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Black carbon in sustainable soils of the Brazilian Amazon region

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Summary

In the Brazilian Amazon, patches of highly fertile anthropogenic soils, known as Terra Preta occur within the Oxisol and Ultisol landscape. Since Terra Preta soils are characterized by a large and stable soil organic matter (SOM) pool, we assumed that this is a key factor for the sustainability of these soils. In the present study, we analyzed finely divided residues from burning (black carbon) in the fine earth and particle size separates in Terra Preta as compared to adjacent Oxisols. The SOM of Terra Preta consists up to 30 % of black carbon, which remains as residue after incomplete burning of biomass. Due to its highly aromatic structure, it is chemically and microbiologically inert and persists in the environment over thousands of years. Thus, a part of the labile carbon pool in the biomass has been converted into a stable SOM pool. Weak oxidation during this time produces carboxylic groups on the edges of the aromatic rings, which increases the cation exchange capacity. Therefore, we conclude that black carbon is a key factor for sustainable and very fertile soils in the humid tropics, which could be established even on highly weathered, very infertile Oxisols.

Introduction

In the Brazilian Amazon region, small patches of sustainable and very fertile black anthropogenic soils, known as Terra Preta, are embedded in a landscape of highly weathered and very infertile Oxisols and Ultisols. The most important factor seems to be the development of stable SOM (Duxbury *et al.* 1989; Zech *et al.* 1990). Normally, in these environments SOM is decomposed very quickly due to the high temperature and high soil moisture content (Sombroek *et al.* 1993). Terra Preta, however, is equipped with a huge A horizon even centuries after forest clearing, but the reasons are still matter of speculation.

The regular occurrence of charcoal in Terra Preta (Sombroek 1966; Saldarriaga and West, 1986) indicates that residues from burning of organic material (pyrogenic carbon, black carbon) probably contributes to the SOM of Terra Preta. To verify if black carbon is a common constituent of SOM of Terra Preta, we developed a method for its specific determination in soil samples (Glaser *et al*. 1998). Our method uses benzenepolycarboxylic acids (BPCA) as specific markers for black carbon. The principle is based on the fact that BPCA are found exclusively after oxidation of charred organic material but not in the original samples. The analytical procedure of soil samples includes acid digestion, oxidation, sample cleanup, derivatization, and gas chromatography.

The objectives of this study were (a) to verify if black carbon is a common constituent of Terra Preta, and (b) to cover textural effects on the black carbon distribution in Terra Preta and Oxisols.

Materials and Methods

Site description and soils

The study was carried out in the Central Amazon region, Brazil, where Oxisols and Ultisols predominate. In addition a peculiar, black earth like anthropogenic soil (Terra Preta) occurs in small areas rarely exceeding 2 ha (Zech *et al.* 1990). Mean annual temperature is 26 ± 3 °C and mean annual rainfall 2050 mm with a dry season between August and November (Otzen 1992). Five profile pairs Terra Preta – Oxisol were sampled near Manaus and Santarem.

Laboratory analyses

Physical particle size fractionation was carried out according to Christensen (1992). Total organic carbon (TOC) and total nitrogen (N) were determined by dry combustion and WLD detection on a Vario EL C/N analyzer. Black carbon was determined in fine earth and particle size fractions using the method of Glaser *et al*. (1998). The sum of the yields of benzene carboxylic acids with three (b3ca) to six (b6ca) carboxylic groups (b3-b6ca) after nitric acid oxidation of commercially available charcoal were adopted as a measure for the black carbon content. For statistical analysis we applied MANOVA followed by the post hoc Scheffé test or Wilcoxon test (Hartung 1993; Sokal and Rohlf 1995).

Results and Discussion

Black carbon as source of stable SOM

The concentrations of black carbon on a soil mass base decreased in all soils with increasing profile depth (not shown here), whereas black carbon on SOM base was more or less equal in the A horizons of Terra Preta soils. In the topsoil horizon of the Oxisols, total organic carbon (TOC) consisted of about 50 to 150 g kg^{-1} of black carbon, rapidly decreasing with decreasing profile depth. In Terra Preta soils, however, black carbon represented 100 to 350 g kg^{-1} of the TOC in the whole A horizon, depending on its thickness.

