

# Organic Matter of the Anthropogenic Dark Earths of Amazônia

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## ABSTRACT

The anthropogenic dark earths (ADE, Terra Preta de Índio or terra preta arqueológica, as are often referred to in Portuguese) feature unique properties that are interesting not only from a pedological point of view but have important agronomic and economic relevance. Among other properties, the organic matter (SOM) of these soils is considerably different from that of other mineral soils. Besides the quantity of SOM, its origin, composition and, consequently, function in the soil is different. Carbonized biomass (pyrogenic carbon) is a principal constituent of ADE that was, to our best knowledge, gradually incorporated into these soils, 4 to 10 thousand years ago, by native dwellers of the Amazon region. The carbon of pyrogenic origin was not only accumulated in ADE, but it also played important role in the transformation of organic matter and the humification process. As a result of this, the SOM of ADE is relatively stable, compared to the SOM of adjacent ferralsols, and at the same time it has chemical reactivity that is the major responsible for the higher cation exchange capacity and good buffer properties of these soils. These properties have very important environmental and agronomic relevance in the tropics due to organic carbon conservation in the soil and enhanced soil fertility. The ADE soils are excellent model for the development of modern soil fertility management practices.

**Keywords:** physical and chemical characteristics of soil organic matter, pyrogenic carbon, soil color, soil fertility, soil organic matter fractions, soil structure, Terra Preta de Índio

**Abbreviations:** ADE, anthropogenic dark earth; CEC, cation exchange capacity; DP/MAS NMR, direct polarization magic angle spinning nuclear magnetic resonance; EPR, electronic paramagnetic resonance; FOR, free organic radicals; HA, humic acid; SOM, soil organic matter; TM, Terra Mulata; TPI, Terra Preta de Índio; VACP/MAS NMR, variable angle cross polarization magic angle spinning nuclear magnetic resonance

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## INTRODUCTION

The organic matter in mineral soils (SOM) rarely exceeds 8%, except some soils in specific climatic or terrain conditions, like Organosols that contain more than 20% organic matter, by definition (IUSS Working Group WRB 2006) to a minimum depth of 40 cm (Embrapa 2006). The distribution of organic matter in the soil is variable, in depth (vertically in the soil profile) and horizontally. This distribution of the C in the soil is dependent on various factors, like soil type, terrain morphology, soil cover or use, climatic conditions, predominant natural vegetation, soil management practices, among others. The quality of organic matter is also of great importance, it is source of nutrients and energy for microorganisms and conditions soil functions. Among these generally great emphasis is given to water retention, soil structure and its stability, porosity, retention and availability of macro- and micronutrients due to the fact that SOM levels are regulating cation exchange capacity (CEC), principally in soils under tropical climate whose mineral

matrix is dominated by low activity clay minerals (kaolinite, iron and aluminum oxides like goethite and hematite). In the soils of Brazil SOM can contribute to CEC even in 80%, considering the whole soil matrix. Hence, variations in the quantity and quality of SOM are able to have a great effect on soil properties and processes. SOM also has an important role in nutrient cycling whose dynamics is still little known. For this reason, SOM management with focus on its conservation and improving its quality is fundamental for the maintenance and sustainability of tropical agroecosystems.

A great proportion of the soils that are suitable for agricultural production at the Amazon Region are acid with low CEC and, consequently, low fertility and production potential, that is a limiting factor for environmental and economic sustainability.

In this same region can be found the so-called anthropogenic dark earths (ADE; also known as Terra Preta de Índio - TPI or simply Terra Preta) that feature an anthropogenic A horizon, also called *archaeo-anthropedogenic* horizon,

denomination proposed by Kämpf *et al.* (2003). Different hypothesis were proposed as possible processes of formation of TPI but the actually most accepted is that these soils were formed by pre-historic populations (Woods and McCann 2001); however, there is still no consolidated opinion whether their activity was intentional (Neves *et al.* 2003). The areas where TPI occur now were places of pre-historic villages where great amounts of residues of vegetal and animal origin together with residues of cooking (fire) places (ash and charcoal). More recently, Birk *et al.* (2011), using biomarkers (5 $\beta$ -cholestan-3 $\beta$ -ol) in TPI compared to reference soils, showed that faeces were deposited on TPI and contributed to their genesis. This great quantity of organic matter contributed, most probably, to the formation of highly fertile soils with high levels of stable SOM of pyrogenic origin and also high levels of available phosphorus, calcium, magnesium and zinc (Kern 1988; Kern and Kämpf 1989; Kern 1996; Costa and Kern 1999). Apparently, in TPI there are proper micro-ecosystems that retain and make macro- and microelements available for a longer period of time than adjacent soils with no *archaeo-anthropedogenic* horizon, even under tropical climate and agricultural use.

Sombroek (1966) mentioned the so called Terra Mulata (TM) that are soils featuring high levels of P and carbon (C) but do not contain artifacts, however their formation was apparently associated to anthropogenic activity. It is believed that areas of TM had been utilized for agriculture and TPI, where high quantity of artifacts can be found, had been the actual day to day living habitat, the village. According to McCann *et al.* (2001) TMs have similar levels of organic C compared to TPI but lower levels of available P and Ca. Examples of TM around the Negro and Urubu Rivers had similar productivities than TPIs of the same regions (Lehmann *et al.* 2003). Because TM was also formed by human activity and has similar characteristics to TPI, Kämpf *et al.* (2003) suggested the use of the term *archeo-anthrosol* for all Amazonian anthropogenic soils.

