BIOCHAR AS A SUSTAINABLE ALTERNATIVE TO AÇAÍ WASTE DISPOSAL IN AMAZON, BRAZIL

ABSTRACT

The açaí palm (*Euterpe oleracea* Mart) is native to the floodplains of central and South America and is cultivated in Brazil for its berries, which are considered to be a ‘superfood’. The waste açaí fiber and seeds obtained after fruit processing pose a challenge since they remain unutilised despite being an abundant waste by-product of açaí processing.This leads to a build-up of waste, regular dumping and environmental management challenges. Here we examine the potential use of açaí seed biochar as a soil conditioner. The biochar was produced from waste seeds in a handmade kiln, incorporated into two soils of different textures and then compacted in volumetric rings with a hydraulic press. The samples were kept in a greenhouse for a 270-day incubation period. After this, the samples were evaluated for their soil physical and chemical attributes. Nine months after the application of the açaí seed biochar, soil physical properties were not affected, except for the soil aggregate size distribution, for which the highest dosage resulted in a larger weighted average diameter. However, biochar increased phosphorus, potassium and magnesium contents, and reduced the aluminum content, which was reflected in an increase of the base saturation and a reduction in aluminum saturation. Therefore, within a relatively short time period, the biochar was found to improve soil chemical quality more so than soil physical properties, thus offering potential as a sustainable solution to manage açaí waste in the Amazon region.

Keywords: Biochar; *Euterpe oleracea* Mart.; Soil physical properties; Soil Fertility

Introduction

The consumption of açaí is part of the traditional diet of a majority of the population of the Amazon region (Oliveira et al., 2000), yet due to its therapeutic and nutritional value, the demand for açaí berries has increased exponentially in both local, domestic and international markets (Rogez, 2000). This growing demand has significantly contributed to the agro-industrial development of the Amazon region. However, such progress has been accompanied by the growth in the generation of unwanted processing residues (seeds and fiber), which are often improperly discarded, impacting the natural landscape and clogging sewers and water courses (Bentes, 2017). Due to this environmental damage, alternative uses for this waste have been explored, such as reworking into handicrafts and use in renewable energy (Rangel, 2015), animal feeds and soil fertilisers (Kabacznik, 1999; Townsend et al., 2001).

Açaí seeds are comprised of 46% carbon, 7% hydrogen, 38% oxygen, 8% nitrogen, 0.1% sulphur (Rangel, 2015), 0.17% phosphorus, 0.48% potassium, 0.03% calcium, 0.02% magnesium, 167 mg kg^{-1} iron, 181 mg kg^{-1} manganese, 22 mg kg^{-1} zinc and 40 mg kg^{-1} boron (Teixeira et al., 2004). The high carbon content reveals a raw material with great potential for the production of biochar (Sato et al., 2019).

Biochar is a product obtained by thermo-chemical decomposition process (pyrolysis) in which organic material (biomass) is converted under conditions of low oxygen availability and high temperatures (300 to 700°C) into a solid material carbon-rich, porous and high-recalcitrant (Lehmann and Joseph, 2009; Devereux et al 2013; Sun and Lu, 2014; Sharma et al., 2015). Although biochar is often discussed as a soil amendment, for agricultural purposes, at present, the biochar technology has pushed its application and related products not only in agriculture, but also, for environmental protection and new material production. Other uses reported include industrial effluent filtration (Barber et al., 2018), feed supplement (Prasai et al., 2016) and remediating metal or chemical contamination (Li et al., 2020, Li et al. 2018).

In fact, biochar is considered an important alternative to support major challenges such as land degradation, food insecurity, climate change, sustainable energy generation and waste management (Shaaban et al., 2018). In this work we focus on the relationship between biochar properties and its applicability as a soil amendment, since this relationship is still unclear (Manyà, 2012).

Several studies have confirmed the beneficial effects resulting from the application of biochar on soil properties, with a concomitant increase in pH, cation exchange capacity and base saturation, aeration porosity, water retention capacity and a decrease in soil bulk density (Laird et al., 2010; Lu et al., 2014; Devereux et al 2013; Castellini et al., 2015).

However, studies in which the addition of biochar did not result in significant changes in soil properties are also reported (Brewer et al., 2012; Ventura et al., 2014; Jeffery et al., 2015). The divergence in the results is probably due to the features of the different raw materials, production conditions, application forms and rates, type of soil, as well as the time taken to evaluate the application of biochar in the soil, all factors that affect the effectiveness of biochar application on soil properties (Kavitha et al. 2018; Shaaban et al., 2018; El-Nagaar et al., 2019). This is because the effect of biochar may vary according to the above mentioned factors (Joseph et al., 2009). Thus, studies that evaluate the efficiency of the addition of biochar as a conditioner of soil properties are needed using different raw materials from different regions.

Agro-processing is a major industry in Brazil, generating an enormous amount of solid waste. Appropriate management of these wastes, for each region, is a challenging issue. In the Amazon region, the production of biochar from açaí seeds can be a feasible and sustainable alternative for the large amount of residues from fruit processing. As mentioned above the rapid increase in the fruit demand increases the waste generation rate, and this waste management becomes an environmental concern.

The objectives of this study were therefore evaluate the effects of the addition of açaí seed biochar, produced in a handmade kiln, on the physical and chemical properties of two Yellow Latosols, sandy loam and clay textural classes, after 270 days of incubation. Our hypotheses are that biochar addition to soil (i) increase soil nutrients availability and (ii) improves soil physical quality through decreasing soil bulk density, increasing porosity, soil water content and the stability of the aggregates.

Material and Methods

Production and characterization of açaí seed biochar

The raw material used for the production of biochar consisted of waste açaí seeds from fruit processing, which were collected from establishments that sell fruit pulp located in the metropolitan region of Belém, Pará state, northern Brazil (1°27' 31" S 48° 26' 04.5" W).

The biochar was produced in a handmade kiln (Figure 1A) similar to that developed by Mia et al. (2015), built with two metal chambers; one internal chamber with 90 cm in height and 20 cm in diameter, intended for the material that was used as a heat source (pieces of wood), and one external chamber (90 cm x 50 cm), where the thermochemical conversion of the biomass was carried out through the slow pyrolysis process.

Preliminary tests in the early kiln design showed the need for modifications in order to enhance the pyrolysis process, as it follows:

- A thermocouple was installed inside the outer chamber for monitoring pyrolysis temperature;
- A screen has been inserted above the exhaust vent to support the açaí seeds at a height where heat could exit from the inner to the outer chamber without obstruction;

- A fan was installed in the air vent in the internal chamber to optimize heat generated from combustion of the material used as a heat source (biomass from a diverse source) (Figure 1A). Further details of kiln operation can be seen in Figure 1B.

