

Mechanisms of C Sequestration in Soils of Latin America

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Carbon (C) sequestration, defined as the process whereby atmospheric CO₂ is transferred into a long-lived C pool, is an important issue not only in the scientific community but also in the society at large because of its potential role in off-setting fossil fuel emissions. Through photosynthesis this C is stored in plants and through decomposition, trunks, branches, leaves and roots are incorporated in the soil via the action of different soil organisms, i.e., bacteria. fungi and invertebrates. This, together with the C exudates from roots that are utilized by microbial populations, constitutes the natural pathways of incorporating biomass-C into the soil. The amount of C stored in terrestrial ecosystems is the third largest among the global C pools. Soil organic carbon (SOC) up to 3 m is 2,344 Pg C (1 Petagram $= 10^{15}$ g), and the SOC pool in tropical soils is approximately 30% of the global pool. Abiotic factors, which moderate C sequestration in soils are clay content, mineralogy, structural stability, landscape position, and soil moisture and temperature regimes. On the other hand, biotic factors involved in soil C sequestration are determined by the activities of soil organisms. However, models do not include the formation, stabilization and lifespan of the aggregates that have been biologically produced, including roots. This is not only due to the lack of studies on this subject, but also to overlooking the role of soil organisms in soil aggregation. Furthermore, there is a lack of comprehensive knowledge regarding the processes that control dissolved organic carbon (DOC) fluxes in soils and its role in the global budget of C sequestration. The boundaries of ecosystems are not considered in the studies of the subject, as it may be the case for terrestrial C sequestration, since the borders around the sites under study constitute pathways for the flow of C between sites and through the landscape. The concentrations of DOC in deep soil horizons and the contribution to DOC fluxes (exports) are relatively small, from 4 to 37 g DOC m⁻² yr⁻¹ retained in the mineral subsoil. In South America, although substantial research has been done under different ecosystems and land use systems in some countries, like Brazil, Colombia, Argentina, there is a need to conduct more studies with agreed standard methodologies in natural ecosystems and agricultural systems, and in other areas of Central America few studies have been undertaken to date. The principal objective of this review was to address the main mechanisms that determine SOC and SIC sequestration in soils of Latin America, and include: physical aggregate protection, SOC-clay interaction, DOC transport, bioturbation by soil organisms, and the formation of secondary carbonates. All of these mechanisms are generally explained by physical and chemical processes. In contrast, this review takes a soil ecological approach to describe the mechanisms listed above.

Keywords carbon sequestration, soil organic carbon, soil inorganic carbon, land management, Latin America, soil aggregation, clay mineralogy, dissolved organic carbon, bioturbation, soil invertebrates, agroecosystems, tropical soils

I. INTRODUCTION

Terrestrial Carbon (C) sequestration is an important issue in both the scientific community and the society at large because of its potential role in offsetting fossil fuel emissions. Terrestrial C sequestration has two principal components: biotic sequestration in plant biomass and soil sequestration in the soil solum. The latter involves two components: soil organic carbon (SOC) and soil inorganic carbon (SIC) sequestration.

A. Terrestrial C Sequestration

Carbon sequestration is defined as the process whereby the atmospheric CO2 is transferred into a long-lived C pool. Photosynthesis is the natural process by which plants fix CO₂ to produce carbohydrates, which are then used in different metabolic pathways. This C is stored in plant components including trunks, branches, leaves and roots. The incorporation of these materials into the soil via the action of different soil organisms, especially the functional group of soil ecosystem engineers (sensu Jones et al., 1994) and inhabitants of the litter, together with the C exudates from roots that are utilized by microbial populations, constitute the natural pathways of incorporating biomass C into the soil. The biomass C enters the soil through the decomposition, a key process in the C cycle due to its two interrelated subprocesses, i.e., mineralization and humification. Mineralization is the process by which organic molecules are converted into inorganic forms assimilable by plants, and humification is the process by which soil organic matter levels are maintained. Humification efficiency ranges from 10 to 20% (Lal, 2004). During mineralization CO₂ is emitted from respiration activities of soil microorganisms.

