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Evaluation of carbon content and humification index of soils under the application of by-products from sugarcane processing

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A R T I C L E I N F O

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A B S T R A C T

The sugarcane processing generates by-product such as, sugarcane bagasse ash and filter cake and their proper disposal is of great environmental responsibility. Nowadays these by-products are being used for soil biofertilization without protocol. This study aimed to evaluate the applying these by-products to a single kind of soil in relation to the amount of carbon (C) and nitrogen (N) and stability of soil organic matter (SOM) through incubations varying the time. The bio-residues were applied to the soil at a proportional dose of 40 Mg ha^{-1} and 10 times periods were defined. Elemental Analysis was used to determine C and N and Fluorescence Spectroscopy was used to evaluate the humification index (H_{LIFS}) of the SOM. The control treatment did not show high variations of C during the experiment and its average value was less than 1.0% (m/m). The highest C values were obtained for fresh filter cake (TF), whose C content was 1.8% in the beginning of the experiment and, after 1 year, it was 1.16%, presenting an exponential decay. The C results were in the range of 1.0% to 1.2% for all the other treatments and did not present a statistically significant difference throughout the experiment. For H_{LIFS}, it was the opposite. The lowest C values were obtained for TF, which also presented an exponential increase over the experiment, showing a fresh OM input in the beginning of the experiment and humification process over the time. For the other treatments, H_{LIFS} had no statistically significant differences. The high levels of C for TF emphasize the importance of studies of SOM regarding the priming effect. Thus, this study indicates the need to create ordinances for the use of these by-products and guide lines for the correct management and application in the soil without any harm to the environment.

1. Introduction

The production of alcohol and sugar generates waste or by-products such as: vinasse, filter cake (FC), sugarcane bagasse ash (SCBA), soot and wastewater. Each ton of processed sugarcane generates about 250 kg of bagasse, which is burned for generating 560,000 kcal of electrical energy and 25 kg of SCBA after the burning process. This heat and energy amount can supply a portion of energy demand from sugar and alcohol production process, which avoids fossil fuel use [1]. For the same amount of sugar cane processed, approximately 50 kg of FC are generated. One ton of sugarcane also produces 70 L of ethanol (which provides 392,000 kcal) and 15 L of vinasse per liter of alcohol generated [1–3].

In Brazil, vinasse is regulated for use in fertigation [4]. On another hand, SCBA and FC have been used for biofertilization, but isn't regulated by councils such as Environmental Sanitation Technology Company. Biofertilizers has a great importance in the economy of agriculture and livestock since mineral fertilizers are sold at high prices [2,5].

The composting practice is well known and has a great importance for compost maturation. It is a suggested alternative and has been used for the management of FC and SCBA [6]. The studies on the characterization and effects of the application of FC and SCBA have been carried out to establish optimized parameters, such as ideal rates, better results, and management without environmental loss [7–9]. Therefore, the correct and adequate management of by-products of the sugarcane production chain is an important matter either by applying excessive rates or by ignoring the concentrations of the elements present in these

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by-products. Studies on the effects of the composting of these residues are not very common in the literature, which can show that the use of these by-products in the soil can be an interesting and economic alternative, as long as it is technically based [6,10,11].

The ideal composting time is an important factor for compost maturation. The application of non-matured compounds would lead to soil damage such as phytotoxicity, nitrogen unavailability and the possible occurrence of carbon (C) priming effect. It is known that these compounds have a high biomass content, which can be added to the soil. Therefore, it reinforces the importance of knowing the optimal rate of these residues to apply them to the soil, due to the possible occurrence of the negative priming effect, that is, the input of fresh material stimulates the decomposition of pre-existing C in the soil [12–14].

The Laser Induced Fluorescence Spectroscopy (LIFS) has some advantages over the traditional techniques [15] for soil organic matter (SOM) evaluation. One of them is the possibility of working with *in natura* samples, that is, whole soils without chemical fractionation and without the interfere of paramagnetic metals, which is a limitation of some spectroscopic techniques since ions like Fe^{3+} (among others) may be present in a great amount of Brazilian Oxisols. This technique also presents low cost and low waste generation apart from being very sensitive for this type of study [16,17].

Performing a search in the main international scientific databases it was not possible to find studies that evaluated the temporal behavior of these by-product when applied to soil. To better understand the effects caused by the application of these by-products to the soil, as well as to evaluate the consequences of previous composting practice and to study the hypothesis of their impact as biofertilizers, the present work aimed at the study of a miniaturized temporal incubation experiment where these residues were applied to a single soil type. We used LIFS to qualitatively assess the humification index of SOM (H_{LIFS}) and Elemental Analysis (CHN/S) to quantitatively determine the C and N contents in an incubation time experiment during one year.