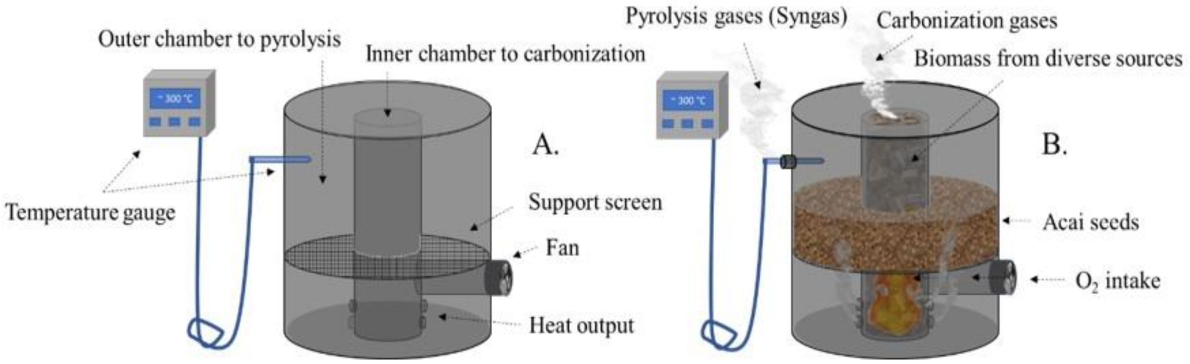

Figure 1. Design of the kiln adapted from Mia et al. (2015) with the adjustments made for our work (A). Detail of the kiln operation during the production of the biochar of Açaí seeds (B).

The heating rate of the kiln was approximately 20°C min^{-1}. The maximum and average temperature were 450 and 300ºC, respectively. The residence time, that is, the time that the biomass remained in the kiln after reaching the average temperature, was 9 h. After this period, the biochar was cooled, crushed and sieved through a 0.5-mm mesh to standardize the particle size. These conditions were adopted from previous experiments (Sato et al., 2019).

The açaí seeds used for the production of biochar were characterized in relation to the extractable and lignin contents according to NBR 7989 (ABNT, 1998) and NBR 14853 (ABNT, 2010), respectively. The determination of ash content, volatile materials, fixed carbon and yield before and after pyrolysis was performed according to NBR 8112 (ABNT 1986). The carbon particle density was determined according to Blake and Hartge (1986). The elemental composition before and after pyrolysis was determined in two replicates using a PE2400 CNHS/O analyzer (Perkin Elmer). From the contents of these elements, the atomic ratios H/C and O/C were calculated (Benites et al., 2005).

Soil collection and characterization

The soil samples used in the experiment were collected in the 0-20 cm layer in two areas. The soil in both areas is classified as dystrophic Yellow Latosol (Santos et al., 2013), one with a sandy loam texture (S1) and the other with a clay texture (S2). Contrasting soil textures were selected to evaluate the biochar effect in representative soils from the acai production areas (natural and planted), with the aim of recommending the use of biochar (byproduct) in these areas, making the productive chain sustainable.

Soil particle size distribution was determined by the pipette method (Gee and Bauder, 1986) and the maximum soil bulk density (Bd_{max}) and the optimum compaction moisture (Ug_{opt}) were obtained for each soil according to NBR 7182 (ABNT, 1986) (Table 1).

Table 1. Distribution of particle size, textural classification, maximum soil bulk density (Bd_{max}) and optimal compaction moisture (Ug_{opt}) of two Latosols with sandy loam (S1) and clay (S2) textural classes.

Soil	**Sand**	**Silt**	**Clay**	**Textural class**	**Bd_{max}**	**Ug_{opt}**
		g kg^{-1}			Mg m^{-3}	kg kg^{-1}
S1	848	92	60	Sandy loam	1.70	0.16
S2	112	151	737	Clay	1.31	0.31

Experimental setting

The treatments consisted of the application of four rates (0, 20, 40 and 60 g kg^{-1}) of biochar, according to Yuan et al. (2011), which were represented by D0, D20, D40 and D60, respectively. For each treatment and soil, four repetitions were prepared (N = 32). Water was added to the soil + biochar mixture until Ug_{opt} and then 5 x 5 cm volumetric metal rings were filled. The soil was compacted in the metal rings with the aid of a hydraulic press until it reached 90% of Bd_{max}.

The metal rings were kept in a greenhouse for 270 days, submitted to weekly wetting and drying cycles (3 days saturating and 4 days drying), in order to simulate field conditions. After this incubation period, the soils were analysed as described below.

Soil physical attributes

The soil water retention curve (SWRC) was determined at nine matric potentials (h):~0, -60, -100, -300, -600, -1000, -6000, -10000 and -15000 hPa (Klute, 1986). The ratio between soil moisture (Ug) and potential (h) was adjusted by the Van Genuchten (1980) model with the restriction (m=1-1/n) proposed by Mualem (1986) according to equation 1:

$$\mathrm{Ug} = \mathrm{Ur} + \frac{(\mathrm{Us}-\mathrm{Ur})}{(1+(\alpha\ \mathrm{h})^{n})^{(m)}} \qquad \text{Equation 1}$$

where: Ug = soil gravimetric water content (kg kg^{-1}); h = soil water matric potential (hPa); Ur = residual soil water content, Us = saturation soil water content; α, n e m are the parameters of the model.

Total soil porosity (TP) was determined considering the volumetric soil water content at saturation (h ~ 0hPa), while microporosity (Mi) was considered as the water content at -6 hPa and macroporosity (Ma) was calculated by the difference between TP and Mi (Teixeira et al., 2017). The available water content (AW) was calculated by the difference between soil moisture at field capacity (FC), considering the water content in the potential of -100 hPa for sandy-loam soil (S1) and -330 hPa for clay soil (S2) (Reichardt, 1988); and permanent wilting point (PWP), which is equivalent to the water content at -15000 hPa potential (Cassel and Nielsen, 1986).

After determining the SWRC and porosity, the samples were once more saturated and allowed to stand in the shade until the point of friability. Once this condition had been reached, the samples were carefully broken manually at their weakness points. The total sample volume was passed through the 9.52-mm and 4.76-mm mesh sieves. The material passed through the 9.52 mm sieve and retained on the 4.76 mm sieve was separated for soil bulk density determination through the paraffin clump method (Kiehl, 1979), and for aggregate stability analysis through wet sieving as described by Salton et al. (2012). For calculations of the weighted mean diameter (WMD), equation 2 was used:

$$WMD = \sum_{i=1}^{n}(xi.wi) \qquad \text{Equation 2}$$

where, wi = mass of each class (g); and xi =average diameter of sieve classes (mm).

