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EFFECTS OF PHOSPHATE, CARBONATE, AND SILICATE ANIONS ON CO₂ EMISSION IN A TYPICAL OXISOL FROM CERRADO REGION

EFEITOS DOS ÂNIONS FOSFATO, CARBONATO E SILICATO NA EMISSÃO DE CO₂ EM UM LATOSSOLO TÍPICO DA REGIÃO DO CERRADO

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ABSTRACT: The effects of agricultural practices on greenhouse gases emissions (e.g. CO_2) at the soil-atmosphere interface have been highlighted worldwide. The use of ground limestone has been considered as the main responsible for CO_2 emission from soils. However, liming is need as conditioner of acidic soils and the CO_2 emission can be compensated due to carbon sequestration by plants. This study simulated under laboratory conditions the effects of two common agricultural practices in Brazil (P-fertilization and liming) on soil CO_2 emission. Columns made of PVC tubes containing 1 kg of a typical Dystrophic Red Latosol from Cerrado region were incubated with $CaCO_3$ (simulating liming), $CaSiO_3$ (simulating slag), and different doses of KH_2PO_4 (simulating P-fertilization). The soil columns were moistened to reach the field capacity (0.30 cm^3 cm^{-3}) and, during 36 days, CO_2 emissions at the soil surface were measured using a portable Licor LI-8100 analyzer coupled to a dynamic chamber. The results showed that CO_2 emission was influenced by phosphate, carbonate, and silicate anions. When using $CaSiO_3$, accumulated CO_2 emission (36-day period) was 20% lower if compared to the use of $CaCO_3$. The same amount of phosphate and liming (Ca-carbonate or Ca-silicate) added to the soil provided the same amount of CO_2 emission. At the same P dose, as Si increased the CO_2 emission increased. The highest CO_2 emission was observed when the soil was amended with the highest phosphate and silicate doses. Based on this experiment, we could oppose the claim that the use of limestone is a major villain for CO_2 emission. Also, we have shown that other practices, such as fertilization using P + $CaSiO_3$, contributed to a higher CO_2 emission. Indeed, it is important to emphasize that the best practices of soil fertility management will undoubtedly contribute to the growth of crops and carbon sequestration.

KEYWORDS: Greenhouse gases. Tropical soils. Soil reaction.

INTRODUCTION

The CO_2 released at soil-atmosphere interface comes from microbial activity (MARCELO et al., 2012), burning and decomposition of soil organic matter (JANZEN, 2004), and direct dissolution of carbonates (RAMNARINE et al., 2012). Soil management practices are strongly related to soil CO_2 production in the soil (SMITH et al. 2008). The role of agricultural activities on CO_2 emissions has been highlighted worldwide as a contributor to the greenhouse effect (global warming) (OERTEL et al., 2016; OZLU; KUMAR, 2018; CASTANHEIRA; FREIRE, 2013). However, this statement must be carefully revised since sustainable agriculture undoubtedly contributes to plant growth and, consequently, to carbon sequestration (SMITH et al., 2008; FORNARA et al., 2011).

Brazil is ranked as one of the top world emitters of greenhouse gases, mainly due to the conversion of preserved areas into croplands for agriculture and livestock (CERRI et al., 2009; BENTO et al., 2018). However, there is some controversy if human activities are capable to promote the warming the Earth's atmosphere and changing the global climate (MOLION, 1995). Also, CO_2 produced in soil is an indicator of biochemical processes, energy flow, carbon storage and decomposition, nutrient cycling, among others (VALLERO, 2014).

Nowadays, the Cerrado Biome (~ 200 million ha) concentrates the most part of the Brazilian agriculture (BATLLE-BAYER, et al., 2010). In the past (1970-80's), this region was considered inappropriate for crop production due the occurrence of highly weathered-leached tropical soils (LOPES et al., 2012), mainly Latosols (almost 50% of the Cerrado). Liming, gypsum, P, K, and micronutrients build-up, and progressive adoption of

no-tillage were crucial for crop production on soils under Cerrado biome (LOPES; GUILHERME, 2016). In particular, the use of ground limestone to correct soil acidity has been frequently targeted as the main contributor to CO_2 emission (BERNOUX et al., 2003). However, crop-livestock-forestry production would definitely be impossible without liming of Cerrado soils. Slags (Ca-silicates) has been successfully used to increase soil pH and as a source of Ca, similarly to the effect of ground limestone in the soil (RAMOS et al., 2006). In the soil environment, the direct dissolution of calcium carbonates acts in two opposite ways: i) releasing CO_2 to the atmosphere, and ii) contributing to crop growth, which leads to increase the carbon sequestration.

