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Soil organic C sequestration and stabilization in karstic soils of Yucatan

C. SHANG[1,2,*] and H. TIESSEN[1]
[1]*Department of Soil Science, University of Saskatchewan, 51 Campus Drive, S7N 5A Saskatoon, SK, Canada;* [2]*Current address: Department of Crop and Soil Environmental Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA; *Author for correspondence*

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Abstract. The tropical semiarid soils of northwestern Yucatan, Mexico, have exceptionally high organic matter (OM) contents, between 50 and 150 g C kg^{-1}. The soils are formed on limestone and form a mosaic of shallow black lithosols surrounding rock outcrops and deeper red rendzinas at slightly lower relief. Traditionally, these soils were managed under shifting cultivation with an uncommonly short cultivation period of only 2 years followed by a long bush fallow. We examined OM mineral associations using size and density fractionations of two soils after 1 and 12 years of fallow in a search for factors responsible for the high OM stability, short cultivation period and poor productivity. Light-fraction OM accounted for up to 38% of total soil OM and was responsible for almost all the OM accretion during fallow. Red soils contained half as much OM as black soils. Lower average OM contents of silt-size aggregates of red soils were due to a lower proportion of OC-rich agregates, not to differences in composition of individual aggregate classes. Expandable clays were practically absent in both soil types and sesquioxides were not related to OM contents or stability. Fine-sized secondary carbonates, undetectable to X-ray, impreganted light fraction OM and stabilized aggregates, and may be the principal cause of the OM accumulation. Mineralisation of coarse OM accumulated during fallow was impeded in both soils, but to a greater extent in the more calcareous black soils, so that relatively undecomposed OM accumulates to well above the levels that are typical for other semiarid tropical soils. Limited OM turnover will limit nutrient release, which may limit the agricultural productivity.

Introduction

The supply of plant nutrients under low input shifting agriculture depends mainly on organic matter (OM) mineralisation. The sustainability of such an agricultural system relies on the restoration of soil fertility through organic matter sequestration during fallow (Tiessen et al. 1992), and information on OM stabilisation and turnover indicates whether the system is sustainable or degrading (Tiessen et al. 1994). Such knowledge is now well developed for temperate soils, where it has been used to model OM budgets not only for land use change but also for such details as different tillage systems (Cole et al. 1989). For weathered tropical soils, a body of knowledge is emerging that points to lower stability of OM, and to a greater dependence of soil fertility on OM stocks (Tiessen et al. 1994).

Soil OM is associated with clay minerals, oxides and carbonates (Parfitt et al. 1999; Shang and Tiessen 1998; Turchenek and Oades 1979), and the degree of this association controls the turnover of OM under the given ecological conditions and land management (Parfitt et al. 1997; Saggar et al. 1996; Shang and Tiessen 2000; Sollins et al. 1996). Under semiarid tropical conditions, undisturbed soils typically contain about 10 g C kg^{-1}, of which some 30% may be lost during 4 to 6 year cultivation. This loss rate is much greater than under temperate conditions, and the difference has been attributed to faster biological reactions at higher temperatures and a lower potential of weathered soils to stabilise organic matter (Shang and Tiessen (1997, 2000)).

The degree of SOM association with mineral components and its turnover under various landuse systems can be studied using physical fractionation (Christensen 1992; Cambardella and Elliott 1992) in combination with chemical and spectroscopic methods. In this way, the association between soil OM and minerals (clays, oxides and Fe/Al cations) and the role soil minerals play in OM stabilization have been demonstrated (Parfitt et al. 1997; Shang and Tiessen 1998; Turchenek and Oades 1979).

The tropical semiarid soils of northwestern Yucatan, Mexico, contain between 50 and 150 g C kg^{-1}. Traditionally, these soils were managed under "Milpa", the Mayan shifting agricultural system with a short cultivation period of only 2 years followed by a long bush fallow of 20–25 years (Perez et al. 1981). Greater demand for land has shortened fallow periods to 6–8 years (Barke 1987; Teran and Rasmussen 1994). Such a short fallow period is insufficient to restore soil fertility and may lead to soil degradation. The unusually short use period, high OM content and significant OM losses during Milpa (Weisbach et al. 2002) indicate that mechanisms of OM turnover and stabilisation may differ substantially from both temperate and other tropical models. This and the widely recognised land degradation under current intensified land use make it important to understand SOM sequestration and stabilisation on these soils.

The soils of Yucatan peninsula are formed on Tertiary limestone in a typical karstic landscape of flat rock outcrops and shallow depressions, and generally fall into two groups: shallow black lithosols surrounding rock outcrops and deeper red rendzinas at slightly lower relief. Organic debris and limestone fragments make up a large portion of soil matrix (Isphording 1984). They also contain amorphous metal oxides and more stable secondary minerals (Isphording 1984) as well as some 2:1 layer minerals such as illites (mica), talc and chlorite inherited from impurities in the weathered calcite and dolomite (Isphording (1978, 1984)).

The present study of organo-mineral associations in the principal soil types under different land use permits a comparision of OM transformation in the calcareous soils of Yucatan with those in the more typical weathered tropical soils of NE Brazil under similar climatic conditions (Shang and Tiessen 1997). The objective is to illustrate the stabilization mechanisms for OM in these tropical calcareous soils in a search for factors responsible for the short cultivation period and poor nutrient availability.

Materials and methods

Study sites and soil sampling

The study sites are in the community of Hocaba (20°45′ N and 89°10′ W), 56 km south of Merida with an elevation of about 20 m a.s.l. The mean annual temperature is 26 °C and mean annual precipitation is 980 mm with a dry season from October to May. The native vegetation is a tropical low to medium deciduous forest.

Data on soil fertility and OM budgets collected from four fields at the different stages of fallow cycle (1, 6, 12 and 25 yr) indicated that much of the nutrients and OM lost during a two-year cropping was recovered after a 12-yr bush fallow (Weisbach et al. 2002). We therefore examined soils from the 1-yr and 12-yr fallow, representing the depletion state at the end of cropping cycle and the state of restoration at which the farmer initiated a new cultivation cycle. The two fields were 50 m apart; within these fields plots of 25 × 25 m were chosen and sampled on a 5 × 5 m giving 36 samples per plot; all plots contained mosaics of black and red soils, which were sampled separately to a depth of 10 cm (or less where soils were too shallow).