Decomposition in terrestrial ecosystems is determined by a set of factors organized in a hierarchy that regulates the activity of soil microorganisms at decreasing scales of time and space in the order: climate—nutrient status + clay mineralogy + quality of resources—role of macroorganisms (i.e., roots and invertebrates) (Lavelle *et al.*, 1993). Soil organic matter participates in the formation of colloids that glue soil particles together and hence C, into solid structural units, the aggregates. Air space surrounds these aggregates of varying sizes so water, gases and solutes can flow. The negative charge of SOM helps retain exchangeable cations, especially in acid soils where clay minerals retain few cations.

The biotic process of C sequestration is natural and occurs above (biota) and below ground (soil + biota). The amount of C stored in terrestrial ecosystems, including above- and belowground components comprises the third largest among the global C pools. The soil C pool up to 1 m is estimated at 2,500 Pg $(Pg = Petagram = 10^{15} g)$, of which 1,550 Pg is SOC and 950 Pg is SIC (Batjes, 1996). These estimates include a large amount of charcoal, especially in areas where vegetation is frequently burnt (Skjemstad et al., 1996). Finally, the above- and below-ground biomass or the biotic pool contains 600 Pg of live biomass and detritus material at some stage of decomposition (Eswaran et al., 1993; Houghton, 1995; Batjes, 1996; Batjes and Sombroek, 1997). Global patterns in SOC were compiled and analyzed by Post et al. (1982). A recent estimate of SOC to 3 m gives a value of 2,344 Pg C; global totals for the second and third meters are 491 and 351 Pg C, and the biomes with the highest contents of SOC are the tropical evergreen forest (158 Pg C) and the tropical savanna (146 Pg C) (Jobággy and Jackson, 2000).

The SOC pool comprises active OM and relatively inert charcoal, and its role is of utmost importance in the global C cycle since it represents a dynamic balance between the input of dead plant material and the output from decomposition (mineralization), erosion and leaching. Abiotic factors that moderate C sequestration in soils are climate, landscape position, mineralogy, clay content, structural stability, and soil moisture and temperature regimes. The SOC pool is transformed biologically by the action of soil organisms (i.e., bacteria, fungi and invertebrates) and is stabilized in each of the clay- or silt-sized organomineral complexes with different turnover rates.

Some of the C is returned to the atmosphere as CO₂ and CH₄ when SOC is decomposed under aerobic and anaerobic environments, respectively. Among the sources that have contributed to CO₂ emissions to the atmosphere, about 50 Pg came from cultivated soils (Paustian et al., 1997), through SOC mineralization. In soils under agricultural practices, part of the SOC pool has already been released into the atmosphere. A 10% reduction in the SOC pool and its emission into the atmosphere is equivalent to the anthropogenic emissions of CO₂ by fossil fuel during 30 vears from 1970 to 2000 (Kirschbaum, 2000). As much as 75% of the antecedent SOC pool is lost following conversion of natural to agricultural systems in tropical regions (Lal, 2004). Since many agricultural lands are no longer productive, new lands are being brought under cultivation through tropical deforestation, causing important soil degradation processes with significant losses of SOC pool.

The flux of CO₂ between soils and the atmosphere has been estimated at 75-77 Pg C yr⁻¹, which is equivalent to 10% of current levels of atmospheric CO₂ (Schlesinger, 1977; Raich and Potter, 1995). Flux of CO₂ from soil to the atmosphere is one of the largest fluxes in the global C cycle, and is equivalent to the net primary productivity (NPP) and litterfall, which are around 50 to 60 Pg C yr⁻¹ (Mattews, 1997; Field *et al.*, 1998). There is a strong direct relationship between soil respiration and NPP (R² = 0.87; Raich and Schlesinger, 1992). Flux due to soil respiration is higher than NPP because it also includes CO₂ emission from plant roots and mycorrhizae. Since the age of C increases with depth (Jenkinson and Rayner, 1977), there is a relatively high amount of C in stable forms that is not affected by land use changes and so it will not be emitted to the atmosphere as CO₂. Sequestration of C as SIC primarily occurs through formation of secondary carbonates. The SIC is an important constituent in soils of the arid and semi-arid regions. Reserves of SIC stored in soils range between 780 and 930 Pg C (Schlesinger, 1982). The SIC comprises elemental C along with carbonates (CO_3^{-2}) and bicarbonates (HCO_3^{-}) of Ca^{+2} , and Mg^{+2} . Important minerals comprising SIC pool include calcite and dolomite. There are two types of carbonates: primary and secondary. Primary carbonates are derived from the weathering of the parent material. In contrast, secondary carbonates are formed through conversion of CO_2 into carbonic acid and its reaction with Ca^{2+} and Mg^{2+} to form pedogenic carbonates (Lal and Kimble, 2000).