Thus, this study was carried out aiming to assess the CO_2 emission under laboratory conditions in a typical Dystrophic Red Latosol from Cerrado region, as affected by two common and needed agricultural practices in Brazil: liming and phosphate fertilization. $CaCO_3$ was used to simulate ground limestone and $CaSiO_3$ for slag.

MATERIAL AND METHODS

Topsoil samples (0-20 cm) were used in this study. The soil is classified as a Dystrophic Red Latosol according to the Brazilian System of Soil Classification (EMBRAPA, 2013), and Hapludox according to the Soil Taxonomy Classification (SOIL SURVEY STAFF, 2014). The soil samples were collected nearby Uberlândia, Minas Gerais state, Brazil (18º59'40" S, 48º25'48" W, and 820 m altitude), then air-dried, ground and sieved (< 2 mm). Soil texture was determined by pipette method (DAY, 1965; DONAGEMMA et al., 2011) after dispersion of a soil suspension (10 g in 190 mL distilled water plus 10 mL 0.1 mol L^{-1} NaOH solution) in a 500-mL plastic bottle using Wagner's shaker for 16 hours. Soil particle density was determined by volumetric flask method (BLACK; HARTGE, 1986). Chemical characterization involved the determination of the following properties: pH in water (ratio 1:2.5); Ca^{2+}, Mg^{2+}, and Al^{3+} exchangeable forms extracted with 1 mol L^{-1} KCl solution; K^+, P, and micronutrient (Cu, Fe, Mn and Zn) extracted with Mehlich-1 solution; soil organic carbon (YEOMANS; BREMNER, 1988); effective cation-exchange capacity (sum of K^+, Ca^{2+}, Mg^{2+}, and Al^{3+}); potential cation-exchange capacity (sum of K^+, Ca^{2+}, Mg^{2+} and $H^+ + Al^{3+}$); and total oxides (SiO_2, Al_2O_3, Fe_2O_3, TiO_2 and P_2O_5) after sulfuric acid digestion analysis. The details of analytical procedures can be found in Donagemma et al. (2011). Table 1 shows the physical and chemical properties of the soil.

Table 1. Physical and chemical properties of soil used in the experiment.

Properties	Value
Clay (g kg^{-1})	380
Silt (g kg^{-1})	45.0
Sand (g kg^{-1})	575
Dp (g cm^{-3})	2.53
pH	4.80
K^+ (mg dm^{-3})	11.0
Ca^{2+} ($cmol_c dm^{-3}$)	0.30
Mg^{2+} ($cmol_c dm^{-3}$)	0.10
Al^{3+} ($cmol_c dm^{-3}$)	0.40
$H^+ + Al^{3+}$ ($cmol_c dm^{-3}$)	1.30
SOC (g kg^{-1})	10.0
CEC[1/] ($cmol_c dm^{-3}$)	1.73
CEC[2/] ($cmol_c dm^{-3}$)	0.83
B (mg dm^{-3})	0.03
Cu (mg dm^{-3})	0.10
Fe (mg dm^{-3})	3.00
Mn (mg dm^{-3})	1.70
Zn (mg dm^{-3})	0,00
SiO_2[3/] (g kg^{-1})	8.80
Al_2O_3[3/] (g kg^{-1})	77.0
Fe_2O_3[3/] (g kg^{-1})	55.0
P_2O_5[3/] (g kg^{-1})	0.10

Soil columns were packed in PVC tubes (12-cm high and 10-cm internal diameter) filled with 1 kg of soil (oven-dried basis). The soil density was standardized at 1.2 g cm^{-3}. Based on soil particle density (Table 1), the total porosity of soil columns was 0.53 cm^3 cm^{-3}. Before packing the columns, the soil samples were treated with phosphate, silicate, and carbonate, establishing the treatments described below. The sources of P and Si (treatments 4 to 8) were KH$_2$PO$_4$ and CaSiO$_3$, respectively.