The TPI is not a homogeneous group of soils regarding fertility and production potential. There might be great differences even between TPIs of a region and there is a great variability within one TPI site (Lehmann *et al.* 2003). Despite these differences some important soil fertility properties are shared by most TPI: high organic C levels, SOM with particular physical-chemical properties and high levels of available P, Ca and micronutrients, compared to adjacent soils like Oxisols among others.

One of the responsible factors for the different behaviours of these anthropogenic soils is the higher organic C content and principally the different quality of this organic C that has pyrogenic origins. The objective of this paper is to describe the organic matrix of TPI in comparison to that in adjacent soils that have no *archaeo-anthropedogenic* horizon, and to investigate the effect of the differences in SOM on the fertility properties of these soils.

### Characterization of the *archaeo-anthropedogenic* horizon of ADE

The characterization of soil horizons that had undergone anthropogenic influence comparing with similar horizons of similar but not anthropogenic soils is important to observe possible functions of SOM in TPI. Hence, characteristics that are different between TPI and adjacent soils are described below.

**Soil color.** The color of TPI in the *archaeo-anthropedogenic* horizon is, in general, as the name of these soils indicate, is black to very dark brownish grey (5YR 2.5/1; 7.5YR 2/0 to 3/1; 10YR 2/0 to 3/2) (Kämpf and Kern 2005), different from the color of adjacent non-anthropogenic soils whose color is generally determined by the color of the clay minerals of the soil matrix. This very characteristic property of TPI is due to the quantity (Kern and Kämpf 1989) and quality of the SOM present in these soils. Data from 56 soil profiles showed that while the mean organic C concentra-

tion in the surface 20 cm of TPIs was 30 g kg<sup>-1</sup> (CV=66%), in non-anthropogenic soils of the Amazon it was 17 g kg<sup>-1</sup> (N=47, CV=58%) at the same depth (Madari *et al.* 2003). In a general manner, the correlation between soil color and SOM concentration is low ( $r^2 = 0.31$ ; Schulze *et al.* 1993), however, there is a tendency for having darker color in SOM rich soils. In TPI the distribution between the chemical SOM fractions is different from that in adjacent soils. In TPI the more recalcitrant fractions, that are also more stable and persistent in the soil (humin and humic acids (HAs)), predominate in relation to the more soluble fractions (fulvic acids). The stability of organic matter is related to some molecular structures that are also responsible for the stability and persistence of SOM in TPI for a longer period of time as these are less sensitive to microbial decomposition. These molecular structures are, for example, hetero-poly-condensed, amorphous structures with high concentration of double conjugated links (Kumada 1965) and poly-aromatic structures. The more stable fractions of SOM, which predominate in TPI, have darker colors than the less stable ones (fulvic acids and low molecular weight organic acids). As mentioned before, the ADE also have elevated concentrations of charred materials (Glaser *et al.* 2000). The presence of these accentuate dark coloration as well (Schmidt and Noack 2000).

**Soil structure.** Chemical aspects of sustainable soil fertility management are very important but soil management for adequate physical status is equally relevant. The physical management of soils is highly relevant to soil fertility, agricultural productivity and the quality of the environment (Lal 2000). Soils under tropical climate feature, in general, good structure under natural vegetation. Examples are the kaolinitic clayey Ferralsols. However, under inadequate management, like frequent plowing, the originally well developed structure rapidly deteriorates, leading to crusting, compaction and subsequent erosion. The ADE also feature excellent physical properties. The bulk density of TPI in the superficial soil layers of the *archaeo-anthropedogenic* horizon is generally low ( $1.08 \pm 0.23$  g cm<sup>-3</sup>, N = 10), the porosity ( $58.83 \pm 9.07\%$ , N = 10) and water retention capacity is high (Teixeira and Martins 2003).

An interesting question is the effect of the pyrogenic carbon on soil physical properties. On one hand char, due to its porosity and, consequently, to its high surface area, can significantly improve water retention, especially in sandy soils. On the other hand, the aromatic structure of char that has hydrophobic characteristics may reduce water penetration into the pore space of soil aggregates, that way increasing aggregate stability (Glaser *et al.* 2002). Probably, due to the mixture of these characteristics the effect of charcoal on the physical properties of medium textured soils in most of the cases is not detectable and in clayey textured soils is negative (Tryon 1948). Almendros *et al.* (1992) described the evolution pathway of humic substances as affected by fire that could significantly contribute to the formation of soils with hydrophobic characteristics (repellent to water). Hence, the high concentration of pyrogenic C in association with its physico-chemical properties, such as high stability and reactivity at the same time (Zech *et al.* 1990; Golchin *et al.* 1997; Schmidt *et al.* 1999; Poirier *et al.* 2000), in fact may have contributed to the improvement of TPI properties, not only the chemical but physical ones as well.

