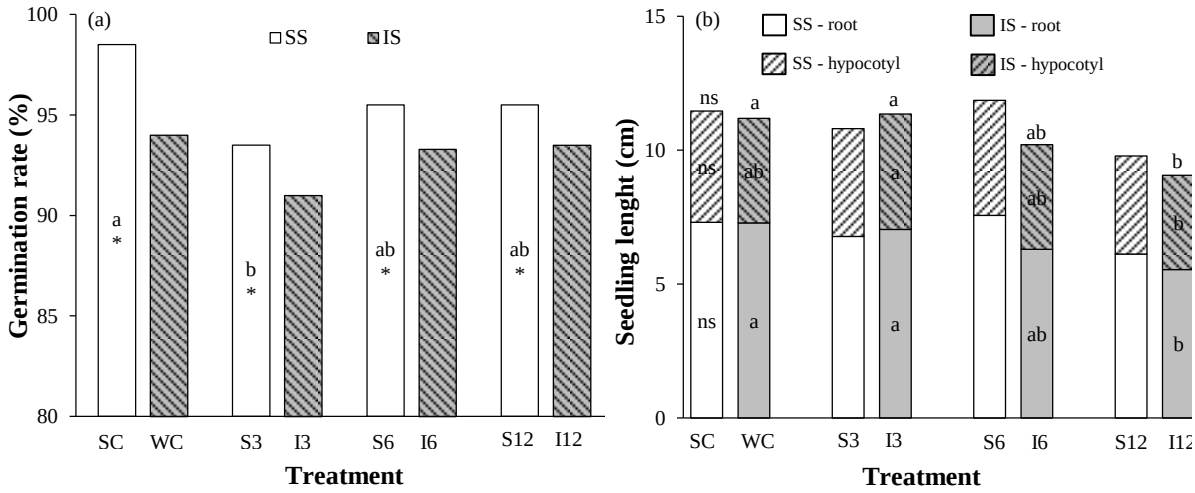

Figure 3 - Soybean seed tests wet with soil solution, or with sugarcane straw solution. a) Germination test; b) Vigor test. SS: soil solution; IS: straw infusion solution; SC: soil control (bare soil); S3: soil solution under 3 Mg ha^{-1} of straw; S6: soil solution under 6 Mg ha^{-1} of straw; S12: soil solution under 12 Mg ha^{-1} of straw; WC: water control; I3: straw infusion solution with 3 Mg ha^{-1} of intensity; I6: straw infusion solution with 6 Mg ha^{-1} of intensity; I12: straw infusion solution with 12 Mg ha^{-1} of intensity. Mean values followed by the same letter in the same variables did not differ significantly (Tukey´s test; $p < 0.05$). *Means significantly different between SS and IS for each straw amount by T-test ($p < 0.1$).

5.4. Discussion

5.4.1. Presence of organic compounds in the solution

Edaphic factors such as precipitation, nutrients, soil and air temperature, and organic matter content affect the availability and action of organic acids in the soil (Cheng, 1995; Inderjit 1996; Kuiters and Denmmaw 1987). Once phenolic acids enter the soil system, processes such as

adsorption, transformation, and transportation may take place (Cheng, 1995). These compounds are known to be strongly associated with soil clay minerals and Fe-oxides (Huang et al. 1977; Kögel and Zech 1985). Therefore, the soil used in this study is rich in Fe-oxides.

Hence, when the straw leachate came into contact with the soil, process as adsorption, transformation, transportation, and degradability quickly occur. Also, the intensity and velocity of the compounds released by straw in natural precipitation and temperature conditions probably are smaller than in a simulated situation (straw infusion). These factors, therefore, justify the fact of these organic acids have not been found even at low intensity in the soil solution, but found in the straw infusion.

The intensity of the organic compounds found in the straw infusion solution was low. At rather low concentrations, phenolic acids may stimulate the growth of a wide range of organisms (Einhellig, 2004). Nevertheless, phenolics are known to show phytotoxic activity at millimolar concentrations (Inderjit 1996; Rice, 1995).

Sugarcane straw leachate is a complex mixture of toxic and non-toxic compounds, thus soil microorganisms could metabolize these alternative C sources more readily than phenolics and become more toxic (Sampietro and Vattuone 2006b). On the other hand, the inhibitory activity of sugarcane straw solution may disappear 10 days after incorporation to soil (Sampietro et al. 2007) due to microbial degradation, chemical decomposition, and/or sorption of these compounds (Inderjit and Weiner 2001). Soil processes are responsible of the decrease of total phenolics over time in soil (Dalton, 1999; Sampietro and Vattuone 2006a).

Soil pH may affect levels of allelopathic activities, in which in lighter-textured soils with higher pH it is more pronounced (Fujita and Kubo 2003). For these reasons, the soil used in experiment needs to be the same as that the soil in the field.

5.4.2. Effects on plant growth

The intensity of the organic compounds found in the straw infusion solution was low. At rather low concentrations, phenolic acids may stimulate the growth of a wide range of organisms (Einhellig, 2004). Nevertheless, phenolics are known to show phytotoxic activity at millimolar concentrations (Inderjit 1996; Rice, 1995). Generally, root growth is more sensitive to toxicity than shoot growth (Inderjit and Dakshini 1995). May occur and inhibition and subsequent recovery of root elongation following removal from ferulic acid solution (Blum et al 1995). It means into the soil the plant can suffer at the moment of the toxic compounds are released and absorbed, but as they are fast adsorbed by the soil minerals, the plant can recover.

