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# IRON OXIDES AND QUALITY OF ORGANIC MATTER IN SUGARCANE HARVESTING SYSTEMS<sup>(1)</sup>

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## SUMMARY

Improvements in working conditions, sustainable production, and competitiveness have led to substantial changes in sugarcane harvesting systems. Such changes have altered a number of soil properties, including iron oxides and organic matter, as well as some chemical properties, such as the maximum P adsorption capacity of the soil. The aim of this study was to characterize the relationship between iron oxides and the quality of organic matter in sugarcane harvesting systems. For that purpose, two 1 ha plots in mechanically and manually harvested fields were used to obtain soil samples from the 0.00-0.25 m soil layer at 126 different points. The mineralogical, chemical, and physical results were subjected to descriptive statistical analyses, such as the mean comparison test, as well as to multivariate statistical and principal component analyses. Multivariate tests allowed soil properties to be classified in two different groups according to the harvesting method: manual harvest with the burning of residual cane, and mechanical harvest without burning. The mechanical harvesting system was found to enhance pedoenvironmental conditions, leading to changes in the crystallinity of iron oxides, an increase in the humification of organic matter, and a relative decrease in phosphorus adsorption in this area compared to the manual harvesting system.

**Index terms:** degree of humification, geochemistry, soil management, sustainable agriculture.

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## RESUMO: ÓXIDOS DE FERRO E QUALIDADE DA MATÉRIA ORGÂNICA EM SISTEMAS DE COLHEITA DE CANA-DE-AÇÚCAR

*Melhores condições de trabalho, produção sustentável e competitividade levaram a mudanças substanciais no sistema de colheita de cana-de-açúcar. Tais mudanças alteraram uma série de atributos do solo, incluindo os óxidos de ferro e a matéria orgânica, assim como alguns atributos químicos como a capacidade máxima de adsorção de P no solo. O objetivo deste trabalho foi caracterizar a relação entre óxidos de ferro e a qualidade da matéria orgânica nos sistemas de colheita de cana-de-açúcar. Para este fim, duas parcelas de 1 ha em áreas colhidas mecanicamente e manualmente foram utilizadas para obter amostras de solo da camada de 0,00-0,25 m em 126 pontos diferentes. Os resultados das análises mineralógicas, químicas e físicas foram submetidos às análises da estatística descritiva, com teste de comparação de médias, estatísticas multivariadas e análises de componentes principais. A aplicação da estatística multivariada possibilitou a divisão de todos os atributos estudados de acordo com o sistema de colheita: colheita manual com a queima dos resíduos da cana e colheita mecanizada sem queima. O sistema de colheita mecânica promoveu condições pedoambientais, que conduzem a mudanças na cristalinidade dos óxidos de ferro, no aumento no grau de humificação da matéria orgânica e na diminuição relativa de adsorção de P nessa área, em relação ao sistema de cana queimada.*

*Termos de indexação: grau de humificação, geoquímica, manejo de solo, agricultura sustentável.*

## INTRODUCTION

Sugarcane has emerged as a major source of clean energy in some countries in tropical areas. The main goal in the production of clean energy from sugarcane is of a social, environmental, and economic nature, and essentially involves improving working conditions, sustainability, and competitiveness in the sugar energy sector. Achieving this goal relies on the development of effective global indices for changes in soil use (Rockström et al., 2009), and tools which support sustainable production.

In regard to soil use, sugarcane has gone through major modifications in traditional cropping systems. For example, sugar energy crops in Brazil are currently being converted from manual harvesting and burning of the cane trash to mechanical harvesting without burning (Cerri et al., 2007). With mechanical harvesting, the heavy machinery and the amount of trash left on the soil surface (13 to 20 t ha<sup>-1</sup>, according to Schultz et al., 2010) cause changes in soil properties (Deickow et al., 2009) that in turn alter sugarcane yield (Tavares et al., 2010).

Leaving cane trash on the soil changes the soil organic matter (OM) content, soil quality (Mendonza et al., 2000; Canellas et al., 2007), and various soil properties, including some of those previously assumed to remain unchanged over long periods, such as the minerals in the clay fraction (Inda Jr. & Kämpf, 2005; Silva Neto et al., 2008). Some authors have shown that the establishment of these environmental conditions can affect the dynamics of iron oxides (Singh & Gilkes, 1992; Inda Jr. & Kämpf, 2005) and lead to a new dynamic equilibrium in the soil system through gradual changes in its mineral fraction (Silva Neto et al., 2008). Thus, Schwertmann & Kämpf (1985) found the dissolution of crystalline Fe oxides

(hematite and goethite) and subsequent neoformation of poorly crystalline species (ferrihydrite) to reflect the establishment of a new pedoenvironment. Moreover, Schwertmann & Carlson (1994) found changes in mean crystal diameter (MCD) of Fe oxides due to differences in their formation environments, the formation rate of Fe oxides, and crystallization inhibitors, such as the presence of OM and mineral age.