**Soil fertility.** Compared to non-anthropogenic soils TPI, in general, feature clear tendency to have higher concentrations of organic C, Ca and Mg, higher pH and base saturation and smaller concentrations or non of exchangeable Al. These properties of TPI are responsible for the better fertility and production potential of TPI. Hence, however there is some overlapping between the fertility properties of TPI and adjacent soils, TPI generally feature higher fertility (Madari *et al.* 2003). The capacity of the soil to adsorb nutrients (Ca, Mg, base saturation), diminish toxicity of Al and the stabilization of pH are processes that are fundamen-

tally controlled by organic matter. Pabst (1992), investigating the principal differences between TPI and regular Ferralsols, also identified that those attributes that are associated with SOM (pH, organic C concentration, "humus structure" – stability to microbial decomposition, N, base saturation, CEC and available P) are the ones that make the most difference. While SOM concentration in TPI is a relevant factor, its composition and characteristics also contribute to the higher fertility of TPI.

### The organic matter of ADE

Processes of stabilization and mobilization affect the accumulation and decomposition of SOM and the equilibrium between these processes are of extreme importance for the formation and maintenance of the fertility of soils under tropical climatic conditions. These processes regulate recalcitrance and reactivity, or in other words, the capacity of SOM to interact with other materials and to be protected against chemical or biological decomposition (Sollins *et al.* 1996). The higher accumulation of organic C in TPI, compared to adjacent soils, indicate that at least a part of its organic matter has characteristics that give stability or little availability to the C associated to it. On the other hand, fertility data on TPI indicate that the SOM in these soils also has elevated chemical reactivity compared to the soils that have no *archaeo-anthropogenic* horizon. In the foregoing paragraphs the characteristics of the different SOM fractions will be described as they are in TPI.

**Chars.** Chars are generally reported as chemically inert and hydrophobic materials and, due to their high porosity, have large surface area (200-400 m<sup>2</sup> g<sup>-1</sup>, Kishimoto and Sugiura 1985). However, the reactivity, hydrophobic characteristics and structure of chars depend greatly on the characteristics of the material of which they are originated, on the conditions of their formation like temperature and duration of carbonization, humidity of the material, availability of oxygen, among others. However chars can be considered stable in the soil, compared to other forms of organic C, they also undergo biodegradation and transformation. Bird *et al.* (1999) suggested that pyrogenic C can be degraded significantly within the timescale of decades or centuries in soil under tropical climate. The half-life of carbonized particles greater than 2 mm was estimated to be shorter than 50 years and of particles larger than 2 mm shorter than 100 years. The degradation of char makes it possible that this material also takes part in the global C cycle. If this is not the case, that would implicate it in the accumulation of C in this form on the surface of the Earth in less than a thousand centuries (Kuhlbusch and Crutzen 1995 in Glaser *et al.* 2002). The biodegradation of chars in soil is a relatively slow process that results in the mobilization of C and in the alteration of the surface properties of chars, hence increasing the concentration of chemically reactive sites.

The quantity of char that is produced during carbonization depends on the originating material and duration and temperature of carbonization. Fearnside *et al.* (1999) reported that char formation during natural fire of a secondary Forest in the Amazon was between 1.6 and 1.8% of the original biomass. Fire in primary Forest resulted in 3.5-4.7% char (Fearnside *et al.* 1993; Graça 1999). In controlled conditions of carbonization, between 300 and 500°C in laboratory or in different carbonizing equipments, char production resulted in about 79.6%. Trompowsky *et al.* (2005), in controlled conditions, demonstrated that two eucalypt species, *E. saligna* and *E. grandis*, had a maximum production of char, 65%, at 300°C carbonization temperature. In that same study, it was also observed that the O/C ratio was higher (0.3) at 300°C and at 500°C it was reduced to 0.06, resulting in a material that contained 90% C in its total mass. The presence of oxygen in higher proportion may indicate higher reactivity of the analyzed char.

Hamer *et al.* (2004) investigated the "priming" effect of pyrogenic C and the mineralization of glucose. According

to these authors the mineralization of the pyrogenic C was stimulated by the addition of glucose to the soil and, vice-versa, the mineralization of glucose was stimulated by the presence of the pyrogenic C. The authors supposed that the effect of the carbonized material occurred because of its high superficial area that served as medium for microbial growth and consequently activity rather than because of higher availability of C since pyrogenic C, being highly aromatic, is not readily available as energy source. Hence, charcoal, however is relatively inert and highly stable in the soil, depending on the conditions of its formation and on the transformations it undergoes, it may have the capacity to contribute to enhance the chemical, physical and consequently biological properties of soils.

**The light fraction of SOM.** There are only a few studies on the contribution of pyrogenic C to the light fraction of SOM in TPI. This fraction is separated on the basis of the density of soil components after their total dispersion. Glaser *et al.* (2000) determined pyrogenic C in three density fractions:  $d < 2.0 \text{ g cm}^{-3}$  (light fraction),  $d = 2.0\text{-}2.4 \text{ g cm}^{-3}$  (medium fraction) and  $d > 2.4 \text{ g cm}^{-3}$  (mineral matrix of the soil to which organic C is associated by chemical and physical mechanisms) in TPI and adjacent non-anthropogenic Ferralsols. The observed that the contribution of pyrogenic C to the soil mass was higher in TPI in each separated fraction, being the largest in the medium fraction. In the Ferralsols the distribution of the pyrogenic C between the fractions was more balanced.