Treatments

1) control;
2) 8.32 mmol kg^{-1} CaCO$_3$;
3) 8.32 mmol kg^{-1} CaSiO$_3$;
4) 8.32 mmol kg^{-1} P;
5) 8.32 mmol kg^{-1} P + 1.04 mmol kg^{-1} Si;
6) 8.32 mmol kg^{-1} P + 2.08 mmol kg^{-1} Si;
7) 8.32 mmol kg^{-1} P + 4.16 mmol kg^{-1} Si;
8) 8.32 mmol kg^{-1} P + 8.32 mmol kg^{-1} Si;
9) 8.32 mmol kg^{-1} P + 8.32 mmol kg^{-1} Si (as H$_4$SiO$_4$).

During the entire experiment, soil moisture was maintained constant at field capacity (0.30 cm^3 cm^{-3}). The experiment was carried out under laboratory conditions, and temperature ranged from 20º to 22º C. The CO$_2$ emission from soil columns was measurement using a portable LI-8100 analyzer (LiCor, EUA) coupled to a dynamic chamber (Figure 1), on the following days: 1st, 3rd, 5th, 8th, 10th, 12th, 15th, 17th, 22nd, 26th, 29th, 31nd and 36th.

The treatments were compared for accumulated CO$_2$ emissions, which were calculated using equation 1.

$$Q = \sum(q\Delta t) \tag{1}$$

Where: Q is the accumulated CO$_2$ (g m^{-2}); q is the average CO$_2$ emission rate (g m^{-2} s^{-1}) for each considered time interval (Δt).
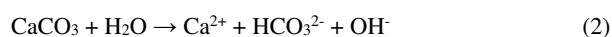

Figure 1. Experimental design and CO$_2$ measurement using a portable LI-8100 analyzer (LiCor, EUA) coupled to a dynamic chamber. Photo: Camila Silva Borges.
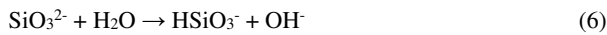
RESULTS AND DISCUSSION

Figure 2A shows the accumulated CO$_2$ emission influenced by CaCO$_3$ and CaSiO$_3$. The control treatment represents the background CO$_2$ emission from soil microbial activity after disturbance sampling, sieving (< 2 mm), and remoistening (0.25 g g^{-1}). A significant difference between CaCO$_3$ amended samples and the control ones was observed. After 36 days, the soil samples treated with CaCO$_3$ emitted 130.7 g m^{-2} (± 13.8), while those of control emitted 64.1 g m^{-2} (± 2.9). The effect of CaCO$_3$ on CO$_2$ emissions from soils are related to the direct dissolution of CaCO$_3$ in soil solution (equations 2 to 4) and also by the increase in soil pH, favoring microbial activity (soil

respiration) (MARCELO et al., 2012; FORNARA et al., 2011). The soil pH increased from 5.2 (control) to 6.9 after CaCO$_3$ application (data not shown). In a long-term field experiment on a Red Latosol (642 g kg^{-1} sand, 315 g kg^{-1} clay, and 43 g kg^{-1} silt), CO$_2$ emission increased linearly with limestone dose (MARCELO et al., 2012).

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^{2-} + OH^- \tag{2}$$

$$HCO_3^{2-} + H_2O \rightarrow H_2CO_3 + OH^- \tag{3}$$

$$H_2CO_3 \rightarrow H_2O + CO_2 \tag{4}$$

After 36 days, the samples treated with CaSiO$_3$ emitted 108.9 g m^{-2} (± 5.2). Compared to

the control, accumulated CO_2 was 70% and 104% higher in treatments using $CaSiO_3$ and $CaCO_3$, respectively. The CO_2 is not produced by direct dissolution of Ca-silicates, as evidenced by equations 5 to 8. Under natural conditions, the weathering of Ca-silicate minerals is considered a sink of atmospheric CO_2 (BRADY, 1991). The effect of $CaSiO_3$ on CO_2 emission is certainly related to microbial activity, which was also favored by the increase in soil pH. Similarly, soil pH also increased when $CaCO_3$ was used, ranging from 5.2 (control) to 6.5 (with $CaSiO_3$ application).

