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Carbon Sink Strength of Subsurface Horizons in Brazilian Oxisols

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Abstract

Interactions with pedogenic oxides are a known mechanism of soil organic matter (SOM) protection, but little is known about how the protective power of pedogenic oxides varies with soil depth in highly weathered tropical soils. To address this issue, we followed the decomposition of a double-labeled plant litter ($^{13}\text{C}/^{15}\text{N}$) in microcosm experiments using samples collected at four depths (0–10, 10–20, 20–40, and 60–100 cm) from six Brazilian Oxisols. These soils were selected to include a range of taxonomic subtypes, spanning wide variations in mineralogy and texture. After a 12-mo incubation, we quantified the proportion of isotopically-labeled SOM ($^{13}\text{C}/^{15}\text{N}$) within the mineral fraction $<53\text{ }\mu\text{m}$ (i.e., clay+silt). We found that litter-C retention increased with depth, while the opposite occurred for litter-N. Correlations between isotopically-labeled SOM and short-range order (SRO) Al-/Fe-(hydr)oxides were insignificant in topsoil (0–10 cm), but increased with depth, reaching peak significance in the 20- to 40-cm interval ($r = 0.64$ and 0.58 , for litter-C and -N, respectively). A similar trend was observed for crystalline Al-/Fe-(hydr)oxides, which were more strongly correlated with the retention of ^{13}C than ^{15}N . We posit that in subsoil, both SRO and crystalline Al-/Fe-(hydr)oxides are more readily involved in the neoformation of mineral-

organic associations. Overall, litter-C is less efficiently transferred into the clay+silt fraction of C-rich topsoil relative to C-depleted subsoil horizons, which may represent a significant C sink for Oxisols.

Abbreviations

AO, ammonium oxalate; Aw, tropical with dry winter; Cwa, temperate moist with dry winter and warm summer; DCB, dithionite-citrate-bicarbonate; DOC, dissolved organic carbon; HHD, Humic Hapludox; IRMS, Isotopic Ratio Mass Spectrometer; MOAs, mineral-organic associations; POM, particulate organic matter; RHT, Rhodic Haplustox; SOC, soil organic carbon; SOM, soil organic matter; SRO, short-range order; THD, Typic Hapludox; THT, Typic Haplustox; WHC, water holding capacity; XHD, Xanthic Hapludox; XHT, Xanthic Haplustox; XRD, x-ray diffraction

Introduction

Tropical regions account for approximately 25 to 30% of the global soil organic C (SOC) stock (Carvalhais et al., 2014). In the tropics, Oxisols are the most widespread soil types containing up to 23% of regional SOC stocks, particularly across South America and Africa (Eswaran, 1993). Oxisols are thought to be among the oldest soils on Earth, undergoing pedogenesis as early as 60 million years ago (Schaefer, 2001). Consequently, present-day Oxisols exhibit deep profiles with a relatively uniform vertical distribution of SOC down to a 2-m depth (Batjes and Sombroek, 1997). This is in sharp contrast to other common tropical soil orders such as Ultisols, where a greater proportion of the SOC tends to be stored in the topsoil (Sombroek et al., 1993; Batjes and Sombroek, 1997). The redistribution of soil organic matter (SOM) from topsoil toward subsoil horizons can result from downward percolating dissolved organic carbon (DOC), bioturbation, or a combination of these factors (Rumpel and Kögel-Knabner, 2011; Maeght et al., 2013). In tropical ecosystems with high annual precipitation and no significant dry season, leaching DOC can be a significant source of C to be stored in subsoil (Veldkamp et al., 2003). Otherwise, bioturbation, including the mixing of soil minerals with organic debris through root growth and the burrowing of aboveground litter by soil fauna, appears to be particularly relevant in Oxisols (Schaefer, 2001).

Once incorporated into the soil, the formation of mineral-organic associations (MOAs) and the occlusion of organic matter within aggregates are the main factors leading to the persistence of SOC (Dungait et al., 2012; Kaiser and Kalbitz, 2012; Stockmann et al., 2013). However, quantitative assessments of the processes involved in the formation of MOAs as a function of properties of the mineral matrix with increasing depth in Oxisols remain scarce. The pedogenesis of Oxisols under persistently warm and moist climate conditions has created unique chemical, physical, and mineralogical properties. As a consequence of the persistent removal of silica and bases, kaolinite is the predominant aluminosilicate found in these soils (Gilkes and Prakongkep, 2016). Depending on the degree of weathering and the

chemical composition of the parent material, gibbsite can be more abundant than kaolinite in some Oxisols (Schaefer et al., 2008). Furthermore, Fe-(hydr)oxides are of ubiquitous occurrence in these soils, mainly goethite and hematite (Schaefer et al., 2008). The combination of a non-expansive aluminosilicate such as kaolinite with gibbsite and Fe-(hydr)oxides contributes to the formation of a unique and strong microgranular structure (“pseudosand”) commonly observed in A and B horizons of Oxisols (Schaefer, 2001; Schaefer et al., 2004). The clay+silt content observed in Oxisols can vary from 150 up to more than 800 g kg⁻¹ soil, but there is no significant clay illuviation from the A into the diagnostic oxic horizon (Bockheim et al., 2014). Therefore, deep C storage in oxic horizons should not be significantly affected by clay illuviation when compared with soils where this feature is expressed (Torres-Sallan et al., 2017). Thus, it can be expected that the formation of MOAs at depth will be more affected by chemical properties of the mineral matrix rather than by differential physical attributes expressed in oxic horizons.