The content and crystallinity of the clay fraction in highly weathered soils (e.g. clayey Latosols [Oxisols]) have a strong influence on their properties (Ghidin et al., 2006), particularly as regards the ability to retain phosphorus (Rolim Neto et al., 2004; Barbieri et al., 2009). Phosphorus adsorption in soil depends markedly on the content and crystallinity of iron oxides, as well as on the content and quality of OM, which can compete with phosphate ions for sorption sites (Mesquita Filho & Torrent, 1993; Heredia & Cirelli, 2007). As a rule, organic substances convert positive charges at active sites in clay minerals and oxides into negative charges, thereby potentially reducing P adsorption (Valladares et al., 2003).

Novais & Smyth (1999) studied P adsorption in Latosols (Oxisols) from the Brazilian cerrado (tropical savannah) which adsorbed more than 2 mg cm<sup>-3</sup> P (equivalent to 4000 kg ha<sup>-1</sup> P or 9200 kg ha<sup>-1</sup> P<sub>2</sub>O<sub>5</sub>) in the 0-0.20 m layer. Goethite, along with hematite, are the predominant iron oxide in Latosols from this region (Inda Jr. & Kämpf, 2005), and are the greatest P sorbent (Motta et al., 2002).

Phosphorus availability is one of the main limiting factors for successful long-term cultivation of sugarcane, and supplying the soil with large amounts of usually expensive P fertilizers requires large investments that compromise economically

sustainable production (Motta et al., 2002; Rolim Neto et al., 2004). In addition to changes in soil use, the global indices proposed by Rockström et al. (2009) to describe the main problems of mankind include the rational usage of P.

The previous arguments testify to the importance of acquiring an improved knowledge of the impact of new sugarcane harvesting methods on soil properties (e.g. the clay mineralogy) and their potential interferences with chemical properties, with a view to ensuring sustainable management of tropical soils. This study was undertaken with the aim of establishing the influence of differences in OM content and quality on iron oxides and of establishing the maximum P adsorption capacity of soil in areas planted to sugarcane with different harvesting systems in the region of Ribeirão Preto, SP, Brazil.

## MATERIALS AND METHODS

The area under study was in Guariba, in the northern region of the state of São Paulo, Brazil. The fields had been cropped with sugarcane for more than 20 years. They were located at 21° 24' S, 48° 09' W, at an average elevation of 550 m above sea level. The climate of the region, according to the Köppen classification, is tropical hot humid (Aw), with dry winters mean annual rainfall of 1,400 mm, and mean annual temperature of 22 °C. In the summer, the maximum monthly temperature rises to 30 °C, rainfall exceeds 200 mm month<sup>-1</sup>, and relative humidity averages 80 %. The minimum average temperature in the winter is about 13 °C, the mean pluvial precipitation is 20-30 mm, and mean relative humidity is approximately 60 %. Vegetation in the Guariba region is sub-deciduous tropical forest.

The study area was located in the geomorphological region of the São Paulo Western Plateau, in the vicinity of the Basalt Slopes of the sandstone-basalt lithostratigraphic division (i.e., the boundary between the basalt in the São Bento Group of the Serra Geral formation and the sandstone in the Bauru Group of the Adamantine formation), as recorded by Souza et al. (2006). The soil was a Latossolo Vermelho eutroférico with a highly clayey texture (LVef-Oxisol) according to the Brazilian System of Soil Classification (Embrapa, 2006).

The study was conducted in two neighboring areas 100 m apart. Area 1 had been mechanically harvested, without burning of sugarcane (Mec), for the last 7 years, and area 2 had been manually harvested, with burning of sugarcane (Man), for the last 30 years. Soil samples for physical and chemical analyses were collected in June 2007, following the first cane cutting. Soil samples were collected from the 0.00-0.25 m topsoil layer at 126 points which were 10 m apart in

each of two georeferenced grids of approximately 1 ha in size (200 × 50 m).