Soil samples were air-dried, and litter and gravel were removed before crushing to 2 mm. Samples from a grid and several transects including all 4 fallow stages were analyzed for organic and inorganic C, total N, total and organic P, exchangeable cations, and pH to document the changes induced during fallow and the field spatial variability (Weisbach et al. 2002). For the present soil OM fractionation and analysis, four composite samples were obtained for each colour group of the 1-yr and 12-yr fallow, i.e. Red-1 yr, Red-12 yr, Black-1 yr, and Black-12 yr (Table 1).

Soil organic matter fractionation

For each composite soil sample, five samples were fractionated, and the five replicates for each OM fraction, after weighing to check mass reproducibility, were combined for chemical analyses. We separated the following fractions (Figure 1), and the separation was conducted at room temperature.

Step 1: Free organic matter

Ten grams of air-dried soil (moisture content was determined separately) was placed on a 50-μm sieve immersed in water, and the soil was gently stirred with a rubber policeman to let < 50-μm particles pass through. The soil on the sieve, after draining, was immersed in a 1.7-g cm^{-3} NaI solution to float free organic matter (FOM), which was not associated with soil mineral particles. The FOM was recovered by vacuum aspiration and filtration, washed and dried at 55 °C.

Step 2: Sand-size fractions

The > 50-μm soil aggregates, remaining on the sieve after Step 1, were disaggregated in water by ultrasonification for 90 seconds at an energy output of 40 watt.

Table 1. Selected soil properties[1].

Soil properties		Red, 1-yr	Red, 12-yr	Black, 1-yr	Black, 12-yr
Sand	g kg^{-1}	20	9	16	36
Silt	g kg^{-1}	118	112	121	97
Clay	g kg^{-1}	742	671	587	505
Organic matter	g kg^{-1}	91	119	179	252
Fe/Al oxides	g kg^{-1}	43	37	25	19
Carbonates	g kg^{-1}	16	11	38	74
Estimated recovery	%	103	96	97	98
pH-water 1:1		8.0	8.0	8.3	8.1
Exchangeable Ca	cmol$_c$ kg^{-1}	39.5	44.5	55.0	58.0
Effective CEC	cmol$_c$ kg^{-1}	47.3	52.6	66.0	70.3
Total N	g kg^{-1}	4.2	5.1	8.7	11.3
Total P	mg kg^{-1}	505	506	730	733

[1] Organic matter contents were calculated assuming a 58% of C content. Carbonate contents (CO$_3$) were converted from inorganic C contents without considering associated cations. Fe/Al oxides were extracted with dithionite.

The sieve serves as a screen or energy boundary to minimize the disruption of silt-size aggregates once they have passed the sieve. The low energy treatment was designed to maximize the production of silt-size aggregates (< 50 μm). The ultrasonification treatment was repeated four times, after which materials retained on the sieve included the heavy sand fraction (HF) and sand-size inter-aggregate organic matter, i.e. the light fraction (LF) originally located between (outside) the < 50-μm aggregates. The two fractions were separated by density floatation (1.7-g cm^{-3} NaI).

Step 3: Free clay

The < 50-μm particles produced from the sonification treatment were combined with the free < 50-μm particles from the Step 1. The silt and silt-size aggregates were separated from clay by sedimentation. The clay in suspension was precipitated with CaCl$_2$ and dried at 55 °C. The clays isolated at this step were not or only loosely associated with aggregates (free clay).

Step 4: Fine light fraction

Part of the OM freed in step 2 passed through the sieve. To recover this fraction, 4 g of oven-dried silt-size fraction was suspended in 35 ml of 1.8-g cm^{-3} sodium metatungstate solution in a 50-ml centrifugation tube and gently dispersed by hand-shaking (Shang and Tiessen 2000). The mixture was centrifuged at 2500 *g* for 10 min. The OM on the top portion of tube was recovered as in Step 1. The fractionation was repeated three times to collect the fine light fraction (LF) from outside the aggregates. This fraction was combined with the fraction isolated at Step 2.

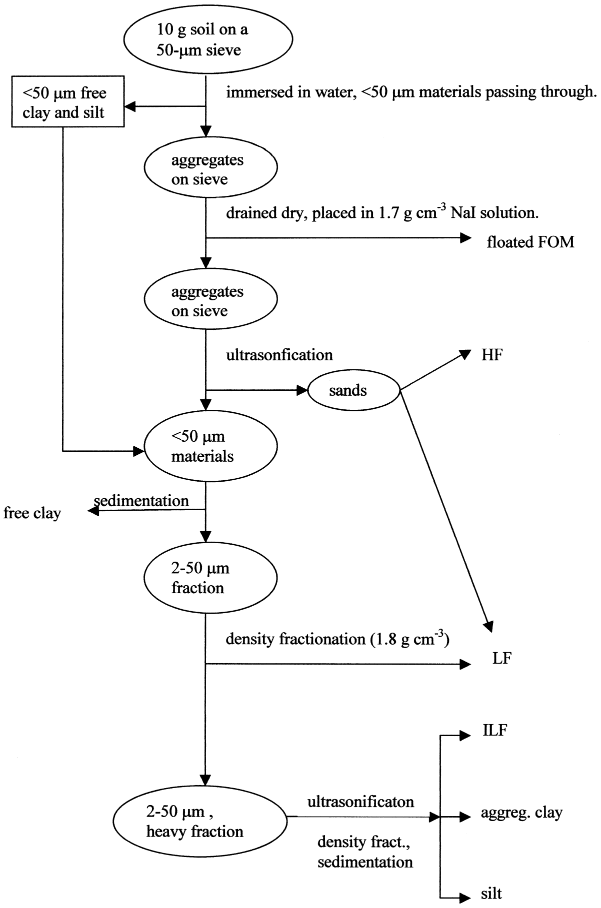

Figure 1. The soil organic matter fractionation scheme.

Step 5: Silt-size (2–50 μm) aggregates

The > 1.8-g cm^{-3} silt fraction from the Step 4 consists of aggregates and silt particles, and two approaches were used in characterizing the aggregate fraction. First, the > 1.8 g cm^{-3} aggregate fraction was treated by ultrasound in 1.8-g cm^{-3} metatungstate solution, and the newly released < 1.8-g cm^{-3} aggregate-internal light fraction (ILF) was recovered by suction from the surface. The > 1.8-g cm^{-3} fractions of the dispersed aggregates were then sedimented to isolate the newly released clays. This dispersion-sedimentation process was repeated four times with increasing ultrasound energy input each time. The silt and clay fractions were termed aggregated clays and silts, as distinct from the free clay fraction from Step 3.