2. Materials and methods

2.1. Description of the experiment

To evaluate the effects of residues from the sugar-alcohol production on Eutrophic Red Latosol (ERL), a smaller scale incubation experiment was executed using vessels filled with soil, residues and water. The vessels were filled with 300 g of soil previously sieved at 2-mm and with 6 g of each bio-residue at 1-mm. This proportion was the same for all the treatments in order to simulate the suggested field dose, equivalent of 40 Mg ha^{-1}.

Six treatments (bio-residues) were defined: fresh SCBA (no previous composting) (CF), composted SCBA (with previous composting) (CC), fresh FC (without previous composting) (TF), composted FC (with previous composting) (TC), Compound A - 50% FC and 50% SCBA (composted together) (CA), Compound B - 75% FC and 25% SCBA (composted together) (CB).

The compositing of TC, CC, CA and CB was performed in rows before the incubation experiment and the compounds were stirred every 90 days and the pH was not corrected. The process was finished when there was no increased in temperature. The six bio-residues were incorporated into the ERL soil, followed by the control intriplicates. The maintenance of the moisture in the vessels was performed by gravimetry.

The samples of the incubation were evaluated at different time periods of 5, 15, 30, 45, 60, 120, 180, 240, 300 and 360 days. Thus, 210 vessels of approximately 300 mL were used, i.e. ((1 control + 6 bio-residues) × 3 replicates × 10 periods times). In Fig. S1, it is represented a generic experimental scheme: the soil vessels of each bio-residue as well as the repetitions and description of the bio-residues.

2.2. Sample preparation

The soil samples were air-dried at room temperature for about two weeks, until the mass was constant. After they dried, they were ground with a mortar and a pestle and the soil was sifted at 0.150-mm (100 mesh) for the subsequent C determination. For LIFS measurements, soil samples were pressed into pellets at approximately 6 tons, resulting in 1 cm diameter, 2 mm thickness and 0.5 g mass.

2.3. Elemental analysis

For C quantifications, a Perkin-Elmer CHN Elemental Analysis equipment (2400 Series II CHN Elemental Analyzer) was used. The measures were obtained in duplicate. For the determinations, about 10 mg (± 0.5 mg) of the samples previously sieved at 0.150 mm was weighed. The C content of the samples was determined for all the incubation times and also for each of the six *in natura* bio-residues.

2.4. To evaluate quality of SOM

A portable LIFS system was designed and produced at Embrapa Instrumentation following the specifications described at the literature [16–22]. The intensity range employed was 0–4000, the integration time 700 ms and, the average and boxcar, 5 and 3, respectively, for all the evaluations.

The methodology used in this work was proposed by Milori et al., 2006 [19]. The humification index, or $H_{LIFS,}$ is defined in Eq. (1), where A_f is the fluorescence area under the spectrum and C_t is the total C content, which, in this study, was determined via Elemental Analysis.

$$H_{LIFS} = \frac{A_f}{C_t} \tag{1}$$

3. Results and discussions

3.1. Elemental analysis

3.1.1. Bio-residues

Fig. S2 shows the average C and N contents and the C/N ratio for the control treatment and the 6 bio-residues used in the incubation experiment.

From this characterization, it can be observed that the C and N contents in all bio-residues is higher than in the control soil. It was not possible to quantify N in CF and CC, since the values are below the limit of detection (LOD) of the technique used. These bio-residues are originated from the combustion of sugarcane bagasse in boilers [6], cites that the average N content in the bagasse is low, about 0.3% and this concentration was possibly lost in the combustion step.

However, when comparing TF and TC, it is possible to notice that higher C and N contents are present in fresh bio-residues, without previous composting, which shows there is C loss due to the composting process, that is, the C/N ratio tends to decrease with composting. This ratio indicates how organic matter (OM) is susceptible to degradation or mineralization. A material with a lower C/N ratio would be more easily decomposed by the microorganisms known as a more labile material. The drop from 29 in TF to 12 in TC shows that there was decomposition of OM as well as an adequate degree of stabilization [11].

The results presented in Fig. S2 also show that higher N concentrations were obtained for TF. There was a small decrease in the N content in TC. This behavior suggests that soil C has been converted into CO_2, and the N fixation in this bio-residue increased due to composting process [23,24].