B. Latin American Soils

The SOC pool in soils of the tropics is estimated at 496 (Kimble et al., 1990) and 506 Pg C (Eswaran et al., 1993), approximately 30% of the global SOC pool. Batjes (1996) estimated the amount of SOC in the tropics as 201 to 213 Pg C in the first 30 cm, 384 to 403 Pg C and 616 to 640 for the top meter and 0-200 cm depth, respectively. The contribution of C in the soil below 1 meter is especially relevant in tropical soils, which are generally deep to very deep (Sombroek et al., 1993). Thus, there is a considerable amount of C stored in tropical soils, higher than in temperate soils (Moraes *et al.*, 1995). The SOC pool in different soils of the tropics represents 66, 80 and 69% of the amount contained to 2-m depth (Table 1). The amount of C in the top 25 cm in Ferralsols and Ferric Acrisols is only one-third of the total pool to 2-m depth (with 43% of the total to 1 m), whereas in non-ferralic Acrisols and Luvisols most of the C pool is concentrated in the top 25 cm layer (Sombroek *et al.*, 1993).

Sombroek *et al.* (1993) estimated the SOC and SIC pools in soils of Latin America at 174 Pg C and 65 Pg C, respectively (Table 2). Basic principles of SOC sequestration apply to soils of the tropics and temperate regions. However, the rates of SOC sequestration are generally lower in the tropics compared with soils of the temperate zone because of high temperatures and the attendant microbial activity throughout the year (Lal, 2002), and

	Andosols		Acrisols		Ferralsols	
Depth (cm)	SOC (kg C m^{-2})	% of total	SOC (kg C m^{-2})	% of total	SOC (kg C m^{-2})	% of total
0–25	14.6	28	5.1	59	2.6	30
25-50	7.3	14	0.6	7	1.4	15
50-75	6.5	13	0.6	7	1.3	15
75-100	5.9	11	0.6	7	0.8	9
100-150	10.1	20	1.0	12	1.5	17
150-200	7.4	14	0.7	8	1.2	14

 TABLE 1

 Distribution of SOC in some tropical soils (adapted from Sombroek *et al.*, 1993)

TABLE 2 The SOC and SIC pools up to 1 m depth in Latin American soils (From Sombroek *et al.*, 1993)

Soil C	Central America	South America
SOC concentration (kg C m^{-2})	9.9	8.3
Total SOC pool (Pg)	26.1	147.5
SIC concentration (kg C m^{-2})	6.9	2.6
Total SIC pool (Pg)	18.6	46.4

¹ Average value of kg C m⁻²

² Pg = Petagram (10^{15} g)

there may be differences in specific C fractions involved (Bayer *et al.*, 2000).

In highly weathered tropical soils, rate of C loss by cultivation is more than that for temperate soils (Shang and Tiessen, 1997), leading to rapid soil degradation. Tropical forest ecosystems account for 20 to 25% of the world terrestrial (soil and vegetation) C (Dixon *et al.*, 1994). Tropical deforestation is a principal source of CO₂, accounting for 20% of the annual global emissions (IPCC, 2001). Cadisch *et al.* (1996) observed that losses of rainforest-derived C amounted to 73% (0 to 2 cm) and 40% (5 to 15 cm) of the initial SOC concentration after 18 years of conversion to pasture. Luizão *et al.* (1992) observed that soil biomass C in 0 to 5 cm depth decreased to 64% within 1 year of slashand-burn. Tropical soils with predominantly low-activity clays like Kaolinite have low ability to sequester C. SOM in many tropical soils may be less stable due to different mechanisms of organomineral stabilization (Shang and Tiessen, 1998).