In an alternative approach, silt-size aggregates were also fractionated into 1.8–2.4 and > 2.4 g cm^{-3} fractions by using a sequential fractionation scheme (Shang and Tiessen 2001). The 1.8–2.4 cm^{-3} fraction is rich in OC, whereas > 2.4 g cm^{-3} fraction is relatively poor. The two density fractions of aggregates were then disintegrated into ILF, aggregated silts and aggregated clays as described previously in a one-step dispersion. This alternative fractionation aimed specifically at characterising the silt sized aggregates, and their constituents forms the basis of Table 4 in the results. Duplicates were used in the density fractionation.

Chemical analysis

Soil organic carbon (OC) was determined by dry combustion at 850 °C on a Leco Carbon analyzer (CR-12, Leco Corp., St. Joseph, MI). A preliminary investigation showed that if combustion time is controlled within 120 s, error from inorganic C is minimal. Inorganic C (carbonates) was obtained from the difference between OC and total C that was combusted at 1100 °C. Total nitrogen was determined by H_2O_2-H_2SO_4 digestion followed by auto-analysis (Thomas et al. 1967). Exchangeable cations were extracted by 1 M NH_4Cl and the sum of extractable cations was taken as effective CEC after correction for water-soluble cations. Soil pH was determined in 1:1 soil/water paste, and texture by pipette after chemical dispersion and sedimentation (Gee and Bauder 1986).

Between 0.1–0.5 g of soil fractions were shaken with 10–25 ml of acidified ammonium oxalate in a 50-ml centrifugation tube at room temperature for 4 h in darkness (McKeague and Day 1966). The sample was then centrifuged for 10 min. at 2500 *g* and 10 °C (Sorvall RC-5B Superspeed Centrifuge, DuPont Instruments), and the supernatant was analyzed for Fe and Al by atomic absorption. The residual sample was then extracted with citrate-bicarbonate-dithionite (CBD) for free Fe and Al oxides (McKeague and Day 1966). Due to smaller sample size the amounts of citrate-bicarbonate buffer and dithionite used were reduced accordingly. The extraction was repeated once, and supernatants were combined for Fe and Al analyses.

Mineralogical analysis

Before K and Mg saturation, clay samples were treated to remove iron oxides, carbonates and OM (Kunze and Dixon 1986). Carbonates were removed by boiling samples in a pH-5.5 acetate buffer for 2 h, and organic matter was oxidized by H_2O_2. The CBD method described above was used to remove free Fe oxides. Treated samples were saturated with 1 M KCl and subsequently washed with alcohol to remove excess cations. K-saturated specimen were examined on a Rigaku x-ray diffractometer (Fe Kα radiation) (Rigaku Corp., Tokyo). To identify carbonate and oxide minerals, powder x-ray diffraction was performed on both untreated and pretreated samples.

Results and discussion

After carbonate, oxide and OM removal, the soils contained 1.2–5.6% sand, 13.4–16.6% silt and 79.1–84.7% clay. When mineral texture, OM, oxides and carbonates

Table 2. Mass and OC concentration of soils and their fractions.

Soils	Whole soil	FOM	Sand-size HF	LF	Silt-size aggregates			Free clay	Recovery
					ILF	Aggreg. Clay	Silt		
Mass, g kg^{-1} soil									%
Red, 1-yr		34	36	25	32	422	167	284	99
Red, 12-yr		45	48	72	34	397	131	286	99
Black, 1-yr		62	37	86	56	352	205	202	97
Black, 12-yr		144	69	130	68	234	158	196	99
OC concentration, mg g^{-1} fraction									
Red, 1-yr	52.9	245	40.7	300	280	33.4	27.7	33.0	
Red, 12-yr	68.9	272	20.6	220	280	36.8	28.3	34.1	
Black, 1-yr	104	284	15.7	278	281	62.8	50.4	74.8	
Black, 12-yr	146	308	19.7	290	285	88.4	60.2	90.9	
OC content, g kg^{-1} soil									
Red, 1-yr	52.9	8.3	1.5	7.6	8.9	14.1	4.6	9.4	103
Red, 12-yr	68.9	12.2	1.0	13.7	9.4	14.6	3.7	9.8	94
Black, 1-yr	104	17.6	0.6	23.8	15.6	22.1	10.4	15.1	101
Black, 12-yr	146	44.2	1.4	38.0	19.4	20.7	9.5	17.9	103

were expressed on a whole soil basis, recovery was between 96% and 103% (Table 1). The Black-12 yr sample had more sand-sized rock fragments and slightly lower clay content. This is consistent with the report by Quinones (1975) on soils from the same region. Black soils had much higher carbonate content than red soils.

Organic matter fractions

The amount of FOM varied with soil type and fallow period. It accounted for 15% of total soil OC in the Red-1 yr soil to 29% in Black-12 yr soil (Table 2). FOM consists of plant residues, up to a few mm long and corresponds to part of the light fraction separated by NaI solution used by Gregorich and Ellert (1993). The FOM pool in these Yucatec soils was much larger than reported for any other soils.