$$CaSiO_3 \rightarrow Ca^{2+} + SiO_3^{2-} \qquad (5)$$

$$SiO_3^{2-} + H_2O \rightarrow HSiO_3^- + OH^- \qquad (6)$$

$$HSiO_3^- + H_2O \rightarrow H_2SiO_3 + OH^- \qquad (7)$$

$$H_2SiO_3 + H_2O \rightarrow H_4SiO_4 \qquad (8)$$

The $CaSiO_3$ (e.g. slag) has been used in Brazilian agriculture (mainly in sugarcane crops) having the same effects of liming: source of Ca and increasing soil pH (BARBOSA FILHO et al., 2001), and promoting Al^{3+} precipitation (MATICHENKOV; BOCHARNIKOVA, 2001). The environmental benefits of Ca-silicates (slags) are their own reuse and less CO_2 emission from soil (ALLEONI et al., 2009). After 36 days, the difference in CO_2 emission between $CaCO_3$ and $CaSiO_3$ treatments was 20% (Figure 2A).
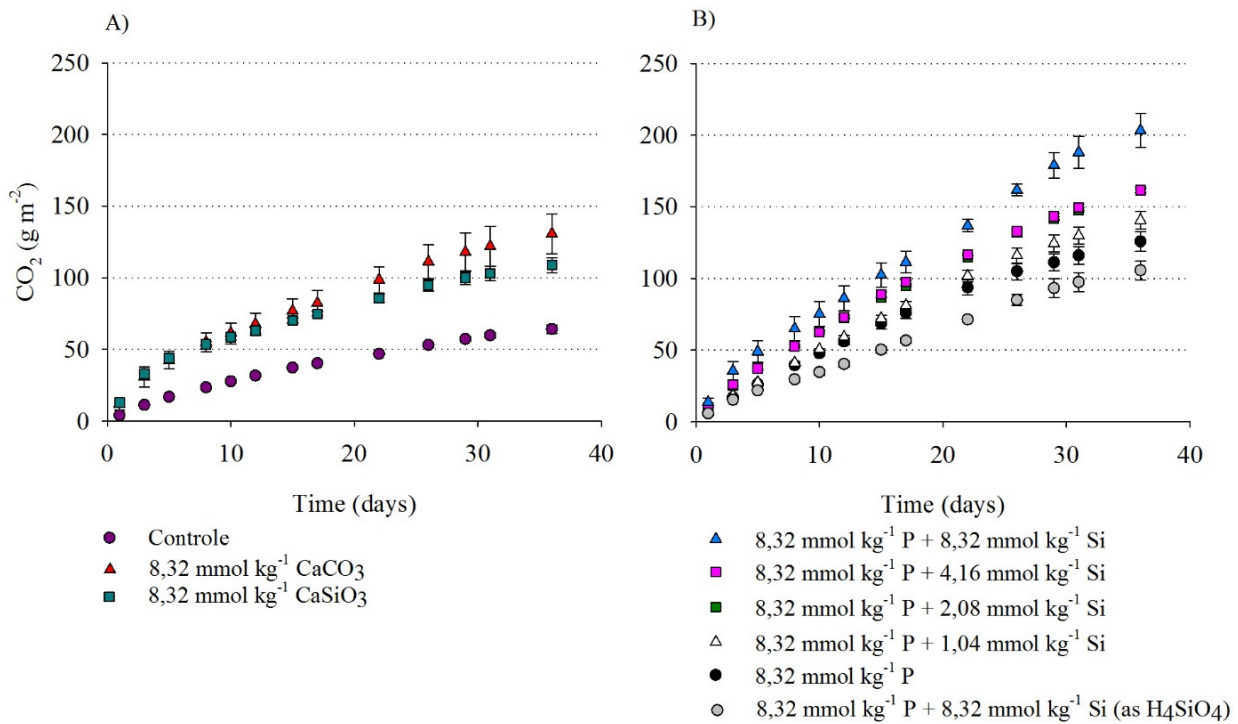

Figure 2. Effects of carbonate and silicate (A) and phosphate (B) on accumulated CO_2 emission of a Dystrophic Red Latosol under lab conditions. Error bars indicate the standard deviation (n = 3).