Soil chemical attributes

The materials <4.76 mm were air dried, passed through a 2-mm sieve, and then separated to determine the pH in water, organic carbon (OC) content, available phosphorus (P), exchangeable potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and aluminum (Al^{3+}), in addition to potential acidity (Al^{3+}+ H^+), all following the methodologies described in Teixeira et al. (2017). The results were used for calculation of the sum of bases (SB = Ca^{2+} + Mg^{2+} + K^+), cation exchange capacity [T = SB + (H^+ + Al^{3+})], base saturation (V% = (100 x SB)/CEC) and aluminum saturation [m% = Al/(SB + A^{3+}].

Statistical Analysis

The effect of the addition of biochar from açaí seeds on the chemical and physical properties of soils was evaluated through an analysis of variance ($p < 0.05$), and when significant, the means were compared using the test of Tukey at 5% significance. The significance of the model parameters for the water retention curve was tested by the t-test at 5% probability.

Results

Açaí seed characterization before and after pyrolysis

The lignin content in fresh açaí seeds was high (Table 2) in comparison to the average range of the 12 to 25% reported for different biomass used for biochar production (Conz, 2015).

The pyrolysis process at an average temperature of 300°C resulted in an increase by 41.3% in fixed carbon content and a reduction by 41.62% in the content of volatile materials in biochar (Table 2). The ash content did not significantly vary ($p > 0.05$). The yield of biochar was 27.8%.

Contents of nitrogen (N) and sulfur (S) did not vary much before and after pyrolysis. Nevertheless, the contents of hydrogen (H) and oxygen (O) reduced considerably, while the carbon content (C) increased (Table 2). As a consequence, the atomic ratios O/C and H/C reduced by 40 and 44%, respectively, after the conversion of açaí seeds into biochar.

Table 2. Characterization of the Açaí seeds before and after the pyrolysis process.

Material	Unit	Before pyrolysis (Açaí seeds)	After pyrolysis (Biochar)
Extractable	%	2.30	-
Lignin		37.2	-
Ashes		2.51 a	2.82 a
Volatile		76.31 a	34.7 b
Fixed carbon		21.18 b	62.48 a
Biochar Yield		-	27.81
Particle density of biochar	$g\ cm^{-3}$	-	0.76
pH	-		5.73
Nitrogen (N)	%	1.60	1.64
Carbon (C)		48.21	69.50
Hydrogen (H)		6.69	4.30
Sulfur (S)		0.21	0.22
Oxygen (O)		43.29	24.58
O/C		0.67	0.27
H/C		1.67	0.74

Means followed by the same letter in the same line do not differ from each other by the t test at 5% significance.

Effects of the biochar on physical attributes of the soils

Regardless of the biochar addition rate, in the soil S1, the largest diameter classes (9.52 to 1.0 mm) accounted for the smallest volume while in soil S2, it corresponded to over 70% of soil aggregates (Table 3). For S1, the addition of biochar increased the proportion of aggregates in the 9.52-4.76 mm and 2-1 mm classes but only for the highest dosage (D60).

Corroborating with the results of relative distribution of aggregates, the application of biochar at the highest dosage (D60) resulted in a larger weighted average diameter (WMP) compared to the other treatments of soil S1, which did not differ from each other. In S2, however, regardless of dosage, the application of biochar had no effect on this attribute (Figure 2).

Table 3. Relative distribution of aggregate size class for two Yellow Latosols, sandy loam and clay, and different rates of biochar addition (D, g kg^{-1}).

	Aggregates size classes (mm)							
TREAT.	9.52-4.76	4.76-2	2-1	1-0.5	0.5-0.25	0.25-0.105	0.105-0.053	<0.053
	%							
S1: Sandy loam								
D0	1.18 b	8.89 a	4.97 b	9.10 a	28.83 a	25.78 a	11.52 a	9.74 a
D20	1.88 b	9.32 a	5.47 b	8.76 a	27.55 a	22.83 ab	12.49 a	11.70 a
D40	1.83 b	9.51 a	5.50 b	9.66 a	25.96 a	23.14 ab	13.22 a	11.18 a
D60	3.95 a	11.06 a	7.59 a	10.62 a	25.02 a	21.61 b	12.67 a	7.50 a
S2: Clay								
D0	19.29 b	31.07 a	18.08 a	11.49 a	7.36 a	3.99 a	2.33 a	6.38 a
D20	21.98 ab	35.79 a	16.11 a	10.97 ab	5.84 a	3.61 ab	2.14 a	3.56 a
D40	23.70 ab	36.05 a	14.92 a	10.11 ab	6.20 a	3.38 ab	2.23 a	3.42 a
D60	27.07 a	34.66 a	14.68 a	8.49 b	5.13 a	2.44 b	1.83 a	5.70 a

Means followed by the same letter in the same column for the same soil do not differ from each other by the Tukey test at 5% significance.

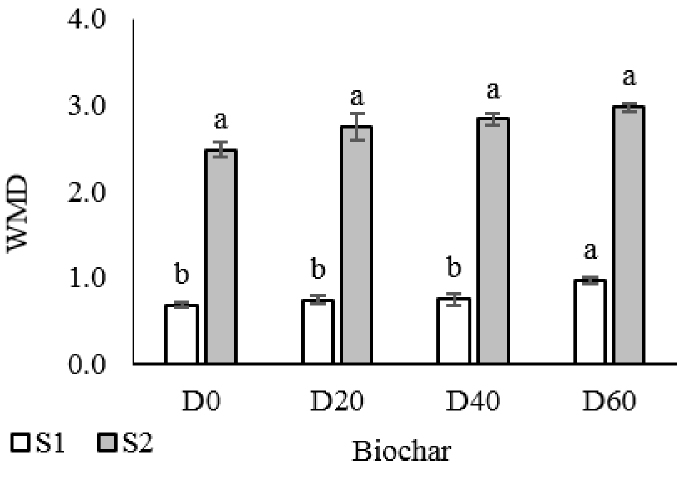

Figure 2. Weighted mean diameter (WMD) of two Yellow Latosols, sandy loam (S1) and clay (S2), with increasing doses of biochar of Açaí seeds (D, g kg^{-1}). Means followed by the same letter in the same soil do not differ between themselves by the Tukey test at 5% significance.