It is possible that the quantities of pyrogenic C were super estimated by the determination of benzenecarboxylic acid with gas chromatography after partial oxidation of the pyrogenic C with nitric acid (Derenne and Largeau 2001). Nevertheless, their results showed the expressed presence of pyrogenic C in the light fraction of SOM of TPIs indicating that the largest proportion of pyrogenic C in TPI is of particulate nature and part of it is physically not protected by soil structure, however, it can be also found in physically or chemically (organo-mineral complexes) protected forms.

The light fraction is one of the most labile ones with a high pre-disposition to microbial decomposition, especially the free light fraction that is not physically protected by soil structure. In relation to chars, and specifically in the case of TPI, there is no exact information about physical protection in its particulate form. There are indications, as mentioned before, that it occurs in protected and non-protected forms as well. The pyrogenic C in particulate form, however, has a much longer half-life in the soil than non-pyrogenic particulate SOM, if not lost by erosion. The fact that it is more preserved even in the particulate form is another indication its higher recalcitrance. However the forms of protection of pyrogenic C and its chemical structure is not fully understood, it can be confirmed, with great certainty, that its higher stability is due to its molecular structure and morphology that varies according to its origin (Poirier *et al.* 2000). Pyrogenic C that was formed from lingo-celulosic materials tends to have micro-structure with basic structural units arranged in a little oriented manner. Formed from materials that have low oxygen concentration like plant waxes or hydrocarbonates as fossil fuels they feature micro-structure where the basic structural units are arranged in a concentric manner (Poirier *et al.* 2000; Derenne and Largeau 2001). The basic structural units, of nanometric scale, are made of condensed polyaromatic structures with low H:C ratio that are highly resistant to biotic and abiotic degradation.

More recently, Liang *et al.* (2010) found that the presence of pyrogenic C (black C) led to more rapid incorporation of freshly added organic matter into aggregate and organo-mineral fractions, the physically and chemically protected organic matter, respectively.

**Humic substances.** The study of the humified organic matter has recently gain new importance due to its role in environmental protection. The disequilibrium caused by the

**Table 1** Variability and distribution of the fulvic acid, HA and humin fractions within a Terra Preta site (Fazenda Roda de Fogo, municipality of Rio Preto da Eva, Amazonas State) (Soares 2007).

| Depth, cm | Fulvic acids          |      |      | HAs                   |      |      | Humin                 |      |      |
|-----------|-----------------------|------|------|-----------------------|------|------|-----------------------|------|------|
|           | C, mg g <sup>-1</sup> | V, % | CV   | C, mg g <sup>-1</sup> | V, % | CV   | C, mg g <sup>-1</sup> | V, % | CV   |
| 0-5       | 11.47                 | 5043 | 0.62 | 5.31                  | 759  | 0.52 | 4.56                  | 176  | 0.29 |
| 5-10      | 12.04                 | 4981 | 0.59 | 6.54                  | 938  | 0.47 | 5.69                  | 193  | 0.24 |
| 10-20     | 10.82                 | 3537 | 0.55 | 9.57                  | 1135 | 0.35 | 4.73                  | 19   | 0.09 |
| 20-40     | 10.00                 | 2390 | 0.49 | 8.39                  | 580  | 0.29 | 3.48                  | 13   | 0.10 |
| 40-60     | 7.85                  | 3519 | 0.76 | 4.81                  | 1127 | 0.70 | 1.95                  | 21   | 0.24 |
| 60-80     | 7.74                  | 3636 | 0.78 | 2.82                  | 1370 | 1.31 | 2.15                  | 71   | 0.39 |
| 80-100    | 7.55                  | 4347 | 0.87 | 1.42                  | 404  | 1.41 | 2.39                  | 99   | 0.42 |

V: Variance, CV: Covariance

**Table 2** Correlation among fertility attributes, sum of bases (SB) and cation exchange capacity (CEC) of a Terra Preta (Fazenda Hatahara, municipality of Iranduba, Amazonas State) and soil organic matter fractions (Cunha 2005).

| Soil fertility attribute | AF                        | AH                  | HUM    | Total of fractions (AF+AH+HUM) | Corg               | Ctot               | Cres                |
|--------------------------|---------------------------|---------------------|--------|--------------------------------|--------------------|--------------------|---------------------|
|                          | mg C.g <sup>-1</sup> soil |                     |        |                                |                    |                    |                     |
| SB                       | R                         | -0.01 <sup>ns</sup> | 0.66** | 0.29 <sup>ns</sup>             | 0.45 <sup>ns</sup> | 0.61 <sup>ns</sup> | 0.72**              |
| CEC                      | R                         | 0.28 <sup>ns</sup>  | 0.85*  | 0.56 <sup>ns</sup>             | 0.69**             | 0.81*              | -0.18 <sup>ns</sup> |