The CB treatment presented an increase of approximately twice the N content in relation to CA. While CA was composted in the proportion of 50%:50%, CB was composted in the proportion of 75%:25%.

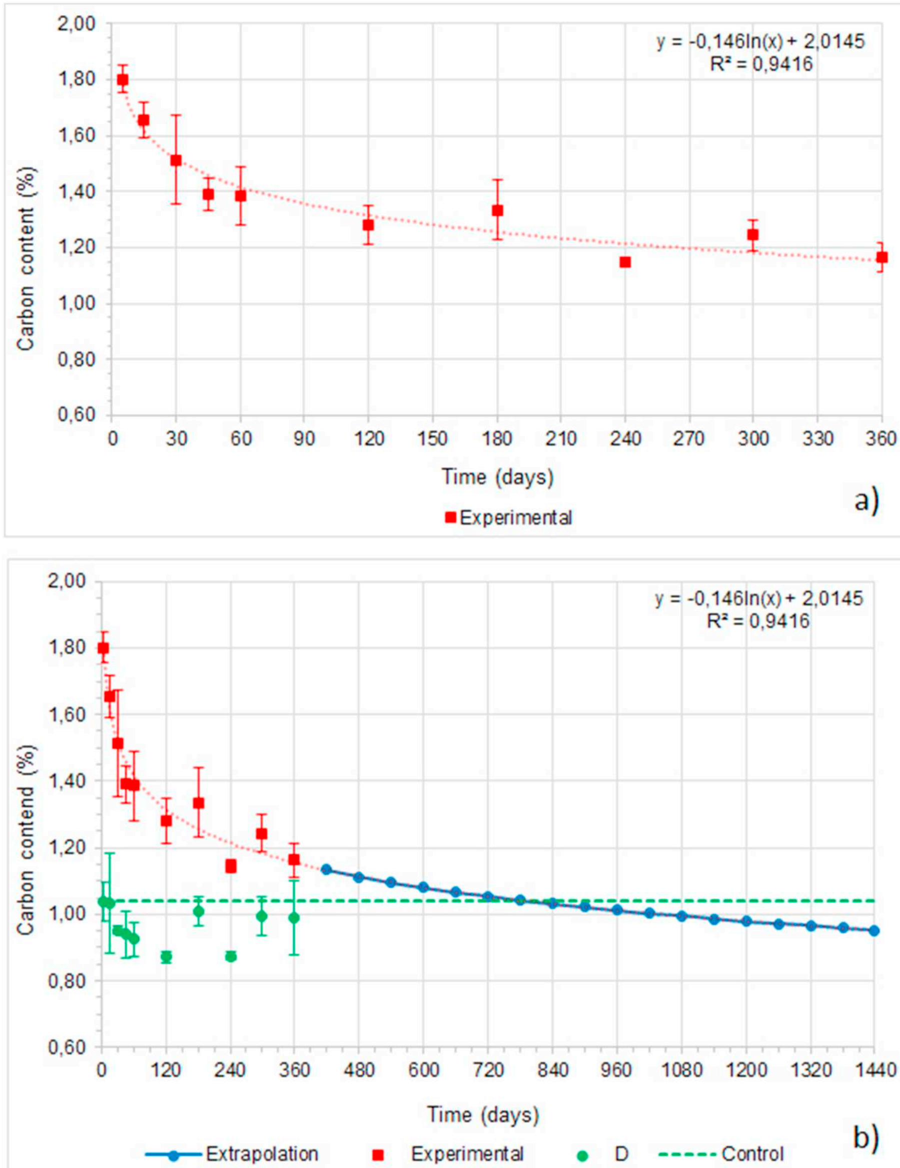

Fig. 1. Exponential decay of C contents for (a) TF treatment and (b) extrapolation decay for TF. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Therefore, there has been an increase in the N concentration in the same proportion of the TF increase in the mixture.

In general, the C and N contents obtained for TF were very similar to the ones obtained in the literature [6,8,25–27]. The composition of by-products is related to several factors, such as: sugarcane species, type of soil in which the crop is grown and sugarcane maturation [3].

3.1.2. Incubated soil samples

Fig. S3 presents the average C content in the incubation samples from 0 to 360-day period, considering the 3 replicates of the incubation.

From Fig. S3(a), one can observe there was a higher decay in the average C contents for treatments D and CF over 120 days. This was more frequently noticed for treatments with no previous composting and it was due to the presence of fresh OM in the soil. The microbial activity became more active due to this less humified and decomposable OM. After 180 days, this could not be noticed and the C concentration over time is more constant. In the bio-residues CC, TC, CA and CB, no great trends were observed over time, that is, the input of this OM through the application of bio-residues at 40 Mg ha^{-1} did not highly impact the soil considering the C content information.