The $CaCO_3$ reaction in the soil released CO_2 to the atmosphere (equations 2 to 4). However, Figure 2B shows that the application of 8.32 mmol kg^{-1} P (KH_2PO_4) + 8.32 mmol kg^{-1} Si ($CaSiO_3$) produced 203.3 g m^{-2} (± 11.8) of CO_2 (217% higher than the $CaCO_3$ amended samples). The single application of 8.32 mmol kg^{-1} P produced the same amount of CO_2 as that of the liming amended samples ($CaCO_3$ or $CaSiO_3$). Vinhal-Freitas et al. (2012) studied the effects of P doses (from 0 up to 600 mg kg^{-1}) on the microbial activity of Cerrado

soil areas (32-year pine plantation, 11-year no-tillage, and native Cerrado). As P doses increased, the CO_2 production by soil microorganisms increased. This effect was more pronounced in non-cultivated soil (native Cerrado).

As the concentration of Si (as $CaSiO_3$ combined with P) increased, CO_2 emission increased (Figure 3). In the presence of P (8.32 mmol kg^{-1}), the increment of 1 mmol kg^{-1} Si increased by 8.61 g m^{-2} the CO_2 emission. Considering the effect of P on CO_2 production in

soils (VINHAL-FREITAS et al., 2012), the effect of Si is certainly related to the increase in the P availability in the soil. The anions silicate and phosphate compete by the same adsorption sites on soil particles (POZZA et al., 2007). It is noteworthy

to mention that when P + Si (as H_4SiO_4) was applied, CO_2 emission was the lowest. H_4SiO_4 has low solubility ($pKa \sim 9.0$). Thus, the anion silicate could not influence P availability.
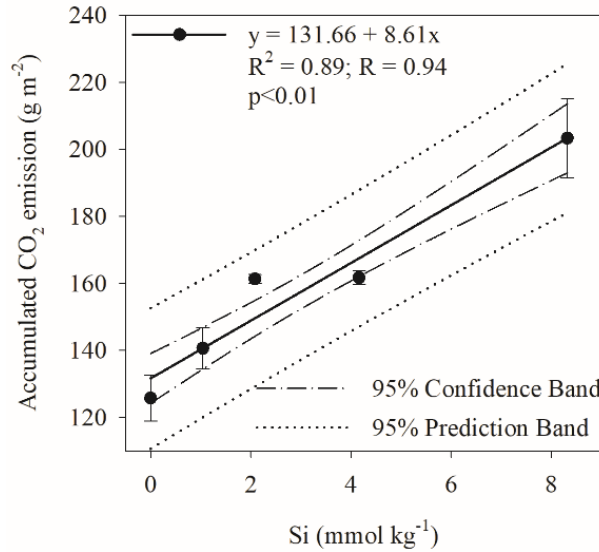

Figure 3. Increasing Si doses combined with a single P dose (8.32 mmol kg^{-1}) on accumulated CO_2 emission. Error bars indicate the standard deviation (n = 3).

In general, the accumulated CO_2 emission decreased as follows: 8.32 mmol kg^{-1} P + 8.32 mmol kg^{-1} Si (CaSiO$_3$) > 8.32 mmol kg^{-1} P + 4.16 mmol kg^{-1} Si (CaSiO$_3$) = 8.32 mmol kg^{-1} P + 2.08 mmol kg^{-1} Si (CaSiO$_3$) > 8.32 mmol kg^{-1} P + 1.04 mmol kg^{-1} Si (CaSiO$_3$) > 8.32 mmol kg^{-1} P = CaCO$_3$ > 8.32 mmol kg^{-1} P + 8.32 mmol kg Si (as H_4SiO_4) = CaSiO$_3$ > control (Figure 4).