In S1, the soil bulk density (Bd), total soil porosity (TP) and microporosity (Mi) were the same in the biochar treatments but lower when compared to the control (D0) while the macroporosity (Ma) was not influenced by the addition of biochar (Table 4). In the S2, the application of biochar did not affect Bd, TP, or even its distribution in Ma and Mi (Table 4). In both soils, biochar doses did not increase water content at field capacity, permanent wilting point and soil water availability when compared to D0.

Table 4. Physical properties of two Yellow Latosols, sandy loam (S1) and clay (S2), with increasing biochar doses of Açaí seeds (D, g kg^{-1}).

TREAT	Bd	TP	Mi	Ma	FC	PWP	AW
	Mg m^{-3}	m^3 m^{-3}			kg kg^{-1}		
	S1: Sandy loam						
D0	1.560 a	0.413 a	0.350 a	0.063 a	0.206 a	0.110 a	0.095 a
D20	1.456 b	0.364 b	0.310 b	0.055 a	0.191 a	0.104 a	0.087 a
D40	1.461 b	0.354 b	0.294 b	0.060 a	0.187 a	0.104 a	0.083 a
D60	1.424 b	0.332 b	0.288 b	0.044 a	0.191 a	0.100 a	0.091 a
	S2: Clay						
D0	0.991 a	0.389 a	0.319 a	0.069 a	0.287 ab	0.223 a	0.064 a
D20	0.998 a	0.389 a	0.332 a	0.057 a	0.295 a	0.223 a	0.072 a
D40	0.962 a	0.364 a	0.310 a	0.055 a	0.275 b	0.203 a	0.072 a
D60	1.090 a	0.417 a	0.354 a	0.063 a	0.286 ab	0.212 a	0.074 a

TREAT: Treatment; Bd: Soil bulk density; TP: Total porosity; Mi: Microporosity; Ma: Macroporosity; FC: Field capacity; PWP: Permanent wilting point; AW: Available Water. Means followed by the same letter in the same soil do not differ among themselves by the Tukey test at 5% significance.

The relationship between the gravimetric soil water content (Ug) as a function of the matric potential (h) was adequately adjusted by van Genuchten's model (1980) in soils with different biochar doses ($p < 0.05$; $R^2 > 0.90$). Moreover, all model parameters were significant by the t-test at 5% probability. When comparing the means by the test of Tukey, it was found that the application of biochar did not change the model parameters in soil S1 (Table 5). However, in S2, it was found that the parameter α was higher in the control than in the biochar treatments, which were the same among themselves.

Table 5. Soil water retention curve parameters of two Yellow Latosols, sandy loam (S1) and clay (S2), with increasing biochar doses of Açaí seeds (D, g kg^{-1}).

TREAT.	UR	US	*a*	n	m
S1: Sandy loam					
D0	0.089 a	0.248 a	0.020 a	1.439 a	0.304 a
D20	0.102 a	0.244 a	0.019 a	1.577 a	0.361 a
D40	0.101 a	0.241 a	0.023 a	1.487 a	0.327 a
D60	0.096 a	0.229 a	0.017 a	1.557 a	0.350 a
S2: Clay					
D0	0.206 a	0.391 a	0.047 a	1.384 a	0.277 a
D20	0.204 a	0.389 a	0.031 b	1.398 a	0.284 a
D40	0.189 a	0.377 a	0.027 b	1.452 a	0.311 a
D60	0.193 a	0.381 a	0.031 b	1.393 a	0.282 a

Means followed by the same letter in the same soil do not differ among themselves by the Tukey test at 5% significance.

The water retention curves in soils with different doses of biochar are shown in Figure 3. In soil S1, a small difference can be observed at the initial part of the curve (saturated condition) at approximately -30 hPa, between the retention curve of treatment D60 and the others. From this potential, the curves showed similar behaviors to the control treatment even at the highest biochar rate.

On the other hand, in soil S2, a slight change is observed in the slope of the curve in the treatments with biochar. Also, small changes are observed in the upper and lower part of the retention curve, especially in treatments D40 and D60 when compared to D0.

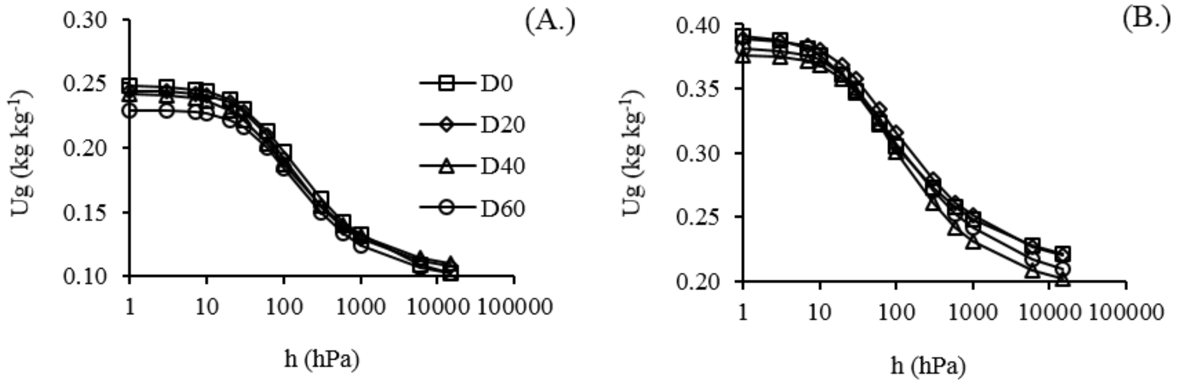

Figure 3. Soil water retention curves for two Yellow Latosols, sandy loam (A) and clay (B) with increasing doses of biochar from Açaí seeds (D, g kg^{-1}).

Biochar hydrophobicity test

In an attempt to elucidate the reasons why the application of biochar to the soil did not influence the soil water retention capacity, the hydrophobicity of the biochar was verified by the water drop penetration test (King, 1981; Bisdom et al., 1993).

The infiltration time of water droplets on the surface of the biochar was longer than 3600 s. Therefore, it is considered to be extremely hydrophobic (EH). This characteristic was confirmed by the contact angle of the water droplet with the biochar surface, which was 114° on average (Figure 4), therefore, greater than 90°, the limit from which the material is considered hydrophobic (Ojeda et al., 2015).