The C content results were subjected to Tukey statistical test ($\alpha = 0.05$) and the statistical analysis showed there was no significant difference, except for TF (Fig. S3(b)).

In the TF application, with a proportional dose of 40 Mg ha^{-1}, it can be observe an increase of 0.8% in C soil (about 1,8%), almost twice the pre-existing C content (about 1% in control treatment). Particularly, for the TF treatment, there was a significant difference in the average C contents throughout the experiment, showing that the decay in the C contents is higher for the bio-residue to which the initial OM percentage added was larger (Fig. S3(b)).

In order to evaluate the decay of C contents over time in the TF treatment, an exponential function ($y = \ln x$) was considered (Fig. 1). In Fig. 1(a) it was observed a correlation coefficient (R^2) close to 0.95, and it was possible to verify an exponential decay of C contents for TF samples.

To determine the time required for the priming effect to occur in the treatment of TF, the curve equation in Fig. 1(a) was used, and this extrapolated decay is shown in Fig. 1(b) (blue line).

Assuming the experiment would continue and the TF decay (red line would behave in the same rate, Fig. 1(b) shows that, in 720 days of

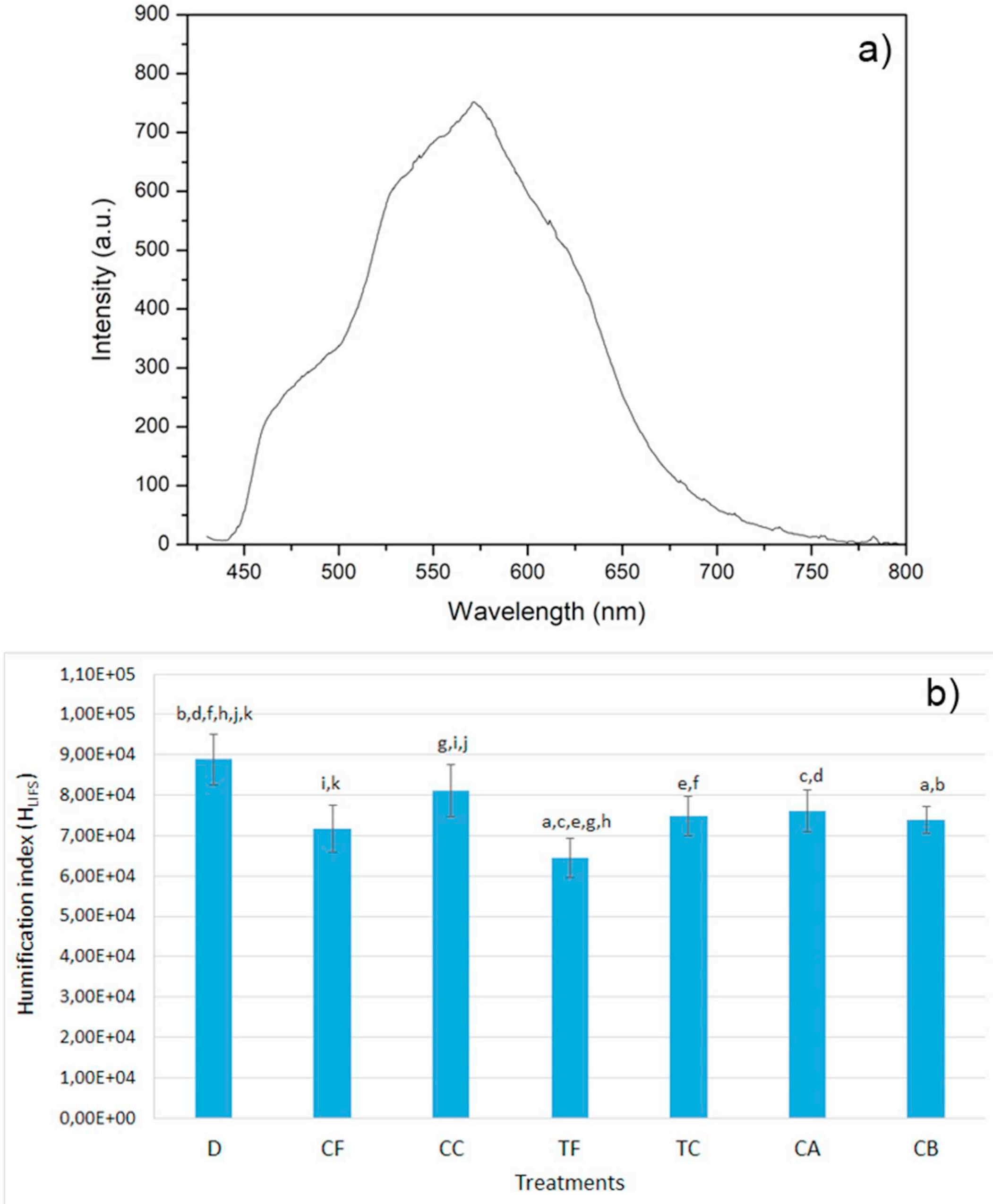

Fig. 2. a) Typical spectrum of whole soil obtained by LIFS; b) average H_{LIFS} throughout the experiment; $^{a\ b\ c\ d\ e\ f\ g\ h\ i\ j\ k}$: *Equal letters indicate comparisons with a statistically significant difference*. CF - fresh SCBA; CC - composted SCBA; TF - fresh FC; TC - composted FC; CA - Compound A - 50% FC and 50% SCBA and CB - compound B - 75% FC and 25% SCBA.

experiment (blue line), the C content in TF would have reached the control (green line). In addition, more detailed studies are needed to evaluate this situation, besides through this result it can be inferred that the addition of TF to the soil at this dose might have caused the priming effect from 720 days after the residue application due to the high C content. The input of OM would stimulate the microbial activity in the soil, resulting in the consumption of this OM and the pre-existing one.

Considering the result of the statistical analysis that compared the C content of the 10 incubation times for each treatment, the average C content for all experiment (during 1 year) was calculated (Fig. S4). In Fig. S4, show statistically significant differences (Tukey test, $\alpha = 0.05$) among bio-residues and controls, except for CC, which shows there was an impact in the soil C with the addition of most of the bio-residues.

3.2. *To evaluate quality of SOM*

Fig. 2 shows the typical spectrum of ERL obtained by LIFS that ranges from 430 to 800 nm. In the LIFS spectrum (Fig. 2), it can observe a shoulder of 462 nm, an intense excitation at 572 nm for aromatic rings, a high electron conjugation due to carbonyl and carboxylic groups as well as organometallic bonds [28]. Fig. S5(a and b) show the H_{LIFS} for the all treatments indifferent incubation times considering the experiment triplicate.