The primary effect of sugarcane straw infusion on soybean growth was a reduction in the germination rate, comparing to the soil solution. The germination was higher at soil control solution than at water control (Fig 3), indicating that soil has organisms and compounds benefic to plant growth. Moreover, straw infusion at higher concentration (I12) caused a significant reduction in the root and in the hypocotyl length of the soybean. These results shows that sugarcane straw leachates can inhibit soybean root growth (Sampietro and Vattuone 2006a; Sampietro et al. 2007). The medium intensity of straw infusion solution (I6) did not affect seedling length so strongly. This indicates that high straw intensities release toxic substances at higher concentration, affecting plant development, as soybean. Variations in sugarcane straw intensities is an important factor that regulates the occurrence of toxic compounds (Liebl and Worsham 1983; Sampietro and Vattuone 2006b).

Phenolic compounds found in sugarcane leachates can cause decreases in root length and initial plants growth plants (Sampietro and Vattuone 2006a; Sampietro et al. 2007), and even in sugarcane regrowth (Villegas et al. 2007). Nevertheless, the results of this study show that soybean initial length was not affected by the soil solution in any straw intensity. Considering also the higher germination rates and the non-presence of any organic acid found in the straw infusion solution, is possible to testify that sugarcane straw leachates into the soil do not negatively affect soybean initial growth. The study made by those authors was using a simulated situation (straw infusion), which was the only solution that presented the organic acids in a considerable concentration. Thus, we suppose that in natural condition of decomposition the sugarcane straw leachate is not toxic to plants growth. In addition, the conjunct of these results lead us to believe that sugarcane straw leachates are not causing damages to sugarcane regrowth.

5.5. Conclusions

Sugarcane straw at high intensity (12 Mg ha^{-1}) release organic acids considered toxic to plant growth. However, in the soil solution, under any straw intensity assessed, these phenolic compounds are not present.

Soil solution from sugarcane straw decomposition did not affect negatively soybean initial growth, but the straw infusion solution at higher intensity did. These findings show that sugarcane straw release organic acids toxic to plants, but in natural conditions of decomposition, the straw leachate does not present toxic effects to soybean growth.

The present study is novel, but more studies in the field conditions need to be done to verify toxic effects in other plants growth and sugarcane regrowth.

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6. SUGARCANE STRAW MANAGEMENT FOR BIOENERGY PRODUCTION: EFFECTS ON SOIL CARBON CAPTURE AND STORAGE

Abstract

Due to the increase in CO_2 emissions, the demand for bioenergy production increased, and thus the interest in using crop residues. Sugarcane residue (straw) has the potential to be used as bioenergy feedstock, however, straw removal from the soil surface can negatively impact C input and storage into the soil. Thereafter, we aimed to evaluate the effects of sugarcane straw removal intensities on soil C balance between inputs and losses. For this, we evaluated: i) the straw decomposition, during one year, into plastic frames placed on the soil surface, in the straw amounts equivalent to 3, 6, and 12 Mg ha^{-1} of dry mass, that represents high removal (HR), medium removal (MR), and no removal (NR), respectively; ii) CO_2 emission, during one year, in chambers consisted of a base and a lid, in the same straw amounts and in bare soil (total removal, TR),; iii) dissolved organic carbon (DOC) leaching, during one year, in PVC lysimeters with 20 ø x 20 cm of soil column, with the same four straw removal rates; soil C stock before and after the experiment. The results show that the decomposition rate was higher with more straw amount on the soil surface. The cumulative CO_2 emission was 128, 188, 103 and 70 g m^{-2} in NR, MR, HR, and TR, but the fraction of CO_2 emitted in relation to the C released by straw decomposition was 13, 25, and 39% in NR, MR, and HR. The DOC leaching was equivalent to 2, 3, and 7% of the C released by decomposition. Jointly, the C losses as CO_2 and DOC were proportionally higher in higher straw removal. Soil C stock showed an increase of 327, 190, and 66, g m^{-2} in NR, MR, and HR, and a reduction of 41 g m^{-2} in TR. Thereby, high sugarcane straw removal rates from the soil surface reduce C input to the soil, which could reduce C stock. Soil under no straw removal can store annually about 3.3 Mg C ha^{-1}. However, the results indicate that keeping a medium straw amount on the soil surface is enough to storage C amounts enable to increase C stocks, and at the same time, can potentially increase the ethanol production.

Keywords: Brazilian sugarcane; C balance; CO_2; DOC; Soil C stock

6.1. Introduction

Global warming is increasing together the rise in the greenhouse gases in the atmosphere. For 2017, estimated CO_2 emission increased 2% from 2016 levels, ~40% higher than 1990 levels (Le Quéré et al. 2017). The C emissions from fossil fuel and industry comprise ~90% of all CO2 emissions from human activities (Jackson et al., 2017). Important advances in Paris Agreement (COP21, December 2015) propose to hold the global warming below 2°C until the second half of this century. In this way, Brazilian government through to its Intended Nationally Determined Contribution (iNDC) committed itself to reduce deforestation and restore forests, and mainly increase the share of sustainable energy and bioenergy, beside promote technologies into bioenergy with carbon capture and storage (Brasil, 2018).