The fields had been renewed in 2006 by removing the stubble after subsoiling. The soil was amended with calcareous dolomite at a rate of 2 t ha<sup>-1</sup> and agricultural gypsum at a rate of 1 t ha<sup>-1</sup> prior to planting. In addition, a 10-25-25 N-P-K fertilizer formula was manually applied at a rate of 500 kg ha<sup>-1</sup> at the time of planting. Prior to the 2006 renewal, the soils in both areas were supplied with 100 m<sup>-3</sup> of vinasse, 300 kg ha<sup>-1</sup> of urea in burnt cane and 200 kg ha<sup>-1</sup> of ammonium nitrate in unburnt cane.

Particle size distribution of the soil was determined according to Embrapa (1997), and pH and OM, P, K, Ca, and Mg contents were determined according to Raij et al. (2001). The sum of bases (SB), cation-exchange capacity (CEC), and base saturation (V%) properties were calculated from the bases and H+Al contents. Phosphorus adsorption was determined according to Casagrande & Camargo (1997) by adding a 100 mg L<sup>-1</sup> P solution to the soil samples and subtracting the amount of P remaining in solution from that initially added.

A total of 20 points in each area were used to determine the degree of humification of soil OM according to Milori et al. (2006). The procedure involved preparing pellets 2 mm thick and 10 mm in diameter (about 0.5 g in weight) by using a hydraulic press at 12 t for 3 min. Laser-induced breakdown spectroscopy (LIBS) is an advanced analytical technique for measuring excited species in a laser-induced plasma. Laser-induced fluorescence spectroscopy (LIFS) relies on excitation of the samples with an emission laser in the UV/blue region to measure the fluorescence of functional groups related to humification in OM. Such fluorescence gives a peak at about 510 nm in the visible spectral region. Total fluorescence as determined from the area under the spectral curve is correlated with the C content of the soil, and weighting it against the organic C content in a sample as determined by LIBS provides a measure of humification in OM.

Goethite and hematite were characterized in powdered samples following treatment of the clay fraction with 5 mol NaOH L<sup>-1</sup> (1 g of clay in 100 mL of solution) in order to concentrate iron oxides through the method of Norrish & Taylor (1961) as modified by Kämpf & Schwertmann (1982). The samples were washed with 0.5 mol L<sup>-1</sup> HCl (1 g of clay per 100 mL of solution) under shaking for 4 h in order to remove sodalite and suppress its potential interference with some X-ray diffraction lines. Position shifts in reflection (*d*) were corrected by supplying the samples with 10 wt% ground sodium chloride screened through 0.10 mm mesh prior to recording of the XRD patterns, which were obtained on a HGZ instrument equipped with a cobalt cathode and iron filter, and operated with K<sub>α</sub> radiation (20 mA, 30 kV) at a rate of 1 °2θ min<sup>-1</sup>

over the range of 23-49 °2 $\theta$ . All samples were ground and screened through 0.10 mm mesh. Table 1 shows the results of the chemical, particle size, and physical characterization analyses of the soil in the two areas under study.

The reflections used for characterization were  $d_{012}$  and  $d_{110}$  for hematite (Hm), and  $d_{110}$  and  $d_{111}$  for goethite (Gt). The mean crystal diameter (MCD) of the two minerals was calculated from width at half height (WHH) and the position of the  $d_{110}$  reflection for both Hm and Gt. MCD was obtained from the Scherrer equation (Schulze, 1984). The Gt/(Gt + Hm) ratio was obtained from the  $d_{012}$  and  $d_{110}$  reflections for Hm and Gt, respectively, the area of

the  $d_{110}$  reflection for Gt being multiplied by 0.35 to correct for the intensity of the  $d_{012}$  line for Hm (35 %) (Kämpf & Schwertmann, 1998). Dithionite-extractable Fe<sub>d</sub> was converted into hematite and goethite contents.

The soil properties were subjected to multivariate statistical analysis following standardization to zero average and unity variance. Principal component analysis (PCA) is typically used to explain the structure of the variance in the results with a reduced number of uncorrelated variables (principal components, PCs) established by linear combination of the original variables (Mardia et al., 1997; Hair et al., 2005).

