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Advances in Biochar Research in Brazil

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ABSTRACT

To mitigate global warming, major changes in the global carbon balance are expected as the world's larger economies migrate to energy matrices that emit less greenhouse gases (GHG). Alternatives of carbon-neutral technologies have led to significant alterations in the global balance of carbon. One example is biochar, which is any source of biomass previously heated under low or no oxygen supply with the purpose of application on soil. This review aims to give an overview about the research carried out in Brazil on biochar-to-soil technology, from its structural characterization to field trials all over the country.

Keywords: black carbon, charred biomass, pyrogenic carbon, pyrolysis

Abbreviations: CEC, cation exchange capacity; **GHG**, greenhouse gases; **OM**, organic matter; **SOM**, soil organic matter; **NMR**, Nuclear Magnetic Resonance; **TPI**, Terras Pretas de Índios; **UNCTAD**, United Nations Conference on Trade and Development

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INTRODUCTION

Within the context of slow global warming, major changes in the global carbon balance are expected as the larger economies of the planet switch to energy matrices that emit less GHG. Besides the ongoing change in the global energy paradigm, from a practical point of view, there are some carbon-neutral or carbon negative technologies that would be of good economic viability and low cost, and that may lead to significant alterations in the global carbon balance, such as what can be expected by adopting the technology currently known as biochar.

In short, biochar is any source of biomass previously heated under low or no oxygen supply, with the purpose of applying to soil in order to improve its agronomic and environmental quality. The process of biochar production is known as pyrolysis and it results in a very stable carbon-rich material not only capable of improving physical and chemical soil properties, and therefore soil productivity, but also of increasing soil carbon storage on a large scale (Sohi *et al.* 2010; Kookana *et al.* 2011) and for a long period of time. From the chemical point of view, to define biochar is a little more complicated due to the wide variety of biomass which can be used for such purpose and due to the large variety of charring conditions used for its production (Lehmann and Joseph 2009; Lehmann *et al*. 2011). Nevertheless, biochar has been considered a very promising technology around the world, especially because it fits perfectly well within the bioenergy approach as a mitigation solution to GHG emissions. Scientific evidence indicates that biochar improves soil biodiversity, enhances soil performance, reduces its susceptibility to weathering, and reduces the need for fertiliser inputs. With its additional suppression of GHG emissions, a biochar-to-soil strategy based on agricultural waste streams offers sustainable carbon-negative energy production, cutting the carbon footprint of farming activity and offering society a rare win-win option for combating climate change (Sohi *et al.* 2010).

WHERE DID THE BIOCHAR IDEA COME FROM?

Terras Pretas de Índios

The idea of biochar as a soil amendment is not new and some occasional scientific publications about charcoal in soils can be found since the early 20th century. Nevertheless, recent studies about Amazonian Dark Earths, the so-called Terras Pretas de Índios (TPI), renewed the scientific interest on pyrogenic carbon in soils. TPI soils are anthropogenic dark earths with a surface horizon enriched in organic matter to variable depth, pottery shards and lithic artifacts (**Fig. 1**), as well as other evidences of human activity (Kämpf *et*

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Fig. 1 Terras Pretas de Índio profiles and pottery artifacts found in these soils. Photographer: EH Novotny.

al. 2003). These archaeological Amazonian sites are characterized by dark soils with high fertility and agronomic potential, which is very unusual when compared to the surrounding highly weathered and very acidic soils of typically low fertility. The first aspect which draws attention to TPI soils, besides the color, is its richness in carbon, up to 150 g kg^{-1} of soil, compared to 20 to 30 g kg^{-1} in adjacent soils (Novotny *et al.* 2009). This additional carbon is presented mainly in pyrogenic form, being around six times more stable than other forms (Glaser *et al.* 2001). Also, the carbon enriched layer can reach a depth of 200 cm, averaging from 40 to 50 cm, while in surrounding soils this is limited to 10 to 20 cm. Therefore, carbon stocks in TPI can be much higher than in surrounding soils. Pyrogenic carbon results from partial carbonization (pyrolysis) of biomass and is rich in condensed polyaromatic compounds of low H/C and O/C ratios. These chemical characteristics confer to pyrogenic carbon high recalcitrance and resistance to thermal-, chemical, and photo-degradation (Novotny *et al.* 2009), which make this material very suitable as a carbon sequester or drainer.