Although the açaí seed biochar has an EH character, the addition of different doses of this material in the evaluated soils (S1 and S2) did not change their affinity with water as the drop of water infiltrated into the soil instantly (<5 s) after its deposition on the surface of the soil-biochar mixture (Figure 4). Corroborating with this result, the evaluation of the contact angle of the water drop with the surface of the soil-biochar mixture was 0 (zero), being considered completely wettable, according to Ojeda et al. (2015).

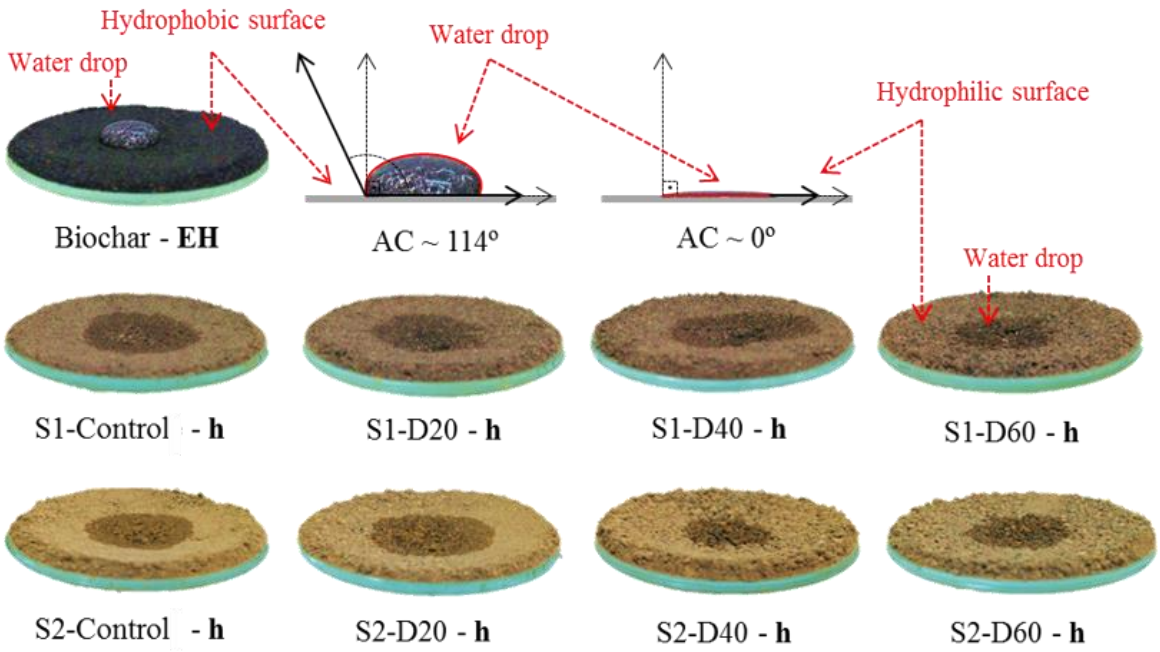

Figure 4. Water drop penetration test for the biochar, for two Yellow Latosols (sandy loam S1, and clay, S2), and for the mixture (soil + biochar). AC: Contact angle; EH: Extremely hydrophobic; h: hydrophilic, D: biochar dose (g kg^{-1}).

Effects of biochar on soil chemical attributes

In contrast to the physical results, the effect of biochar application on the chemical properties was observed in both soils (Table 6). In soil S1, the pH significantly increased as biochar was added, regardless of the applied rate. However, the same effect was not observed in soil S2 where the addition of biochar did not change soil pH. However, for the other evaluated chemical attributes, the behaviour was similar in both soils.

The content of the organic carbon (OC) linearly increased in both soils (S1 and S2) as biochar dose was incremented (Table 6). Regarding the nutrient elements for the plants, the available phosphorous content in the soil (P) increased from 40 g kg^{-1} in S1 while in S2, it was from 20 g kg^{-1} there was a significant increase in this nutrient in the soil. The same behaviour was observed for exchangeable potassium (K^{+}). In relation to exchangeable magnesium (Mg^{2+}), only the highest dosage (D60) resulted in a relevant increase in its content in both soils.

While the addition of biochar provided an increase in OC, P, K^{+} and Mg^{2+} content in soils, a reduction was observed in Ca content (Table 6). Biochar also reduced exchangeable aluminum (Al^{3+}) content in soil S1, but it had no significant effect on soil S2.

Table 6. Soil chemical properties of two Yellow Latosols, sandy loam (S1) and clay (S2), with increasing biochar doses of Açaí seeds (D, g kg^{-1}).

TREAT.	pH$_{H2O}$	OC	P	K^{+}	Ca^{2+}	Mg^{2+}	Al^{3+}
	-	g kg^{-1}	mg dm^{-3}	cmol$_c$ dm^{-3}			
S1: Sandy loam							
D0	4.63 c	24.65 d	15.53 c	0.42 b	2.30 a	0.40 b	0.62 a
D20	5.02 b	28.99 c	16.80 c	0.49 b	1.63 b	0.50 ab	0.56 ab
D40	5.09 ab	32.01 b	21.59 b	0.64 a	1.67 b	0.73 ab	0.47 b
D60	5.17 a	36.48 a	30.99 a	0.69 a	1.63 b	1.85 a	0.30 c
S2: Clay							
D0	6.21 a	36.12 c	1.26 d	0.73 c	9.93 a	1.30 b	0.22 a
D20	6.16 a	37.81 bc	2.38 c	0.93 b	8.73 ab	1.27 b	0.15 a
D40	6.19 a	40.23 b	3.90 b	1.21 a	7.63 b	1.77 b	0.10 a
D60	6.13 a	48.57 a	4.67 a	1.31 a	7.40 b	2.23 a	0.10 a

OC: organic carbon. Means followed by the same letter in the same soil do not differ among themselves by the Tukey test at 5% significance.

The application of biochar affected potential acidity (H + Al^{3+}) and cation exchange capacity (T) only in S1 soil ($p < 0.05$). The H $^{+}$+ Al^{3+} was lower in the biochar treatments compared to the control, however, no differences were found between the doses (Figure 5).

The treatment D60 had the highest average among the applied doses. Nevertheless, there was no difference when this treatment was compared with the control (D0) (Figure 5A and B).

For base saturation (V%) in the S1, only in D60 treatment this attribute increased in relation to D0. Still considering D0 as a comparative factor, no increase was observed in SB in S2. Aluminum saturation (m%) was reduced from dose D40 in both evaluated soils. Moreover, it was found that only in S1, the increase from this dose resulted in an even greater reduction in this attribute (Figure 5C and D).