**Table 1. Characterization, mean, maximum and minimum values; and coefficient of variation properties of chemical, grain size and physical of the soils in the two zones under study**

Property	Harvesting system	Mean	Minimum	Maximum	CV <sup>(4)</sup>
					%
pH	Mec <sup>(5)</sup>	4.9 b	4.3	5.5	5.0
	Man <sup>(6)</sup>	5.3 a	4.7	6.0	4.7
P <sub>available</sub> (mg dm <sup>-3</sup> )	Mec	36.0 b	22.0	52.0	16.2
	Man	67.0 a	17.0	143.0	51.6
Ca <sup>2+</sup> (mmol <sub>c</sub> dm <sup>-3</sup> )	Mec	28.0 b	11.0	45.0	26.0
	Man	43.0 a	23.0	59.0	16.6
Mg <sup>2+</sup> (mmol <sub>c</sub> dm <sup>-3</sup> )	Mec	8.0 b	4.0	15.0	28.4
	Man	10.0 a	5.0	14.0	19.4
K <sup>+</sup> (mmol <sub>c</sub> dm <sup>-3</sup> )	Mec	1.4 b	0.4	3.2	47.5
	Man	3.2 a	0.5	6.5	37.7
H+Al (mmol <sub>c</sub> dm <sup>-3</sup> )	Mec	37.0 a	22.0	52.0	16.5
	Man	30.0 b	18.0	47.0	18.7
SB (mmol <sub>c</sub> dm <sup>-3</sup> ) <sup>(1)</sup>	Mec	37.7 b	15.0	64.0	25.6
	Man	55.7 a	30.0	84.0	16.7
CEC (mmol <sub>c</sub> dm <sup>-3</sup> ) <sup>(2)</sup>	Mec	75.4 b	57.0	94.0	11.2
	Man	86.1 a	53.0	115.0	11.1
V (%) <sup>(3)</sup>	Mec	50.0 b	28.0	71.0	18.9
	Man	65.0 a	51.0	76.0	8.4
Clay (g kg <sup>-1</sup> )	Mec	637.0 a	580.0	690.0	3.2
	Man	613.0 b	560.0	660.0	3.4
Silt (g kg <sup>-1</sup> )	Mec	75.0	40.0	120.0	22.2
	Man	58.0	30.0	90.0	23.9
Total sand (g kg <sup>-1</sup> )	Mec	289.0	24.0	35.0	7.6
	Man	328.0	29.0	37.0	5.3
Bulk density (kg dm <sup>-3</sup> )	Mec	1.29 b	1.14	1.42	5.0
	Man	1.35 a	1.01	1.55	9.8
Macroporosity (%)	Mec	14.0 a	6.0	26.0	30.5
	Man	11.0 b	4.0	27.0	50.2
Microporosity (%)	Mec	37.0 a	30.0	41.0	6.1
	Man	36.0 a	28.0	44.0	7.5
Total pore volume (%)	Mec	50.0 a	43.0	58.0	6.2
	Man	47.0 b	37.0	58.0	9.2

<sup>(1)</sup> Sum of bases; <sup>(2)</sup> cation exchange capacity; <sup>(3)</sup> base saturation; <sup>(4)</sup> coefficient of variation; <sup>(5)</sup> mechanical harvesting without burning; <sup>(6)</sup> manual harvesting with burning. Means followed by the same letter in the same property are not significantly different by the Student t-test at 5 %.



The results were also subjected to hierarchical cluster analysis according to Sneath & Sokal (1973) in order to establish groups, each containing similar samples in terms of specific variables and differing from all others in this respect (Webster & Oliver, 2009). Dissimilarity coefficients were calculated from Euclidean distance (Hair et al., 2005).

The clustering strategy applied to the target soil properties was the complete linkage algorithm, which allows the number of clusters formed to be defined in various ways, including assisted selection and intuitive selection (Mardia et al., 1997), by which the researcher establishes the clustering level according to an easily understood criterion. So, in this study, the Euclidean distance of 3.25 was chosen since it can identify the influence of both management practices under study.