Usually these soils occur in small patches, many of them not larger than 2 ha, although sites of up to 350 ha have been registered (Kern *et al.* 2003). According to geographer William I. Woods, the total area of TPI sites overtakes around 10% of the Amazonian tropical forest, equivalent to the territory of France (Mann 2002), though this might be an overestimation.

It is currently accepted that TPI soils can date back to the pre-Columbian era and that their enrichment in char resulted from the activity of human communities such as bonfires or field burning, but it is still not clear so far whether intentional or not. What is certainly known is that the origin of the high nutrient content of these soils is the intense accumulation of fire-managed organic wastes (from plants or animals). Phosphorus, magnesium, zinc, copper, calcium, strontium and barium are all representative of the geochemical signature of human occupation (Costa and Kern 1999). This accumulation process and the slow environmental alteration of this material explain the higher values for pH, Ca, Mg, P, CEC and base saturation in TPI when compared to surrounding soils (Novotny *et al.* 2009).

Pyrogenic or black carbon

Soil fertility, especially in tropical soils, is substantially influenced by organic matter and its physical and chemical properties. SOM is a complex miscellany of organic compounds, of plant or animal origin, in gradual decomposition stage due to chemical or biological transformation. Pyrogenic carbon is the most recalcitrant fraction of SOM and, according to Seiler and Crutzen (1980) can be described as "a continuum from partly charred plant material, through char and charcoal, to soot and graphite particles without distinct". Pyrogenic carbon is derived from partial carbonization mainly of ligno-cellulosic materials, resulting in different sizes of hydrogen and oxygen deficient condensed polyaromatic units, which form small cross-linked aromatic clusters that give way to larger graphene sheets and tend to form stacks with disordered packing. Soot particles that condense from the gas phase typically develop as concentric shells of these graphene stacks ("onion-like" structure, Preston and Schmidt 2006). Pyrogenic carbon is highly resistant to thermal-, chemical- and photo-degradation (Skjemstad *et al.* 1996), an excellent characteristic for soil carbon sequestration (Glaser *et al.* 2001; Masiello 2004). However, partial oxidation of peripheral aromatic units may produce carboxylic groups that elevate the total acidity of SOM and, therefore, their CEC and soil fertility (Novotny *et al.* 2009). The high condensation degree of pyrogenic fraction is supported by elemental composition data, which indicate a low H/C atomic ratio and NMR data (Novotny *et al.* 2007). Its persistence was proven by radiocarbon analysis as being aged from 500 to 3,000 years (Glaser *et al.* 2001).

In Brazil, pyrogenic carbon is not restricted to TPI and its origin is not always anthropogenic. Pyrogenic carbon is highly common in soils under vegetation that was historically burnt with high frequency by natural fires as in, for example, the Brazilian savannah (*Cerrado*) (Roscoe *et al.* 2001). According to some estimates, char may represent up to 40% of total carbon in the *Cerrado* soils (Jantalia *et al.* 2007). Due to their high stability and reactivity after environmental aging, weathered pyrogenic organic fractions are of great importance for tropical soils usually characterized by low CEC clays (**Table 1**).

Humic acids extracted from TPI and analyzed by ^{13}C NMR spectroscopy (Kramer *et al.* 2004; Novotny *et al.* 2007) revealed that this fraction is rich in condensed aromatic structures and functionalized with carboxylic groups linked directly to the recalcitrant polyaromatic rings (**Fig. 2A**). In contrast, humic acids from adjacent non-anthropogenic soils have a higher content of labile compounds, such as carbohydrates, aminoacids and lignin (**Fig. 2B**). The content of recalcitrant and reactive structures correlates with its thermal stability, determined by thermo gravimetric analysis.

