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## SOIL CHEMICAL CHANGES AND RESEMBLANCES IN A CHRONOSEQUENCE RAINFOREST-SUGARCANE-PASTURELAND IN THE ATLANTIC FOREST BIOME

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### HIGHLIGHTS

The conversion of the forest into agricultural lands reduced soil acidity.

Cation exchange capacity was mostly influenced by  $K^+$ ,  $Ca^{+2}$  and  $Mg^{+2}$ .

Soil  $\delta^{13}C$  was enriched by the conversion of forest to agricultural lands.

Pastures and sugarcane had similar isotopic profile compared to forest soils.

### ABSTRACT

This study evaluated soil chemical and isotopic changes in soils of a chronosequence rainforest-sugarcane-pasture in the Atlantic Forest biome, Brazil. Soil samples were collected (0-20 cm) in areas of native Brazilian Atlantic rainforest, sugarcane plantation and pastures of *Brachiaria decumbens*. The soil analyses performed were: pH (water 1:2.5), P (Mehlich-I), ( $Al^{+3}$ , H+Al,  $K^+$ ,  $Ca^{+2}$ ,  $Mg^{+2}$  and  $Na^+$ ), soil organic matter (SOM), N, organic carbon and  $\delta^{13}C$  and  $\delta^{15}N$  stable isotopes. The conversion of rainforest to sugarcane and pastures resulted in a reduction of the soil natural acidity. Forest areas had greater  $Al^{+3}$  and H+Al concentrations than cultivated areas. The conversion from forest to agricultural soil reduced  $Al^{+3}$  (44%) and H+Al (11%), approximately. Soils from pasture had a greater percentage of base saturation (37.3%) than forest soils (25.4%). Cation exchange capacity was strongly influenced by concentrations of  $K^+$ ,  $Ca^{+2}$  and  $Mg^{+2}$ , but not by  $Na^+$ . Carbon stable isotope ( $\delta^{13}C$ ) was more depleted in forest areas (-28.14‰), followed by sugarcane (-21.33‰), and pastures (-19.54‰). The greatest  $\delta^{15}N$  values were found in sugarcane areas. The short chronosequence studied, had a strong influence of the conversion of the forest on the decrease of the natural acidity and modifications of the isotopic profile. The enrichment of soil  $\delta^{13}C$  was attributed to the changes from predominant  $C_3$  vegetation to  $C_4$  grasses.

#### Keywords:

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## INTRODUCTION

The conversion of native vegetations into agricultural lands is considered one of the main factors that can drastically impact changes in the physical-chemical and biological characteristics of the soil. Soil alterations due to conversion of native vegetation to agricultural lands can include modifications in soil carbon stocks, changing in nutrient cycles, possibility of nutrient and/or heavy metals accumulations, reduction of the natural soil acidity, increase of exchangeable bases and bulk density, soil compaction, increase of available N and changes in soil biodiversity (Don et al., 2011; Rodrigues et al., 2013; Allen et al., 2015; Fujisaki et al., 2015). Nevertheless, due to intrinsic characteristics of each type of native vegetation and soil that was subjected to the conversion of its natural cover, as also, to the different types of crops/agricultural system adopted after conversion, these soil alterations might have a different pattern according to each specific case. These alterations could be even more complex if more than one type of crop/agricultural system followed the conversion of the natural system.

In Brazil, the conversion of native forests into agricultural lands was one of the cheapest ways of expanding food production during the past centuries (Gibbs et al., 2010). Among the native biomes in Brazil that were drastically affected by the conversion, the Atlantic Forest suffered severe losses of its original covered area. It is estimated that only 12% of the original forest area remains conserved (Ribeiro et al., 2009). In Brazil, the conversion of the Atlantic Forest into agricultural lands was strongly influenced by the expansion of sugarcane plantations since the colonial period, especially in the Northeastern coastal region. After the conversion, most of these areas underwent predatory agriculture with inadequate soil management practices for several years, as backdate poor understanding about the dynamic between soil-plant interface and fertilization practices were achieved. Nevertheless, in the last decades, sugarcane production in Northern Brazil stagnated in its productivity and competitiveness, while the sugarcane production in Southern Brazil expanded due to higher levels of competitiveness (Rudorff et al., 2010; Moraes et al., 2016). These factors combined, have contributed to the conversion of sugarcane areas into other crops cultures or pasturelands in Northern Brazil.

Due to practices such as fertilization, liming, nutrient exportation by cultures, and changes in nutrient cycles (Don et al., 2011; Allen et al., 2015; Fujisaki et al., 2015), forest conversion to agricultural lands can have a considerable impact over the soil chemistry. The degree of these soil chemical changes due to different land use can be understood by analyzing soil fertility indicators such as the sum of exchangeable bases, effective cations exchange capacity (CEC), potential cations exchange

capacity (PCEC), percentage of Al saturation (m%), percentage of base saturation (V%), soil organic matter (SOM) and the isotopic composition, compared to the native soils. These soil fertility indicators are dependent on the concentrations and the balance of a range of nutrients and ions such as available P, K<sup>+</sup>, Al<sup>+3</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+</sup> that are strongly influenced by a sort of soil management strategies adopted such as fertilization (McLaughlin et al., 2011; Bindraban et al., 2015), liming (Alleoni et al., 2010; Buni, 2014), grazing (Vendramini et al., 2007) and type of crop (Bindraban et al., 2015). Understand the complexity of these soil chemical changes due to land-use changes is useful to support strategies for adequate soil fertility management in areas that underwent use conversion.

The objective of this study was to evaluate the chemical and isotopic changes in areas of a short-chronosequence, rainforest-sugarcane-pastureland in the Atlantic Forest biome, after approximately 30 years from the conversion of the native vegetation into agricultural lands. Additionally, this study outlines the interaction between soil chemical composition and fertility indicators, and their correlation with the type of vegetation cover.