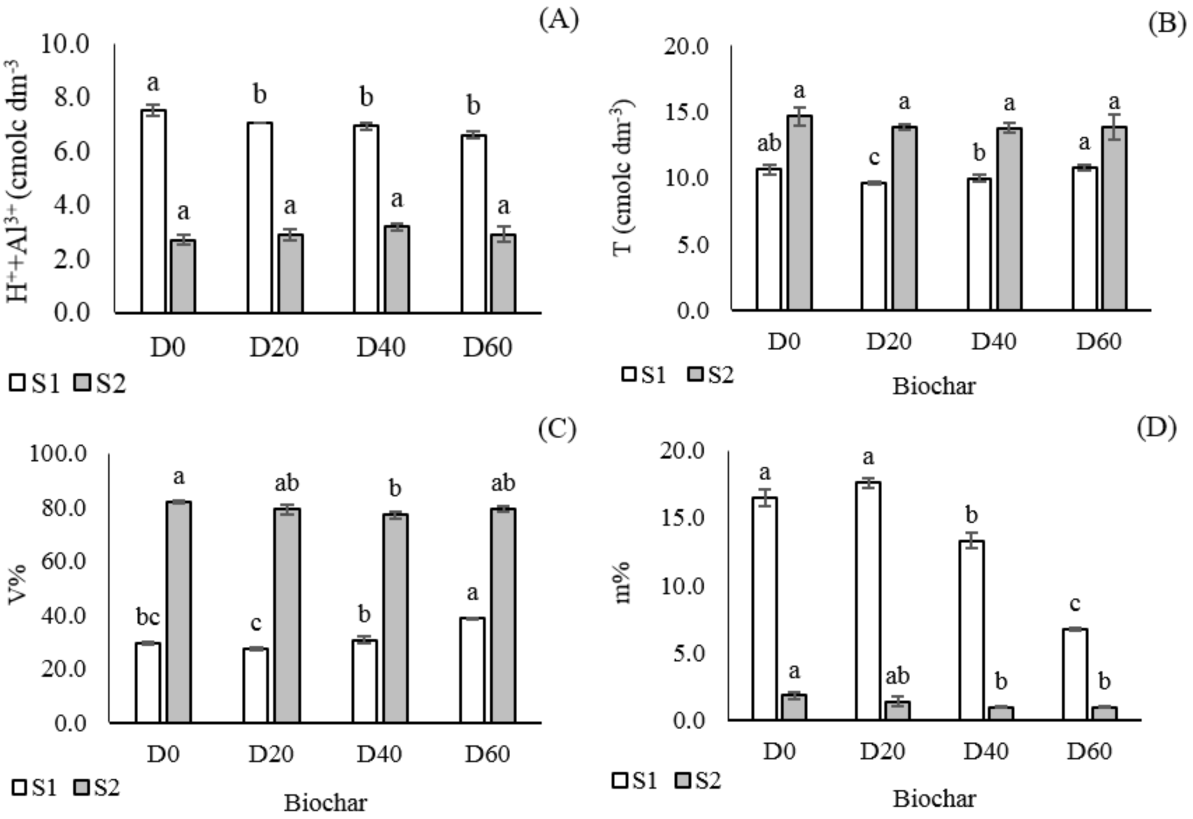

Figure 5. Soil fertility parameters of two Yellow Latosols, sandy loam (S1) and clay (S2), with increasing biochar doses of açaí seeds (D, g kg^{-1}). Means followed by the same letter in the same soil do not differ among themselves by the Tukey test at 5% significance.

Discussion

Characteristics of açaí seeds in nature and after pyrolysis

The high lignin content in açaí seeds indicates a potential for carbon sequestration. According to Maia et al. (2011), the highly complex aromatic structure of this biomass component conferes high resistance to the thermal degradation of the residue, which is directly related to the stability of the biochar when applied to the soil, that is, over time, the carbon will remain sequestered in the soil, therefore, contributing to the mitigation of emission of greenhouse gases (Joseph et al., 2009).

The reduction in volatile materials and the consequent increase in the proportion of fixed carbon after biomassas pyrolysis resulted from loss of mass caused by the release of volatile molecules (methanol, acetic acid, CO, H_2 and CO_2) and extractables besides decomposition of chemicelluloses and water release occurring between 120 to 300°C (Amonette and Joseph, 2009; Róz et al., 2015). Thus, the carbon remaining in the biochar is reorganized into a predominantly aromatic structure with high recalcitrance.

The biochar yield of 27.8% means that, considering the production conditions used, for each 100 kg of açaí seeds, 27.8 kg of biochar can be produced. This is in agreement with Dias et al. (2019) who tested the rate of biochar production under similar conditions and temperatures for different sources of biomass characteristic of the Amazon region, including açaí seeds (25.4% at 400 °C). The alternative kiln used here for the production of biochar proved to be efficient, since the production rates are similar to those of Sato et al. (2019) under laboratory conditions.Considering the municipality of Belém in Brazil, with about 3000 establishments that process and sell fruit pulp, the daily demand is around 440 tons of the fruit *in natura*. As only around 17% of the fruit is usable, the rest (83%) is discarded as residues (seeds and fibers of the fruit) (Bentes, 2017), leading to around 365 tons of waste generated daily. Taking into account our results, these residues could be converted to approximately 101.5 tons of biochar, which could be used by smallholders of the region to improve soil conditions and enhance production. Beyond the environmental benefits, this could also avoid the accumulation of this wastes in the streets, sewage networks and rivers (Townsend et al., 2001).

The maintenance of ash content is associated with the preservation of inorganic biomass components, such as Ca, Mg, Si, K, S and P, which are not degraded with the biochar production temperature. Also, they are only transformed into oxides, hydroxides and carbonates that remain part of the material (Novak et al., 2009).

The losses of H and O from biomass components due to dehydration (loss of H_2O), demethylation (loss of $-CH_3$) and decarboxylation (loss of COOH) during the pyrolysis process resulted in the accumulation of C, as previously discussed. Reductions in O/C and H/C atomic ratios confirm this behaviour, which is caused by the loss of functional groups with polar surface and the development of the aromatic structure of the biochar (Cantrell et al., 2012).

Although this condition is desirable, considering the potential of the biochar for carbon sequestration in the soil due to its high recalcitrance, the reduction in O/C and H/C atomic ratios indicates a lower ability to interact with soil. This limits its potential for the retention of water and nutrients, or as an immobilizer of soil contaminants. Higher values in these ratios suggest a biochar with more diversified organic characteristic, including aliphatic and cellulose structures, which can be used as substrates used by bacteria and fungi in nutrient renewal processes and formation of soil aggregate (Novak et al., 2009).