## RESULTS AND DISCUSSION

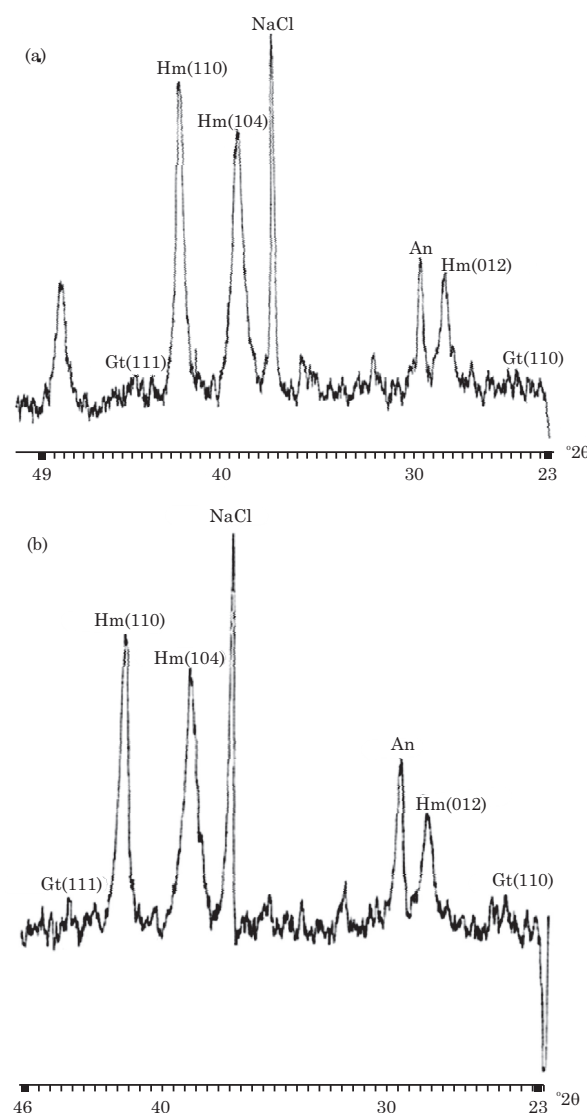
Hematite had a higher degree of crystallinity than goethite in both areas sampled (Table 3). In addition, the manually harvested area exhibited a higher MCD compared to the mechanically harvested one. The XRD patterns of both areas are shown in figure 1. Conversely, Gt exhibited a lower MCD in the manually harvested area - it was, in fact, the lowest level of this property found in this study. According to Fitzpatrick & Schwertmann (1982), a higher MCD value also reflects a higher degree of crystallinity.

The MCD values are very similar to those previously found by Camargo et al. (2008) in clayey Latosols. Ghidin et al. (2006) reported MCDs of 19-39 nm for Hm in various types of Brazilian Latosols. These results confirm previous reports by several authors (Inda Jr. & Kämpf, 2005; Silva Neto et al., 2008) that switching to a different harvesting system can alter major clay minerals in Latosols and various other soil properties as a result. As can be seen from table 2, Gt exhibited greater differences between harvesting systems than did Hm, which is consistent with previous results from Camargo et al. (2008) and suggests that Hm is less sensitive to environmental changes than is Gt.

There were significant differences in Hm contents between the two areas, but not in Gt; furthermore, Hm contents exceeded Gt contents in both. The prevalence of Hm over Gt was previously observed by Silva Neto et al. (2008) and Ghidin et al. (2006), who ascribed this to differences in chemical and mineralogical composition between the original materials, the climate of the sampling zones, the drainage conditions, and removal of Si from the soil. However, the difference in Hm contents between the two zones cannot be solely ascribed to the original material or to climate since both zones were very close

and differed merely in the harvesting method used. Our results suggest that the environmental differences arising from the large amounts of trash left on the soil in the mechanically harvested zone may affect not only properties related to crystallinity but also the contents in clay minerals. The prevalence of Hm in the manually harvested area was confirmed by the  $Gt/(Gt+Hm)$  ratio, which was lower in the mechanically harvested zone (Table 3).

Fed levels were higher in the mechanically harvested zone. Although the Fed contents include all pedogenic forms of iron in the soils, the difference found in this study among its contents can be attributed mainly to crystalline iron oxides. The higher Fed values in the mechanized harvesting area are related to better crystallized goethite. The OM content in the soil environment favors the formation of goethite relative to hematite (Inda Jr. et al., 2013).



**Figure 1. Diffractogram of iron oxide concentrated in the clay fraction of Latosols. (a) Mechanical harvesting; (b) Manual harvesting.**

**Table 2. Mean, maximum and minimum values, and coefficients of variation, of the chemical and mineralogical properties in the 0.00-0.25 m layer of the soils under the two harvesting systems**