AF: fulvic acids, AH: HAs, HUM: humin, Total of fractions: sum of C in the three humic fractions (chemical fractions), Corg: organic C measured by the modified Walkley-Black method (Embrapa 1997), Ctot: total carbon measured by dry combustion, Cres: Ctot-Corg, SB: sum of bases, CEC: cation exchange capacity, r: coefficient of correlation (Pearson's), ns: not significant at p&lt;0.01, \*: significant at p&lt;0.0001, \*\*: significant at p&lt;0.005, \*\*\*: significant at p&lt;0.01.

elimination of the natural vegetation and the introduction and inappropriate practice of agricultural activities promoted soil degradation and diminished its capacity to sustain life in long term (Mielniczuk *et al.* 2003). The humic substances are among the most important SOM fractions, having fundamental role in the sustainability of soil functions. The largest proportion of humic substances represent a pool of SOM that has small transformation or degradation rate or is recalcitrant and makes 70-80% SOM (Stevenson 1994). These have important role in C accumulation and to retain and make available plant nutrients.

For these reasons the distribution of C among the fractions of humic substances and their molecular characteristics in TPI will be discussed in detail further in the text, always compared with non-anthropogenic soils.

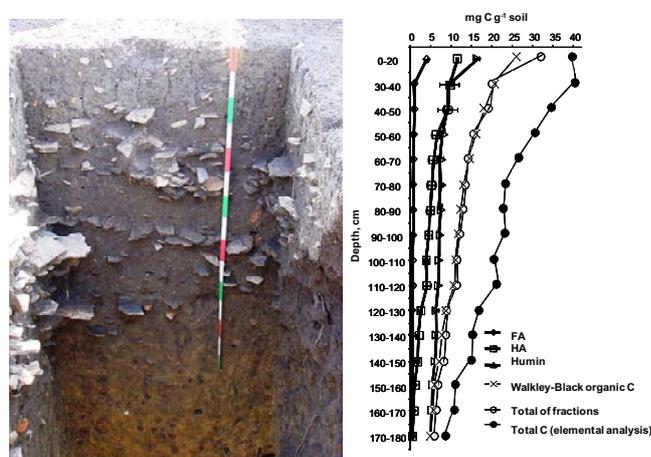
### The distribution of C among humic substances fractions in ADE

The most abundant humic fraction is the humin, both in TPI and non-anthropogenic soils under tropical climate. The TPI, however, has a larger proportion of C in the HA fraction (Fig. 1) than in the fulvic acid fraction, in this being different from non-anthropogenic soils. Hence, in TPI, those humic fractions (HAs and humins) that are conventionally considered to be chemically more stable in function of the presence of aromatic groups and benzene rings, higher degree of polymerization and lower susceptibility to microbial decomposition predominate. In Fig. 1 it is also presented that TPI has a great proportion of C (~50% in the whole soil profile) that is not oxidizable by the Walkley-Black method (Nelson and Sommers 1996). This C is chemically stable and consequently has longer persistence in the soil.

The variability of the distribution of the three humic fractions (fulvic acids, HAs and humin) of the humic substances within one TPI site is however great (Table 1), and the fulvic acid fraction has the largest and the humin the smallest variability of all. This variability, similarly to those observed in the case of the fertility properties of TPI, is probably due to the proper anthropogenic origin of these soils that is the cause of the uneven and irregular deposition of the carbonized material within these sites.

### Composition and physical-chemical properties of the HA fraction of ADE

In the profile of TPI (Fig. 1) total and organic C showed significant correlations to CEC and with the sum of basic cations (Table 2). Among the chemical fractions of SOM only the HA fraction correlated with these fertility para-

**Fig. 1** Anthropogenic dark earth (Terra Preta) profile at Hatahara Farm, Iranduba, Amazonas State. Concentration of carbon in the chemical fractions of soil organic matter (n = 3). Error bars indicate standard deviation. FA: fulvic acids, HA: HAs, Total of fractions: HA+FA+Humin.

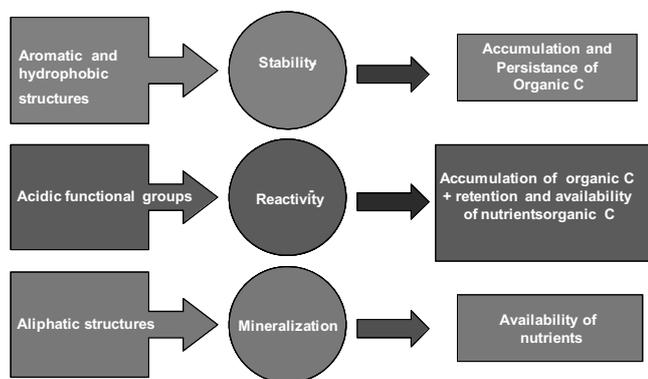
eters. These data demonstrate the importance of the HA fraction in conditioning some soil fertility attributes in the studied TPIs. Also suggest that to be able to better understand the effect of SOM on the fertility of TPI it is important to investigate, among other aspects, the molecular composition and physical-chemical characteristics of the HA fraction.