Effects of biochar application of Açaí seed on soil physical attributes

Although the application of biochar did not affect all aggregate classes, or even the proportion of macro and microaggregates, the increase in relative mass of some classes, such as 9.52-4.76 and 2-1 mm in S1 and 9.52 -4.76 and 1-0.5 mm in S2, and a reduction in the 0.25-0.105 mm class (in both soils) at the application of the highest rate of biochar (D60), suggests an improvement in stability of some macro-aggregate classes. This was confirmed by the higher WMD in soil S1 using this dosage. This improvement in soil structure may promote the formation of environments with more complex structures and many diversified and expanded niches, ensuring better conditions which may enhance microbial activity.

The lack of effect of the application of biochar on the WMD of soil S2 is likely to be related to the high stability of naturally-occurring aggregates found in clay soils due to the high cohesion of clay particles. In this case, the aggregates of S2 tended to be more resistant to water breakage, causing most of the relative mass to be retained in the larger open sieves.

The contribution of biochar may have been minimal, unlike in S1, where the low clay content resulted in low cohesion between soil particles, resulting in a reduced aggregate stability. In this case, there is a direct beneficial influence of biochar on the physicochemical quality and, consequently, on the soil microbiology, which may result in the indirect provision of more habitats and niches for microorganisms such as litter and roots, through better plant growth (Gul et al., 2015).

The reduction in Bd with the application of biochar in S1 corroborates the work of Bruun et al. (2014), which reported a reduction of this attribute as doses of wheat straw biochar and timber by-products (sawdust) were added in a sandy soil. This behaviour is caused by the extremely porous structure of the biochar, which is a consequence of the loss of volatile materials that are part of the original material structure, leaving empty spaces in the biochar structure after biomass pyrolysis. Barnes et al. (2014), Herath et al. (2013), Ouyang et al. (2013) and Peake et al. (2014) also support the results observed in the study.

Similar to our study, Castellini et al. (2015) did not observe differences in the density of a clay soil (43% clay) due to the addition of doses of commercial biochar produced with fruit tree pruning after about 900 days (30 months) of application.Likewise, Haefele et al. (2011) found that the effect of biochar application on soil density was undetectable even after two growing seasons. This may be related to the natural disposition of soil particles, resulting in a more porous system, typical of soils with clay texture (Brady and Weil, 2008). Such conditions may have resulted in a soil mass/volume ratio similar to that of biochar, which justifies the lack of the effect of its application on this soil.

Based on the Bd results in S1, an inconsistency was found in the TP values since their inverse relationship with Bd is recognized. Similarly, the application of biochar also reduced Mi, contrary to that assumption. According to Steiner et al. (2011) the pores of the biochar are added to the soil, resulting in greater porosity and, therefore, a greater soil water storage capacity.

The increase in the water retention is commonly reported in several papers that evaluate the effect of the addition of biochar on soil water characteristics (Castellini et al., 2015; Sun and Lu, 2014). These results may be related to the method used for determining these attributes in which water is used to fill the pores, and subsequent quantification of their volume. Thus, the hydrophobic characteristic of biochar may have prevented the water from entering into the additional pores of the material, underestimating the real volume of soil pores in biochar treatments. In addition, the application of biochar increased the ratio of hydrophobic (biochar) in relation to the hydrophilic (soil), thereby reducing water retention at tensions where water volume is considered equal to the total volume of the pores and micropores. This may also have been the reason for the lack of effect of biochar on FC, PWP and AW, regardless of the soil type.

Despite the contradictory results, studies such as those by Brewer et al. (2012), Karhu et al. (2011), Ventura et al. (2014) found similar to us, reporting that the addition of biochar did not cause any changes in soil water retention characteristics unlike Devereux et al. (2013). Jeffery et al. (2015) and Herarth et al. (2013) also attributed the lack of relationship between biochar and soil water retention to the hydrophobic character of biochar, which prevents water retention within the pore space, regardless of the size or structure of the soil.

Although the behaviour of SWRC in the soil S1 shows some absolute differences in its wetter part as a function of doses, the addition of biochar did not significantly affect the SWRC configuration. For S2 soil, the lower values of parameter α in biochar treatments suggest changes in the structure of this soil. According to Coelho et al. (1999) parameter α is inversely related to aeration porosity. In this perspective, Mota et al. (2017) suggest that α is very dependent on soil structure and, therefore, small changes in structure cause changes in the value of this parameter. According to those authors, this parameter is associated with the inverse of the value of the matric potential through which air enters into the larger pores. Since the entrance of air in these pores occurs at the matric potential closest to saturation, that is, at a location on the curve where it is most dependent on the structure of the soil, it can be stated that, based on the parameters of van Genuchten's equation, α is the most sensitive and shows a high spatial variability.

Effect of biochar hydrophobicity and its soil and water

The high degree of hydrophobicity of the Açaí-seed biochar is likely related to the nonpolar compounds in the composition of these seeds. According to Rogez (2000), the Açaí seed is surrounded by fiber bundles covered by a thin oily cuticle. In addition, they highlight the high contents of insoluble fibers that can range from 63 to 81%, and an endosperm in which most of the seed lipids are concentrated. According to Gray et al. (2014) and Jeffery et al. (2015), the temperature used in the biochar production and the presence of remaining nonpolar compounds on the material surface are directly related to the biochar hydrophobicity, and the magnitude of this effect is dependent on the raw material.

The lack of effect of biochar hydrophobicity on soil and water interactions explains why the water retention characteristics were not altered by the addition of Açaí seeds biochar. It is likely that the proportion of this material in relation to the soil is not sufficient to express its hydrophobic potential in the soil. Thus, as long as the content of up to 60 g of biochar per 1 kg of soil is maintained, the application of Açaí seed biochar does not compromise the soil affinity with water and, therefore, does not influence the soil water characteristics.

Effects of açaí seed biochar application on soil fertility

The increase in the soil pH (in S1) and OC (in S1 and S2) as the dosages of biochar were incremented is attributed to the increase in the proportion of basic substances such as oxides, hydroxides and carbonates that make up the ashes of the soil and the increasing contribution of C contained in biochar as the dosage is increased (Novak et al., 2009).

The lack of effect of the application of biochar on the pH of S2 is related to its naturally high pH, even higher than the pH of the biochar. In this case, the addition of biochar may result in a reduction in the soil pH. Although this reduction was not significant ($p > 0.05$), we observed a tendency for a reduction in the pH of S2 as a function of the addition of biochar.