On a whole soil basis, red soils had less OM but more clays than black soils (Table 2). Organic C concentrations in the light fractions (FOM, LF and ILF) were similar across soils (Table 2) except for some variations in coarse LF fractions, which contained black particulate matter of various densities, possibly charcoal. Therefore, differences in OC content between soils were determined by the differences in fraction weight. The light fractions accounted for 30 to 38% of total soil OC. By scanning electron microscopy (not shown), parts of vegetation were clearly identifiable in LF with increasing decomposition in finer particle sizes, but could

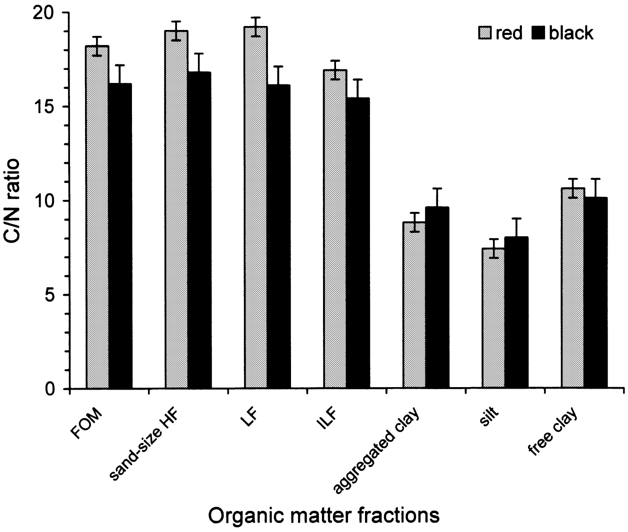

Figure 2. Carbon to nitrogen ratios of organic materials in various soil fractions.

no longer be identified in ILF, although some very fine (about 1 μm diameter) hyphae were seen. High C/N ratios in the LF also indicated the presence of plant residues (Figure 2).

The OC concentration of the free and aggregated clays did not differ consistently. It appears that the OC in the free clays was clay-bound humus rather than free OM that settled with clay particles, since no significant amount of light fraction could be isolated from free clays by density fractionation.

Organic C sequestration

The difference in OC content between samples taken at 1 and 12 yr fallow periods was taken as C sequestered during 11 years of fallow. Because OM is a significant portion of total soil mass, mineral-associated OC may be under-estimated for the soils with a higher OC content if a whole-soil basis is used. The OC content was thus expressed on the basis of mineral-phase weight (the soils have similar textures, Table 1) for the calculation of C sequestration. Figure 3 shows the distribution of OC and the newly sequestered C among soil fractions. The black and red soils had a similar percentage (18–19%) of new C in mineral-associated forms (clay and silt fractions), although the amount of mineral-associated C for the black soil was 5 times as much as that for the red soil (13.7 g kg^{-1} vs. 2.5 g kg^{-1} mineral particles, calculated from Figure 3).

The most striking difference between these Yucatec and other tropical soils is that most newly sequestered C is in FOM and LF (Figure 3). Amongst these, FOM is the predominant fraction in black soil, whereas LF is the main one in red soil (Figure 3). This suggests a faster disintegration of incoming OM (FOM) into LF in

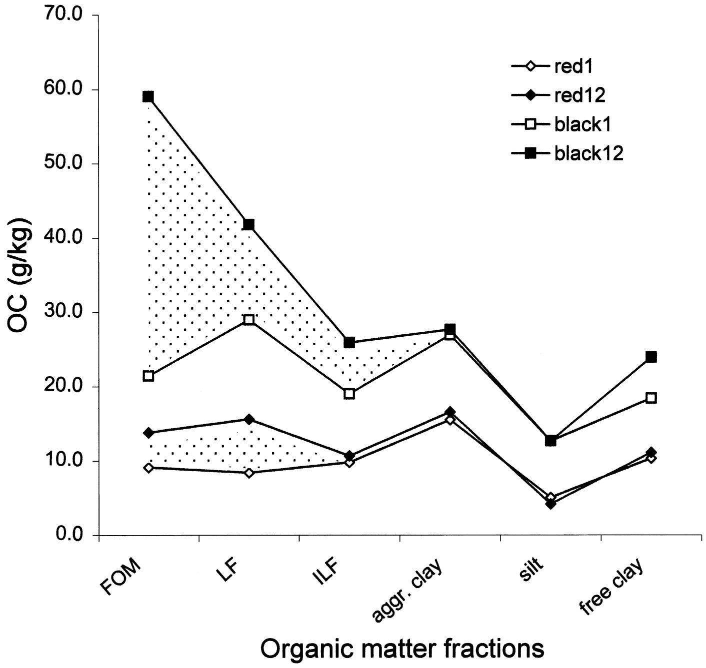

Figure 3. Distribution of organic carbon after 1 and 12 years of bush fallow in red and black soils (g OC kg^{-1} mineral mass). The shaded area represents new C sequestered during the intervening 11 years of fallow.

red soils. In the black 12-yr soil, 30% of total soil OC is contained in FOM, and 56% are in FOM + LF. Even at the end of the cultivation cycle (1-yr), at a 30% reduced soil OC content, FOM + LF still account for 40% of the soils OC. This implies an exceptional stability of the relatively undecomposed organic materials in the black soils. In the red 12-yr soil 38% of OC was in the FOM + LF, which was reduced to 30% in the 1-yr fallow. Although the mineral associated and aggregate-protected fractions respond somewhat to OC accretion by the soils, the properties that distinguish these calcareous soils from other tropical soils are clearly related to the stability of relatively coarse materials, i.e. to an inhibition of both decomposition and formation of humified soil OC.

Bush fallow consistently increased the OC concentration of free clays, aggregated clays and silt fractions, ranging from 2–10% in red soils to 19–41% in black soils, with the greatest increase in aggregated clays of both soil types (Table 2). The results suggest that OC sequestration coincided with silt-size aggregate formation. The LF has some similarities to the intra-aggregate particulate OM described by Six et al. (1998), who suggested that these organic materials acted as binding agents for macroaggregates.

Table 3. Distribution of carbonates (CO_3) among soil fractions.

Soils	FOM	Sand-size HF	Light fraction[1]	Aggregated clay	Free clay	Silt	Sum	Recovery
	g kg^{-1} soil							%
Red soil	1.2 ± 1.0[2]	1.9 ± 1.4	0.8 ± 0.5	6.0 ± 0.2	1.4 ± 1.4	1.7 ± 0.0	13.0	96
Black soil	4.9 ± 4.6	25.3 ± 9.4	6.3 ± 3.9	5.8 ± 0.6	2.6 ± 1.8	7.4 ± 4.7	52.3	94

[1] The sum of LF and ILF.

[2] Mean (of soils from two fallow periods) ± absolute deviation.

Stability of silt-size aggregates

About half the LF + clay were released from silt-size aggregates during the initial ultrasonification, followed by smaller increments during subsequent sonifications. Red soil aggregates consistently released more material than black aggregates during the first three dispersions, resulting in a smaller silt-size residual fraction (Figure 4). Hence, black aggregates were more resistant to mechanical dispersion than red aggregates. Red and black aggregates contained similar amounts of clay-associated carbonates (Table 3), but the black soil aggregates had more silt-sized carbonates and OM which acts as a binding agent for aggregates (Tisdall and Oades 1982).