To demonstrate the principal differences between the HAs of TPI and non-anthropogenic soils, the respective physical-chemical and molecular properties, that define their function in the soil, will be discussed in the following. The properties that determine the function and transformations of the HAs are their stability, reactivity and susceptibility to mineralization. The stability of HAs in relation to decomposition and leaching is important for the accumulation and persistence of organic C in the soil. The reactivity of HAs is responsible for the interaction of these molecules with other soil components via the formation of organo-metallic complexes whose linkages between the mineral and organic matrix of the soil favor organic C accumulation and stabilization. Via adsorption and desorption reactions occurs the retention and availability of plant nutrients. Via mineralization of HAs, the liberation of nutrients occurs and also the diminution of organic C concentration in the soil. The stability of HAs is determined, principally, by their aromatic and hydrophobic structures. Their chemical reactivity

**Table 3** Indices that describe composition and physical-chemical properties of HAs in Terra Preta (TPI) and adjacent non-anthropogenic soils (Non-TPI) of the Amazon (Cunha 2005).

| Soils   | TGI   | IA     | Total acidity, $\text{cmol}_e \text{ kg}^{-1}$ | Carboxylic acidity, $\text{cmol}_e \text{ kg}^{-1}$ | O:H    | E <sub>4</sub> :E <sub>6</sub> | FOR, Spin $\text{g}^{-1}$ | C:N    | A <sub>4</sub> :A <sub>1</sub> | I <sub>485</sub> :I <sub>400</sub> |
|---------|-------|--------|--|---|--------|--------------------------------|---------------------------|--------|--------------------------------|------------------------------------|
| TPI     | 3.2 a | 0.86 a | 673 a  | 445 a   | 7.42 a | 4.2 b                          | 5.75 a                    | 12.2 a | 3.067 a                        | 2.109 a                            |
| Non-TPI | 2.3 b | 0.77 b | 575 b  | 320 b   | 4.76 b | 6.0 a                          | 2.11 b                    | 8.8 b  | 1.713 b                        | 1.510 b                            |

TPI: Terra Preta under natural forest and cultivated (N=18), Non-TPI: Non-anthropogenic soil, adjacent to TPI under forest (N=4), The numbers followed by different letters within a column are different at  $p \leq 0.05$  by Tukey's test. TGI: Thermogravimetric index, IA: Index of aromaticity obtained by infrared spectroscopy (DRIFT), Total acidity: Concentration of all acidic functional groups on molecular surfaces, Carboxylic acidity: Concentration of carboxylic groups, O:H: Atomic ratio Oxygen: Hydrogen, E<sub>4</sub>:E<sub>6</sub>: Obtained by UV-Visivel spectroscopy, indicate condensed aromatic rings, FOR: Obtained by electron paramagnetic resonance spectroscopy (EPR), used to describe humification degree, C:N: atomic ratio Carbon: Nitrogen, A<sub>4</sub>:A<sub>1</sub> e I<sub>485</sub>:I<sub>400</sub>: Indices obtained by fluorescence spectroscopy, describe degree of humification of humic substances.

**Fig. 2** Properties that determine function and transformation of humic substances in soil.

is determined by the concentration of acidic functional groups on the molecular surfaces. The susceptibility of HAs to mineralization depends, greatly, on the quantity of hydrophilic aliphatic structures in their molecular associations (Fig. 2).

The principal differences between the HAs of TPI and non-anthropogenic soils, is presented in Tables 3 and 4. The methods used to obtain the indices presented in the respective tables are listed in Table 5 (Cunha 2005). The localization of the respective TPIS and adjacent non-anthropogenic soils is described in Fig. 3.

The humification process results in ever-increasing molecules or molecular associations, increasing the degree of condensation and concentration of free organic radicals. The different humification indices that were obtained via degradative, basically chemical, and non-degradative physical, principally spectroscopic techniques, methods indicated higher humification degree and higher concentration of aromatic poly-condensed structures in HAs extracted from TPIS. The HAs of TPI are more resistant to thermo-degradation, compared to the HAs of adjacent soils, that is expressed by the thermogravimetric index (TGI). This property indicates that the HAs of TPI have greater proportion of stable structural elements such as condensed aromatic nuclei. The index of aromaticity (IA), obtained by infrared spectroscopy, and the distribution of C among the structural elements of humic substances determined by <sup>13</sup>C nuclear magnetic resonance spectroscopy (Tables 3, 4) confirmed a greater proportion of aromatic structures in the HAs of TPI. The E<sub>4</sub>/E<sub>6</sub> ratio that has an inverse relation to the condensed aromatic rings was smaller in TPI HAs than in those of adjacent soils. The concentration of the free organic radicals (FOR), data obtained by electronic paramagnetic resonance (EPR), is also frequently utilized to estimate the degree of humification. The higher the concentration of FOR in the HA fraction, the higher is the degree of humification, and HAs of TPI showed a higher concentration of FOR compared to adjacent soils. Additionally, the humification indices obtained by fluorescence spectroscopy (A<sub>4</sub>:A<sub>1</sub> and I<sub>485</sub>:I<sub>400</sub>) also indicated higher degree of humification in TPI. The C:N ratio indicate the degree of incorporation of nitrogen, in this case, into the structure of humic substances and also the degree of humification. High C:N ratios normally

**Fig. 3** Localization (▲) of the Amazonian anthropogenic dark earths and adjacent soils described in Table 5.

signify low levels of N incorporation and low degree of humification. In the case of TPI, however, the C:N ratio of the HAs falls within the range considered "normal" for stable organic compounds in soils that is between 10 and 12 (Stevenson 1994). It means little secondary mineralization of SOM (Rossel *et al.* 1989). The low (8.8) C:N ratio obtained for the non-anthropogenic soils suggests lower biological stability and the possible presence of secondary mineralization of SOM. The higher total acidity and the presence of carboxylic radicals together with the higher O:H ratio of the HAs of TPI indicate the higher concentration of acidic functional groups that are responsible for the chemical reactivity and, consequently, for the interactions of HAs with other soil components.