The energy produced from biomass plays an important role in this scenario of C capture, mainly through the utilization of the crop residues (EPE, 2016). Brazil has a successful energy policy with Ethanol Fuel Program (ProAlcool) for renewable energy production based in the

sugarcane. Nowadays, the area to sugarcane production is about 10.2 Mha resulting in 635 thousand tons of sugarcane stalks (CONAB, 2018), that produces 38 million tons of sugar, 28 billion liters of the ethanol (25% of the World) and 620 TW of bioelectricity co-generated (8% of the national demand) (EPE, 2016). In addition to stalk bagasse, large amount (10-20 Mg ha^{-1}) of leaves and tops (straw) left on field after harvesting, has raised the industrial interest as a complementary cellulosic feedstock to increase bioenergy production (Seebaluck, 2009; Menandro et al. 2017). Brazilian governmental projections indicate a potential for the production of about 10 Bi liters of cellulosic bioethanol from sugarcane straw by 2025 (UNCTAD, 2016), and near to 20% of the domestic electric energy demand will be provided by sugarcane biomass by 2023 (Brasil, 2015).

Although sugarcane straw has potential to be used as a bioenergy feedstock, depending on the removal strategy adopted, there are negative impacts on soil organic carbon (SOC) dynamics (Bordonal et al. 2018; Satiro et al, 2017; Sousa Jr et al. 2018; Vasconcelos et al. 2018). The global SOC pool contains about 1,325 Pg C (topsoil - 1 m), is greater than the combined mass of C contained in the atmosphere and living biomass (Ciais et al. 2013; Lal, 2004). Changes in SOC pool depend on the balance between inputs (*e.g.* litter, crop residues, organic compounds) and losses (*e.g.* mineralization, leaching, erosion), when inputs are higher than losses, there are C sequestration, i.e., CO_2 capture from the atmosphere (through photosynthesis), and stored into the soil (through deposition, decomposition and humification processes) as soil organic matter (Lal et al. 2015). On the other hand, small changes in SOC have as direct consequence increases on the CO_2 concentration into the atmosphere (Myhre et al. 2013). Therefore, loss of SOC, besides being the most significant threats to soil functions and health, directly affects global warming (Montanarella et al. 2016).

Thereby, given the importance of SOC, straw removal management cannot be treated as a "lucky-strike", so, this study was motivated by the hypothesis that there is a suitable removal strategy to target a "win-win" situation, where in addition to feedstock to bioenergy production, others important soil functions are kept, *e.g.*; CO_2 mitigation through increasing soil C capture and storage, and reducing C losses by erosion and leaching. These environmental benefits should be put in place to consolidate the suitable removal management as an effectively strategy to global warming mitigation. Thus, our aim was evaluated the effects of the straw removal intensities on soil C (stored) balance between C input by straw decomposition, and C losses (as gas emissions and dissolved organic carbon).

6.2. Material and methods

6.2.1. Study site and treatments

The studies were located in the municipality of Piracicaba (22°42'27.6" S; 47°38'36.6" W; 547 m.s.l.), São Paulo state, Brazil. The climate is classified as Cwa – humid subtropical with dry winters and rainy summers, average annual rainfall of 1400 mm and an average annual temperature of 22.4 °C. Soil is classified as Rhodic Kandiudox (Soil Survey Staff, 2014) with a sandy clay loam texture with 33% clay, bulk density of 1.32 and 1.37 in 0-10 and 10-20 cm respectively, pH (water) of 5.8, 27 mg dm^{-3} of available phosphorus, and 52% of base saturation.

The treatments used corresponded to four sugarcane straw removal levels from soil surface: total removal (TR), high removal (HR), medium removal (MR), and no removal (NR), that represent the amounts (in dry mass) of 0, 3, 6, and 12 Mg ha^{-1}, respectively. We used freshly harvested straw (cv. SP 80-3280), with ~40% moisture content, composed of 40% tops and green leaves and 60% dried leaves in a heterogeneous shredded mixture. Total C and N from straw were 420 g kg^{-1} and 8.2 g kg^{-1}, respectively.

6.2.2. Straw decomposition sampling and analysis

The straw decomposition experiment started after the sugarcane harvest. Into plastic frames were added the sugarcane straw amounts, equivalent to 3, 6 and 12 Mg ha^{-1} (dry mass). Destructive straw samples were collected of the 30th, 70th, 120th, 180th, 270th and 365th days after the experiment installation (3 treatments x 4 replications x 6 sampling times = totaling 72 boxes). All material inside the boxes was collected and takes on the laboratory to be dried at 60°C until a constant weight reached. The dry matter results were corrected by the ash content in order to exclude the effects of straw contamination by soil.