Minerals exhibiting particle size <53 µm are the main drivers of the formation and persistence of MOAs in soils (Kleber et al., 2015). The mechanisms by which silt- and clay-sized minerals interact and ultimately protect SOC against decomposition vary from adsorption or co-precipitation (Eusterhues et al., 2014) to physical occlusion within soil aggregates (Six and Paustian, 2014; Gupta and Germida, 2015). The contribution of these mechanisms for the formation of MOAs may vary as function of many factors. For instance, adsorption or co-precipitation of SOC should predominate in soils that are enriched in SRO minerals (Xiao et al., 2015). Conversely, physical protection of SOC because of microaggregation should become progressively more relevant as soil pedogenesis reaches advanced stages, such as in Oxisols (Kinyangi et al., 2006). Nevertheless, it can be expected that even in Oxisols the relative importance of reactive minerals for the formation of MOAs should increase with depth (Kaiser and Kalbitz, 2012). Because Oxisols are characterized by both deep profiles and large amounts of reactive Al-/Fe-(hydr)oxides (Schaefer et al., 2008), it is critical to evaluate how a combination of these factors affect the formation of MOAs.

The central objective of this research was to obtain a quantitative assessment of the potential C-sink of the deep profiles of Oxisols as a function of their physical and chemical properties. We hypothesized that the availability of reactive pedogenic Al-/Fe-(hydr)oxides to interact with litter-derived C and N should increase with soil depth. Our conceptual approach consisted of sampling six representative and very contrasting Oxisols profiles at 0- to 10-, 10- to 20-, 20- to 40, and 60- to 100-cm depth. These samples were incubated with a double-labeled (¹³C and ¹⁵N) eucalypt (*Eucalyptus urophylla* x *Eucalyptus grandis*) litter for 12 mo under controlled conditions. Following the incubation, we determined the proportion of the stable isotopes transferred into MOAs within the soil particle-size fraction <53 µm.

MATERIALS AND METHODS

¹³C and ¹⁵N Isotope Labeling of Eucalypt Seedlings

Three seedlings of a eucalypt hybrid aged 120 d were grown hydroponically into a nutrient solution (pH 5.5) with continuous oxygen supply during 126 d. We chose Eucalypt because this is a typical tropical plant that is widely grown in Brazil. During the isotope labeling, the seedlings were kept in a 448-dm³ chamber in which the CO₂ concentration was maintained at approximately 500 mg L⁻¹. Once a week, the seedlings were submitted to five pulses of ¹³CO₂ applied over a 10-h interval. Afterward, the plants were kept in the dark for 12 h. The ¹³CO₂ labeling was achieved by using Na₂CO₃ solution (0.18 mol L⁻¹) prepared from Na₂¹³CO₃ (¹³C at 99 atom%, Isotec Inc. Miamisburg, OH), acidified with H₂SO₄ at 3.8 mol L⁻¹. The ¹⁵N label was added via nutrient solution (N-NH₄⁺ 0.9 mmol L⁻¹) applied once a week, prepared from (¹⁵NH₄)₂SO₄ (98 atom% excess, Sigma-Aldrich, St. Louis, MO). After isotope labeling, the seedlings were collected and separated into leaves, twigs, stem, and roots (Ø < 2 mm), and dried under forced air circulation at 45°C for 2 wk. Afterward, the plant material was milled to achieve a final particle-size between 250 and 149 µm. For characterization, subsamples were analyzed using an Isotopic Ratio Mass Spectrometer (IRMS) with continuous flux (20-20, ANCA-GLS, Sercon, Crewe, UK). The C and N content, and respective stable isotope enrichment (¹³C and ¹⁵N) for each plant components are shown in Table 1.

Table 1. Components of the plant litter, C and N contents, and stable isotopes enrichment.

Component	Mass†	C	δ ¹³ C	N	¹⁵ N	C/N
	g	g kg ⁻¹	‰	g kg ⁻¹	atom %	
Bark	21.9	425.0	318.6	5.2	81.4	82
Leaves	135.9	455.0	508.5	18.3	76.2	25
Twigs	40.5	427.0	423.1	7.6	72.3	56
Stem	52.3	452.0	210.4	2.2	70.7	205
Roots	58.5	457.0	358.4	10.4	66.7	44
Corrected mean‡	–	449.0	405.5	11.8	74.3	38

† The mass of each component produced (grams per plant). The plant litter was added to the soils as a mixture, in which the amount of each component was proportional to their content the plant grown for ¹³C and ¹⁵N labeling.

‡ Mean values was corrected considering the C and N content and the proportion of each component for total dry matter of the labeled plant. The corrected means for C and N contents and their respective abundance of ¹³C and ¹⁵N were used to calculate litter-derived C and N remaining within the clay+silt fraction after the incubation.

Soil Sampling and Characterization

Six representative Oxisols were collected across Southeastern Brazil, under native vegetation within the biomes Mata Atlântica (Atlantic Forest) and Cerrado (Savanna-like). According to the Köppen classification, the climate within the Atlantic Forest is predominantly tropical with dry winter (Aw), while for the Cerrado, the climate is temperate moist with dry winter and warm summer (Cwa). Total annual precipitation for both climate types is

similar, ranging from 1300 to 1600 mm. However, for the area under Cwa climate, the rainy season is typically concentrated from October to March. We classified each soil by Soil Taxonomy (Soil Survey Staff, 2014); the soils collected across the Atlantic Forest were classified as a Typic Hapludox (THD), a Humic Hapludox (HHD), and a Xanthic Hapludox (XHD). The soils collected in the Cerrado were classified as a Xanthic Haplustox (XHT), a Rhodic Haplustox (RHT), and a Typic Haplustox (THT). We also classified the soils according to the FAO WRB system (IUSS Working Group WRB, 2015) (Table 2). For convenience, we refer to these soils as ‘Oxisols’ throughout this text. At each site, soil samples were collected at depths of 0 to 10, 10 to 20, 20 to 40, and 60 to 100 cm. Classification, particle-size distribution, mineralogy, and texture class of the selected soils are provided in Table 2. Chemical characterization of the soils is in Supplementary Table 1.

Table 2. Oxisols texture (sand, silt and clay content), extractable Al and Fe by ammonium oxalate (AO) and dithionite-citrate-bicarbonate (DCB), and kaolinite and gibbsite content within the clay fraction.