Pyrogenic carbon is not only found in tropical soils, but

Table 1 Typical values for cation exchange capacity (CEC) of clay minerals and organics colloids from temperate and tropical soils.

Soil	**Constituent**	**CEC (cmol$_c$ kg^{-1})**
Temperate climate	Montmorilonite	80-120
	Vermiculite	120-150
Tropical climate	Kaolinite	3-15
	Sesquioxides	2-4
Organic fraction	Soil organic matter (SOM)	100-300
	Humic fraction (2/3 of SOM)	400-800

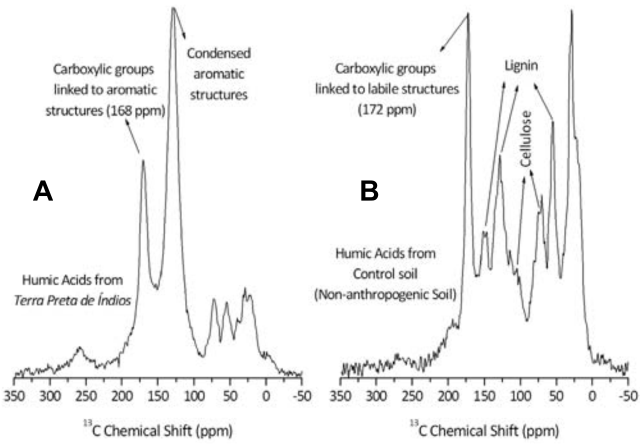

Fig. 2 ^{13}C-NMR spectra of humic acids from Amazon Region soils. (**A**) TPI; (**B**) Non-anthropogenic soil. Source: EH Novotny.

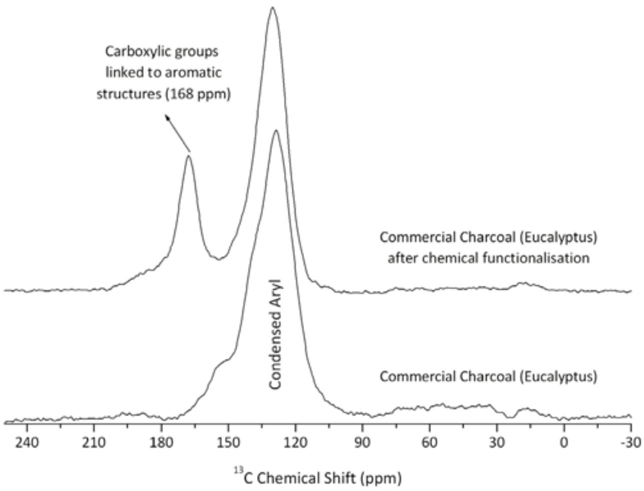

Fig. 3 ^{13}C-NMR spectra of charcoal before and after chemical oxidation. Source: EH Novotny.

is widespread around the world. It is estimated that it represents 1 to 6% of the total world SOM (González-Pérez *et al.* 2004) and can reach 18% of total SOM in native grasslands of the USA (Glaser and Amelung 2003); up to 30% in Australian soils (Skjemstad *et al.* 2002); up to 45% in German Chernozems (Schmidt *et al.* 1999) and 65% in Canadian Chernozems (Ponomarenko and Anderson 2001).

Soil organic matter from Terras Pretas de Índios as a model

Ancient indigenous production systems can provide insights and a basis for a sustainable agricultural management model that promotes carbon sequestration and is particularly suitable for tropical ecosystems. Once the model is established, the next step is to pursue materials and techniques to mimic it and as such, charcoal is a natural answer. Even though charcoal is an efficient material for carbon sequestration (its half-life ranging from decades to millennia) it is not provided with carboxylic groups that could improve its reactivity and CEC (**Fig. 3A**). Therefore, some functionalization of the aryl backbone is desirable, which can be obtained naturally (but slowly) or through oxidation processes, chemically (**Fig. 3B**), thermally or biologically.