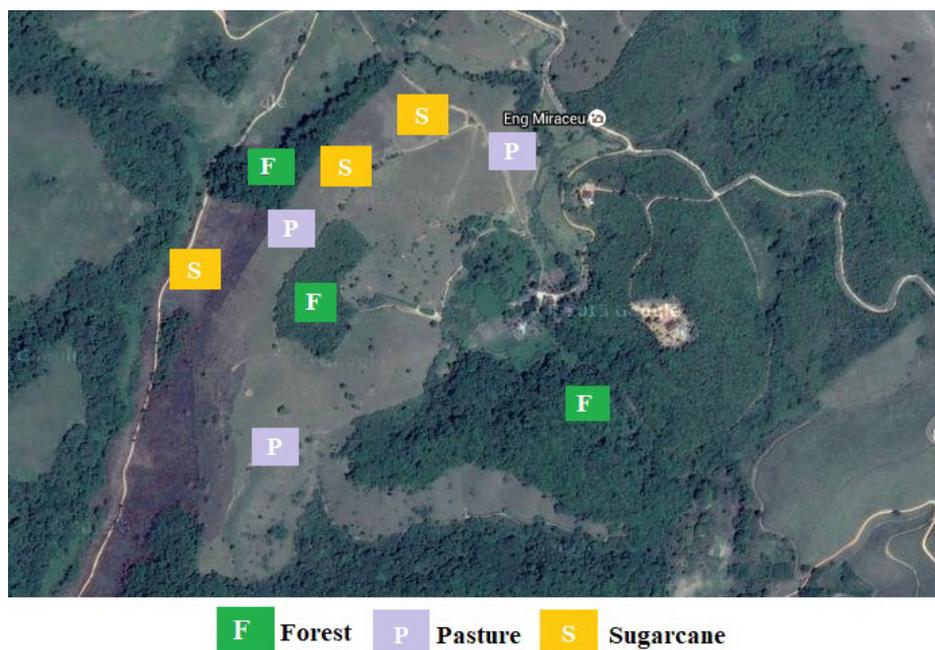
## MATERIAL AND METHODS

### Site location

This study was carried out at Miracéu Farm (S 08 ° 29 '147", W 035 ° 37' 054"), located at the coastal zone of Atlantic forest biome, microregion of the Mata Sul of Pernambuco State, Northeast region, Brazil. The land is situated at 302-m a.s.l. The climate of the region is considered tropical with a dry season, according to Köppen-Geiger climate classification. The average annual temperature is 25°C, with an average yearly rainfall of 1000-2200 mm (Embrapa, 2020). The predominant rocks types of the study area are igneous and metamorphic rocks (Carmo Leal, 2020). Oxisols dominate the soils of this region in the flat tops that are generally deep and well-drained. Spodosols prevails on steep slopes, moderately deep and drained. The lowlands are composed by Entisol rich in organic matter and typically poorly drained. Soils classification were based on (USDA, 1960, Soil Survey Staff, 2014). The soils at the farm have a clay texture.

### Land use description and sampling

The sampling area included three types of land use: sugarcane plantation subjected to chemical fertilization and annual fire, pastures of *Brachiaria decumbens* used for beef cattle production, and native/conserved Atlantic rainforest (Figure 1). The area correspondent to the native Atlantic forest had approximately 28 ha, dispersed in distinct areas of flat and sloping topography. The pasture



Note: Soil samples were collected over the whole area of each vegetation tagged. A minimum of 30 m distance between soils from different vegetations was used as border limit between different sampling areas.

**FIGURE I** Map of the sampling areas of forest, sugarcane and pasture.

areas were established between 4 to 12 years before sampling, with a monoculture of *Brachiaria decumbens* Stapf, totaling 31 ha. Before conversion to pastures, these areas were used for sugarcane cultivation, and prior sugarcane the areas were unaltered native Atlantic rainforest. Since the establishment of the pastures, no fertilization or liming were performed. Pastures had been managed under rotational stocking in a semi-intensive beef cattle production system. The sugarcane areas sampled totaled 9 ha and were established around 30 years before the evaluation. These areas of sugarcane were improved in 2005, they underwent tillage, and its pH was corrected with lime at a rate of 2 Mg·ha<sup>-1</sup>. Sugarcane has been fertilized annually with 200 kg·ha<sup>-1</sup> of 20-10-20 (NPK). This area had been subject to annual fire before harvesting. Soil samples were collected in the first semester of 2013, at a depth of 0-20 cm. Sampling included flat top areas, steep slopes and lowlands equally distributed for each type of vegetation. Twenty-four samples were collected in each treatment, where 8 soil samples were collected along each experimental unit tagged in Figure 1. A minimum distance of 8 m between samplings points within the same experimental unit was used. During sampling, transitional areas between vegetations were avoided, allowing a minimum distance of 30 m.

### Soil chemical and isotope analyses

Soil samples were analyzed at the Federal Rural University of Pernambuco, Recife, Brazil. Soil samples were air-dried and sieved at 2 mm as a standard procedure before the analyses. The soil chemical analyses followed methods described in Donagema et al. (2011), they included:

soil pH (water 1:2.5) based on a ratio (10 ml soil + 25 ml of distilled water) and readings performed in pH meter; H+Al (cmolc·dm<sup>-3</sup>), extracted using 0.5 mol·L<sup>-1</sup> calcium acetate at pH 7.0; Al<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> (cmolc·dm<sup>-3</sup>), extracted using 1 mol·L<sup>-1</sup> KCl N, followed by dilution in a volumetric solution of NaOH 0.025 N for Al<sup>3+</sup> determination, and addition of bromine water, buffer solution, eriochrome black and titration with EDTA 0.0125 N; Na<sup>+</sup> and K<sup>+</sup> (cmolc·dm<sup>-3</sup>) were determined by extraction with HCL 0.05 followed by flame spectrophotometry using specific filters; P was extracted using Mehlich I (HCl 0.05 N + H<sub>2</sub>SO<sub>4</sub> 0.025 N) solution, followed by addition of 10 ml acid solution of ammonium molybdate and 30 mg of ascorbic acid, readings by optical density on the photocolormeter, using a red filter (660 mμ wavelengths). Organic carbon was estimated via organic matter oxidation in dichromate potassium in sulfuric medium, followed by titration with Ammonium Iron (II) sulfate (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>, then the soil organic matter was calculated using the equation 1.724 x % organic carbon.

Soil fertility indicators were estimated: total exchangeable bases (cmolc/dm<sup>3</sup>) = Ca<sup>2+</sup> + Mg<sup>2+</sup> + K<sup>+</sup> + Na<sup>+</sup>; effective cation exchange capacity (ECEC) (cmol<sub>c</sub>·dm<sup>-3</sup>) = Ca<sup>2+</sup> + Mg<sup>2+</sup> + K<sup>+</sup> + Na<sup>+</sup> + Al<sup>3+</sup>; potential cation exchange capacity (PCEC) (cmol<sub>c</sub>·dm<sup>-3</sup>) = Ca<sup>2+</sup> + Mg<sup>2+</sup> + K<sup>+</sup> + Na<sup>+</sup> + (H + Al<sup>3+</sup>); Aluminium saturation (m%) = (100 x Al<sup>3+</sup>) / (Ca<sup>2+</sup> + Mg<sup>2+</sup> + K<sup>+</sup> + Na<sup>+</sup> + Al<sup>3+</sup>); percentage of bases saturation (V%) = [100 x (Ca<sup>2+</sup> + Mg<sup>2+</sup> + K<sup>+</sup> + Na<sup>+</sup>)] / (Ca<sup>2+</sup> + Mg<sup>2+</sup> + K<sup>+</sup> + Na<sup>+</sup> + Al<sup>3+</sup>).