Factors affecting rate of SOC sequestration are similar in soils of the tropics and in temperate environments. Soil texture plays an important role in the below-ground C storage in the lowland Amazonian forest ecosystem (Silver *et al.*, 2000). The effect of texture on SOC storage is related to its impact on ability of soils to retain C, water, and nutrients and on soil air permeability for gaseous exchange.

The objective of this review is to address the principal mechanisms that determine SOC and SIC sequestration in soils with a focus in Latin America. Four mechanisms addressed in this review include the following:

- 1. physical protection within soil aggregates,
- 2. interaction of SOC with clay fractions,
- 3. transport of dissolved organic C (DOC) into subsoil, bioturbation, and
- 4. formation of secondary carbonates.

These mechanisms are generally addressed as physical and chemical processes. In contrast, this review takes a soil ecological approach to describe the five mechanisms listed above, and provides a unifying conceptual framework that combines all mechanisms into a single and provocative model (Figure 1).

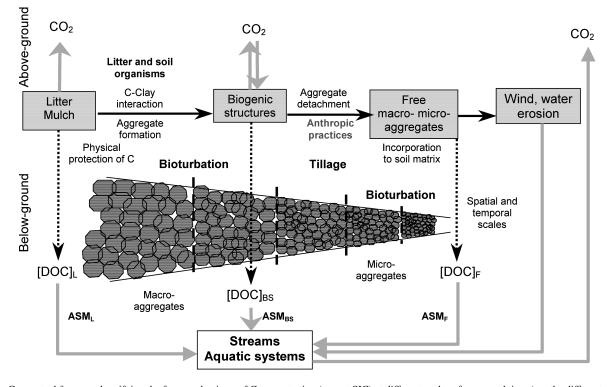


FIG. 1. Conceptual framework unifying the four mechanisms of C sequestration (except SIC) at different scales of space and time (see the different sections in the text for explanation of each of the mechanisms) DOC = Dissolved organic C; L = litter, BS = biogenic structure; F = free aggregates; ASM = Activation of soil microorganisms. Biotic processes associated to any of the mechanisms are indicated in green while those abiotic processes are indicated by gray letters.

Briefly, processes at different spatial and temporal scales occur above- and belowground and involve either a biotic factor or control (indicated in green), or and abiotic factor (indicated in gray). In the soil, clay-C interactions and aggregate formation together with the activities of soil invertebrates determine the formation and properties of biogenic structures that later degrade due to environmental factors, i.e., rainfall or management (for example, cattle trampling in pastures). In the soil, bioturbation also creates aggregates of different sizes (macro- and microaggregates), whereas in agricultural systems continuous tillage leads to a reduced mean weight diameter of aggregates that may exacerbate in the medium-term wind and water erosion problems. The DOC has several sources from above (litter and biogenic structures) and below ground (aggregates) and flows through the soil to the water streams and aquatic systems.

II. SOIL AGGREGATION AND C SEQUESTRATION

Soil aggregation implies the formation of secondary particles or aggregates through flocculation of clay colloids and the cementation of floccules by organic and inorganic materials. The process of aggregation is affected by a range of factors which affect the formation of stable aggregates, i.e., land use and management, soil mineralogy, texture, quantity and quality of the organic matter (OM) incorporated, diversity and abundance of soil macrofauna.¹ Soils can be fractionated according to the aggregates that configure their structure. Sand-size $(20 - 2000 \,\mu\text{m})$ macroaggregates are important in the short-term dynamics of OM, while clay (<2 μ m) and silt-size $(2 - 20 \,\mu\text{m})$ separates on microaggregates are important in the longer term due to the complex associations of C with the structure of clays (see next section).