6.2.3. Soil C gases sampling and analysis

The sampling chambers consisted of a base and a lid. Into bases were added the sugarcane straw equivalent to 3, 6 and 12 Mg DM ha^{-1}, and a set without straw (bare soil) (HR, MR, NR, and TR, respectively), all with four replication – totaling 16 sampling chambers (details, see Vasconcelos et al., 2018). Over the year, soil gas sampling were taken with a 20 mL nylon syringe at four sampling times (0, 10, 20 and 30 min) counted from the closing of the chambers. All sampling was performed in the morning, between 10:00 and 11:00 h. CO_2 and CH_4 concentration were measured by gas chromatography (SRI-GC-110®, Torrance, USA) with a HAYESP™ packed column (80-100 mesh) maintained at 82°C to separate molecular gases, and were determined by a flame ionization detector (FID).

Gas fluxes were calculated by the linear change in the amount of each gas in the chambers (obtained by the Clapeyron equation) as a function of closing time (30 min). Cumulative gases were calculated by linear interpolation of the daily gas fluxes between two successive samples by the trapezoidal rule (Whittaker and Robinson, 1967), with the numerical integration considering the days after the start of sampling until the end of the experiment.

6.2.4. Dissolved organic C (DOC) sampling and analysis

To measure DOC fluxes, a set of lysimeters was built with PVC tubes with 20 ø x ~25 cm of height. To fill the tubes with soil, soil was placed 10 by 10 cm 20 cm. In the bottom, was placed perforated stainless-steel plates with a thickness of 2 mm to hold the soil and a sieve mesh (125 μm) to prevent soil loss. Below, a funnel stuck with a rubber ring, connecting to a hose that conducted the soil solution to the glass collector. Onto soil surface were added the same sugarcane straw amounts than to gas sampling, equivalent to 3, 6 and 12 Mg DM ha^{-1}, and a set without straw (bare soil), all with four replication – totaling 16 lysimeters. The lysimeters were placed in the field receiving natural rainfall.

Over the year, the entire percolated soil solution was collected and quantified. After collecting the solution, was made the syringe filtration with Millipore 0.45 μm filter opening and then the solution was analyzed in automatic analyzer TOC Shimadzu® (Kyoto, Japan) to quantify total DOC concentration. Fluxes of DOC were calculated by multiplying DOC concentration with the volume of leached water, as done by Sparling et al. (2016).

6.2.5. Soil C stock sampling and analysis

Soil C stock (0-20 cm) was measured before the beginning of the experiment (initial C stock, sampled to soil characterization) and after one year in each treatment (final C stock). Undisturbed soil samples were collected to determine soil C content and bulk density using volumetric stainless steel cylinder in the center of the boxes used to the straw decomposition experiment at 365th sampling. Samples were dried at 60°C until a constant weight to determine total soil mass, and an aliquot of 5 g was ground to a fine powder and sieved through a 250 μm prior to the total C determination by dry combustion, using an elemental analyzer (LECO© TruSpec® CN, Michigan, USA). Soil bulk density was calculated as describe by Blake and Hartge (1986). The C stocks (g m^{-1}) were calculated using C concentration, bulk density and soil layer as describe by Bernoux et al. (1998). The ΔC stock was calculated from C stocks for each treatment sampling at the 365 days discounted for the initial soil sampling.

6.3. Results

The remaining dry mass percentages indicated a greater decomposition rate for the NR decreasing with removal levels (Fig. 1). This pattern also was in directed related with the decomposition constant (k) that showed high value for the NR (k = 0.005; t1/2 = 139 days) and decreased with higher straw removal (k = 0.004; t1/2 = 173 days to MR, and k = 0.003; t1/2 = 231 days to HR), while the half-life (t1/2) presented the inverse relationship. After one year, 17% (NR), 23% (MR) and 33% (TR) of the initial straw amount remained on the soil surface. Therefore, the C release from straw decomposition (unaccounted in remained straw mass) were estimated of 85; 195 and 419 g C m-2 for NR, MR and HR, respectively (Table 1).