Six composite samples (0.25 g) of each treatment were prepared for  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  stable isotopes analyses, being two composite samples from a mix of 8 individual samples of each experimental unit. Samples were previously oven-dried at  $50^\circ\text{C}$  and ball-milled to be reduced to a fine powder. Before the isotopes analyses, samples were acidified in 1.5 N HCl to remove organic carbon. Nitrogen and carbon % were analyzed based on mass spectrophotometry using Vario Micro Cube (CHNS analyzer using the Dumas dry combustion method Elementar, Hanau, Germany) combined with an ISOPRIME 100 Isotope Ratio Mass Spectrometer (Elementar, Manchester, UK). The isotopes values are expressed in ‰,  $\delta^{13}\text{C}$  to the PDB (Pee Dee Belemite) standard, and  $\delta^{15}\text{N}$  to the atmospheric  $\text{N}_2$ . The analyses were performed at the Nuclear Energy Center, USP-CENA.

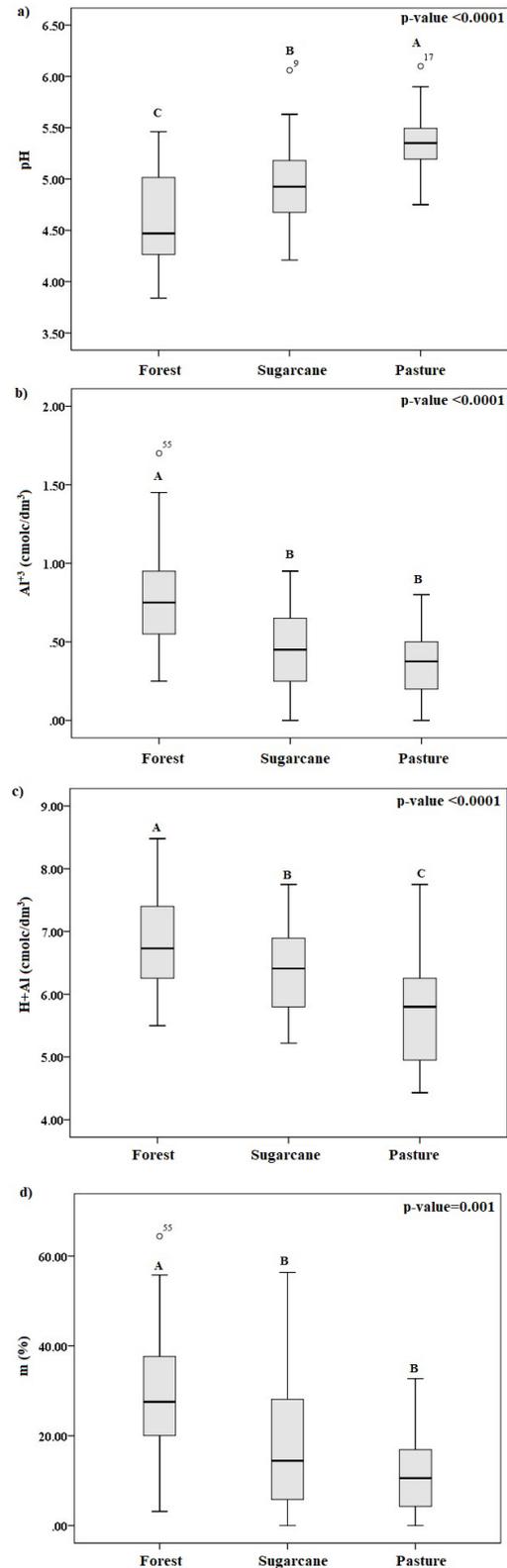
### Statistical analyses

The data were tested for normality using the Kolmogorov-Smirnov and Shapiro-Wilk tests. Comparison between soil attributes from different land use was analyzed by independent Kruskal-Wallis H Test ( $p < 0.05$ ) using the software SPSS 24 IBM®. Pearson's correlations were performed ( $p < 0.05$ ) between all soil physical-chemical variables analyzed, excepted for  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ . Relationships between soil nutrients, soil fertility indicators and vegetation type were analyzed by correspondence analysis using XLSTAT®. For the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  stable isotopes, cluster analysis (Bray-Curtis similarities matrix) were performed to detect similarities between the isotopic profiles in the different land uses.

## RESULTS

### Soil fertility

Forest soils showed the lowest pH average between the types of land use (pH = 4.6), followed by sugarcane soils (pH 5.0), and higher pH values were found in pasture soils (pH = 5.4) ( $p < 0.0001$ ) (Figure 2.a). It was observed that forest areas had greater concentrations of  $\text{Al}^{+3}$  ( $0.8 \text{ cmol}_c \cdot \text{dm}^{-3}$ ), H+Al ( $6.8 \text{ cmol}_c \cdot \text{dm}^{-3}$ ) and m% (28.9) than the areas of sugarcane ( $\text{Al}^{+3} = 0.5$ ; H+Al =  $6.4 \text{ cmol}_c \cdot \text{dm}^{-3}$  and m% = 19.1) and pastures ( $\text{Al}^{+3} = 0.4$ ; H+Al =  $5.7 \text{ cmol}_c \cdot \text{dm}^{-3}$  and m% = 12.0) ( $p < 0.001$ ) (Figure 2 b-d). The greater concentrations of  $\text{Al}^{+3}$  and H+Al in forest soils effectively contributed to their lower pH levels compared to sugarcane and pasture soils. It can be observed in the correspondence analysis map (Figure 4) that soil pH was plotted in opposition to  $\text{Al}^{+3}$  and H+Al. Also, it can be visualized a predominance of forest samples in the biplot that  $\text{Al}^{+3}$  and H+Al were located.



Box-plots with different letters differed significantly in the independent Kruskal-Wallis H Test ( $p < 0.05$ ). (n samples = 72)

**FIGURE 2** a.b.c.d. Soil pH (water – 1:2.5) (a),  $\text{Al}^{+3}$  (cmol<sub>c</sub>/dm<sup>3</sup>) (b), H+Al (cmol<sub>c</sub>/dm<sup>3</sup>) (c) and m% (d), from a chronosequence forest-sugarcane-pastureland in the Atlantic Forest biome.