This result fits well with previous results on black carbon contents in soils with large amounts of stable SOM, using solid state ^{13}C CP/MAS nuclear magnetic resonance (n.m.r.) spectroscopy. Skjemstad *et al.* (1996) estimated up to 8 g charcoal-C kg^{-1} dry mass in four Australian soils with contrasting properties, corresponding to up to 300 g kg^{-1} TOC as charcoal in a black earth in Queensland, Australia. They mentioned, however, that their method has some analytical constraints. E.g. the main aryl band (160 - 110 ppm) of n.m.r. spectra consists of a combination of structures from lignin, tannin and other non-oxygen substituted aromatics such as those in charcoal. Also non protonated, aromatic carbons give no effective cross polarization leading to an underestimation of aromatic carbon. This could be avoided using Bloch decay. Due to long time of data acquisition, analyzing all samples with Bloch decay would be totally impractical. Therefore, the authors used a conversion factor of 1.5 for all samples measured with CP/MAS technique.

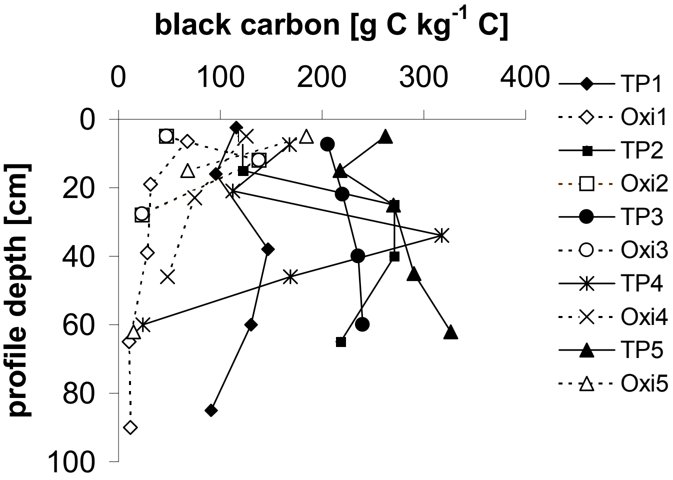

Figure 1. Concentrations of black carbon in the soil organic matter of Terra Preta soils (TP) and adjacent Oxisols (Oxi) of the Brazilian Amazon region with increasing profile depth.

Schmidt *et al*. (1998) investigated A horizons from a catena of Chernozems south of Hannover (Germany) using a suite of complementary methods (high energy ultraviolet photo-oxidation and solid state ^{13}C n.m.r.). They found that charcoal contributed up to 450 g kg^{-1} to TOC and up to about 8 g kg^{-1} to the bulk soil of the Chernozems. They did not detect charcoal in two reference soils (Alfisol, Gleysol). Additionally they found a strong relationship between soil color and the content of charred organic carbon. The authors concluded that besides climate, vegetation and bioturbation, also fire history plays an important role in the pedogenesis of Chernozems.

The stocks of black carbon in the soil profile to one meter profile depth was 4 to 11 times higher in Terra Preta than in Oxisols and increased with increasing clay content (Figure 2). Terra Preta contained 22 (sandy soil) to 110 (clayey soil) Mg black carbon ha^{-1} m^{-1}, and the Oxisols 4 (sandy soil) to 13 (clayey soil).

Distribution of black carbon among particle size separates

In the topsoil horizon of Terra Preta and Oxisols, the SOM of fine sand and silt had the highest black carbon concentrations (Table 1), whereas in the subsoil horizon, no significant differences were observed within different particle size classes (not shown here). TP 5 had the highest black carbon concentrations in all particle size classes. This could be due to longer or to more intensive human occupation of this site.

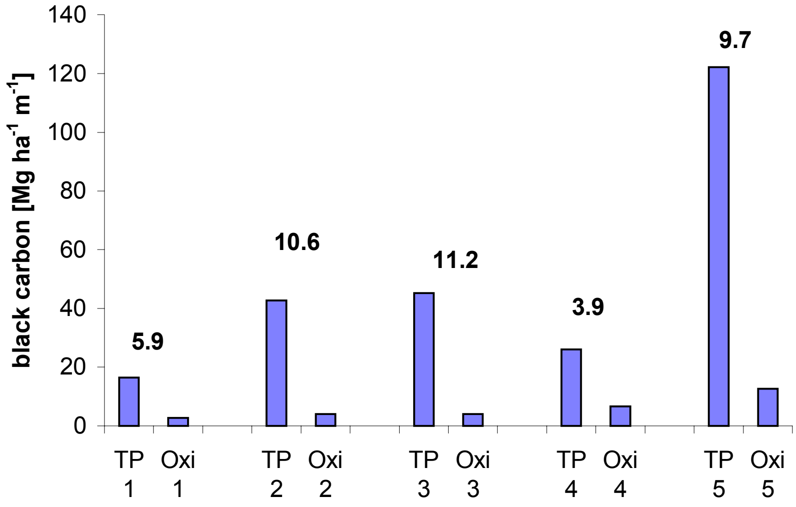

Figure 2. Stocks of black carbon in profiles of Terra Preta (TP) and Oxisols (Oxi) down to 1 m profile depth. Numbers above the columns indicate the ratio of the black carbon content of a Terra Preta to its adjacent Oxisol.