The aggregates remaining after repeated dispersions presumably were more resistant. The OC concentration of clays isolated with increasing energy decreased, and the decrease was more significant for black than red soil aggregates (Figure 5). This implies that the clay-associated humified OM was not the stabilizing agent for silt-sized aggregates, and there was no significant difference in OC concentration between aggregated and free clays except for Black 1 soil, for which aggregated clays even had a lower OC concentration than free clays (Table 2). This leaves ILF as a candidate for the stabilizing agent, in contrast to models proposed by Jastrow et al. (1996) and Oades (1984), Tisdall and Oades (1982) which implicate light OM in the stabilisation only of macroaggregates (> 250 μm), while microaggregates of 50–250 μm are thought to be stabilized by transient (mainly polysaccharides) and persistent humified OM. It is possible that with decreasing aggregate size and depletion of ILF, the stability of aggregates might be more dependent on inorganic components (carbonates and oxides) so that the clays isolated at the end of the sequence contained more inorganic cements and less OM.

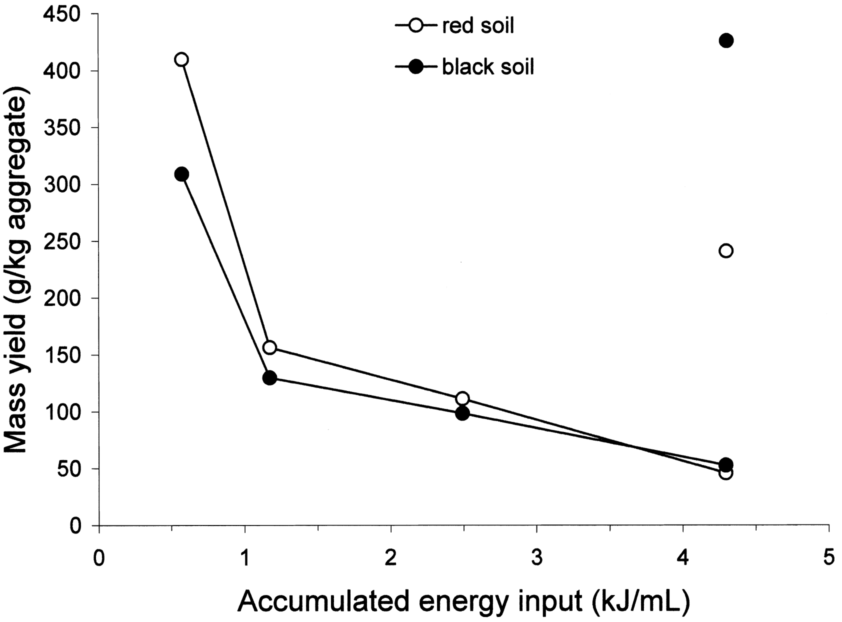

Figure 4. Production of released materials from silt-size aggregates as a function of ultrasonic energy input. The separate points represent the amounts of silt-sized residues after four dispersions. The data are the average of two replicates, and the absolute deviations are smaller than the font size used.

Organic C-rich and low-OC aggregates

The OC concentration of 1.8–2.4 g cm^{-3} fractions was 3 to 4 times higher than that of > 2.4-g cm^{-3} aggregates (Table 4). The OC enrichment in 1.8–2.4 g cm^{-3} aggregates was mainly due to the presence of ILF, which was nearly absent in > 2.4 cm^{-3} aggregates. The clays in OC-rich aggregates also had higher OC concentrations than those in low-OC aggregates. The silt-size residues of 1.8–2.4-g cm^{-3} aggregates probably still contained some aggregates resistant to ultrasonic dispersion, with OC concentrations similar to those of whole aggregates, whereas true silt particles were exclusively present in > 2.4 g cm^{-3} fractions. The results showed that the aggregates of two density fractions were qualitatively different, regardless of soil type.

Organic C-rich (1.8–2.4 g cm^{-3}) aggregates made up 64% of the mass of black soil aggregates whereas the red soils contained only 31% of organic C-rich aggregates (Table 4). Therefore, a low average OC content in red soil aggregates was the result of small amounts of OC-rich aggregates (1.8–2.4 g cm^{-3}) present. Total N distribution was similar to that of total organic C, and the C/N ratio decreased in the order: LF > C-rich aggregates > low-OC aggregates (Table 4).

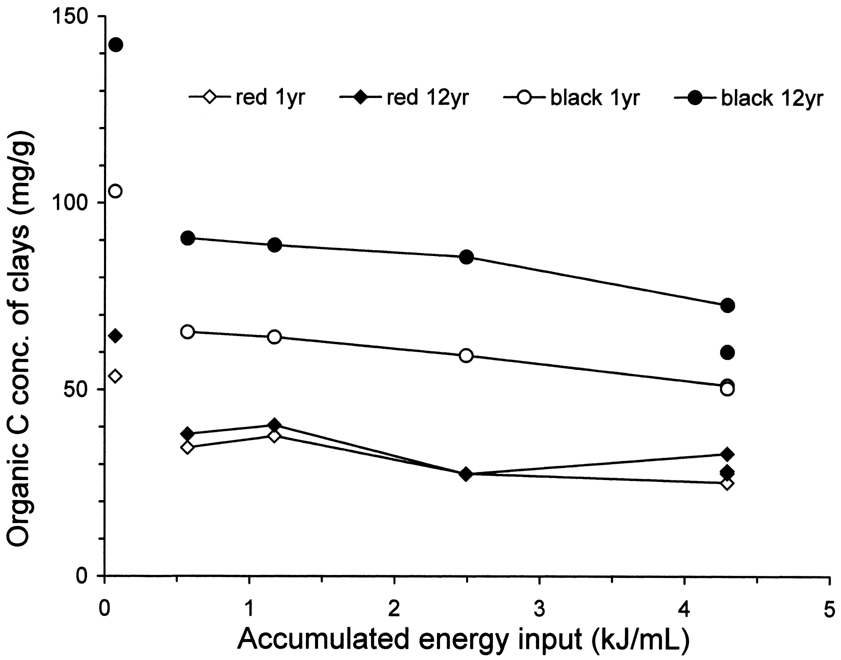

Figure 5. Change in the OC concentration of released clays at various energy levels. Two separate points at the low-energy end represent free clays and those at the high-energy end represent silt-sized residues. The data are the average of two replicates, and the absolute deviations are smaller than the font size used.