A higher number of sugarcane samples compared to pasture were found in the biplot where  $Al^{+3}$ ,  $H+Al$  and  $m\%$  were plotted in (Figure 3). However, the concentration of  $Al^{+3}$  and  $m\%$  in the soil did not have any significant difference between sugarcane and pasture soils ( $p>0.05$ ) (Figure 2 b.d).

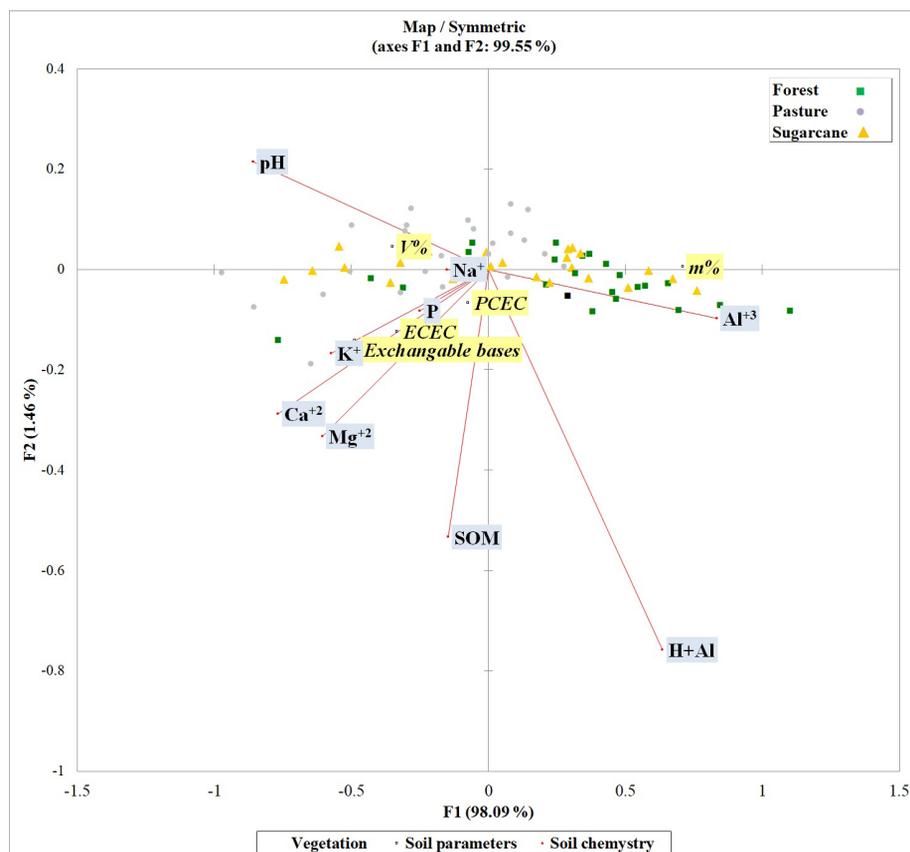
It was not observed significant differences between the types of land use on the potential cation exchange capacity (PCEC), effective cation exchange capacity (ECEC) and the sum of exchangeable bases of the soil (Figure 4 a.c.d) ( $p>0.05$ ). Only  $V\%$  showed a significant difference between vegetation types ( $p<0.006$ ) (Figure 4 b), with pasture areas showing higher  $V\%$  (37.3%) than forest (25.4%), and sugarcane being an intermediated (29.9%). For the exchangeable bases analyzed individually, it was found a greater average of soil P concentrations in sugarcane soils ( $6.4 \text{ mg}\cdot\text{dm}^{-3}$ ) ( $p<0.05$ ) than in pasture and forest soils ( $1.9$  and  $0.8 \text{ mg}\cdot\text{dm}^{-3}$ , respectively). Greater  $K^+$  concentrations were found in pastures soils ( $0.12 \text{ cmol}_c\cdot\text{dm}^{-3}$ ) in comparison to sugarcane ( $0.07 \text{ cmol}_c\cdot\text{dm}^{-3}$ ), with forest being intermediate ( $0.08 \text{ cmol}_c\cdot\text{dm}^{-3}$ ) ( $p<0.05$ ) (Figure 5 a.b). Forest and pasture soils had the greatest

$Na^+$  concentrations ( $0.19 \text{ cmol}_c\cdot\text{dm}^{-3}$ ) ( $p<0.0001$ ) (Figure 5 c). Soil  $Mg^{+2}$ ,  $Ca^{+2}$  and SOM did not differ significantly between land uses ( $p>0.05$ ) (Figure 6 d.e.f).

It was observed in the correspondence analysis map (Figure 3), that most of the samples that were in the same biplot as exchangeable bases, PCEC and ECEC were from pastures and sugarcane, only a few number were from the forest. Nevertheless, PCEC and ECEC did not show any significant difference between the different types of vegetation (Figure 4 c.d). Correlation analyses revealed that  $K^+$ ,  $Ca^{+2}$  and  $Mg^{+2}$  were the exchangeable bases with higher linear correlation coefficients with PCEC and ECEC, between  $r=0.5$  to  $0.8$  (Table I). Among the exchangeable bases, soil  $Na^+$  showed no significant correlation ( $p>0.05$ ) with exchangeable bases, PCEC and ECEC. Higher soil pH correlated moderately with ECEC ( $r=0.6$ ), and SOM moderately with PCEC ( $r=0.5$ ).