Besides carbon sequestration, charcoal amendments to soil can provide other benefits such as productivity enhancement (from 0 to 300%), decreased emission of methane and nitrous oxide (up to 50% estimations), decrease of nutrient leaching and enhanced water-holding capacity (Gaunt and Lehmann 2007).

WHY IS BRAZIL INVESTING IN BIOCHAR?

According to the UNCTAD, by the end of next decade Brazil will become the largest agriculture and livestock producer in the world (Lourenço and Lima 2009). It is also forecasted that Brazil's agricultural output will grow faster than any other countries in the world in the coming decade, increasing by 40% by 2019 (Tollefson 2010). The country is already a leader in exports of sugar and ethanol, coffee and orange juice. Recently, Brazilian beef and chicken surpassed traditional competing exporters such as Australia and North America. According to Lora and Andrade (2009), in 2001, grains (corn, soybean, rice, wheat and coffee), cotton and manioc production was 100 million tons, the equivalent to around 130 million tons of residues (straw, stems and husks). Moreover, 45.1% of the Brazilian energetic matrix is based on renewable resources (compared with a world average of 15%), from which 27.2 % is supplied by biomass (Lora and Andrade 2009). The Brazilian agro energy chain involves around 200 million tons of bagasse from sugar cane industry and, as the largest charcoal producer and consumer in the world (38.5% from the global production in 2005), around 1.9 million tons per year of charcoal powder which is lost during the charcoal production and distribution steps (Benites *et al.* 2009). With this huge amount of wasted biomass, biochar comes as an obvious solution for urgent problems: a fast, inexpensive and opportune way to stock carbon and improve soil quality.

It is important to mention that biochar technology is being studied by Embrapa and their partners together with other low carbon practices such as no-tillage cropping systems, integrated crop-livestock-forestry systems, forestation and degraded land restoration. To produce biochar from native forest destruction is nonsense in any environmental analysis. Besides, sustainability is a concept that is increasingly present in industrial management, with recent initiatives taking place in the private forestry sector. For example, the Sustainability Pact established in the state of Minas Gerais, the highest charcoal consumer in Brazil, between its industries and the Forestry State Association, declares that within five years, plantations will supply 95% of feedstock for charcoal production. A second case concerns the Carajás Pig Iron Pole, where around U$ 200 million was invested in 150 thousand hectares of eucalyptus plantations in degraded lands, and the recovery of 50 thousand ha of native forest in Pará State, the largest deforester state in Brazil, is expected. It is interesting to note that the Carajás Pole works together with the Citizen Charcoal Institute, whose main concern is the compliance of labor laws for charcoal workers, and has already achieved 90% of conformity with regulations.

CHARACTERIZATION OF BIOCHAR

Generally, all plant is formed mainly by lignin, cellulose and hemicelluloses. In the charring process the structural differences between the sources tend to diminish. Nevertheless, biomass chemical constitution is highly variable according to the botanical species and plant part (leaves, branches, wood, bagasse, residues from vegetable oil extraction, etc.). Trees, for example, usually have higher lignin content than herbs, and conifers have lignin type different from hardwoods. Therefore, different biomass sources result in different biochar, with further anatomic differences in the residues that confer particularities to the obtained charcoal (such as porosity, grain size etc.). Similarly, physical properties such as density and porosity are variable and depend on the pyrolysis process, which can also vary drastically according to the heating rate and intensity, from traditional slow pyrolysis methods for charcoal production to high temperature gasification processes, which produce just around 10% of solid biochar. In Brazil, most of the charcoal is produced by a traditionally slow pyrolysis process of low efficiency and average yield of around 30%.