Soils classification	Horizon	Depth cm	Sand	Silt	Clay	Al _{AO} [†]	Fe _{AO} [†]	Al _{DCB} [†]	Fe _{DCB} [†]	Kaolinite [‡]	Gibbsite [‡]	Texture class
g kg ⁻¹												
Typic Hapludox-THD§	A	0–10	363.8	33.1	603.2	0.8	0.7	12.2	49.1	439.5	32.1	Clay
	A	10–20	289.8	33.7	676.7	0.9	0.9	15.1	54.3	493.1	36.1	Clay
Haplic Ferralsol¶	BA	20–40	249.3	31.6	719.2	1.0	0.8	13.2	54.8	524.1	38.3	Clay
	B	60–100	234.4	31.1	734.6	1.1	0.5	14.0	56.9	535.2	39.1	Clay
Humic Hapludox-HHD§	A	0–10	324.9	78.4	596.8	4.1	2.2	14.5	36.2	354.4	136.3	Clay
	A	10–20	355.3	55.4	589.4	3.9	2.2	13.6	37.9	350.0	134.6	Clay
Umbric Ferralsol¶	A	20–40	316.0	51.4	632.7	4.4	2.5	15.2	40.2	375.8	144.5	Clay
	AB	60–100	307.9	34.7	657.5	3.3	1.7	15.2	47.7	390.5	150.2	Clay
Xanthic Hapludox-XHD§	A	0–10	752.8	24.2	223.1	0.4	0.2	1.6	4.9	200.9	1.2	Sand clay loam
	A	10–20	629.0	38.2	332.9	0.6	0.3	2.7	7.6	299.8	1.8	Sandy clay
Xanthic Ferralsol¶	BA	20–40	622.8	38.0	339.3	0.5	0.3	2.5	7.9	305.5	1.8	Sandy clay
	B	60–100	606.8	35.7	357.6	0.7	0.2	2.8	9.2	322.0	1.9	Sandy clay
Xanthic Haplustox-XHT§	A	0–10	395.9	86.6	517.6	2.5	0.6	4.2	11.7	176.3	303.8	Clay
	A	10–20	388.6	80.0	531.5	1.8	0.5	3.6	10.7	181.3	311.9	Clay
Gibbsic Ferralsol¶	BA	20–40	378.6	59.4	562.1	2.4	0.7	3.9	11.8	191.5	329.9	Clay
	B	60–100	393.0	44.4	562.6	2.3	0.6	3.6	11.3	191.7	330.2	Clay
Rhodic Haplustox-RHT§	A	0–10	195.5	205.1	599.4	3.9	3.7	12.2	103.6	224.5	122.8	Clay
	A	10–20	154.9	236.6	608.6	3.6	3.8	12.8	103.6	227.9	124.7	Clay
Ferritic Ferralsol¶	AB	20–40	169.2	223.5	607.4	3.2	3.7	13.0	105.2	227.5	124.5	Clay
	B	60–100	212.1	202.2	585.8	2.8	3.4	12.8	106.8	219.4	120.1	Clay
Typic Haplustox-THT§	A	0–10	580.1	60.0	359.9	1.0	0.8	2.2	24.6	297.3	1.3	Sandy clay
	A	10–20	635.0	51.1	313.9	0.9	0.6	2.0	22.2	259.0	1.1	Sandy clay loam
Rhodic Ferralsol¶	BA	20–40	644.1	53.5	302.5	0.8	0.5	1.7	19.0	249.6	1.1	Sandy clay loam
	B	60–100	553.0	72.1	375.0	0.7	0.4	2.0	22.1	309.4	1.3	Sandy clay

[†]Element content within the clay fraction, expressed in g kg⁻¹ soil.

[‡]Estimated by thermogravimetry using the clay fraction after treating the samples with DCB for Fe-(hydr)oxides dissolution. The presence of all minerals was confirmed by XRD (data not shown).

§Soil classification according to Soil Taxonomy (Soil Survey Staff, 2014).

¶FAO WRB (IUSS Working Group WRB, 2015).

Physical and Mineralogical Analyses

Air-dried soil samples were sieved to yield the fine earth fraction (<2 mm). Water holding capacity (WHC) was estimated by saturating 20 g of the fine earth fraction for 24 h with deionized water in a 25.4-mm diameter and 10-mm high steel cylinder. Later, the samples were submitted to a tension

equivalent to -30 kPa and after reaching equilibrium, the samples were weighed and dried at 105°C for 48 h.

Texture was determined after dispersing 5 g of the fine earth fraction using 5 mL of 0.1 mol L⁻¹ NaOH and 25 mL of deionized water in a 50-mL centrifuge tube, and continuously shaken for 16 h at 120 rpm. After dispersion, the samples were wet-sieved through a 53-μm mesh screen to separate sand (>53 μm) from the clay- and silt-sized fractions (<53 μm). Subsequently, clay and silt content was determined using the pipette method and the fractions obtained were dried at 105°C for 48 h and then weighed (Table 2).

For mineralogical analysis, 1 g of the fraction <53 μm was treated with 50 mL of 6% (v/v) NaOCl at pH 8 under continuous shaking for 18 h at 25°C to remove SOM. Subsequently, the samples were centrifuged at 1308 × *g* (3000 rpm) for 30 min and rinsed with deionized water. These procedures were repeated three times. Afterward, the clay fraction was separated using siphoning after the sedimentation of the silt fraction according to the Stoke's Law. After the siphoning, both clay- and silt-sized fractions were dried at 60°C. The mineralogical composition of these fractions was qualitatively assessed by X-ray diffraction (XRD) using fine powdered samples (<149 μm). X-ray diffraction analyses for non-oriented samples were conducted using Co-Kα radiation ($\lambda = 0.178896$ nm) at 30 mA and 40 kV with a Rigaku D-MAX vertical goniometer equipped with a graphite monochromator. X-ray diffraction patterns were obtained between 4 and 60° 2θ in 0.02° steps at a scan rate of 10° 2θ/min for accurate measurements of the d-spacing (data not shown).