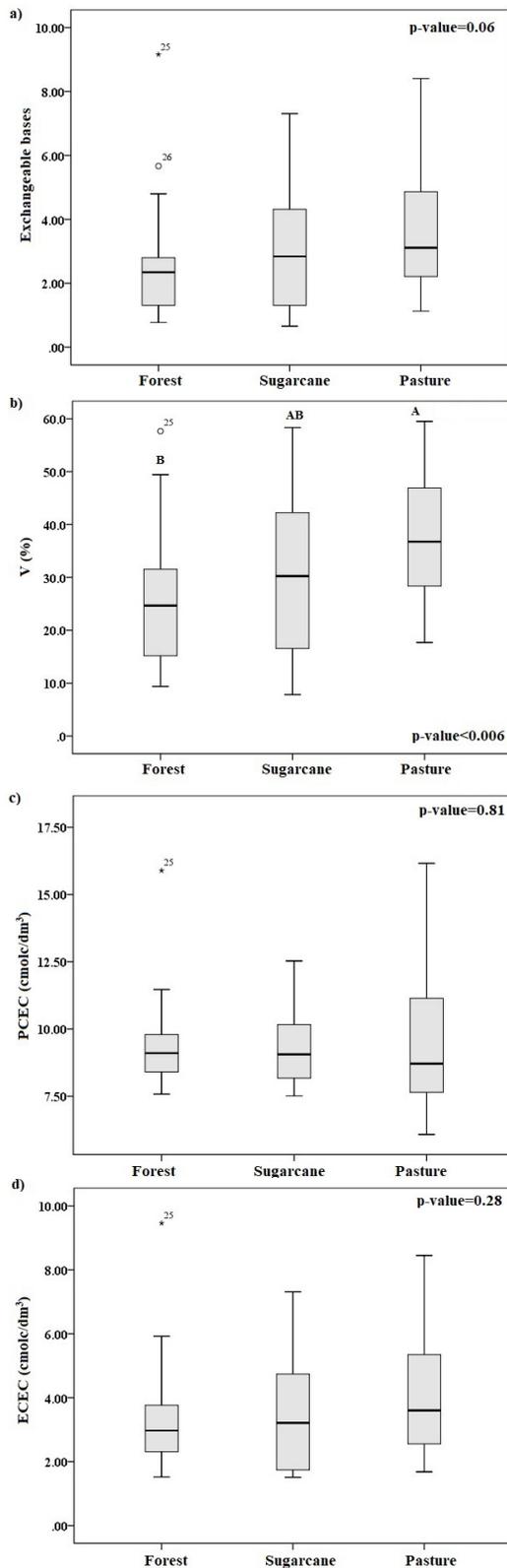
### Soil C and N isotopic profiles

The isotopic analyses showed that soil  $\delta^{13}C$  was more depleted in areas of forest ( $-28.1\text{‰}$ ), followed by sugarcane ( $-21.3\text{‰}$ ) and pastures ( $-19.5\text{‰}$ ) areas



Potential and effective cations exchange capacity (PCEC and ECEC, respectively) ( $\text{cmol}/\text{dm}^3$ ), percentage of base saturation ( $V\%$ ), potential acidity  $H+Al$  ( $\text{cmol}/\text{dm}^3$ ), percentage of Al saturation ( $m\%$ ), soil organic matter (SOM). (n samples=72).

**FIGURE 3** Correspondence analysis of soil nutrients and fertility indicators in areas of a chronosequence forest-sugarcane-pastureland in the Atlantic Forest biome.



Box-plots with different letters differed significantly in the independent Kruskal-Wallis H Test ( $p < 0.05$ ). (n samples=72).

**FIGURE 4** a.b.c.d. Soil exchangeable bases (a), percentage of base saturation (V%) (b) potential and effective cations exchange capacity (PCEC and ECEC, respectively) ( $\text{cmol}/\text{dm}^3$ ) (c,d), from a chronosequence forest-sugarcane-pastureland in the Atlantic Forest biome.

that did not differ significantly (Figure 6a) ( $p = 0.002$ ). Increased soil  $\delta^{15}\text{N}$  values were found in sugarcane soils (7.5 ‰), with pastures and forest not showing any significant difference (5.8 and 5.2 ‰, respectively) ( $p > 0.05$ ) (Figure 7 b). Soil C% was greater in forest and pastures (5.3 and 5.5%, respectively) compared to sugarcane soils (2.6%) ( $p < 0.05$ ) (Figure 6c.). The same was observed for N%, with forest and pastures (0.28 and 0.27%, respectively) showing greater concentrations than sugarcane (0.15%) ( $p < 0.05$ ) (Figure 6d.). Cluster analysis of the isotopic profiles ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) evidenced that sugarcane and pastures soils showed more similarities between their isotopic compositions in comparison to forest soils (Figure 7).

## DISCUSSION

### Soil fertility

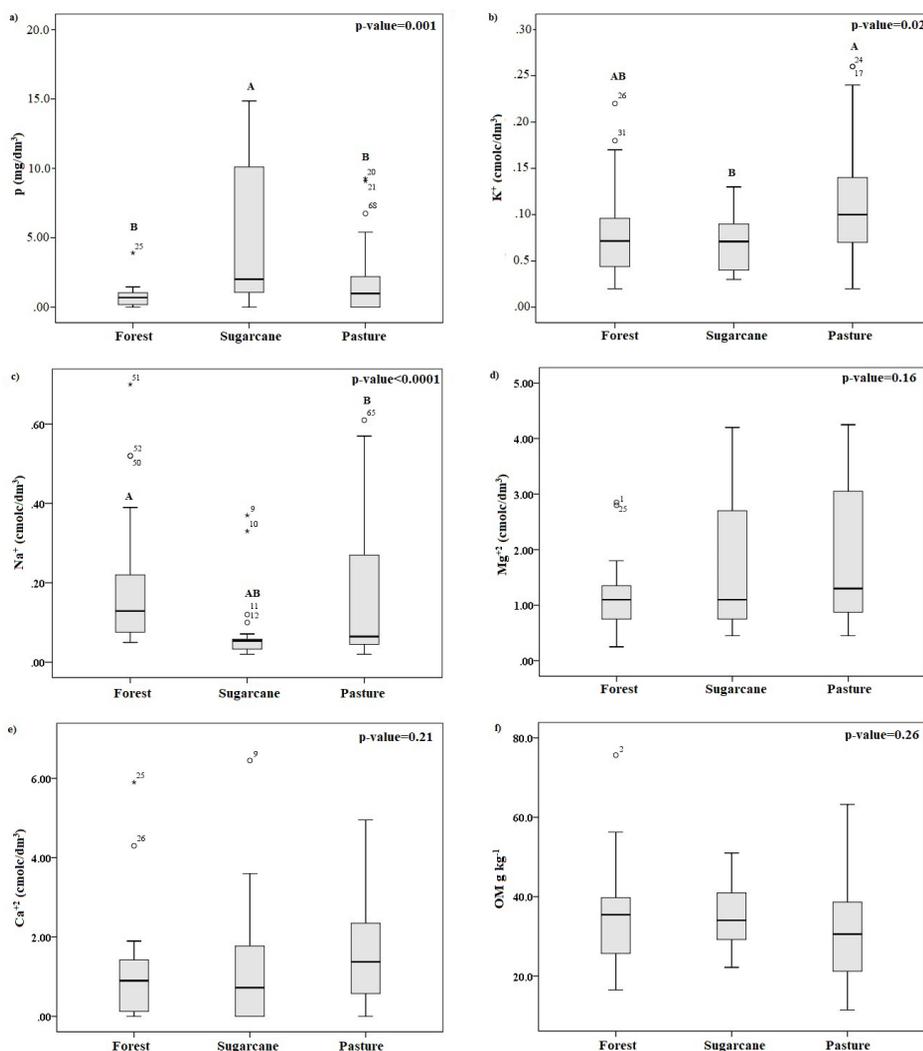
Differences in acidity levels between forest and cultivated soils can be associated with the fact that the areas of sugarcane and pasture in a given period received lime or fertilizer after forest conversion. In previous studies in the Atlantic biome, a consequence of the conversion of the forest to agricultural lands was the increment in the pH levels and the reduction of acidity parameters (Barreto et al., 2006; Barreto et al., 2008). The usual lower pH of forest soils in comparison to cultivated lands is generally associated with the natural acidity from organic matter mineralization, and acid exudates ( $\text{H}^+$ ) released by the roots of the forest vegetation (Barreto et al., 2006).