Chemical aspects of the pyrolysis process are complicated not only due to the large variation of biomass components but also because the chemical reactions involved are poorly understood. Chemical components found in plants – mostly cellulose, hemicellulose and lignin – all undergo different reactions during pyrolysis. The carbonization process can be described as the following degradation steps: a) dehydration, an endothermic step that generally occurs from 50 to 150°C, where free water molecules and low molecular mass organic compounds are lost; b) hemicellulose degradation, a exothermic phase starting around 150°C and mass loss apex around 275°C yielding predominantly volatile products such as carbon oxides; c) cellulose degradation, an endothermic step occurring from 280 to 500°C and reaching a peak around 350°C; d) lignin degradation, a slow exothermic process between 200 to 500°C and maximum of energy release around 365°C (Bridgwater 2001; Taccini 2010). These reactions combine in complex ways that go beyond the simple superposition of their individual characteristics (Antal 1989). All studies conducted about the degradation of wood point to free radical reactions, which can be characterized by a number of generalized reactions such as:

1. Initiation: One molecule breaks into two free radicals and propagates the reaction further;
   $CH_3CH_3 \rightarrow 2\ CH_3\bullet$
2. Hydrogen Abstraction: a free radical pulls hydrogen from another molecule, creating another radical that will react further;
   $CH_3\bullet + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2\bullet$
3. Radical Decomposition: a free radical breaks into two separate molecules, often creating an alkene;
   $CH_3CH_2\bullet \rightarrow CH_2{=}CH_2 + H\bullet$
4. Radical Addition: the reaction of a radical with an alkene produces a larger free radical. Aromatic products are probably created through this reaction;
   $CH_3CH_2\bullet + CH_2{=}CH_2 \rightarrow CH_3CH_2CH_2CH_2\bullet$
5. Termination: two free radicals interact to form one molecule with no radical left over. Two types of this reaction are:
   Recombination: $CH_3\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_3$
   Disproportionation:
   $CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_2{=}CH_2 + CH_3CH_3$

Pyrolysis results in a graphite-like structure, low O/C and H/C ratios and, therefore, few organic functional groups. In short, it can be considered a drastic process of dehydration, decarboxylation and condensation.

AGRONOMIC USE AND FIELD EXPERIMENTATION IN BRAZIL

Biochar use in order to improve soil properties has been widely studied but its real potential as conditioner and carbon sequester is still little understood. Many studies confirm that biochar improves various chemical, physical and biological soil characteristics. Productivity increases of soybean have been testified since 1948 (Tryon 1948) and in other recent works (Iswaran *et al.* 1980; Kishimoto and Sigiura 1985; Petter 2010). Oguntunde *et al.* (2004) observed that the grain and biomass yield of maize increased by 91 and 44%, respectively, on charcoal amended soils when compared to adjacent field soil. Major *et al.* (2005) found an increase of 53% in biomass yields of rice on soils that received charcoal. Others studies confirm a positive effect on rice and grass yields when cultivated on soil amended with charcoal (Rondon *et al.* 2006; Yamato *et al.* 2006). Maia and Sohi (2010) found an increase of 17% in the biomass yield of maize on plots with biochar plus fertilizer as compared to fertilized plots without biochar.

In Brazil, field experimentation started about 10 years ago. The first studies were focused on Amazonian lands. In Amazonian soils, charcoal significantly improved plant growth and doubled rice grain production if fertilized with NPK in comparison to the NPK-fertilizer without charcoal (Steiner *et al.* 2007).

The largest research network, headed by Embrapa, includes charring studies of different biomass sources and field experiments in different Brazilian biomes: the Amazon, the Atlantic Forest, the *Cerrado* and the transition zones between *Cerrado*-Amazon and *Cerrado-Pantanal* (wetlands).