Selective Dissolution of Al-/Fe-(hydr)oxides

Because the silt fraction was mainly composed of quartz (XRD data, not shown), only the clay fraction was submitted to selective dissolution of both SRO and crystalline Fe-(hydr)oxides. Thus, samples of the clay fraction were treated with ammonium oxalate (AO) and dithionite-citrate-bicarbonate (DCB) to dissolve SRO and crystalline minerals, respectively. To dissolve SRO minerals, 0.25 g of the clay fraction was treated with 10 mL of 0.2 mol L⁻¹ AO at pH 3.0 in the dark, using centrifuge tubes covered with aluminum foils. Samples were shaken for 2 h at 120 rpm. Subsequently, the samples were centrifuged at 1308 × *g* (3000 rpm) and the supernatant was collected to quantify the amount of Fe and Al released during the treatment. To dissolve crystalline Fe-(hydr)oxides, 0.25 g of clay was treated with 10 mL of 0.2 mol L⁻¹ DCB in centrifuge tubes kept in water bath for 30 min at 50°C. Afterward, the samples were centrifuged at 1308 × *g* (3000 rpm) for 20 min, and the supernatant was collected and stored. The DCB dissolution was repeated three times. Total Fe and Al released by AO and DCB was determined by Atomic Absorption Spectrometry (Varian Spectra AA, 220FS, Agilent Corp., Santa Clara, CA).

After removal of Fe, kaolinite and gibbsite contents in the clay fraction were estimated by thermogravimetry (Karathanasis and Harris, 1994). For this

procedure, 5 mg of clay was deposited in an alumina crucible and submitted to heat flow from 25 up to 750°C under a N₂ atmosphere flowing at 50 mL min⁻¹ using a Shimadzu (Model DTG60H, Shimadzu Corp., Kyoto, Japan). Kaolinite and gibbsite contents are shown in Table 2.

Incubation Experiment

Soil samples were incubated in air tight vials (150 mL) containing 20 g of the fine earth fraction (<2 mm). The incubation experiment was set up with a complete randomized block design arranged according to a complete factorial scheme. The factorial included: six Oxisols, four sampling depths (0-10, 10-20, 20-40, and 60-100 cm), and four levels of plant litter inputs (0-, 10-, 20-, and 40-mg g⁻¹ soil). Each treatment had three replicates, yielding a total of 288 experimental units. For C inputs, the mass of the components of the litter added was equivalent to their proportion in the whole plant, as shown in Table 1. The incubation was performed for 12 mo under controlled temperature (25°C ± 1). During the first month, the microcosms were opened three times a week for 1 h to avoid O₂ depletion in the headspace. After the first month, the microcosms were opened only once a week and the weight of the experimental units was monitored to avoid water limitation. When necessary, deionized water was added to maintain the moisture content within 60 to 70% of the WHC. In an attempt to standardize the composition of the microbial community at the beginning of the experiment, we prepared an inoculum by mixing 2 g of soil from the 0- to 10-cm depth into 200 mL of deionized water, and used this to inoculate the samples from the other soil layers (10- to 20-, 20- to 40-, and 60- to 100-cm depth). After shaking overnight, an aliquot of 1 mL of the suspension was used for inoculation. This procedure was done for each soil separately.

Soil Physical Fractionation

After the 12-mo incubation, samples were air-dried and physically fractionated to isolate the SOM fraction >53 µm, that is, particulate organic matter (POM) from the SOM within the clay+silt fraction (<53 µm). The physical fractionation approach consisted of dispersing a 5-g soil subsample into a 50-mL centrifuge tube containing 15 mL of sodium hexametaphosphate (5 g L⁻¹). We then added a 10-mm diameter glass bead into each tube and kept the samples under continuous shaking for 16 h at 120 rpm. After dispersion, the samples were wet-sieved through a 53-µm screen, and the fractions were dried at 45°C for 7 d. Afterward, the samples were weighed and finely ground using an agate mortar and pestle to achieve a final particle-size of <149 µm. The C, N content and their respective stable isotope abundance (¹³C and ¹⁵N content) were determined using an IRMS. The ¹³C results were expressed as δ¹³C in parts per mil (‰) with reference to the international standard (Pee Dee Belemnite) and the ¹⁵N abundance was expressed in atom%.

Litter-Derived C and N within the Fraction <53 µm

The proportion (f) of litter-derived C and N in the fraction <53 μm was calculated as follows

$$f = \frac{\delta_t - \delta_c}{\delta_{pl} - \delta_c}$$

in which δ_t is the $\delta^{13}\text{C}$ of the soil fraction <53 μm for the treatments receiving plant-litter, δ_c is the $\delta^{13}\text{C}$ of the soil fraction <53 μm in the control treatments (no plant litter addition), and δ_{pl} is the $\delta^{13}\text{C}$ of the plant litter (405.50‰). The same formula was used to assess the litter-derived N, for which the δ_{pl} was 74.30 atom%. The total amount of litter-derived C and N associated to the soil fraction <53 μm was calculated as

$$\text{ER, \%} = \left(\frac{f \times E}{\text{total input}} \right) 100$$

where ER is the percentage (%) of the element added (C or N) that was recovered after the incubation period, E is the total element content (C or N) associated with the fraction <53 μm in the whole 20-gram of soil sample after the incubation experiment, and total input is the total C or N added via plant litter.

Data Analysis

We used ANOVA to test for the main effects of soil (sub)type, depth of sampling, litter input, and their interactions on the proportion of the initial litter-C and -N that was transferred into the fraction <53 μm . Because of the dependence structure of soil type and depth of sampling, the experiment was analyzed as a split-plot design (Table 3). The effects of mineralogy on litter derived-C and -N within the clay + silt fraction were assessed by correlation analysis. The statistical analyses were performed using the software Statistica 13 (Quest, Aliso Viejo, CA) and the figures were prepared with Sigma Plot 11 (Sigma Plot, San Jose, CA).