In contrast to agricultural areas, the high concentrations of  $\text{Al}^{+3}$  and  $\text{H}+\text{Al}$  found forest soils had a significant influence on the lower pH values found. The levels of the ion  $\text{Al}^{+3}$  is considered a critical factor for causing excessive acidity in soils (Alleoni et al., 2010; Haling et al., 2010). In practical terms, the  $\text{Al}^{+3}$  range levels between sugarcane and pasture were comparable, while the forest soil showed a slightly higher range for  $\text{Al}^{+3}$  which was associated with the lower pH. The relationship between soil pH and  $\text{Al}^{+3}$  levels in the present study was found to be expressed by the equation  $\text{Al}^{+3} = -0.5488 \cdot \text{pH} + 3.2718$  ( $R^2 = 0.61$ ;  $p < .0001$ ). According to Bojórquez-Quintal et al. (2017), under a low  $\text{pH} < 4.3$ ,  $\text{Al}^{+3}$  can have a major impact on plants in terms of toxicity and growth inhibition. Forest soils had the lowest pH found in the present ( $\text{pH} = 3.84$ ), which is associated with one of the greatest  $\text{Al}^{+3}$  concentrations ( $1.7 \text{ cmol}_c \cdot \text{dm}^{-3}$ ) found in the study. According to Nicolodi et al. (2008), crops can

**TABLE I** Coefficient of correlation between Soil pH (water – 1:2,5), Al<sup>3+</sup>, H+Al, P (Mellich I) (mg·dm<sup>-3</sup>), K<sup>+</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+</sup> (cmol<sub>c</sub>·dm<sup>-3</sup>); the sum of exchangeable bases, potential and effective cations exchange capacity (PCEC and ECEC, respectively) (cmol<sub>c</sub>·dm<sup>-3</sup>), percentage of base saturation (V%), potential acidity H+Al (cmol<sub>c</sub>·dm<sup>-3</sup>), percentage of Al saturation (m%), soil organic matter (SOM) g·kg<sup>-1</sup>, from a chronosequence forest-sugarcane-pastureland in the Atlantic Forest biome.

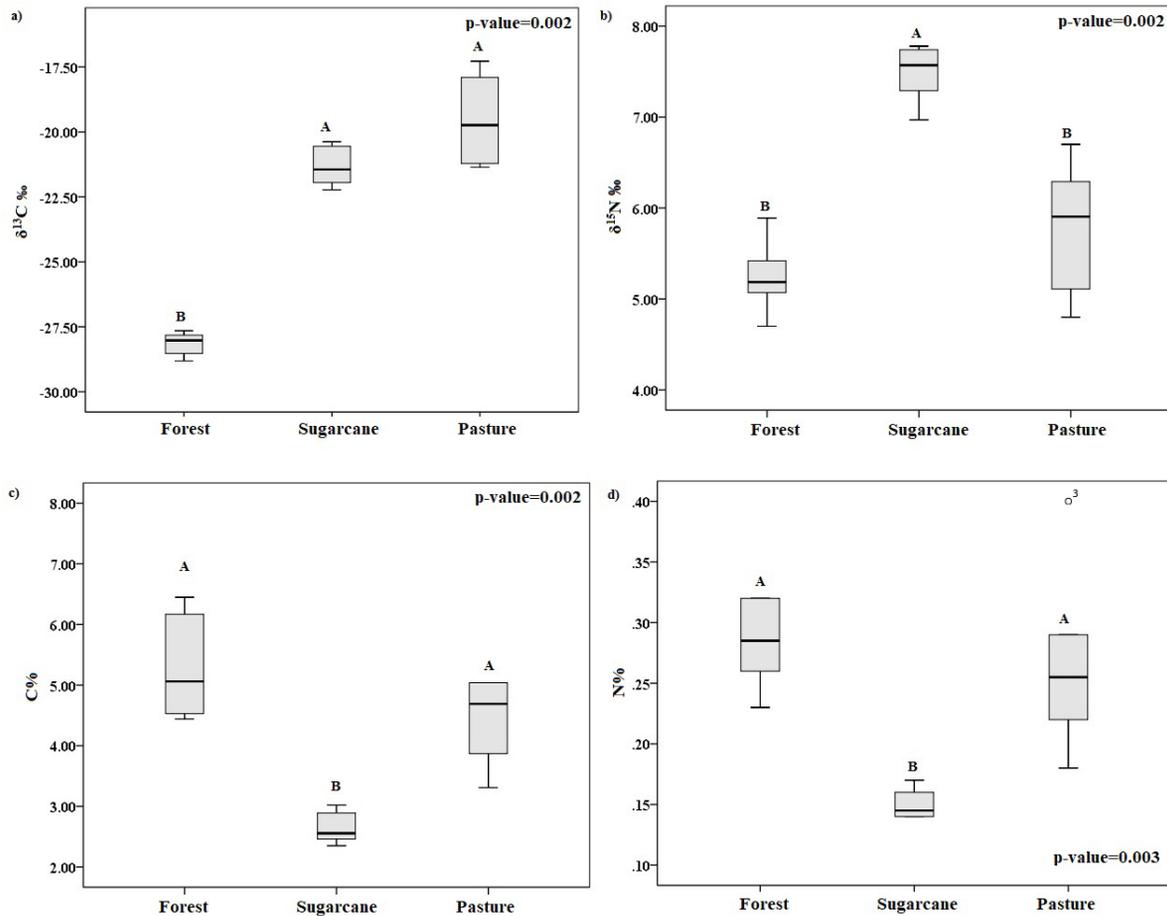
	Exchangeable Bases	PCEC	ECEC	V%	m%	pH	P	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Al <sup>+3</sup>	H+Al
PCEC	<b>0.9</b>												
ECEC	<b>1.0</b>	<b>0.9</b>											
V%	<b>0.9</b>	<b>0.7</b>	<b>0.9</b>										
m%	<b>-0.8</b>	<b>-0.5</b>	<b>-0.7</b>	<b>0.9</b>									
pH	<b>0.6</b>	<b>0.3</b>	<b>0.6</b>	<b>0.8</b>	<b>0.8</b>								
P	<b>0.2</b>	<b>0.2</b>	<b>0.2</b>	<b>0.2</b>	<b>0.2</b>	<b>0.3</b>							
Na <sup>+</sup>	<b>0.2</b>	<b>0.1</b>	<b>0.2</b>	<b>0.2</b>	<b>0.1</b>	<b>0.2</b>	<b>0.2</b>						
K <sup>+</sup>	<b>0.6</b>	<b>0.5</b>	<b>0.6</b>	<b>0.6</b>	<b>0.5</b>	<b>0.4</b>	<b>0.1</b>	<b>0.1</b>					
Ca <sup>+2</sup>	<b>0.8</b>	<b>0.7</b>	<b>0.8</b>	<b>0.8</b>	<b>0.7</b>	<b>0.6</b>	<b>0.4</b>	<b>0.2</b>	<b>0.5</b>				
Mg <sup>+2</sup>	<b>0.7</b>	<b>0.7</b>	<b>0.7</b>	<b>0.6</b>	<b>0.5</b>	<b>0.3</b>	<b>0.1</b>	<b>0.1</b>	<b>0.4</b>	<b>0.2</b>			
Al <sup>+3</sup>	<b>-0.6</b>	<b>-0.3</b>	<b>-0.4</b>	<b>0.6</b>	<b>0.9</b>	<b>0.8</b>	<b>0.3</b>	<b>0.0</b>	<b>0.3</b>	<b>0.6</b>	<b>0.3</b>		
H+Al	<b>-0.3</b>	<b>0.2</b>	<b>-0.2</b>	<b>0.5</b>	<b>0.6</b>	<b>0.7</b>	<b>0.1</b>	<b>0.2</b>	<b>0.2</b>	<b>0.3</b>	<b>0.0</b>	<b>0.6</b>	
SOM	<b>0.3</b>	<b>0.5</b>	<b>0.3</b>	<b>0.1</b>	<b>0.1</b>	<b>0.0</b>	<b>0.1</b>	<b>0.3</b>	<b>0.1</b>	<b>0.1</b>	<b>0.4</b>	<b>0.1</b>	<b>0.4</b>