The concepts of micro- $(20 - 250 \,\mu\text{m})$ and macroaggregates (>250 μ m) are only useful for some soil types. Oades and Waters (1991) proposed an aggregate hierarchy in soils where aggregate stability is determined by OM. The hierarchy concept does not apply to all soil types, for instance, in Oxisols where oxides and hydroxides are the dominant stabilizing agents of aggregates. The hierarchy is created by the physical attachment of particles by living roots and hyphae into macroaggregates. Nonetheless it seems a general process since Cambardella and Elliot (1994) documented that microbial byproducts are the key binding agents of microaggregates into macroaggregates. For example, Gijsman and Thomas (1995) and Gijsman (1996) observed a strong non-linear relationship between aggregate stability and hot-water extractable carbohydrates of microbial or plant-derived origin in a tropical Latin American Oxisol. An increase of microbially derived carbohydrates in the clay and silt-sized fractions has been observed by Feller et al. (1991) and Guggenberger et al. (1995). Microbially derived carbohydrates

¹A soil macrofauna taxon is an invertebrate group found within terrestrial soil samples which has more than 90% of its specimens in such samples visible to the naked eye (or those invertebrates in general >2 mm) (IBOY meeting).

can be separated from those sugars of plant origin. In the former group, galactose (G) and mannose (M) accumulate preferentially in the fine fractions, whereas plant-derived sugars arabinose (A) and xylose (X) are dominant in coarse fractions. The G+M/A+X ratio is high in clay-size separates.

On the death of roots and hyphae the stability of macroaggregates declines at about the same rate at which plant material decomposes in soils. The degradation of macroaggregates creates microaggregates that are considerably more stable than macroaggregates. For aggregates $<20 \,\mu\text{m}$ Ø there appears to be a random mixture of clay microstructures, biopolymers and microorganisms (Oades and Waters, 1991).

Studies under laboratory conditions have shown that particles of fine clay ($<0.2 \,\mu m \,\emptyset$) are aligned parallel to fungal hyphae and stick firmly to the hyphae by a mucilage of polysaccharides (Clough and Sutton 1978; Tisdall and Oades 1979). Research is needed on the mechanisms of sorption of clay to hyphae in natural soils. The sorption of clay to fungal hyphae may affect the stability of aggregates, not only through the strength and persistence of bonds in soil, but also through the ability of the hyphae to survive and grow through soil (Stotzky, 1986).

A. Biologically Formed Stable Aggregates

A review on the abiotic mechanisms of C sequestration in soil aggregates was recently published (Blanco-Canqui and Lal, 2004; Bronick and Lal, 2005). In the present review we address the biological processes involved in the formation of aggregates. Soil aggregates physically protect some fractions of the soil organic matter (SOM), thus increasing the residence time of C in soil (Beare *et al.*, 1994; Golchin *et al.*, 1994a; Guggenberger *et al.*, 1996; Blanchart *et al.*, 1997). The general structure of an aggregate is outlined in Figure 2. The SOM, which is in very different forms and stages of decomposition, is included within these aggregates, sometimes within microaggregates (20-250 $\emptyset \ \mu$ m) that are included in larger aggregates (>250 μ m). Microaggregates are formed at the center of the macroaggregates (Oades, 1984; Elliot and Coleman, 1988; Beare *et al.*, 1994; Bossuyt *et al.*, 2002). Sometimes, SOM (iPOM) is

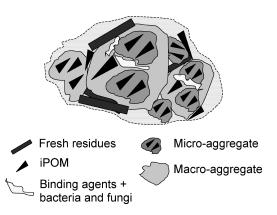


FIG. 2. Pictorial representation of a soil aggregate.

attached to these microaggregates by the action of soil macrofauna through their feeding and casting activities (Lavelle and Spain, 2001) or through abiotic processes like drying and rewetting. The SOM included in these microaggregates is physically preserved from further mineralization processes, until these aggregates are broken either by natural processes like the reingestion by soil macrofauna and other soil organisms, or by agricultural practices like tillage. Due to the three-dimensional structure of soil, different processes may occur at very short scales, i.e., macroaggregates, where mineralization can be reduced or enhanced due to the presence of microbial population which is in intimate contact with the organic resources, or where SOM can be protected in microaggregates included in the macroaggregates.