Table 3. ANOVA for the main effects of soil, depth of sampling, plant litter additions, and their interactions on the mass proportion of litter-C and -N remaining (percentage of recovered C and N) within the soil fraction < 53 μ m after 12-mo incubation

Source of variation	df	C recovered, %				N recovered, %			
		SS	MS	F	P-value	SS	MS	F	P-value
Block	2	45	22	7	0.011	190	95	12	0.00
Soil	5	647	129	42	0.000	3506	701	90	0.00
Error (A)	10	31	3			78	8		
Depth	3	360	120	29	0.000	1374	458	26	0.00
Soil $\times$ Depth	15	225	15	4	0.001	1627	108	6	0.00
Error (B)	36	148	4			631	18		
Litter	2	86	43	12	0.000	3065	1533	124	0.00
Soil $\times$ Litter	10	136	14	4	0.000	1092	109	9	0.00
Depth $\times$ Litter	6	51	8	2	0.029	111	18	1	0.19
Soil $\times$ Depth $\times$ Litter	30	135	4	1	0.167	1252	42	3	0.00
Error (C)	96	330	3			1191	12		
Total	215								

RESULTS

Incorporation of ^{13}C and ^{15}N within the Soil Fraction <53 μ m

The transfer of litter-C and -N into the soil fraction <53 μ m was significantly affected by all factors tested and their interactions (Table 3). For the recovery of litter-C, the strongest influence was noted for Oxisol subtype, followed by depth of sampling, and litter-C inputs (Fig. 1a-c; Table 3, $P < 0.01$). The average litter-C remaining within the fraction <53 μ m was approximately 23.7% of the initial input (Fig. 1d). Among individual soils, the litter-C recovered was significantly higher in the RHT and in the HHD, averaging 25.2 and 26.1%, respectively (Fig. 1a). In these soils, the litter-C recovered in the clay+silt fraction was consistently above the average for this study (Fig. 1d). The proportion of litter-C recovered within the fraction <53 μ m was significantly lower in the THT and in the XHT. The mean amount of litter-C recovered in these soils was 21.0 and 22.1%, respectively (Fig. 1a). For the THD and the XHD soils, the average amount of litter-C remaining within the mineral fraction was 23.2 and 24.3%, respectively. Overall, the efficiency of conversion of litter-C into the fraction <53 μ m increased significantly ($P < 0.01$) from the topsoil toward the subsoil (Fig. 1b,d).

Fig. 1.

Mass proportion of litter-C and -N (percentage of initial input) remaining within the clay+silt fraction (<53 μm) after the 12-mo incubation as function of (a) soil type: Typic Hapludox (THD), Humic Hapludox (HHD), Xanthic Hapludox (XHD), Xanthic Haplustox (XHT), Rhodic Haplustox (RHT), and Typic Haplustox (THT); (b) depth of sampling: 0–10, 10–20, 20–40, and 60–100 cm; (c) plant litter inputs: 10, 20, and 40 mg g^{-1} soil. Means followed by the same lowercase letter do not differ according to the Tukey's test at $P < 0.05$; (d) the average amount of litter-C transferred into the clay+silt fraction was 23.7% and (e) 37.3% for litter-N. The vertical bars denote the standard error of the means, $n = 3$.

Interestingly, the incorporation of litter-N into the fraction <53 μm was approximately 60% greater than that observed for litter-C. The average amount of litter-N recovered within the clay+silt fraction was 37.3% (Fig. 1e). The variability observed for the transfer of litter-N into the clay+silt fraction was a function of the magnitude of litter-N inputs, followed by soil subtype, and depth of sampling (Table 3, $P < 0.01$). The HHD and RHT soils also had the highest recovery of litter-N (Fig. 1a,e; $P < 0.01$), averaging 42% relative to the initial inputs (Fig. 1e). Intermediate values occurred in the XHD, where the recovered litter-N was 39.3% (Fig. 1a,e). Lower accumulation of litter-N was observed for the other Oxisols (THT, XHT and THD). In the latter soils, the recovered litter-N within the clay+silt fraction was 32.2, 33.2, and 35.1% of the initial input, respectively (Fig. 1a, e). In contrast to the recovery of litter-C, the conversion efficiency of the litter-N into the fraction <53 μm decreased significantly ($P < 0.01$) with increasing depth of sampling (Fig.

1b). For both elements, however, we measured proportionally less incorporation into the clay+silt fraction as the plant litter inputs increased (Fig. 1c). Soil organic C and SON content within the clay + silt fraction as affected by the soil subtype, depth of sampling and plant litter inputs is shown in Table 4. Because of the differential incorporation of litter-C and -N as a function of depth, the C/N ratio tended to increase toward the subsoil of the selected Oxisols (Supplementary Table 2).

Table 4. Soil organic carbon (SOC) and soil organic nitrogen (SON) content within the clay + silt fraction as affected by plant litter inputs to soil samples collected at 0–10, 10–20, 20–40 and 60–100 cm depth of six Oxisols after the 12-mo incubation.†