Property	Harvesting system	Mean	Minimum	Maximum	CV <sup>(8)</sup>
					%
MCD <sup>(1)</sup> Hm <sup>(2)</sup> (110) (nm)	Mec <sup>(9)</sup>	53.93 b	53.78	54.02	0.1
	Man <sup>(10)</sup>	57.27 a	52.57	90.88	18.6
MCD Gt <sup>(3)</sup> (110) (nm)	Mec	41.34 a	23.28	86.91	45.2
	Man	28.23 b	19.69	86.85	30.6
Hm (110) (g kg <sup>-1</sup> )	Mec	167.90 a	132.0	195.10	7.6
	Man	115.30 b	48.20	152.50	15.8
Gt (110) (g kg <sup>-1</sup> )	Mec	25.70 a	10.50	61.60	39.0
	Man	26.70 a	9.50	64.30	43.7
Ratio Gt/(Gt+Hm)	Mec	0.12 b	0.05	0.22	29.8
	Man	0.17 a	0.01	0.55	44.6
Fed <sup>(4)</sup> (g kg <sup>-1</sup> )	Mec	14.00 a	11.00	15.00	5.0
	Man	9.00 b	6.00	13.00	13.1
OM <sup>(5)</sup> (g dm <sup>-3</sup> )	Mec	24.00.a	15.00	34.00	3.5
	Man	25.00 a	16.00	34.00	2.7
H <sub>LIFS</sub> <sup>(6)</sup>	Mec	231.00 a	198.00	280.00	9.0
	Man	180.00 b	158.00	204.00	8.0
P <sub>ads</sub> <sup>(7)</sup> (mg kg <sup>-1</sup> )	Mec	373.00 b	171.00	514.00	19.0
	Man	415.00 a	129.00	790.00	39.5

<sup>(1)</sup> Mean crystal diameter; <sup>(2)</sup> hematite; <sup>(3)</sup> goethite; <sup>(4)</sup> dithionite-extracted iron; <sup>(5)</sup> organic matter; <sup>(6)</sup> degree of humification; <sup>(7)</sup> adsorbed phosphorus; <sup>(8)</sup> coefficient of variation; <sup>(9)</sup> mechanical harvesting; <sup>(10)</sup> manual harvesting. Means followed by the same letter in the same property are not significantly different by the Student t-test at 5 %.

Silva Neto et al. (2008) found the distribution of Fe forms and the Feo/Fed ratio to be negatively correlated with the carbon contents in OM and the humin fraction; they ascribed these relationships to redistribution of iron oxides, possibly through reductive dissolution. Inda Jr. et al. (2013) studied the dynamics of iron oxides based on management systems and found negative correlations between soil crystalline iron oxides and organic carbon content in areas with no-tillage.

Unlike previously reported values for OM contents (Canellas et al., 2007; Silva Neto et al., 2008), ours exhibited no significant differences between the two areas. In contrast, the degree of humification differed markedly (Mendonza et al., 2000; Guimarães et al., 2013) and was higher in the mechanically harvested area. The increased humification of this area, together with the increased MCD values of goethite in it, suggests a tendency toward a new dynamic equilibrium via gradual mineralogical changes in the soil system (Karathanasis & Wells, 1989). Inda Jr. & Kämpf (2005) examined the selective dissolution of Fe oxides and concluded that goethite heterogeneity was possibly a result of pedoenviromental changes during the pedogenetic process; such changes altered the factors governing Al<sup>3+</sup> activity in the soil solution (e.g. pH, the contents in organic compounds, base saturation, and Si concentration).

The crystallinity of these minerals affects their specific surface area and hence their ability to adsorb P and various other surface phenomena (Rolim Neto et al., 2004). The adsorbed phosphorus (P<sub>ads</sub>) was significantly lower in the mechanically harvested zone, which was that which exhibited greater MDC, Gt, and OM humification values. These results strengthen the hypothesis that P adsorption is only affected by the quality of OM in the soil, not only because OM competes with phosphate ions for adsorption sites (Mesquita Filho & Torrent, 1993; Heredia & Cirelli, 2007), but also because it provides pedoenviromental conditions that potentially affect the dynamics of pedogenic iron oxides (Kämpf & Curi, 2000) by favoring their main reactions: dissolution, reduction, and complexation (Schwertmann, 1991; Silva Neto et al., 2008).

Valladares et al. (2003) examined P adsorption in soils with low clay activity and found that those with a clayey texture adsorb higher amounts of P. Our highest P<sub>ads</sub> levels were those of the soils with the lowest clay contents (Table 1), which strengthens the hypothesis that the quality of the clay is as influential as or even more so than its content in the soil (particularly in highly clayey, weathered soils).