Microaggregates $(2 - 250 \,\mu \text{m} \,\text{\emptyset})$ are highly stable in soil. It is not well understood how macroaggregates (>250 μ m) form from a group of these microaggregates before being stabilized. Microorganisms (bacteria and fungi) are important agents in the formation and stabilization of aggregates. Fungal hyphae form macroaggregates, which are then stabilized by the hyphae or other microorganisms and fungal polysaccharides (Saini and MacLean, 1966; Tisdall and Oades, 1980; Elliott and Coleman, 1988; Gupta and Germida, 1988; Chenu, 1989). Scanning Electron Microscope (SEM) images have provided visual evidence of fungal hyphae entangling particles into macroaggregates, which were stabilized by polysaccharides (Tisdall and Oades, 1979; Gupta and Germida, 1988). Particles of clay can be found firmly attached to hyphal fragments even after disruption by ultrasound, suggesting that the hyphal network hold the macroaggregates intact. Under field conditions, extracellular polysaccharides of fungi probably stabilize existing aggregates (Tisdall and Oades, 1980). Elliott and Coleman (1988) proposed that roots and fungal hyphae physically form macroaggregates, and that microorganisms at the centre of each macroaggregate produce polysaccharides, which add to the stability of the macroaggregates.

Fungi, bacteria, roots and larger soil organisms, like earthworms and invertebrates, that the top soil layers are key actors in the active formation and regulation of soil structure, and they all probably interact in more than one mechanism of stabilization at different spatial and temporal scales. Most models do not include the processes and mechanisms of formation, stabilization and lifespan of the aggregates that have been produced by the action of organisms in the soil, including roots. This is not only due to the lack of studies on this subject but also to continuously overlooking the role of soil organisms in aggregation. Bacteria are not always active since they are not in contact with the resource, and the movement of larger soil organisms in the soil profile or the growth of roots provide sites where there is an activation of microbial communities. This process was named the "sleeping beauty paradox" (Lavelle, 1996).

These mechanisms of physical protection of C within the aggregates are important determinants of SOM stabilization (Ladd *et al.*, 1993), and have been reinforced by the provision of images of the process by SEM studies. For example, in a study conducted on a Vertisol under pasture from Martinique, Feller *et al.* (1996) observed that plant cell wall debris, bacteria colonies and amorphous SOM were included in the microaggregates and protected from the attack of soil microorganisms since they were encrusted in a dense clay fabric. Guggenberger *et al.* (1996) and Decaëns (2000) also observed strong evidence to support the hypothesis of physical protection of SOM in a tropical Oxisol from the Colombian "Llanos." Hence, physical controls of SOM protection, storage and/or loss are determined by biological processes.

The functional group of soil ecosystem engineers sensu Jones et al. (1994), e.g., roots, earthworms, and also the contribution of fungal hyphae of VAM or micro-arthropods, strongly influence the formation and stabilization of aggregates (Oades and Waters, 1991; Tisdall, 1991; Tisdall and Oades, 1982; Lavelle and Martin, 1992; Beare et al., 1997; Decaëns et al., 2001). The effects of aggregation on SOM mineralization have been addressed in tropical situations with an observed increase in C content and aggregate stability in earthworm casts (Blanchart et al., 1997). Decaëns et al. (1999) also showed that C content increased in field incubated earthworm casts, probably as a consequence of CO₂ respired by microorganisms in the surface of casts (Hedde et al., 2005). This process may have important consequences in SOC dynamics since, under pastures, the production of large amounts of surface casts by earthworms lead to an annual accumulation of 8.6 Mg C ha⁻¹ (Decaëns et al., 1999).