Soil#	Litter input	Depth, cm							
		0-10	10-20	20-40	60-100	0-10	10-20	20-40	60-100
		SOC [‡]				SON [‡]			
mg g ⁻¹ soil		g kg ⁻¹ soil							
THD§	0	17.5 Abc	15.8 Ab	12.7 Bc	7.3 Cc	1.5 Ab	1.3 Bb	1.0 Cb	0.6 Da
	10	18.6 Ab	16.9 Aab	13.5 Bbc	8.3 Cbc	1.9 Aa	1.5 Bb	1.1 Cab	0.7 Da
	20	19.6 Aab	18.3 Aa	14.8 Bab	9.7 Cb	1.9 Aa	1.7 Ba	1.3 Ca	0.7 Da
	40	21.3 Ab	18.3 Aa	16.4 Ba	12.1 Ca	1.8 Aa	1.5 Bb	1.3 Ca	0.8 Da
HHD§	0	38.2 Aa	32.8 Bb	28.4 Cb	14.6 Dc	2.7 Ac	2.2 Ba	1.9 Cb	0.8 Db
	10	39.0 Aa	34.1 Bab	29.6 Cb	16.5 Dbc	2.8 Abc	2.4 Ba	2.2 Ca	1.0 Dab
	20	42.0 Ab	35.1 Bab	30.4 Cab	18.0 Dab	3.0 Aa	2.3 Ba	1.8 Cb	0.8 Da
	40	42.3 Ab	35.9 Ba	33.1 Ba	19.7 Ca	3.0 Aab	2.3 Ba	2.1 Ca	1.0 Da
XHD§	0	13.4 Aa	8.8 Ba	7.0 Ca	4.0 Da	1.2 Ac	0.6 Bc	0.5 Bb	0.3 Cb
	10	13.7 Ab	9.6 Bb	8.0 Bb	5.1 Cb	1.3 Ab	0.9 Bb	0.7 Ca	0.4 Da
	20	16.4 Ac	11.8 Bc	8.7 Cbc	6.7 Dc	1.5 Aa	1.1 Ba	0.7 Ca	0.5 Da
	40	18.9 Ac	13.4 Bc	12.1 Bc	9.6 Cc	1.5 Aa	0.8 Bb	0.7 Ca	0.5 Da
XHT§	0	16.2 Bb	18.3 Ab	15.3 Bc	9.8 Cc	0.9 Ac	1.2 Bb	1.1 Cb	0.6 Db
	10	16.3 Bb	19.0 Ab	16.4 Bbc	11.6 Cb	1.2 Ab	1.3 ABab	1.1 Bab	0.7 Cab
	20	18.9 Ba	20.8 Ba	17.1 Cb	12.2 Db	1.3 Aa	1.4 Aba	1.2 Ba	0.7 Ca
	40	19.9 ABa	20.9 Aa	19.1 Ba	15.0 Ca	1.1 Aab	1.3 Aab	1.2 Bab	0.8 Cab
RHT§	0	37.7 Ab	26.9 Bc	17.8 Cc	9.8 Dd	3.6 Ab	2.4 Bb	1.5 Cb	0.7 Db
	10	38.4 Ab	28.3 Bbc	20.3 Cb	11.4 Dc	3.8 Aa	2.6 Bb	1.7 Ca	0.8 Db
	20	40.0 Aa	29.1 Bb	22.5 Ca	13.2 Db	3.9 Aa	2.5 Bab	1.8 Ca	0.8 Dab
	40	41.0 Aa	31.8 Ba	23.4 Ca	15.7 Da	3.7 Aa	2.7 Ba	1.8 Ca	1.0 Da
THT§	0	15.9 Ac	10.5 Bc	7.7 Cc	2.9 Dc	1.2 Ab	0.8 Bc	0.6 Cc	0.2 Dd
	10	17.2 Abc	10.6 Bc	8.6 Cbc	4.2 Dbc	1.3 Aa	0.8 Bbc	0.6 Cbc	0.3 Dc
	20	18.4 Aab	12.2 Bb	9.4 Cb	5.3 Db	1.4 Aa	0.8 Bb	0.6 Cb	0.3 Db
	40	19.0 Aa	14.4 Ba	11.9 Ca	8.1 Da	1.4 Aa	1.0 Ba	0.8 Ca	0.4 Da

†For a given soil and litter input, means followed by capital letters, do not differ according to the Tukey's test at $P < 0.05$. For a given depth within each soil, means followed by the same lowercase letter do not differ according to the Tukey's test at $P < 0.05$.

‡The full classification of the soils is provided in Table 2.

§ SOC, soil organic carbon; SON, soil organic nitrogen; THD, Typic Hapludox; HHD, Humic Hapludox; XHD, Xanthic Hapludox; XHT, Xanthic Hapludox; RHT, Rhodic Hapludox; THT, Typic Hapludox.

Correlations between the mass proportion of litter-C versus litter-N remaining within the clay+silt fraction, while statistically significant, were generally weak (Fig. 2a–d). Even when the effects of sampling depth and plant litter inputs were accounted for, there was still a significant dispersion of the data for the litter-C and -N within the clay+silt fraction (Fig. 2).

Fig. 2.

Relationship between the mass proportion of litter-C versus litter-N remaining within the clay+silt fraction as affected by plant litter inputs of 10; 20; and 40 mg g⁻¹ soil and depth of sampling (a) 0-10 cm; (b) 10-20 cm; (c) 20-40; and (d) 60-100 cm.

Influence of Mineralogy on the Retention of Litter-C and -N

The transfer of litter-C and -N into the fraction <53 μm was best explained by variations in clay, Al-/Fe-DCB, Al-/Fe-AO and Al+Fe-AO throughout the profiles of the selected Oxisols (Fig. 3a). The only exception was in the topsoil (0-10 cm, Fig. 3a), where none of these variables were positively correlated with the retention of litter-C and -N. For the 10- to 20-cm soil layer, only Al-/Fe-AO exhibited positive correlation with the retention of litter-C. The predictive power of clay, Al-DCB and Al-AO increased significantly from the topsoil toward the subsoil, while the predictive capacity of Fe-AO and Al+Fe-AO was lower for the 60- to 100-cm layer as compared with the 20- to 40-cm layer (Fig. 1a). The only instance where kaolinite content was significantly correlated with the retention of the litter-C was in the deepest soil layer (60-100 cm). Of the variables we measured, only gibbsite had no significant effect on litter-C retention (Fig. 3a). Plots of the mass proportion of litter-C and -N remaining within the clay+silt fraction versus Al-/Fe-AO, Al-/Fe-DCB, kaolinite and gibbsite content are provided in Supplementary Information 1; Fig. S1-S3.

Fig. 3.

Pearson's correlation coefficients (r) between mineralogical parameters (clay, Al-DCB, Fe-DCB, Fe-AO, Al-AO, Al+Fe-AO, kaolinite and gibbsite) and the percentage of initial inputs of (a) the litter-C; and (b) litter-N remaining within the clay+silt fraction as related to depth of sampling (0-10, 10-20, 20-40, and 60-100 cm). Correlation coefficients followed by ***, **, * are significant at $P < 0.01$, $P < 0.05$ and $P < 0.10$ level respectively; ns, nonsignificant ($P > 0.10$).