The manually harvested zone exhibited higher pH and V% values than the mechanically harvested area (Table 1). Guilherme et al. (2000) found an increase in pH to result in a decrease in the amount of positive

charge in the soil colloid fraction and hence in a reduction in P adsorption. In this study,  $P_{ads}$  was greater in the manually harvested zone, which exhibited more suitable chemical conditions (pH and V%). This further supports the previous results and suggests that if the chemical properties of the soil in the two areas had been similar, the differences in  $P_{ads}$  between the two harvesting systems would have been even greater than those obtained in this study.

The cycling and use of P is one of the major obstacles for the future of agriculture. In tropical soils, this problem is even greater. In these regions, there are real sinks for applied P, such as the iron oxides of hematite and goethite (Camargo et al., 2013). The reactivity of these oxides is related to the size of the crystals. Smaller crystals have greater specific surface area, reactivity, and P-adsorption. Our results suggest that change in the sugarcane harvesting system (with or without burning) promotes changes in the quality of OM, represented by the humic substances. Changes in the subfractions of OM promote the selective dissolution of the most reactive iron oxides, causing the release of previously adsorbed P. This information may assist the understanding of other systems, such as no-till farming and natural forest systems (Zhang et al., 2006; Wei et al., 2011) enabling better understanding of P cycling in these management systems.

The first component (PC1) explained 33.16 % of the variance in the target soil properties and the first two (PC1 and PC2) jointly explained 53.98 % (Figure 2). Siqueira et al. (2010), in a previous study of some soil properties, found the first two PCs to account for 57.62 % of the variance in combination; in addition, Carvalho Jr. et al. (2008) examined various physical and chemical properties of soil and found PC1 to explain 28.29 % of their variance. The main goal of

PCA is to find a data set for a property explaining, to a significant extent, the variance in the whole sample population via linear correlations. According to Theodoropoulos et al. (1997), PCA is useful in soil science to select the specific variables most markedly influencing pedogenetic processes.

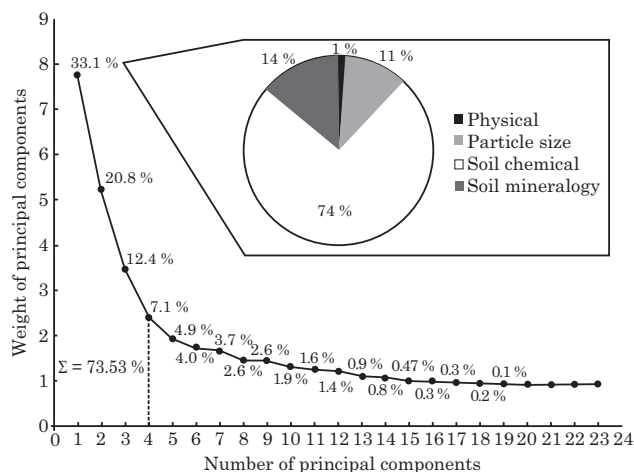
The chemical properties were the greatest contributors to PC1, with 74 %, followed by particle size distribution (14 %) and mineralogical properties (11 %), and, far behind, the physical properties (1 %). Carvalho Jr. et al. (2008) applied PCA to Brazilian Ultisols and found the chemical properties to be greater contributors than the physical properties to PC1. The 23 soil properties studied here can be grouped into as few as four components. This may provide a better understanding of causal relationships between soil properties and the management strategies used by the sugar energy sector with a view to their improvement.

The first two PCs were used to construct the biplot of figure 3. As can be seen, the results clustered in two groups, coinciding with the harvesting methods: mechanical (X) and manual (O). Campos et al. (2012), in a previous study, used PCA to examine soil properties in various geomorphically different surfaces and obtained three groups coinciding with the three surfaces assessed.

As can be seen, the soil growing manually harvested sugarcane (O) exhibited higher levels of available P, pH, and K but lower hematite contents and goethite mean crystal diameters. This harvesting system is known to result in increased levels of adsorbed P, degree of OM humification, and goethite MCD. As previously shown by Camargo et al. (2008), the minerals in the clay fraction in tropical soils are effective pedoenvironmental indicators by virtue of their neoformation in well-defined locations. Our results also indicate that mineralogical properties can be used as environmental indicators by the sugar energy sector. This can be useful towards better understanding of the mid- and long-term relationships between OM quality, crystallinity-related properties, and nutrient availability, as determined by selective dissolution, by the effect of switching to a different harvesting system for sugarcane, or, in general, any crop type producing an increasing amount of agricultural residues left on the soil each year.

Recent studies have demonstrated the potential of PCA for elucidating pedology-geomorphology relationships (Barrios et al., 2012; Campos et al., 2012). Based on our results, such relationships can be effectively used to better understand the relationships between edaphic, geochemical and soil management factors.