Values in bold were significant for 2-tailed Pearson's correlation (p<0.05). (n samples=72).



Box-plots with different letters differed significantly in the independent Kruskal-Wallis H Test (p<0.05). (n samples=72).

**FIGURE 5** a.b.c.d.e.f. Soil P (Mellich I) (mg·dm<sup>-3</sup>), K<sup>+</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+</sup> (cmol<sub>c</sub>·dm<sup>-3</sup>) and organic matter (SOM) g·kg<sup>-1</sup>, from a chronosequence forest-sugarcane-pastureland in the Atlantic Forest biome.



Box-plots with different letters differed significantly in the independent Kruskal-Wallis H Test ( $p < 0.05$ ). (n samples = 18).

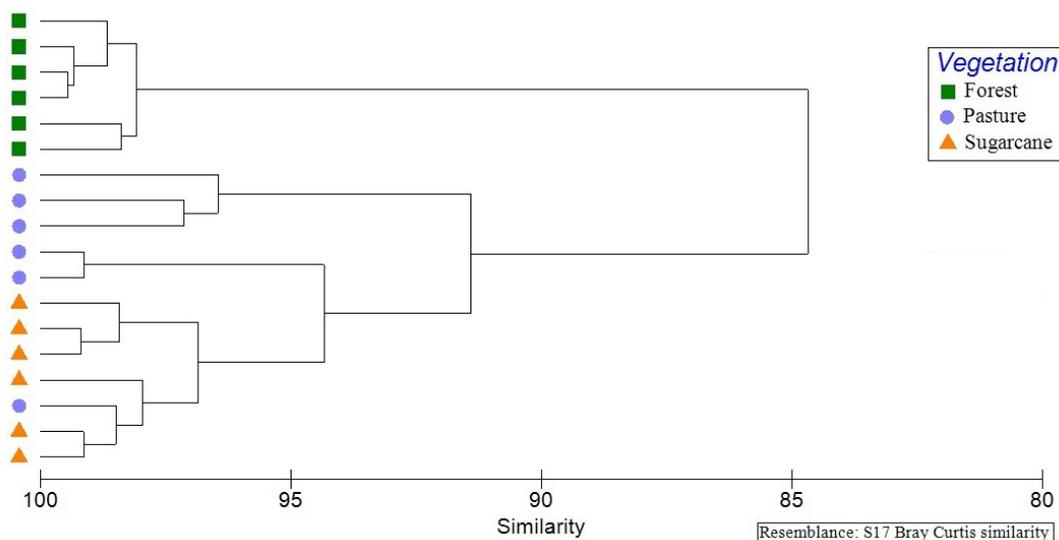
**FIGURE 6** a.b.c.d.  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  Soil isotopes, C% and N%, from a chronosequence forest-sugarcane-pastureland in the Atlantic Forest biome.

have their yields dropped by a slight increase from 0 to  $0.5 \text{ cmol}_c \cdot \text{dm}^{-3}$  of  $\text{Al}^{+3}$  in the soil.

The slightly higher pH levels found in sugarcane and pastures areas in comparison to the forest soils were a consequence of the management practices performed along the years after forest conversion. Among these practices, liming, fertilization, biomass harvesting and nutrient cycling via animal excreta are perhaps the most important ones. Liming is known for raising soil pH by neutralizing the active acidity ( $\text{H}^+$ ), and for precipitating  $\text{Al}^{+3}$  ions (Alleoni et al., 2010; Buni, 2014). The annual greater fertilizer inputs of the sugarcane that has been performed possibly contributed to the lower soil pH values found in comparison to pastures. Yearly applied NPK inputs via fertilization has been associated with decrements in pH of agricultural lands (Meng et al., 2013; Zhou et al., 2017). Annual harvesting is another factor that also might have contributed to the lower pH observed in the sugarcane soils compared to the pasture. Sugarcane vegetation has been entirely harvested yearly,

differently from the pastures that have been managed to allow enough residual mass for regrowth and have been maintained below the maximum stocking rate capacity. The harvesting of the crops leads removal and exportation of soil nutrients which can contribute to increasing soil alkalinity (Avila-Segura et al., 2011; Hao et al., 2019).