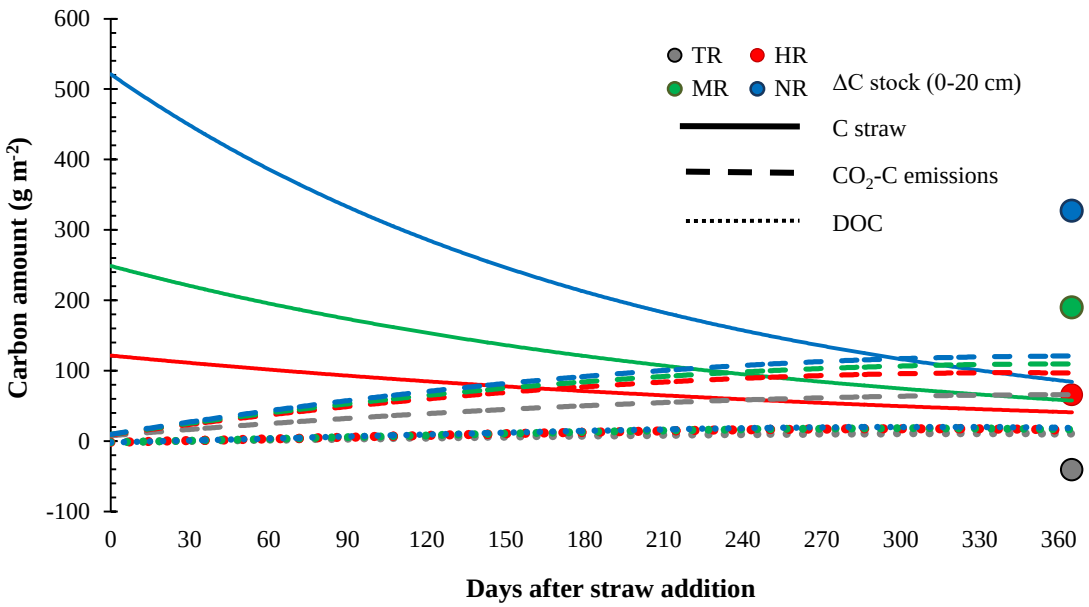

Figure 1. Quantity of C cycled (g m^{-2}) on the soil-atmosphere in the sugarcane field with different straw removal levels, in 365 days after straw deposition on soil surface from sugarcane harvest: C remained in the straw (solid lines); accumulated CO_2-C emissions (dashed lines); dissolved organic carbon (dotted lines); and ΔC stock on soil (colored circles).

The C emission recovered as CO_2 showed higher peaks and differences up to the first 180 days. In fact, almost 20% of the total precipitation of the experimental year occurred in the first 30 days, which impulse decomposition and gas emission. The cumulative CO_2 emission was lower under bare soil (TR) and increased with decreasing straw removal (Fig. 1; Table 1). However, a net recovery as CO_2 fraction show that the emissions were 13, 25, and 39% of the total of straw decomposed in NR, MR and HR, respectively. Likewise, the DOC leaching (below 20 cm) was equivalent to 2, 3, and 7% of the total C released by straw decomposition in NR, MR and HR, respectively. Higher gas emission recovery and DOC leaching rates were positively

related to the straw removal intensity. In bare soil (TR) about 12 g m^{-2} of DOC were leached (Table 1) without C inputs, indicating a loss of SOC.

Soil C stock before starting the experiment (initial) was 3099.5 g m^{-2} in the 0-20 cm layer. Indeed, bare soil lost C from stock over the year and had a negative variation (ΔC stock = -40.6 g m^{-2}). The other treatments, with straw maintenance, had a positive ΔC stock (Table 1).

The net C balance showed that even with higher cumulative CO_2 emissions under the no straw removal, the amounts of C released to the system (soil + atmosphere) during decomposition was higher when less straw was removed. Moreover, C balance showed that HR and MR had a negative value, while NR presented a positive balance.

The C released by decomposed straw at 365 days (unaccounted on straw remaining) was estimated as about 419, 195, and 85 g m^{-2} for NR, MR, and HR, respectively (Table 1). Of this total, about 58, 48, and 33 g m^{-2} were recovered as CO_2 emission; and about 9, 7 and 6 g m^{-2} were leached in the DOC form.

The lowest values of CO_2 emitted found for bare soil (TR) and the highest for NR. Thus, with an increase in sugarcane straw removal, cumulative CO_2 emissions decreased. In cumulative CO_2 emission, there was a reduction of 45% between TR (70.1 g m^{-2}) and NR (127.8 g m^{-2}) (Fig 1). However, a net recovery as CO_2 fraction ranged from 13 to 40%, being 13, 25, and 39% of the total of straw decomposed in NR, MR and HR, respectively. Higher recovery rates were inversely related to the straw removal intensity.

The DOC leaching (below 20 cm) was equivalent to 2, 3, and 7% of the total C released during straw decomposition in NR, MR and HR, respectively. In bare soil (TR) about 12 g m^{-2} of DOC were leached (Table 1) (without C inputs), indicating a loss of SOC.

Soil C stock before starting the experiment (initial) was 3099.5 g m^{-2}. Indeed, bare soil lost C from stock over the year and had a negative variation (ΔC stock = -40.6 g m^{-2}). The other treatments, with straw maintenance, had a positive ΔC stock (Table 1).

The net C balance showed that even with higher cumulative CO_2 emissions under the no straw removal, the amounts of C released to the system (soil + atmosphere) during decomposition was higher when less straw was removed. Moreover, C balance showed that HR and MR had a negative value, while NR presented a positive balance.

Table 1. Accumulated balance of C from added straw and accumulated CO_2-C emitted, dissolved organic C and ΔC stock in the sugarcane field with different straw removal levels, 365 days after straw deposition on soil surface from sugarcane harvest.

Measurement	TR	HR	MR	NR
	g m^{-2}			
Straw add and decomposition				
Straw C added [a]	0.0	126.0	252.0	504.0
Straw C remaining [b] (still in straw mass)	…	41.4	57.4	84.9
Straw C lost [c] (unaccounted in straw mass)	…	84.6	194.6	419.1
Soil C stocks				
Total C stock [d]	3,058.8	3,165.2	3,289.4	3,426.5
ΔC stock [e]	-40.6	65.8	189.9	327.0
Cumulative C gases				
Total CO_2-C emitted [f]	70.1	103.3	118.2	127.8
Net straw CO_2-C emitted [g]	…	33.2	48.1	57.7
Total CH_4-C sink [h]	[0.07]	[0.07]	[0.07]	[0.08]
Net straw CH_4-C sink [i]	…	[0.00]	[0.01]	[0.02]
Cumulative DOC				
Total DOC [j]	12.2	18.3	18.8	21.3
Net straw DOC [k]	…	6.1	6.6	9.1
Straw-soil-atmosphere C balance				
Current C in the field [l]	3,058.8	3,206.3	3,346.8	3,511.4
C balance [m]	-40.6	18.8	4.7	92.1
System C losses [n]	82.3	121.6	137.0	149.1
Net system C losses [o]	…	39.3	54.7	66.8
Net C balance [p] (unaccounted in system)	…	-20.5	-50.0	25.3