Overall, the mineralogical variables controlling litter-C retention exerted similar effects on litter-N retention within the fraction $< 53 \mu\text{m}$ (Fig. 3b). However, increasing contents of clay and gibbsite in the topsoil reduced the efficiency of the litter-N incorporation within the clay+silt fraction. This effect was not observed for the litter-C (Fig. 3a). With increasing depth (below 20 cm), we measured significant and positive correlations between gibbsite content and the recovered litter-N (Fig. 3b). For clay content, despite its positive relationship with the retention of litter-N with increasing soil depth (60-100 cm), this pattern had no relationship with kaolinite, which is the predominant mineral found in Oxisols (Table 2). This was because the only significant correlation between kaolinite and the retention of litter-N was negative, and occurred at the 20- to 40-cm depth. As observed for the retention of litter-C, only Al-/Fe-AO or Al+Fe-AO exhibited positive correlations with the retention of litter-N from 10 to 20 cm downward. For

soil layers below 40 cm, increasing content Al-/Fe-DCB was associated with higher litter-N retention (Fig. 3b).

The data shown in Fig. 3 allowed us to constrain the most likely drivers of the development of MOAs in Oxisols. We recognize, however, that we have not probed MOAs directly in this study. Moreover, we acknowledge that the results shown in Fig. 3 would not unequivocally prove that the minerals leading to $^{13}\text{C}/^{15}\text{N}$ retention in our incubation would have been similarly involved in the formation of MOAs under field conditions. Thus, in a follow-up step, we performed correlation analysis for the variables shown in Fig. 3 versus the unlabeled SOM, that is, after subtracting the amount of litter-derived C remaining after the incubation (Supplementary Fig. S4). According to these correlations, it seems that both labeled and unlabeled SOM were affected by the same variables as shown in Fig. 3. Plots of the unlabeled SOC content versus the mineralogical variables clearly illustrate that minerals in the topsoil were associated with greater amounts of unlabeled SOC than those in subsoil (Supplementary Fig. S4). This trend was most evident for Al-/Fe-DCB and Al-/Fe-AO (Supplementary Fig. S4b-f), which were the variables most closely correlated with high efficiency of retention of the labeled SOM with increasing depth (Fig. 3).

DISCUSSION

Transfer of C and N from Plant Litter into the Mineral Soil

With increasing inputs of plant litter, the proportion of both C and N transferred into the clay+silt fraction declined (Fig. 1c). Generally, increased plant litter inputs, whether as roots or shoots, seem to favor increased mineralization rather than sustained accumulation of SOM (Shahbaz et al., 2017). It seems reasonable that this same pattern occurred in our study, although we evaluated the components of the plant litter as a mixture. Despite similar behavior of litter-C and -N with respect to increasing plant litter inputs, our data indicate a significant decoupling between C and N dynamics during the incubation (Fig. 2a-d). Previous studies indicated that ^{15}N is generally incorporated into the SOM at higher efficiency than ^{13}C during the decomposition of plant litter (Garcia-Pausas et al., 2012; Hatton et al., 2015). In our study, we found that with increasing inputs of plant litter, there was a concomitant increase in litter-C in the POM fraction, which was not observed for litter-N (Supplementary Tables 3 and 4). The transfer of litter-C to POM increased from 21 to 25% for samples collected at 0 to 10 and 60 to 100 cm, respectively, while the retention of litter-N decreased from 21 to 12% in those layers (Supplementary Tables 3 and 4). Similar differences also occurred in the clay+silt fraction (Fig. 1a-e). Thus, with increasing depth of sampling, the transfer of litter-N into the fraction $<53\text{ }\mu\text{m}$ was reduced while the opposite occurred for litter-C in most of our Oxisols (Fig. 1d,e). One possible explanation is that at the moisture content that our soils were kept during the incubation (60–70% of WHC), some of the litter-N was lost as N_2O (Pilegaard, 2013). Indeed, at 60 to 70% of WHC, the release of N as N_2O from

soils is favored (Cameron et al., 2013). Ideally, such dynamics should be directly measured by quantifying the release of N₂O from the soils during the incubation. However, our mass balance indicates that a significant fraction of the litter-N was lost with increasing plant litter inputs, particularly in subsoil samples.

The Retention of Litter-C and -N by Al-/Fe-(hydr)oxides Varies with Soil Depth

The incorporation of litter-C into the clay+silt fraction increased with depth (Fig. 1b), but also varied substantially among the Oxisols we analyzed (Fig. 1a,d). We interpret our data to indicate that two major factors accounted for the above observations: (i) the retention of litter-C and -N in MOAs was constrained by reactive species of Al-/Fe-(hydr)oxides and (ii) the availability of Al-/Fe-(hydr)oxides to form MOAs increased with depth. To date, many studies have indicated a similarly strong effect of Al-/Fe-(hydr)oxides on the retention of SOM in a wide range of soil types and horizons (Kleber et al., 2005; Zinn et al., 2007; Xiao et al., 2015; Van De Vreken et al., 2016). Hydroxyl groups at the surface of Al-/Fe-(hydr)oxides can form inner-sphere coordination, that is, ligand-exchange reactions with functional groups of SOM (e.g., carboxylic acids), rendering the latter less accessible to microbial decomposition (Kleber et al., 2015). However, because the formation of MOAs depends on the availability of reactive surface sites, even highly reactive SRO minerals have an upper limit for their capacity to interact and protect SOM (Kleber et al., 2005). Our results are consistent with such findings; in the C-rich topsoil neither SRO nor crystalline Al-/Fe-(hydr)oxides had detectable effects on the retention of the labeled SOM (Fig. 3a,b). Possibly, Al-/Fe-(hydr)oxides were associated with higher amounts of unlabeled SOM in topsoil than in subsoil (Supplementary Fig. S4d-f). Consequently, the effect of all forms of Al-/Fe-(hydr)oxides on the retention of isotopically-labeled SOM increased significantly from the topsoil toward the subsoil (Fig. 3). Although the amount of remaining litter-N decreased with depth (Fig. 1b,e), the retention of this element also was strongly affected by Al-/Fe-(hydr)oxides (Fig. 3). Despite SRO forms of Al-/Fe-(hydr)oxides presenting better correlations with SOC content throughout the Oxisols profiles (Supplementary Fig. S4e-f), at deep horizons abundant crystalline forms of Al-/Fe-(hydr)oxides also should be important for the formation of MOAs (Fig. 3a-b). Moreover, isomorphic substitution of Fe by Al as inferred from Al-DCB, appears to increase the ability of crystalline Fe-(hydr)oxides to form MOAs (Fig. 3; Supplementary Fig. S4b). Probably, Al-substituted Fe-(hydr)oxides exhibit lower crystallinity degree and by extension, larger SSA than non-substituted counterparts (Fitzpatrick and Schwertmann, 1982).