The degree of humification, hematite content, and adsorbed P values clustered (Figure 3) in such a way that they allowed the two harvesting systems to be

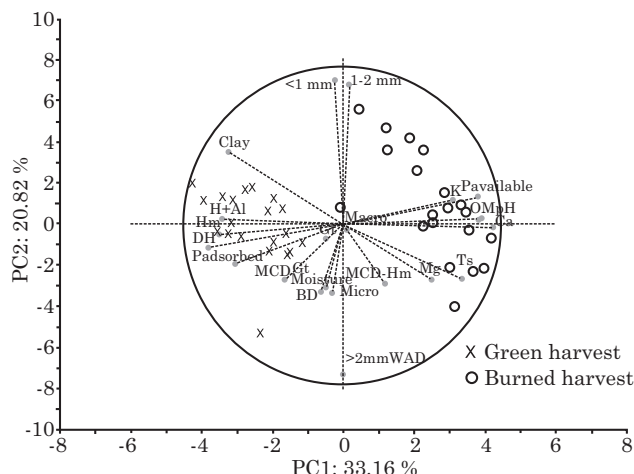


**Figure 2.** Variance in the body of properties explained by each principal component and contribution of soil chemistry, particle size distribution, soil physical and soil mineralogical properties to PC1.

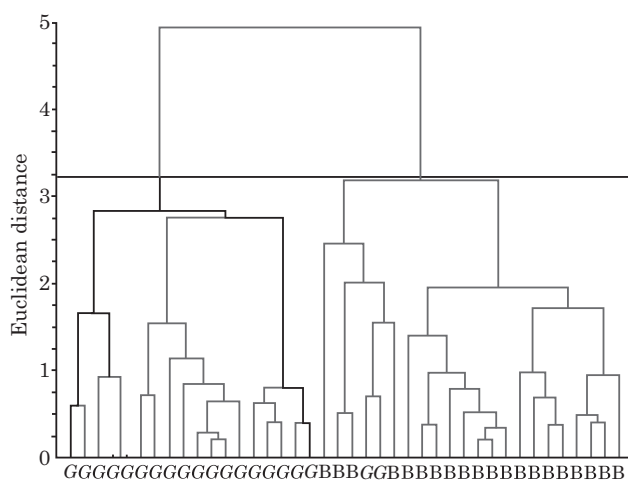


clearly distinguished (Figure 4). Therefore, cluster analysis allowed the successful identification and separation of the two harvesting systems; in fact, the target properties were similar for the soils harvested

with each method but differed from those of the soils harvested with other (Webster & Oliver, 2009). This confirms that multivariate statistical analysis allows minimal variability within a group and maximal variability with another to be detected (Yemefack et al., 2005).



**Figure 3. Scatter biplot of PC1 and PC2: clay content, total sand (TS), weighted average diameter (WAD), aggregates greater than 2 mm in size (> 2 mm), aggregates smaller than 1 mm (< 1 mm), aggregates 1-2 mm in size (1-2 mm), macropores (macro), micropores (micro), soil density (BD), moisture, Ca, Mg, K, H+Al, pH, P adsorbed, P available, degree of humification (DH), hematite content (Hm), goethite content (Gt), mean crystal diameter of hematite (MCD-Hm), and mean crystal diameter of goethite (MCD-Gt) in the 0.00-0.25 m soil layer. n = 40.**



**Figure 4. Dendrogram illustrating the mutual relationships between the two harvesting systems considering physical, chemical and mineralogical properties in the 0.00-0.25 m layer of soil. G: mechanical (green) harvesting, B: manual harvesting (with burning). n = 40.**

## CONCLUSIONS

1. All the soil properties in this study allowed the formation of two groups, coinciding with the harvesting systems used in the two areas (mechanical and manual) as established by multivariate statistical analysis. Therefore, this analytical tool can be useful for strategic planning of changes in current harvesting methods for sugar energy crops without altering soil properties to the extent of compromising their yield.

2. The pedoenviromental conditions resulting from the presence of large amounts of cane trash left on the soil with the mechanical harvesting system altered goethite crystallinity, increased organic matter humification, and reduced phosphorus adsorption in relation to the manual harvesting system.

3. The mean crystal diameter of goethite can be used as a pedoenviromental indicator of the relationship between organic matter quality, crystallinity related properties, and nutrient availability as determined by selective dissolution in similar locations.

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