[a] Straw intensity * 420 g C kg^{-1} (see Materials and methods)
[b] Straw intensity remaining at 365 days (see Fig. 1)
[c] Straw C lost (a – b)
[d] Total C stock at 365 days (see Figure 1)
[e] ΔC stock (Current soil C stock – initial soil C stock (3,099.5 g m^{-2}; see Materials and methods)
[f] Cumulative CO_2-C emitted at 365 days (see Fig. 1)
[g] Net straw CO_2-C emitted (f – TR)
[h] Cumulative CH_4-C sinks at 365 days (data not showed)
[i] Net straw CH_4-C sink (h – TR)
[j] Total DOC leachate below 20 cm soil layer, at 365 days (see Figure 1)
[k] Net straw DOC (j – TR)
[l] Current C in the field (b+d)
[m] C balance (c-e)
[n] System C losses (f+j)
[o] Net system C losses (n-TR)
[p] Net C balance (m-o)

6.4. Discussion

The main factors responsible for straw decomposition are temperature, soil moisture, and the quality and quantity of residues, as well as the surface of contact between the residue and the soil (Thorburn et al. 2001). Therefore, higher soil-straw contact and higher soil moisture due to straw maintenance leads to increases on decomposition rates (Sousa Jr et al. 2018), releasing C and nutrients to the soil and atmosphere (Fortes et al. 2013). The intensity of straw removal changed the dynamics of decomposition (83, 77, and 67% in NR, MR and HR, respectively), being relatively more intensive with more straw. In this sense, the CO_2 emission was effectively higher in soil with more straw (Vasconcelos et al. 2018), due to increases in microbial activity, consequently respiration rates (Sousa Junior et al. 2018), but was proportionally smaller in relation to the C released (unaccounted) by straw decomposition (14, 25, and 39% for the NR, MR and HR, respectively).

The C released from straw decomposition has two mains destinations: the atmosphere as CO_2; or the soil. The entrance of the C in the soil is an available source of energy to the microbial activity (De Troyer et al. 2011) whose metabolic products maintain the turnover of the soil organic matter (Blair, 2000). One part of this C will be retained (through aggregates formation; Six et al. 2002) due to the strong adsorption to the surfaces of soil minerals, such as clays and oxides (Fujii et al. 2013; Kaiser et al. 1996) increasing soil C storage (Fröberg et al. 2007). While, because also microbial activity, part will be returned to the atmosphere from soil respiration, increasing CO_2 emission (Deng et al. 2017), besides too may be leachate to deeper soil layers reaching aquatic systems (Sparling et al. 2016). In this sense, the long-term storage of C released from straw decomposition into soil profile is an important way to sequester C and decrease environmental losses (Lal, 2004; Smith, 2004).

The dissolved organic C (DOC) measured below 20 cm represented 2% (NR), 3% (MR) and 7% (HR) of the total C released by straw decomposition. Thus, more straw removal promoted higher proportional losses as DOC (below 20 cm) and CO_2, representing together 46% (HR), 28% (MR), and 16% (NR) of the total C released by straw decomposition. These results indicated that the losses of C related to the SOC turnover presented a relative steady state, *i.e.*, in this short-term, regardless the amount of C input from straw amounts onto soil, the losses (CO_2 and DOC) showed similar.

In this way, soil C stock changes (accumulation/losses) are associated by the amount of C that enters in soil, mainly crop residues (Paustian et al., 2016). Thereby, high removal rates of sugarcane straw reduce C input to the soil, and could reduce soil C stock on a long-term perspective, which lead to soil degradation (Blanco-Canqui and Lal, 2009). Our results showed

increases in the C stocks when more straw was maintained onto soil surface. Soils cultivated with sugarcane under straw maintenance can potential to accumulate between 0.73 to 2.0 Mg C ha^{-1} $year^{-1}$ compared with those under no residue (Cerri et al. 2011). In contrast, in bare soil (TR) we observed reduction of C stock in one year without straw addition, similarly as found by Bordonal et al. (2018).

The net C balance showed negative value to HR and MR, while NR was positive. A correct balance should be equal to zero, but in the case of a field experiment it becomes difficult, for some of the measured variables are quite unstable; *e.g.*, CO_2 emission is a non-physical estimate, being difficult to express absolutely real values; some measurement errors in the laboratory; there are some sudden changes in the weather and environment, insects and small animals present, and other factors. Furthermore, depending on the straw removal, the machinery traffic causes soil compaction (Satiro et al. 2017), which affects the distribution of the root system (Chopart et al. 2010) impacting C input into upper soil layers.