Potential and Challenges for C Sequestration in the Subsoil of Oxisols

We posit that three general aspects of Oxisols highlight their significant potential for promoting subsoil C sequestration: (i) their deeply developed

profiles, (ii) their generally strong microaggregation and high porosity, and (iii) besides SRO, the more abundant crystalline forms of Al-/Fe-(hydr)oxides also can develop associations with SOM in subsoil (Fig. 3). All else being equal, soils with deep profiles inherently present a higher potential for C storage in subsoil than shallower types. Not coincidentally, deep B horizons of Oxisols (down to 2 m) have been reported to store from 40 up to 75% of the total C stock within the solum, that is, A and B horizons combined (Andrade et al., 2004). Beyond directly binding organic molecules, Al-/Fe-(hydr)oxides also favor aggregation (Schaefer et al., 2004), which in turn can provide physical protection to SOM within and around microaggregates (Kinyangi et al., 2006; Lehmann et al., 2007). Physical protection of SOM in Oxisols is another potentially important mechanism since crystalline forms of Al-/Fe-(hydro)oxides are much more abundant than SRO minerals in these soils (Table 2). Moreover, by assuming a linear relation between Al-AO and SOC content ($r = 0.81$, Supplementary Fig. S4), the former cannot explain more than 65% of the total variation in the latter.

The main constraints to increase deep C storage in Oxisols can be summarized as (i) the contribution of DOC percolation to subsoil C accumulation is seemingly restricted, (ii) burial of organic matter via bioturbation appears to operate in rather long timescales, (iii) lack of experimental data on deep C storage via mechanical incorporation of organic matter across the tropics, (iv) 'priming' effects induced by roots. Generally, significant DOC percolation throughout the soil profile seems to be restricted to areas of active rain forest (Veldkamp et al., 2003; Schwendenmann and Veldkamp, 2005). Other than DOC percolation, C fixed aboveground can reach the subsoil mainly through the burial of organic debris by soil fauna, particularly termites (Jouquet et al., 2016). The contribution of this mechanism for deep SOC storage is probably better expressed over long timescales, for example, from 100 to 1000 yr (Schaefer, 2001; Araujo et al., 2017). Otherwise, mechanical incorporation of aboveground plant litter deep into the soil profile by ploughing (down to a 90-cm depth) may reportedly increase subsoil C stocks in temperate soils on short timescales (35–50 yr) (Alcántara et al., 2016). To the best of our knowledge, there is no experimental data evaluating the effect of deep ploughing on C stocks in tropical soils. For root litter produced belowground in tropical regions, the potential to increase deep C storage appears to be more realistic (Stahl et al., 2016). Perhaps, under acidic conditions of subsoils, the retention of root-derived C in MOAs (Rumpel et al., 2015) is high enough to overcome eventual C losses caused by the release of exudates that can trigger the decomposition of indigenous SOM (Stockmann et al., 2013; Keiluweit et al., 2015). Despite such potential negative side effects, the transfer of root-C and -N into SOM can be facilitated by the presence of reactive minerals with high capacity to form MOAs, particularly in subsoil horizons (Fig. 3; Supplementary Fig. S4). Generally, we can infer that the subsoil of Oxisols can be a significant C sink (Fig. 3), but deep accumulation of SOM must be

understood as a complex environmental service that can be affected or depend on a range of factors. Overall, the potential for deep C storage in Oxisols must be further evaluated, particularly in field-based studies. Furthermore, the C sink strength of Oxisols will depend strongly on the dynamics of N, particularly in subsoil.

CONCLUSIONS

Our results highlight the potential for deep C storage in subsoil of Oxisols, although this is a complex issue bringing about many considerable challenges. Both litter-C and -N were less efficiently converted to SOM with increasing plant litter inputs. While the retention of litter-C increased with depth, the opposite occurred for litter-N. With increasing depth, the incorporation of both ^{13}C and ^{15}N was mostly correlated with Al-/Fe-(hydr)oxides. Thus, it is likely that SRO and crystalline forms of Al-/Fe-(hydr)oxides can favor the formation of MOAs in the subsoil of Oxisols. If further corroborated (e.g., in field-based experiments), the combination of deep profiles of Oxisols and abundant minerals capable of developing protective associations with SOM would indicate a quantitatively relevant, yet underappreciated C sink in tropical ecosystems.

SUPPLEMENTAL MATERIAL

Supplementary Information 1. Retention efficiency of litter-C and -N versus mineralogical variables for samples collected at different depths, including Al-/Fe-(hydr)oxides dissolved by ammonium oxalate (Fig. S1); Al-/Fe-(hydr)oxides dissolved by dithionite-citrate-bicarbonate (Fig. S2); kaolinite and gibbsite contents (Fig. S3). Correlations of unlabeled SOC versus mineralogical variables at different depths (Fig. S4). Supplementary Table 1. Chemical properties of the selected Oxisols. Supplementary Table 2. C/N ratio of total SOM after the 12-month incubation. Supplementary Table 3. ANOVA for the main effects of soil, depth of sampling, plant litter additions and their interactions on the retention efficiency of C and N within the soil fraction $>53\ \mu\text{m}$ after the 12-month incubation. Only means for the main effects of soil, depth of sampling, and plant litter additions are presented. Supplementary Table 4. Percentage of initial input of litter-C and -N remaining within the soil fraction $>53\ \mu\text{m}$ (sand-sized) of each Oxisol for depths of sampling of 0–10 and 60–100 cm.

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