Saldariaga and West (1986) found on Terra firme soils of the upper Rio Negro area of the Colombian and Venezuelan Amazon region 3 to 24 Mg charcoal ha^{-1}, with 33 to 86 % of it concentrated in the upper 50 cm, which is in the range of our investigated Oxisols.

Table 1. Contribution of black carbon to soil organic matter [g C kg^{-1} C] in particle size fractions of topsoil horizons (0-10 cm) of soils in the Brazilian Amazon region with various texture.

cs coarse sand (2000 - 250 µm); fs fine sand (250 - 20 µm); silt (20 - 2 µm); clay (<2 µm); different letters indicate significant ($p<0.05$) differences between different particle size classes. nd not detected.

Profile	cs	fs	Silt	Clay	Profile	cs	fs	Silt	Clay
Terra Preta	a	ab	b	a	Oxisol	ab	ab	b	a
TP1	9	89	151	69	Oxi1	32	8	126	86
TP2	nd	36	53	64	Oxi2	nd	48	48	nd
TP3	28	138	173	58	Oxi3	nd	48	48	nd
TP4	89	226	146	77	Oxi4	114	142	111	28
TP5	291	245	288	222	Oxi5	116	116	97	24

In the topsoil horizons, most of the stocks of black carbon was located in the silt and clay fractions in Terra Preta soils (86%) and Oxisols (80%, Table 2). In Terra Preta soils, the silt fraction contributed significantly ($p<0.01$) more to the total black carbon content than in the Oxisols. In the subsoil horizons, the clay fraction of Terra Preta represented on average 92 % of the total black carbon stock. In the other fractions, black carbon is distributed homogeneously and contributes only a minor amount (not shown here). Skjemstad *et al.* (1996) calculated that 64 to 97% of charcoal in four Australian soils occurred in the < 53 µm fraction. In spite the analytical differences of both studies, their results are consistent with our findings.

Table 2. Distribution of black carbon [%] in particle size fractions of topsoil horizons (0-10 cm) of soils in the Brazilian Amazon region. cs coarse sand (2000 - 250 µm); fs fine sand (250 - 20 µm); silt (20 - 2 µm); clay (<2 µm). Different letters indicate significant ($p<0.05$) differences between different particle size classes.

Profile	cs	fs	Silt	Clay	Profile	cs	fs	Silt	Clay
Terra Preta	a	a	b	b	Oxisol	a	a	a	b
TP 1	nd	21	53	25	Oxi 1	2	4	19	76
TP 2	nd	4	19	78	Oxi 2	nd	11	nd	89
TP 3	1	10	38	51	Oxi 3	nd	11	nd	89
TP 4	2	16	36	46	Oxi 4	23	30	17	30
TP 5	1	5	36	59	Oxi 5	8	15	4	73

The enrichment of black carbon in clay sized separates in the subsoil make it probable that black carbon could be leached into deeper horizons by eluviation processes, as also assumed by Skjemstad *et al*. (1996) and Schmidt *et al.* (1998). Such processes could be responsible for the huge A horizons of Terra Preta. Leaching, however, does not explain the occurence of potsherds in deeper horizons of Terra Preta soils. As it is known that Terra Preta sites received no tillage, turbation could be also responsible for the transport of black carbon and potsherds into deeper soil horizons. Further research, however, is desirable to clarify the dynamics of black carbon in soils.

Conclusions

Our results showed that black carbon form a major SOM pool in Terra Preta. With time, black carbon is partly oxidized at the surface, and carboxylic groups with partly low pKa values (e.g. pKa of mellitic acid 1.40) are produced (Glaser *et al.*, 1998). Hence, black carbon is a sustainable and effective cation exchanger and probably responsible for the high nutrient storage capacity of Terra Preta compared to the Oxisols they originated from. This high nutrient storage capacity of Terra Preta arising from partly microbially oxidized burning residues may be responsible that these soils maintain their high soil fertility even after their abandonment centuries ago. Enhanced biomass production on these sites still may result in larger carbon inputs in the topsoil. Further research is desirable to study the SOM enrichment process on Terra Preta and to develop a large-scale field program for the stimulation of SOM storage in tropical and subtropical soils.

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