1) control
2) 8.32 mmol kg^{-1} CaCO$_3$
3) 8.32 mmol kg^{-1} CaSiO$_3$
4) 8.32 mmol kg^{-1} de P
5) 8.32 mmol kg^{-1} de P + 1.04 mmol kg^{-1} de Si
6) 8.32 mmol kg^{-1} de P + 2.08 mmol kg^{-1} de Si
7) 8.32 mmol kg^{-1} de P + 4.16 mmol kg^{-1} de Si
8) 8.32 mmol kg^{-1} de P + 8.32 mmol kg^{-1} de Si
9) 8.32 mmol kg^{-1} de P + 8.32 mmol kg^{-1} de Si (as H_4SiO_4)
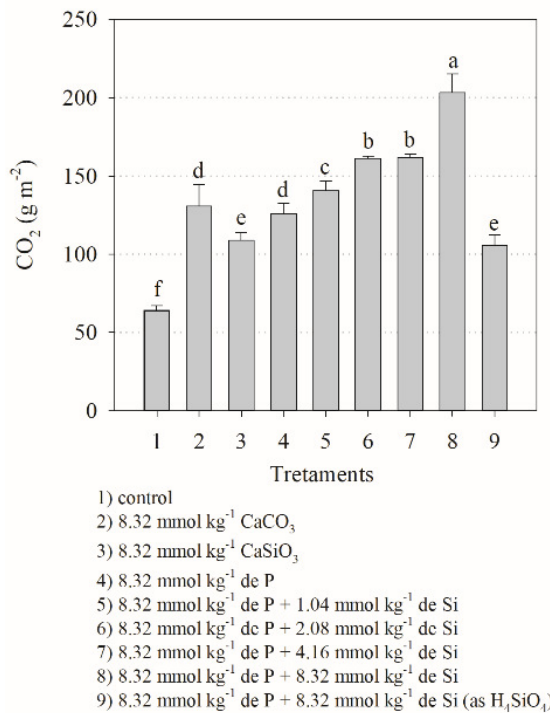
Figure 4. Accumulated CO_2 emission after 36-day incubation period as affected by CaCO$_3$, CaSiO$_3$ and P addition. Error bars indicate the standard deviation (n=3) and the letters compare the treatments by Scott-Knott test ($p<0.05$).

CONCLUSIONS

The use of $CaSiO_3$ contributed to decrease CO_2 emission compared to $CaCO_3$. However, the combination of P and $CaSiO_3$ contributed to the highest CO_2 emission. Based on this experiment, we could oppose the claim that the use of limestone is a major villain for CO_2 emission from soils. Also, we could show that other practices, such as fertilization using P+$CaSiO_3$, contributed to a higher CO_2 emission. Indeed, it is important to emphasize that the best practices of soil fertility management will undoubtedly contribute to crop growth and carbon sequestration

RESUMO: Os efeitos das práticas agrícolas nas emissões de gases de efeito estufa (e.g., CO_2) na interface solo-atmosfera têm sido destacados em todo o mundo. O uso de calcário tem sido considerado o principal responsável pela emissão de CO_2 em solos. Entretanto, a calagem é necessária como condicionador de solos ácidos e a emissão de CO_2 pode ser compensada devido ao sequestro de carbono pelas plantas. Este estudo simulou, em condições de laboratório, os efeitos de duas práticas agrícolas comuns no Brasil (adubação fosfatada e calagem) na emissão de CO_2 do solo. Colunas de tubos de PVC, contendo 1 kg de amostra de um Latossolo Vermelho Distrófico típico da região de Cerrado, foram incubadas com $CaCO_3$ (simulando calagem), $CaSiO_3$ (simulando escória) e diferentes doses de KH_2PO_4 (simulando fertilização com P). As colunas de solo foram umedecidas para atingir a capacidade de campo ($0,30$ cm^3 cm^{-3}) e, durante 36 dias, as emissões de CO_2 na superfície do solo foram medidas usando um analisador portátil Licor LI-8100 acoplado a uma câmara dinâmica. Os resultados mostraram que a emissão de CO_2 foi influenciada pelos ânions fosfato, carbonato e silicato. Ao usar $CaSiO_3$, a emissão de CO_2 acumulada (período de 36 dias) foi 20% menor se comparado ao uso de $CaCO_3$. A mesma quantidade de fosfato e calcário (Ca-carbonato ou Ca-silicato) adicionado ao solo proporcionou a mesma quantidade de emissão de CO_2. Na mesma dose de P, o Si aumentou a emissão de CO_2. A maior emissão de CO_2 foi observada quando o solo foi alterado com as maiores doses de fosfato e silicato. Com base neste experimento, nega-se que o uso de calcário em solos é um grande vilão para a emissão de CO_2. Além disso, foi mostrado que outras práticas, como a fertilização usando P + $CaSiO_3$, contribuíram para uma maior emissão de CO_2. Assim, é importante enfatizar que práticas adequadas de manejo da fertilidade do solo, sem dúvida, contribuirão para o crescimento das culturas e o sequestro de carbono.

PALAVRAS-CHAVE: Gases de efeito de estufa. Solos tropicais. Reação do solo.

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