The slightly higher exchangeable bases concentrations and V% in the pastures and sugarcane soils in comparison to the forest soils is also an associative effect of management practices performed after conversion, especially fertilization and liming. Fertilization had been performed using NPK, that contributed for inputs of the exchangeable base  $\text{K}^+$  while liming ( $\text{CaCO}_3$ ), provided inputs of  $\text{Ca}^{+2}$ . These nutrient inputs were performed yearly in sugarcane areas, and as the pasture areas followed sugarcane in the chronosequence, possibly a residual effect of fertilization on sugarcane remained. It also should be considered that in the pasture areas, there is a tendency for a greater nutrient return to the soil compared to sugarcane, due to the contribution of the litter deposition (Vendramini



(n samples = 18)

**FIGURE 7** Cluster analysis of the soil based on  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  stable isotopes from a chronosequence forest-sugarcane-pastureland in the Atlantic Forest biome.

et al., 2007) and animal excreta (Faccio Carvalho et al., 2010). Despite there was no significant difference in SOM between land use (Figure 5 f), it also correlated positively with the potential cation exchange capacity (PCEC). Fageria (2012) reported that organic matter has a significant contribution to the soil cation exchange capacity, especially in soils with elevated pH.

### Soil C and N isotopic profiles

The natural abundance of  $\delta^{13}\text{C}$  in the soil reflects the plant material that mostly contributed to the soil organic matter (SOM). The greater depletion  $\delta^{13}\text{C}$  in forest soils in comparison with to the isotopic values found in both cultivated lands (sugarcane and pasture) is a consequence of the vegetation predominant in the area, and also the age that the soil organic matter was formed (Malone et al., 2018). The forest is mostly dominated by plants of metabolism  $\text{C}_3$  and the pasture and sugarcane  $\text{C}_4$ . Species with metabolism  $\text{C}_3$  have  $\delta^{13}\text{C}$  values in between -20 and -34 ‰, while  $\text{C}_4$  species vary between -9 and -17 ‰ (Alves et al., 2005; Liu et al., 2011). Malone et al. (2018) reported that the initial values of  $\delta^{13}\text{C}$  in a given plant material will depend on its photosynthetic pathway, where the  $\text{C}_3$  photosynthesis is known for discriminating strongly against the  $\delta^{13}\text{C}$  than plants with  $\text{C}_4$  metabolism during the isotopic fractioning. The influence of the type of predominant vegetation metabolism explains the greater isotopic similarities showed by sugarcane and pastures soils.

The succession of the forest by sugarcane and later by pasture modified the isotopic composition

of the original  $\delta^{13}\text{C}$  of the soil, via enrichment of the  $\delta^{13}\text{C}$  isotope. Nevertheless, a residual contribution of the original soil organic matter formed by the forest vegetation on the isotopic composition of sugarcane and pasture soils is speculated, as the  $\delta^{13}\text{C}$  of plant material from  $\text{C}_4$  is close to -13 ‰ (Liu et al., 2011), and the cultivated lands showed a  $\delta^{13}\text{C}$  between -19 ‰ to 21 ‰. Costa et al. (2009) noticed enrichment of  $\delta^{13}\text{C}$  from -29.08 ‰ to -18.83 ‰ in soils of Atlantic Forest converted into pastures of *Brachiaria brizantha* after 20 years from conversion. Desjardins et al. (2004) reported that the enrichment of  $\delta^{13}\text{C}$  in soils of pastures areas that followed a conversion from Amazon rainforest was time-dependent, increasing with the advance of the time. Differences observed in the soil isotopic composition ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ), especially concerning the forest, indicates that for this short chronosequence analyzed, detectable differences in the C and N profiles were mostly associated to the change between  $\text{C}_3$  dominant vegetation to  $\text{C}_4$ .

The greater  $\delta^{15}\text{N}$  in soils of sugarcane compared to forest and pastures soils can be associated with the annual nitrogen inputs via inorganic fertilization that the sugarcane has received over the years. Nitrogen fertilizer is enriched in  $\delta^{14}\text{N}$  when compared to soils. Once N fertilizer is applied in soils, soil bacteria will likely utilize the greater amount of  $\delta^{14}\text{N}$  in the fertilizer, leaving the  $\delta^{15}\text{N}$  behind. According to Stevenson et al. (2010), others processes that fractionate the  $\delta^{15}\text{N}$  in the soil are nitrification are denitrification and ammonia volatilization, in their study, there were greater  $\delta^{15}\text{N}$  in cultivated soils compared to native forests.

The  $\delta^{15}\text{N}$  signature in plants can also increase when N fertilizer is applied (Santos et al., 2018). Santos et al. (2018) reported an enrichment of the  $\delta^{15}\text{N}$  of *Paspalum notatum* roots after two years of N fertilization, the response was credited to a possible increase in the availability of SOM-N (rich in  $\delta^{15}\text{N}$ ) after N fertilization, and due to the decrease in the C:N ratio. Similar to our results, Franco et al. (2015) evaluating areas of a chronosequence (forest-pasture-sugarcane) also reported higher  $\delta^{15}\text{N}$  in sugarcane areas. The isotopic composition in our present trial was only measured in the depth of 0-20 cm, possibly, the soil  $\delta^{15}\text{N}$  could have a different profile in deeper soils horizons, as  $\delta^{15}\text{N}$  has been reported to increase with soil depth. The increment of  $\delta^{15}\text{N}$  in the function of the soil depth is attributed to the isotopic fractionation during litter decomposition and SOM formation (Marin-Spiotta et al., 2009; Franco et al., 2015).

## CONCLUSIONS

The short chronosequence of approximately 30 years after the forest conversion investigated in this study, pointed a strong influence of the alteration of the native forest into agricultural lands in to decreasing the natural acidity and modifying the original isotopic profile of the soil. Lime application after the conversion was possibly the main factor which contributed to the decrements of the concentrations of  $\text{Al}^{+3}$  and  $\text{H}+\text{Al}$  in the native soils converted. In terms of isotopes, there was an enrichment of  $\delta^{13}\text{C}$  in sugarcane (-21.3‰) and pastures (-19.5‰) areas, compared to forest soils (-28.1‰). As there is much interest in restoring forests, in areas currently occupied by sugarcane and pastures, forest managers should keep in mind that some agricultural soils possibly were too modified in terms of their chemical composition, which might impose a limitation on the establishment and development of previous native forest species.

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