Hence, the HAs of TPI are more stable and at the same time have higher chemical reactivity than those in adjacent, non-anthropogenic, soils. Through their physical-chemical and molecular structural properties the humic substances formed in TPI facilitate organic C accumulation and higher fertility and production potential, so much desired in soils under tropical climate where soils without this organic matter are often obstacles to sustainable agricultural production.

### The origin of the molecular structural characteristics of the HAs in ADE

The edaphic and climatic conditions that control humification processes are similar for TPI and adjacent soils. The difference is in the higher concentration of char or pyrogenic C in TPIS. The pyrogenic C is considered inert and little susceptible to decomposition but, as mentioned before, it also undergoes some degradation and transformation in the soil. Trompowsky *et al.* (2005), using <sup>13</sup>C direct polarization magic angle spinning nuclear magnetic resonance (DP/MAS NMR) on HAs extracted from charcoal made from eucalypt wood showed that C was present in two principal structures: aromatic (aryl-C, condensed and deficient in H, at 130 ppm) and carboxylic (-COO<sup>-</sup>, at 169 ppm) groups and a significant part of the carboxylic groups was

**Table 4** Distribution of  $^{13}\text{C}$  among carbon containing chemical structures of the humic acids of Terra Preta and adjacent non-anthropogenic soils of the Amazon obtained by nuclear magnetic resonance spectroscopy ( $^{13}\text{C}$  VACP/MAS NMR).

| Soils   | Alkyl           | Methoxyl | O-Alkyl | Aromatic | Carboxyl | Carbonyl | Aliphatic | Aromatic |
|---------|-----------------|----------|---------|----------|----------|----------|-----------|----------|
|         | ----- ppm ----- |          |         |          |          |          |           |          |
| TPI     | 23 b            | 10 b     | 18 b    | 29 b     | 11 a     | 7 a      | 64 b      | 36 b     |
| Non-TPI | 29 a            | 12 a     | 26 a    | 22 a     | 11 a     | 2 b      | 75 a      | 25 a     |

TPI: Terra Preta under natural forest and cultivated (N=18); Non-TPI: Non-anthropogenic soil, adjacent to TPI under forest (N=4); The numbers followed by different letters within a column are different at  $P \leq 0.05$  by Tukey's test. Source: Cunha (2005).

**Table 5** List of techniques and methods used to obtain humification indices and reactivity, quantify and describing the properties of soil organic matter, of humic substances and, specifically, of the HAs (Cunha 2005), discussed in the text.

| Technique/Method   | Purpose/Index/Property  | Specification  |
|--|---|--|
| Modified Walkley-Black method Embrapa (1997)   | Quantification of organic C in soil   | Oxidation of SOM by potassium dichromate   |
| Benites <i>et al.</i> (2003) modified from Yeomans and Bremner (1988)  | Quantification of humic substances  | Oxidation of SOM by potassium dichromate   |
| Method recommended by IHSS (International Humic Substances Society) (Swift 1996)   | Extraction and separation of humic substances                               | Operational separation of humic substances based on solubility in aqueous solutions of acid and base   |
| Thermogravimetry   | Thermogravimetric index (TGI) (Benites <i>et al.</i> 2005b)                 | Ratio of the weight loss of HAs in the temperature ( $^{\circ}\text{C}$ ) ranges (350-650) and (105-305)   |
| Fourier Transform Infrared Spectroscopy with diffuse reflectance (DRIFT)   | Index of aromaticity (IA) (Freixo <i>et al.</i> 2002)                       | Ratio of the absorbance of the bands ( $3057\text{-}3055\text{ cm}^{-1}$ ) and ( $2934\text{-}2928\text{ cm}^{-1}$ )   |
| Ba(OH) <sub>2</sub>  | Total acidity and carboxylic acidity (Schnitzer and Gupta 1965)             | Total acidity = (titrated volume for blank – titrated volume for sample) $\times$ N of HCl $\times$ 1000/mass of the sample (mg)<br>Carboxylic acidity = (titrated volume for blank – titrated volume for sample) $\times$ N of NaOH $\times$ 1000/mass of the sample (mg)                 |
| Elemental analysis by high temperature combustion (Dumas method; Nelson and Sommer 1996)   | O:H and C:N ratios  |  |
| UV-Visible Spectroscopy  | E <sub>4</sub> /E <sub>6</sub> ratio (Kononova 1966)                        | Ratio of absorbance at 465 and 665 nm  |
| Electron paramagnetic Resonance Spectroscopy (EPR)   | Free Organic Radicals (FOR)   | Obtained by the integration of the signal of the first derivative of the free radical, compared to a standard (KCl) of known concentration of spins ( $3 \times 10^{15}$ spins $\text{g}^{-1}$ ), using synthetic rubi as secondary standard (Singer 1959; Martin-Neto <i>et al.</i> 1994) |
| Fluorescence spectroscopy  | A <sub>4</sub> :A <sub>1</sub> e I <sub>485</sub> :I <sub>400</sub> indices | A <sub>4</sub> :A <sub>1</sub> : ratio of absorbance at (665-585 nm) and (425-345 nm) (Zsolnay <i>et al.</i> 1999).<br>I <sub>485</sub> :I <sub>400</sub> : ratio of absorbance at 480 nm and 400 nm (Kalbitz <i>et al.</i> 1999)  |
| Nuclear Magnetic Resonance Spectroscopy with Cross Polarization, Variable Amplitude Magic Angle Spinning ( $^{13}\text{C}$ VACP/MAS NMR) | Table 3 (Knicker <i>et al.</i> 2005a, 2005b; Dick <i>et al.</i> 2005)       |  |