The variation in available or exchangeable macronutrient contents as a function of biochar application is related to the total contents of these elements in the original material. According to Teixeira et al. (2004) and Rangel (2015), the defibrated Açaí seed has 46% carbon, 7% hydrogen, 38% oxygen, 8% nitrogen, 0.1% sulfur, 0.17% phosphorus, 0.48% potassium, 0.03% calcium, 0.02% magnesium, 167 mg kg^{-1} iron, 181 mg kg^{-1} manganese, 22 mg kg^{-1} zinc and 40 mg kg^{-1} boron. Based on that perspective, because the total P and K^+ contents in the Açaí seed are higher when compared to Mg, the contents of available P and exchangeable K in the soil are increased through the lower-dose biochar application than the content of exchangeable Mg^{2+}.

Besides the advantage of adding P to the soil, the application of biochar promotes the increase in the availability of this element through competition reactions with its surface acid functional groups for adsorption sites and precipitation of free cations (Al^{3+} and Ca^{2+}) (Guppy et al. 2005).

The temperature in the production of the biochar used in this work (~ 300 ºC) may have been decisive for the increase in P availability in both soils, as, according to Singh et al. (2010), biochars produced at low temperatures present surfaces with higher concentration of acid functional groups (such as carboxylic, phenolic and alkyl groups) than those produced at higher temperatures. The disadvantage was the reduction in the contents of Ca^{2+} which may have occurred due to the complexation of this cation with carboxylic and phenolic groups of biochar, resulting in a decrease in its availability (Novais and Mello, 2007).

The reduction in the content of Al^{3+} in S1 soil with the addition of biochar results from hydrolysis caused by the increase in the pH and complexation by organic acids. According to Silva and Mendonça (2007), the efficiency of organic acids in complexing Al is determined by the stability of the complex formed, which is increased by the dissociation of functional groups from organic compounds with the increase in the soil pH.

Based on this, the absence of significant differences in Al^{3+} content in treatments with and without biochar in S2 soil may be justified by the fact that the application of biochar did not change the pH of this soil, as previously discussed. Therefore, it does not affect its potential acidity (H^++Al^{3+}), considered average (2.51-5.00 cmolc dm^{-3}) in all its treatments (Novais and Melo, 2007).

Regardless of treatment, H^++Al^{3+} in soil S1 is considered high by Novais and Melo (2007) (5.01-9.00 cmolc dm^{-3}), although this attribute had been reduced in biochar treatments compared to control. The reduction in H^++Al^{3+} in biochar treatments is a consequence of the decrease in exchangeable acidity, mainly regarding exchangeable aluminum, that is bound to soil colloids by electrostatic forces (Al^{3+}), and non-exchangeable acidity, which refers to hydrogen dissociated only by the rise in the soil pH (Cravo et al., 2007).

The result of T in both soils contrasts with many studies that report the increase in this attribute with the application of biochar, an effect caused by the contribution of functional groups with negative biochar residual charge (Novak et al., 2009; Gul et al., 2015). In this study, the absence of effect on the T of both soils, when compared to control (D0) with biochar treatments (D20, D40 and D60) may be related to the dissociation of functional groups of biochar (such as carboxylic and phenolic groups) with the rise in pH, and metal complexation in these clusters, so that these additional sites of biochar do not take part in the cation exchange (Silva and Mendonça, 2007).

Another explanation might be the interaction of biochar charges with the residual fatty acids in Açaí, which results in the annulment of biochar charges (Doerr et al., 2000). In this case, an increase in the biochar production temperature may promote the removal of these substances from the biochar surfaces, which would result in a greater contribution of the biochar charges to the T in the soil.

The predominance of positive charges on the surface of the biochar functional groups will result in a competition with cations for exchange sites in the soil colloids to form organometallic complexes which may reduce the amount of soil cation exchange sites and affect their base saturation (V%) as occurred in D20 in S1 (Gul et al., 2015). Also in S1, the increase in V% in D60 and the reduction in aluminum saturation (m%) starting from D40, when compared to D0 is mainly due to the increase in K^+ and Mg^{2+} levels and reduction in the content of Al^{3+} (Table 2).

Similarities in SB values between treatments (except D40) in the soil S2 are due to small variations in cation contents, despite being sometimes significant. The increase in K^+ and Mg^{2+} contents with the application of biochar in this soil resulted in a reduction in m% from D40 treatment, even though there was no difference in Al^{3+} content between treatments with and without biochar.

Future Potential for the use of Açaí seeds as biochar

An important issue to consider in the production and use of biochar is the cost of the material acquisition and its homogeneity. In this sense, Açaí agroindustrial residues represent a very advantageous material, since they are easily acquired and are disposed of in large plastic bags without mixing with other residues. Our results provide positive evidence that the production of biochar from the Açaí agroindustry residues and its addition to the soil can result in environmental, economic and social benefits. Such improvements can be addressed to the Açaí production areas that have been intensively altered while sustainable conservation practices have not been adopted.

Although the proposal of using açaí seeds for biochar production is incipient, our results show its potential as a soil conditioner, especially for the soils of the Amazon region, that are, in general, coarser textured, acidic and low in fertility. The increase in soil pH and the improvement in the availability of some macronutrients verified for the sandy loam soil (S1) confirm our hypothesis. In fact, current research has clearly indicated the greater benefits of biochar application to nutrient-poor and degraded soils than to fertile or healthy soils (El-Naggar et al., 2019).

However, in order to meet demand and application, some limitations need to be considered. For example, the long-term influence of biochar on soil physicochemical properties needs to be ascertained. To consider biochar as an inducer of positive changes in soil properties further studies are needed in contrasting controlled conditions (e.g. laboratory, greenhouse, field trials). Such comparisons will help to underline the benefits of biochar. The liimited effect of the biochar addition on soil physical properties is not at this stage a reason to discourage the use of this technology as soil physical properties often take longer to respond than in the duration of this study (270 d).

Conclusions

Nine months (270 d) after the application of biochar from Açaí seeds to a sandy loam and clay soil, the levels of available phosphorus, exchangeable potassium and magnesium were increased and exchangeable aluminum reduced, mainly in a sandy loam textured soil. Biochar addition to soil improved soil physical quality to a certain, limited extent, primarily through increasing macroporosity and improving soil aggregation. However, this was not reflected with increased water retention for either soil texture. Longer-term studiess are needed to further verify the benefits of Açaí derived biochar as a soil amendment. The use of biochar from Açaí seeds as soil conditioner in the Brazilian Amazon is a promising future alternative based on the improvements to soil chemical properties supporting the production of Açaí in a sustainable manner.

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