The role of the mineral phase in C stabilization

Carbonates

On average black soils contained four times as much carbonates as red soils (Table 3). In black soils close to 50% of carbonates was in HF fraction as rock residues, and the carbonate distribution was quite uniform among the rest of fractions. If we consider red soils as advanced stages formed from black soils, carbonates have been lost during soil weathering from every fractions except clays in 2–53 μm aggregates. Carbonates probably were partially responsible for aggregation because carbonate content of aggregated clay was greater than that of free clay (Table 3).

The FOM of the 12-yr black soil contained about 5 g carbonate per kg of soil (Table 3), corresponding to 35 g carbonate per kg of fraction mass (Table 2). This is a substantial amount of carbonate impregnation, which is visible as a coating on organic materials in electron micrographs (not shown). We suggest that this carbonate impregnation may play a major role in the stability and accumulation of FOM and LF in the black, and to a lesser extend also in the red soils (Figure 3).

Table 4. Organic C and N contents of silt-size aggregates and OC-rich (light) and low-OC (heavy) subfractions.

Fraction		Mass		OC concentration		OC amount		Total N	
		Red	Black	Red	Black	Red	Black	Red	Black
		g kg^{-1} aggregate		mg g^{-1} fraction		g kg^{-1} aggregate		g kg^{-1} aggregate	
Aggregate total		1000	1000	59 ± 5	123 ± 20	59 ± 5	123 ± 20	5.3 ± 0.1	9.0 ± 1.7
< 1.8 g cm^{-3}		41 ± 5[1]	121 ± 24	278 ± 20	301 ± 1	12 ± 2	38 ± 8	0.9 ± 0.2	2.2 ± 0.7
1.8–2.4 g cm^{-3}		312 ± 10	639 ± 1	94 ± 4	113 ± 13	29 ± 2	72 ± 8	2.4 ± 0.2	6.8 ± 0.5
	LF	30 ± 3	83 ± 12	231 ± 37	249 ± 30	7 ± 0	22 ± 6	0.4 ± 0.0	1.5 ± 0.3
	Clay	175 ± 4	343 ± 6	45 ± 4	60 ± 22	8 ± 0	27 ± 2	1.0 ± 0.0	2.8 ± 0.3
	Silt	103 ± 21	221 ± 1	126 ± 9	103 ± 3	14 ± 2	24 ± 1	1.1 ± 0.3	2.5 ± 0.1
> 2.4 g cm^{-3}		669 ± 27	230 ± 45	25 ± 1	38 ± 11	17 ± 0	8 ± 1	2.1 ± 0.0	1.0 ± 0.2
	LF	<1	3 ± 0	nd[2]	249 ± 0	nd	<1 ± 0	nd	nd
	Clay	389 ± 60	93 ± 24	23 ± 1	42 ± 14	10 ± 2	4 ± 1	1.1 ± 0.3	0.4 ± 0.1
	Silt	269 ± 75	136 ± 22	23 ± 0	27 ± 4	7 ± 2	4 ± 0	0.9 ± 0.3	0.5 ± 0.1
sum of fractions		1022 ± 12	995 ± 16			58 ± 4	118 ± 18	5.2 ± 0.3	10.1 ± 1.0

[1] Mean ± absolute deviation

[2] nd = not detectable.

Iron and aluminium

Table 5 shows the mean metal concentrations for two groupings of soil fractions, the OC-rich group with an OC content near 30% and the low-OC group with $<$ 10% OC (see the footnote of Table 5). For both red and black soils, the concentrations of extracted Fe and Al of the low-OC were either higher than or equal to those of the OC-rich group. The CBD-Fe contents of red soils (low-OC fractions) were significantly higher than those of black soils because of the more advanced weathering in red soils. The CBD-Fe concentration of aggregated clay in red soils was 50 μg g^{-1} vs. 36 μg g^{-1} of black soil clays, and a similar difference also existed between two soils' free-clay fractions (not shown). CBD-Fe and CBD-Al were also enriched in low-OC fractions and have been shown to interact only weakly with OM in Brazilian soils (Shang and Tiessen 1998). For oxalate-Fe, there was essentially no difference between red and black soils even though the latter had twice as much OM as red soils (Table 5). In contrast, corresponding data from Brazilian soils (Figure 6) show a linear correlation between OC and metal concentrations. Stabilization of OM by interaction with aluminum was also reported in other tropical soils (Parfitt et al. 1999). Higher concentrations of oxalate-Fe and -Al in low-OC fractions and the lack of correlation between OC and metal concentrations suggest that oxalate-Fe and Al were extracted mostly from clay surfaces or inorganic phases rather than from metal-OM complexes. This indirectly points to the role of Ca and Mg cations and carbonates in these soils in stabilising OM.

Within silt-size aggregates there also was no correlation between extracted Fe and Al and organic C (Table 5). For both soil aggregates, free oxides extracted by CBD were more concentrated in $>$ 2.4-g cm^{-3} fractions, particularly for red soils, and thus free oxides were not actively involved in OM stabilization in accordance with our previous findings (Shang and Tiessen 1998). For both density fractions, red soil aggregates consistently contained 20 to 30% more CBD-Fe than black soil aggregates.

Crystalline minerals

The soils' HFs consist of calcite and quartz (x-ray spectra not shown), and the relative peak intensity of calcite between two soils is in accordance with the carbonate contents given in Table 3. Both quartz and calcite were also present as impurities in soil light fractions, but the peak intensity decreased with decreasing particle size and none was detectable in the ILF (spectra not shown). No crystalline iron-containing minerals were detected in these organic fractions by powder x-ray diffraction, in comparison with the presence of goethite in similar fractionated materials from Brazilian soils (Shang and Tiessen 1998).

Quartz was mainly concentrated in silt fractions (spectra not shown). Calcite was found only in the free-clay fraction of black soil but not in other fine fractions, although they had higher carbonate contents than the black free clay (Table 3). The carbonates in these fractions might be in very fine particles to be detected. This indicates that there is considerable carbonate mobility and transformation in these soils, which can explain the impregnation of coarser OM with carbonates.