The LIFS results showed that, by using the Tukey test ($\alpha = 0.05$), none of the treatments presented a significant difference in the behavior of the average humification index among the incubation times during all the experiment. This fact can be associated with the input of stable organic substances from the bio-residues that are less susceptible to microbial activity.

The highest value of the H_{LIFS} average was observed for control treatment (D), which presented the most statistical differences, as shown in Fig. 2. The addition of bio-residues to the soil resulted in a decrease of the humification index in relation to the control treatment due the fresh OM input.

TF and CF presented the lowest H_{LIFS} since both bio-residues were submitted to the previous composting process when compared to TC and CC. Lastly, CA and CB presented almost the same H_{LIFS}, which means that the concentration of bio-residues in the compounds did not influence the average humification index throughout the experiment.

For TF (Fig. S5), there was a constant exponential increase in the humification index and it behaved inversely compared to the decay of C contents. Therefore, over time, the OM applied to the soil went through a stabilization process and became more recalcitrant. In this stabilization process, there was a greater condensation of the organic groups present in the OM structure, which were hindering the C loss to the atmosphere.

4. Conclusions

The N content in TF indicated the possibility of using this residue as a bio-fertilizer, however the C high levels showed that the treatment demands a lot of attention since there is a risk of priming effect, which was evident as carbon decayed. The H_{LIFS} results reinforced the importance of composting the fresh bio-residues when they are used as fertilizers in agriculture. These results also showed there is a stabilization of the OM in the soil, which hinders C loss to the atmosphere, keeping it stable in the soil. The mixed composting (CA and CB) with both bio-residues (filter cake (FC) + sugarcane bagasse ash (SCBA)) is an interesting alternative because it accelerates the maturation process and, at the same time, it keeps some of the N content of FC available in the compound.

Elemental Analysis (CHN/S) and LIFS showed potential and complementary tools for the analysis of soils under the application of by-products from the sugarcane processing. Additionally, this study emphasizes the importance of the correct management of the bio-residues as well as the need to create ordinances and laws for such uses.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2019.104041.

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