chemically linked to aromatic structures. As the condensed aromatic structures are highly resistant to degradation the carboxylic groups associated to them are also expected to be resistant and persistent once in the soil.

Benites *et al.* (2005b) examined, using  $^{13}\text{C}$  variable angle cross polarization magic angle spinning nuclear magnetic resonance (VACP/MAS NMR), HAs extracted from a soils that were naturally (no anthropogenic effect) enriched in pyrogenic C. The principal structures identified in these HAs were, similarly to the spectra of HAs extracted from charcoals, C in aromatic structures (130 ppm) and in carboxylic groups (169 ppm) probably linked to the aromatic components. In this material the contribution of C in alkyl structures (0-45 ppm) was, however, greater than in the HA extracted from charcoals.

Novotny *et al.* (2007) compared the spectra, also using  $^{13}\text{C}$  NMR spectroscopy, of HAs extracted from TPI and from an adjacent Ferralsol. The HA fraction of TPI presented two principal peaks, at 130 ppm, correspondent to aryl-C and at 169 ppm, corresponding to C in carboxylic groups, similarly to the HAs extracted from eucalypt charcoals and from the soil naturally enriched in pyrogenic C. There was a smaller contribution of aliphatic structures such as C in O-alkyl structures of carbohydrates (60-90 ppm), C in methoxyl groups of lignin (45-60 ppm) and alkyl-C (0-45 ppm). The HAs of the non-anthropogenic soil (Ferralsol) consisted of, in basis of the spectrum, significant proportions of C in aliphatic structures, specifically at 0-45 ppm (alkyl-C) and at 45-60 ppm (methoxyl). The presence of O-aryl C (140-160 ppm), together with methoxyl-C, indicate higher contribution of lignin to the structure of the HAs in the non-anthropogenic soil. In the ADE the peak of the O-aryl C was

smaller and the contribution of aryl-C (poly-condensed aromatic structures) greater. Additionally, the carboxylic groups that were present in TPI HAs, in great proportion were associated with poly-aromatic condensed structures. Hence, the HAs of TPI, besides showing a certain degree of recalcitrance, also had C in functional groups that represent chemical reactivity.

Using data obtained by  $^{13}\text{C}$  VACP/MAS NMR and multivariate analysis, Novotny *et al.* (2007) verified that the HAs in TPI had C in their structures that are of pyrogenic origin. This signifies that the HAs of TPI are in fact originated, at least partially, from the pyrogenic C (charcoal) that was incorporated, accumulated and transforming in the soil during long periods of time. This way, charcoal directly contributed to the enhancing of the chemical and physical properties and, consequently, for the formation of more fertile and productive soils.

## FINAL CONSIDERATIONS

The organic matter of the Amazonian ADE has a key role in the formation of the chemical, physical and biological properties of these soils. Because of its high concentration, and principally due to its chemical-physical properties, TPIs feature unique fertility properties and so agricultural potential in humid tropical environments where soils are frequently obstacles of sustainable production.

The ADE are rich in humified and stable organic matter that, at the same time gives higher fertility to the soil, making viable the existence of an environment that is favorable to cation exchange reactions, with organic and inorganic colloids, and the complexation of metallic ions,

among others. For having stable organic matter, in the TPI predominate processes that favor organic C accumulation. However, the effect of the pyrogenic C and of the fractions of SOM in TPI that inherited some properties of the pyrogenic C on the biological processes in the soil and on the proper accumulation of C is still basically unknown. The mechanisms by which pyrogenic C affects plant growth are also still mainly unknown.

The ADE of the Amazon, due to their favorable properties for agricultural use, are usually utilized by local communities. The promotion of the agricultural utilization of TPIs, these being national patrimony of Brazil (IPHAN 1988), is not desirable. However, using scientific investigation, important information can be obtained about the functioning of these soils that could be used, as model (Novotny *et al.* 2009; Renard *et al.* 2011), in the development of sustainable soil fertility management systems for TPIs already under utilization and for the development of new soil management systems for tropical soils for the benefit of, principally, small producers, family farms and local communities of the Amazon and other tropical regions.

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