In the Amazon region, Steiner *et al.* (2007) described the effect of charcoal use alone and in combination with synthetic fertilizer and chicken manure. They have concluded that the better result, in terms of yields (maize and upland rice), is the combination of charcoal with poultry manure. On the effect of charcoal on soil physical properties, Teixeira *et al.* (2003) are progressing with investigations. Another priority in the research agenda in this biome is the comparison of three different management systems: slash and burn, slash and mulch ("*Tipitamba*") and slash and char.

BRAZILIAN BIOCHAR EXPERIMENT NETWORK

In the Savanna biome (*Cerrado*) the effect of biochar has been studied since 2006 in different soil types and textures: sandy clay Haplic Ferralsol, sandy loam Dystric Cambisol and clayey Rhodic Ferralsol. The effects of different doses of fine of charcoal (0 to 32 Mg ha^{-1}) in combination with a mineral fertilizer (NPK, 0 to 400 kg ha^{-1}) is being evaluated on soybean, common beans and upland rice yields regarding the synthetic fertilizer use efficiency, the soil fertility, the physical, chemical and biological properties of the soil, and the C dynamics, as well as plant growth, biomass production and nutrient uptake. Amongst environmental parameters, N_2O emission and emission factor are evaluated as affected by biochar-synthetic fertilizer interaction. In these experiments charcoal was incorporated to soil only once, at the time of the experiment implementation. The main objective is to evaluate the extended effect of biochar on the above-mentioned soil and crop properties over a number of years (residual effects). As the most important agronomic observations, the effect of charcoal on crop yield and on nutrient use efficiency should be mentioned.

According to Madari *et al.* (2010) charcoal had dramatic effects on soybean and upland rice yields over time in the sandy and sandy loam textured soils. Charcoal had a significant separate effect on soybean yields that can be described by a quadratic equation ($f=y_0+ax+bx^2$, x=charcoal dose, $r^2=0.96$, $p=0.016$), even after four years of its application to the soil. Charcoal had similar effects on upland rice yields, which increased in a linear manner with increasing charcoal doses. In the second year after its application to the soil, the equation that describes the effect of charcoal on upland rice yields in a sandy loam soil was $f=y_0+ax$, (x=charcoal dose, $r^2=0.99$, $p<0.0001$). The effect of charcoal was, in most cases, much stronger than the effect of the synthetic fertilizers (P e K in case of soybean and N, P and K in case of upland rice). The high r^2 and low p values suggest high predictability of the effect of charred material on crop yield, an important aspect for its practical implementation in agriculture.

The effect of charcoal on the agronomic efficiency of synthetic N, P and K is demonstrated in **Table 2**. The data shows that elevated doses of charcoal incorporated to the soil increased N, P and K use efficiency by upland rice.

However, the positive effect of charcoal on yields and nutrient use efficiency by the crop cannot be explained fully by the effect of charcoal on soil fertility properties, since on these, synthetic fertilizer had greater effects than charcoal and there was no significant correlation between soil fertility properties and crop yield (Madari *et al.* 2010).

As for soil physical properties, over time charcoal increased water holding capacity and microporosity in the medium textured soil. However, immediately after its application in the first year, it seemed to decrease water-holding capacity, especially at the higher application rates. On sandy soil however, already in the first year the highest charcoal dose (32 Mg ha^{-1}) increased both plant available and fixed water (Silva *et al.* 2010).

Table 2 Agronomic efficiency* of N, P and K application as affected by charcoal application to the soil (immediate effect of charcoal) in a sandy Dystric Cambisol, in Nova Xavantina, MT.