Thus, negative values to the net C balance indicate that the C lost as CO_2 and DOC was higher than the C released by straw decomposition. That difference may have been caused by some factors, such as: i) the maintenance of the straw on the soils may have lost more CO_2 than bare soil (control) due to the increase in microbial activity (Graham and Haynes, 2006), besides ii) the soils may have lost an amount of DOC from the soil (SOM) due to small/medium organic material addition. Positive values, as found to NR, mean the C lost was lower than C released by decomposition. However, it is necessary must consider measurement errors.

The findings suggest, considering our study conditions that about 3 Mg ha^{-1} of straw are necessary to neutralize C loss from soil C turnover and straw decomposition. However, considering C storage in soil, keeping about 6 Mg ha^{-1} on the soil surface could be a suitable management strategy, because presents similar CO_2 emission than more straw removal, but does not leachate more DOC, since that storage three times more C, besides allowed adequate soil cover over time. This amount seems to be enough to sustain soil quality, plant growth and others related soil services (Carvalho et al. 2017).

Regards to the soil functioning, the maintenance of a medium straw amount on the soil surface (~6 Mg ha^{-1}), an amount of 190 g C m^{-2} $year^{-1}$ may be stored (1.9 Mg ha^{-1}). In Brazilian conditions, sugarcane cycle lasts an average of 5 years, with one harvest per year. Thereafter, is made the renovation of sugarcane field, using conventional tillage with disk harrowing operations, which reaches to emit 95 g C m^{-2} to the atmosphere (Silva-Olaya et al. 2013), *e.g.*, which represents 10% of the C that likely is stored over the 5 years. However, it is important to highlight that through the successive harvestings (with mean reduction of the ~10% in stalks

productive), the vegetative vigor of the plants will decrease, which implies in even further reduction of stalks production (Lisboa et al. 2018), and considering the straw/stalk ration of ~12% (Menandro et al. 2017), the estimated straw production also reduce. Thus, the losses by field renovation may reach ~15% of the C stored.

In relation to the bioenergy production, according to Vasconcelos et al. (2018), implementing medium intensity of straw removal strategy to bioenergy production (~6 Mg ha^{-1}) in São Paulo state, an additional of 1.5 to 2.3 GW of bioelectricity, or 6.3 to 8.6 billion liters of cellulosic ethanol could be produced. This additional cellulosic ethanol could directly reduce the CO_2 emission equivalent to 340 million liters of gasoline.

Based on these projections, we are allowed to say that a medium amount of sugarcane straw kept on soil surface (~6 Mg ha^{-1}) has the potential to obtain the C storage, maintaining soil functioning and benefits, likewise to supply feedstock for bioenergy production. Reinforcing, straw removal management may be a suitable strategy to effectively mitigate global warming.

6.5. Conclusion

The straw management that aims the total removal from the soil surface leads to a negative input of C into the soil, causing degradation. Whereas no straw removal (12 Mg ha^{-1}) enables an annual increase of about 330 g C m^{-2} (3.3 Mg C ha^{-1}). However, the results indicate that keeping a medium amount (~6 Mg ha^{-1}) of straw on the soil surface can ensure the maintenance of soil C stock in short-term. Therefore, the removal of a medium amount of straw, keeping a range of 6 Mg ha^{-1} may be a potential strategy to make possible the "win-win" situation, both by the capture and storage of C into the soil, and the high increase in ethanol production.

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7. FINAL CONSIDERATIONS

Global efforts to replace fossil fuels sources by renewables considerably increase. Bioenergy production derived from crop residues has become increasingly important, and consequently has increased the concerns about soil and plant growth. In Brazil, the world's largest sugarcane producer, sugarcane area has expanded by 35% in the last decade. It means an increase in bioenergy production. However, the intensification in straw removal has direct implications on soil C inputs, reflecting on a potential threat to the soil functioning. In this work, we hypothesized that high sugarcane straw removal rates from the soil surface for bioenergy purposes leads to overall soil degradation, reducing soil quality.

The overall findings of this study show that: in Chapter 3 we concluded that the drainage lysimeter system efficiently works. The straw maintenance on the soil surface is necessary to maintain suitable soil water availability, mitigating drought effects on plants. As well as, maintains soil structure favoring water drainage, reducing losses by evaporation. However, to leave large amounts of straw on soil surface is not necessary, since a medium amount (~6 Mg ha^{-1}) was enough to maintain soil moisture and available water to plants. Even so, the ideal intensity of straw removal depends on the harvest season, due to the seasonality of the rainfalls in this region. In Chapter 4, our results indicate that high straw removal considerably reduces the DOC production by straw decomposition, and consequently reduces the C inputs into soil. The DOC translocation and flux is strictly linked to soil water infiltration in the soil, thus problems in soil structure and drainage may cause a C reduction in deeper soil. The DOC retention was stronger in the first 20 cm in soil with no straw removal, which had an increase in the C stock in the upper soil layer, while for medium and high removal the retention was stronger in 20-50 cm, what indicates different composition of DOC according to straw amount. The SOC in medium and high removal were similar, smaller than in soil with no removal, but higher than in bare soil. Increment in SOC along the soil profile takes more time to appear. Bare soil showed a C release from the upper soil to the deeper soil, indicating C loss over time. Large amounts of straw on the soil surface, despite producing more DOC do not provide higher C loss by leaching than bare soil, due to high DOC retention by clays and oxides.