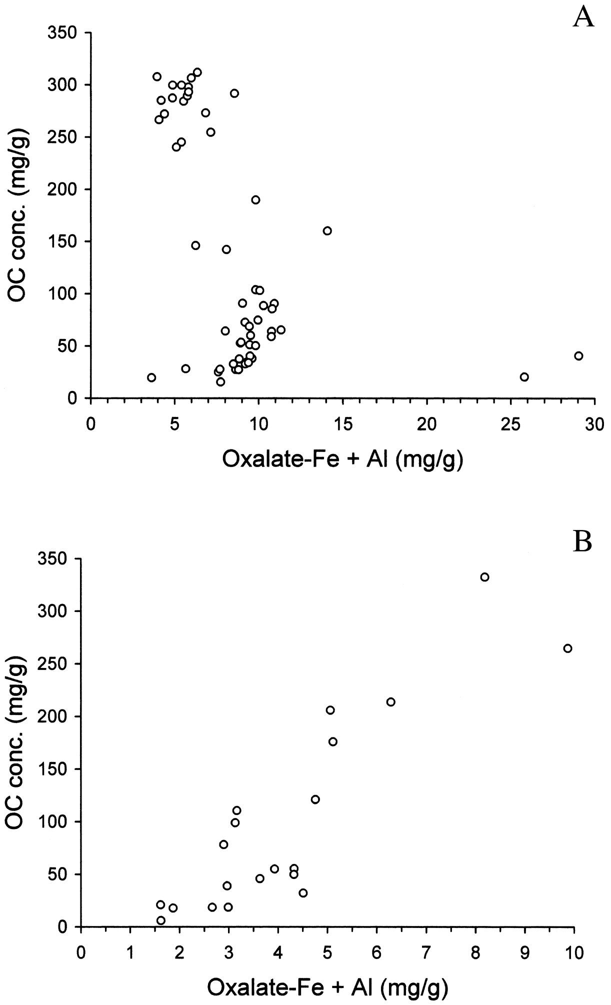

Figure 6. Correlation between the OC and total oxalate-extracted metal concentrations for the soil fractions (a) from the current study, and (b) from Brazilian Alfisol and Oxisol.

The x-ray diffraction patterns of K-saturated aggregated and free-clay samples show illites (mica) (1.008, 0.499 and 0.332 nm), kaolinite (0.716 and 0.357 nm) and boehmite (0.610 nm) as major minerals (Figure 7). A high long tail at the low-angle side of the 1.0-nm-peak probably indicates the poor crystallinity of illites caused by weathering. The 1.0-nm peak in the free clay of red soil is not as sharp as that of black soil (at 25 °C) and diminished further after heating (Figure 7a). The peak intensity of kaolinite and boehmite are relatively stronger in red soils than in black soils if they are all compared with 1.0-nm illite peak, and this suggests that the two minerals are more abundant in red than in black soils. This was also observed for aggregated clays (Figure 7b). The red soils are at a more advanced

Table 5. Concentrations of extracted Fe and Al in OC-rich and low-OC soil fractions of red and black soils.

Soil	Fraction	Oxalate-Fe mg g^{-1}	Oxalate-Al mg g^{-1}	CBD-Fe mg g^{-1}	CBD-Al mg g^{-1}
Fractions for whole soil					
Red	OC-rich[1]	1.2 ± 0.6[2]	5.1 ± 2.4	17.8 ± 7.0	2.9 ± 1.3
	low-OC[1]	2.4 ± 1.8	9.1 ± 5.1	50.9 ± 3.5	6.2 ± 1.1
Black	OC-rich	1.4 ± 0.4	4.6 ± 1.2	13.4 ± 2.6	2.6 ± 0.8
	low-OC	2.0 ± 0.5	7.5 ± 1.7	33.6 ± 7.6	5.3 ± 1.9
Fractions from silt-size aggregates					
Red	1.8–2.4 g cm^{-3}	1.5 ± 0.0	6.8 ± 0.1	42.4 ± 2.1	4.5 ± 0.2
	> 2.4 g cm^{-3}	1.7 ± 0.0	7.2 ± 0.0	54.1 ± 4.0	4.9 ± 0.2
Black	1.8–2.4 g cm^{-3}	2.1 ± 0.1	7.9 ± 0.2	34.6 ± 2.5	4.4 ± 0.2
	> 2.4 g cm^{-3}	2.3 ± 0.4	6.3 ± 1.0	38.2 ± 6.1	4.9 ± 0.3

[1] The organic C-rich group includes free organic matter (FOM) and all light fractions (LF + ILF), while the OC-poor group includes sand-size heavy fraction, free clay, aggregated clay and silt fractions.
[2] Mean ± standard deviation.

stage of weathering and naturally contain more kaolinite and boehmite. Broadening in the kaolinite basal reflection confirms the previous reports by Isphording (1978, 1984) that in these relatively young soils kaolinite has poor crystallinity. The small peak appearing at 1.41 nm in the spectra at room temperature indicates the presence of expandable clays, perhaps hydroxy interlayered minerals (Barnhisel and Bertsch 1989). Isphording (1974, 1978) suggested that chlorites, present in trace amounts in some soils and parent limestones from the region, serves as the source material for most of the residual clay minerals that develop from weathering of these limestones. The hydroxy-interlayered minerals may have derived from chlorite.

The mineral distributions in silt-size aggregates (Table 6) were based on the basal diffraction intensity and therefore have no quantitative significance within a group or sample. However, the comparison between any two or more groups illustrates a quantitative change in mineral composition. The mineralogical composition of the clay fraction was found to be similar in all density fractions of black soil aggregates with illite dominant and quartz a minor constituent. For the red soil, kaolinite was more abundant in the > 2.4-g cm^{-3} fraction than in the 1.8–2.4-g cm^{-3} fraction. This change in mineralogy may determine the low quantity of OC-rich aggregates in the red soil discussed above. Quartz was largely present in silt fractions and was more concentrated in > 2.4-g cm^{-3} fractions than in low-density fractions. Calcite was found only in the heavy fraction of black soil and apparently was lost during weathering to red soils. Weathering has also resulted in relative increases in quartz or decrease in illite abundance in the silts of 1.8–2.4-g cm^{-3} aggregates.