Charcoal (Mg ha^{-1})	**Applied nutrient doses (kg ha^{-1})**		
		Nitrogen	
	20	**37**	**55**
8	13.11 A	7.41 A	1.10 A
16	16.76 A	8.47 A	2.53 A
32	25.67 B	13.04 A	10.17 B
		Phosphorus	
	11	**22**	**33**
8	24.03 A	12.56 A	1.85 A
16	30.72 A	14.36 A	4.25 A
32	47.06 B	22.10 A	17.08 B
		Potassium	
	12	**25**	**37**
8	21.06 Ba	11.01 A	1.62 A
16	26.92 Ba	12.59 A	3.72 A
32	41.24 Aa	19.37 A	14.97 B

*Agronomic efficiency = (PGcf - PGsf)/(QNa), in kg kg-1; where: PGcf = yield of grains with the application of synthetic fertilizero, PGsf = yield of grains without applying synthetic fertilizer e QNa = amount of nutrient applied, in kg. Means followed by the same capital letters in the columns and by the same small letters in the rows do not differ by Tukey's t-test at $p \leq 0.05$.
Source: Madari *et al.* 2010

As for the environmental consequences of charcoal application to soil, little doubt can be drawn in relation to its positive effect on carbon sequestration in the soil, although little can be affirmed about the biochar half-life once in the soil. Also, reasonable doubt exists about its efficiency in nitrous oxide (N_2O) emissions reduction. According to Carvalho *et al.* (2010) in the clayey Rhodic Ferralsol, charcoal had no effect on N_2O emissions. In the sandy Dystric Cambisol, however, at the highest rate of its application (32 Mg ha^{-1}) charcoal induced more N_2O emission compared to the control (no charcoal addition). It is worth mentioning that the latter soil represents a rather degraded environment. Improving soil conditions with the introduction of pyrogenic carbon (charcoal) might have had a great effect on biological activity (not measured) that, in turn, led to higher N_2O emissions.

The usefulness of pyrogenic carbon therefore has to be evaluated on a multidimensional level, including the agronomic and environmental aspects (not mentioning socio-economic parameters that go beyond the scope of this paper). Some of the factors to be evaluated are doses of application, combination with synthetic or other type of fertilizers, soil and climatic conditions of the site of application. According to this, site-specific combined with biochar-specific recommendations would be desirable for planned and predictable agronomic use of this material.

RESEARCH CHALLENGES AND PERSPECTIVES

Brazil is now the world's largest exporter not only of coffee, sugar, orange juice and tobacco but also of ethanol, beef and chicken, and the second-largest source of soybean products (The Economist 2010). With such huge amounts of agricultural production, the first challenge comes with the large variety of biomass sources available to char. Each biomass source has its specific ideal conditions to produce biochar that are physically and chemically different, and thus lead to different soil responses. The variability comes not only from that, but also from the large climate variation in the country. With all these possibilities, it is necessary to prioritize certain biomass sources. At the moment, it seems that amongst the most important challenges is to find biochar techniques (sources, pyrolysis parameters and application) adapted to the Brazilian Savannah biome that experiences accentuated dry periods (dry season, May to September/October) and, frequently, short but limiting dry periods (dry spells) within the rainy season (October/November to April) and is characterized by specific production systems with specific problems. Within this biome the most vulnerable areas are those with sandy soils that have low water holding capacity and low organic matter and nutrient levels, many times also in bad physical conditions, especially under prolonged agricultural use without soil conservation practices (Resende *et al.* 1996). The Savannah and the Savannah-Amazon transition zone are today the major frontiers for agricultural expansion in Brazil.

As carbonization (pyrolysis) can be a viable solution not only for agricultural waste management but also for the waste management of municipalities, this can be an interesting option for city administration as well, and in some places interest has arisen already in relation to the management of municipal gardens. However, for the use of municipal waste, several prerequisites must be fulfilled such as selective waste collection, among others.

Caution needs to be taken when biochar production capacity is evaluated. Charred material that may come from deforestation of natural areas must not be considered. However, a positive scenario comes through the great potential to expand forest plantations since its 5.5 million ha represent only 0.2% of all cultivated land in the country. Therefore, besides the scientific challenges of processes, mechanisms, agronomic and environmental effects, biochar research needs to be carried according to each regional or even local peculiarity.

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