In Chapter 5, we verified the presence of several phenolic acids in the sugarcane straw solution, that commonly have allelopathic effects in plants growth. But these compounds were not found in the soil solution under any straw amount. It indicates that in natural decomposition conditions, sugarcane straw release rather low intensities of these compounds and which may be quickly adsorbed by the soil minerals. Thereby, the soil solution derived from sugarcane straw did

not affect the germination and initial growth of soybean seed, suggesting that it do not affect sugarcane regrowth. Finally, in Chapter 6 we made a C balance with C inputs and losses found in this study, to estimate an ideal straw removal management, under the conditions of this study, taking into accounts both soil benefits and bioenergy production benefits. Considering straw decomposition rates and its products, such as CO_2 emission, C released (DOC), and C stored into soil, the soil under medium intensity of straw removal (~6 Mg ha^{-1}) has the potential to maintain and increase SOC, while raising the ethanol production. Approximately 6 to 8 billion liters of cellulosic ethanol can be produced with a removal of 6 Mg ha-1 in São Paulo state.

Overall, our results indicate that keeping high straw amount on the soil surface provides better soil water infiltration and consequently percolation (Fig. 1). Furthermore, it retains and storage larger water amounts, increasing soil moisture and soil water availability. With higher soil moisture, the decomposition tends to be faster releasing C into the soil. More straw releases more C amounts, which is retained in the soil minerals increasing C stock, or may translocate within the soil with the water, being stored in deep soil layers. High straw amounts do not release toxic compounds to the soil. More water percolation does not mean higher C leaching (DOC) to the deeper soil layer, due to the strong C retention.

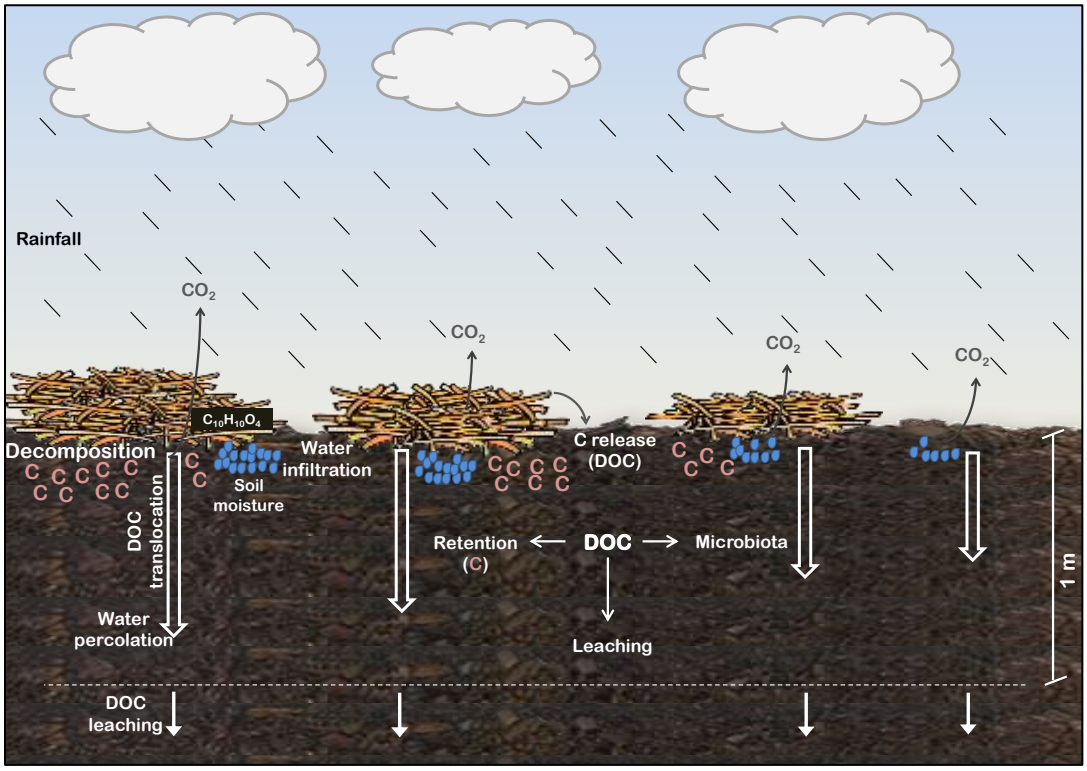

Figure 1 – Evaluated soil and water variables under sugarcane straw removal. The magnitude of the arrows and numbers of symbols (such as water drops and C), under each treatment, reflects illustratively the amounts found in this study.

Thus, in order to maintain soil functioning in terms of soil organic carbon, soil water availability, and other variables evaluated in this study, assuming this soil type and climate conditions, it is not necessary to maintain large amounts of straw on the soil surface, being a medium amount enough (i.e., 6 Mg ha^{-1}). Thus a portion can be removed for bioenergy production, by keeping soil quality, maintaining a double gain path and contributing to reduce CO_2 emissions to the atmosphere.

We believe sugarcane production has a great potential to mitigate global warming due to its potential to produce cleaner energy. Therefore, we suggest more studies in soils under sugarcane production with straw removal management practices, involving sugarcane productivity and water storage, carbon inputs and biodiversity, and carbon balance in a long-term experiment, for better understanding the sugarcane production system, aiming at environmental sustainability.