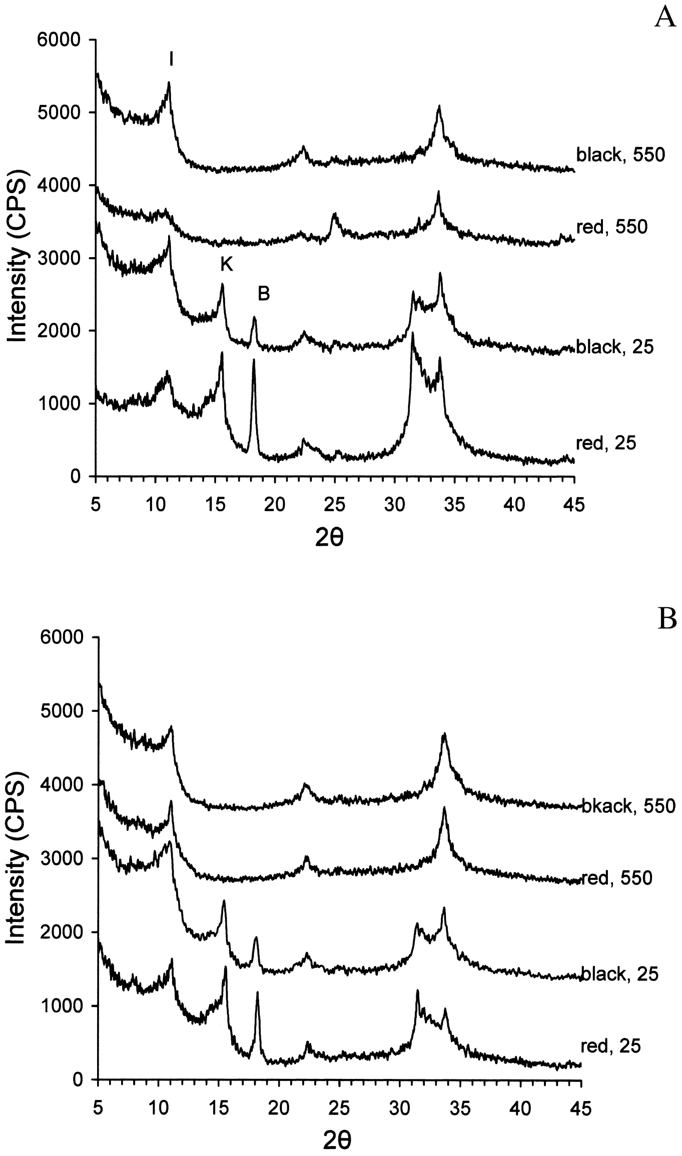

Figure 7. X-ray diffraction patterns of K-saturated aggregated (7a) and free (7b) clays at 25 °C and heated at 550 °C.

Conclusions

The OM pools obtained in this study reveal a path of OM disintegration from FOM, to LF, into ILF. The LF was located within sand-size or larger structures between silt-sized aggregates and is believed to be responsible for stabilizing larger struc-

Table 6. Occurrence of minerals in the density and size fractions of silt-sized aggregates.

Density fraction	Clay		Silt	
	Black soil	Red soil	Black soil	Red soil
1.8–2.4 g cm^{-3}	I, K, B, Q[1]	I, K, B, Q	I, Q, K, B	Q = I, K, B
> 2.4 g cm^{-3}	I, K, B, Q	K, I, B, Q	Q, Cal, I, K, B	Q, I, K, B

[1] I = illite, K = kaolinite, Q = quartz, Cal = calcite, B = boehmite. The minerals are arranged in the order of decreasing intensity of their strongest diffraction peak.

tures (Oades 1984; Six et al. 1998). There was a link between OM within silt-sized aggregates, ILF and aggregate stability as described by Jastrow (1996) and Jastrow et al. (1996).

The clay kaolinite, boehmite and illite made up 80% of the soil mineral phase. No significant amounts of expandable minerals were found, and there was no correlation between OC and oxalate-Al and -Fe concentrations that could explain the stabilisation of OM in these calcareous soils. Kaolinite and boehmite contain variable charges and are capable of interacting with OM through their edge sites forming chemical bonding (Dixon 1989; Hsu 1989) but their stabilisation capacity is relatively low. Fine particle-sized carbonates may act as a cementing agent in the silt-sized aggregates. We also detected up to 3.5% of carbonate in the FOM, possibly an impregnation with fine particle-sized carbonates that may in part explain the exceptional stability of relatively undecomposed OM in these soils. The presence of carbonates in recent organic materials indicates a relatively high mobility of carbonates which may therefore be active in the stabilisation of organic matter and soil structure.

The physical distribution of OM is uneven within soil matrix (Cambardella and Elliott 1994), as demonstrated by the silt-size aggregates. There is a compositional difference between organic C-rich and -poor aggregates, the former contained organic C-rich clays and all the intra-aggregate ILF of the silt size aggregates (Table 4). This difference between organic C-rich and -poor aggregates did not vary with soil type. The higher average OC content for the silt-size aggregates of the black soil was therefore due to a greater proportion of OC-rich aggregates.

It seems that physical, chemical and biological processes in red soils are more active resulting in faster turnover of OM, and the predominant low-activity minerals are unable to stabilize as much OM through formation of OC-rich aggregates. High OC levels and an accumulation of coarse fractions in black soils indicate a slow decomposition, which might be related to carbonate impregnation, an unfavorable field moisture regime and the presence of charcoal. Soil OC turnover in the tropics is normally faster than in the temperate zone under similar management practices (Tiessen et al. 1994), and equilibrium levels may therefore be lower. Under similar semiarid climate and shifting cultivation two Brazilian soils (an Oxisol and an Alfisol) were found to contain only one tenth as much OC as these soils from Yucatan (Shang and Tiessen (1997, 1998)). The calcareous Yucatec soils impede OC turnover, so that substantial amounts of relatively undecomposed OM accumulate, well above the OC levels typical for other semiarid tropical soils.

The OM accumulation and limited turnover will limit nutrient release which may limit the agricultural productivity of these soils. In addition, the high OM content of the black soil, accounting for more than 20% of total soil mass, affects the water retention and availability in these soils. We have observed hydrophobicity of some black soils and are studying the role of OM in the soils' moisture regime further.

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