The importance of the biotic processes in aggregate formation and SOC accumulation has been addressed by several authors. For example, Villenave et al. (1999) studied the SOC budget in different agroecosystems under kaolinitic soils of the Peruvian Amazonia by inoculating soil organisms to follow the fate and dynamics of C incorporated from mulching. Under continuous maize (Zea mays L.) cultivation, the amount of SOC in the first 30 cm decreased 15% in 6 years and in all particle size fractions. The C incorporated into the soil after this period was 8.3% of the total SOC pool (Table 3). This retention of maize litter resulted in the addition of 0.25 kg C m^{-2} into the SOC pool representing 11.1% of the measured maize input (Villenave et al., 1999). On the contrary, in the noninoculated system, only 0.18 kg C m^{-2} was incorporated, representing 6.2% of total SOC pool. In conclusion, the activity of earthworms lead to a slight increase in the incorporation of fresh litter into the total SOC pool in mulched maize plots, with most of the C incorporated from roots (Villenave et al., 1999).

The SOM has been chemically fractionated since the early 1900s. Physical fractionation has been used to separate the different fractions since 1990. With the advent of new tools like NIRS, aggregates formed by different organisms and processes can be discriminated followed by a physical fractionation, in order to study differences in SOM dynamics and assess SOC contents in biologically and nonbiologically originated aggregates.

	c inputs				
C loss in 6 years	C stock 6 th year (0–30 cm)	C ₄ in SOC	Mulch	Roots	Incorporation (%)
Without earthworms 18 With earthworms	2.9	6.2	1.8	0.2	8.9
12	3.1	8.3	2.0	0.3	11.1

 TABLE 3

 SOC budget under 6-year continuous maize (Zea mays L.) plot at Yurimaguas (Peruvian Amazonia) (redrawn from Villenave et al., 1999)

The C content in the soil and in aggregates that have been produced by the action of soil organisms can be determined by using several techniques, e.g., Nuclear Magnetic Resonance (NMR), Near Infrared Spectroscopy (NIRS), isotope C labeling like δ^{13} C (very useful in studies on the origin and fate of C from C₃ or C₄ plants). NIRS also has the advantage to discriminate those aggregates, which have been created biologically by, for example, earthworms, ants, or termites. There is a functional specificity of the biologically-originated aggregates (Decaëns *et al.*, 2001; Hedde *et al.*, 2005). There is a need to conduct relevant studies on this issue for different soil types that may harbor different species or functional groups of organisms.

B. Aggregate Stability and Soil Organic Carbon Pool

A positive relationship exists between SOC pool and aggregate stability. Polysaccharides glue soil particles inside aggregates (Cheshire, 1979; Tisdall and Oades, 1982). Gijsman and Thomas (1995) reported that aggregate stability is more related to hot water-extractable carbohydrates than to total SOC pool in a tropical Oxisol. These polysaccharides can be of microbial origin or derived from plants. Cheshire et al. (1984) showed that plant-derived polysaccharides were less important in aggregate stability than microbial-derived carbohydrates. In those aggregates from biogenic structures produced by some soil invertebrates there may be no correlation between structural stability and hydrosoluble carbohydrates (Decaëns et al., 2001). In a study conducted on the degradation dynamics of biogenic structures produced by a native savanna earthworm in Oxisol under different land use systems, Decaëns (2000) observed important differences regarding the mean weight diameter (MWD) of constituting casts' aggregates. In fresh casts produced in a grass-legume pasture, almost 50% of the total volume was occupied by identifiable plant fragments together with quartz crystals (ca. 5%) and the remaining space was occupied by dark, amorphous material (Figure 3). In the original system, fresh casts were comprised of amorphous plasma in which few quartz crystals and plant fragments were observed (5%). A combination of abiotic and biotic factors lead to the degradation of these structures across time and where cracks or cavities were observed, together with the presence of small fecal pellets indicating the activity of smaller invertebrates, i.e., termites (Decaëns, 2000).

These casts have a higher structural stability than the surrounding soil due to the stabilization of the SOM included in the constituting cast aggregates (Guggenberger et al., 1996). A similar stabilization process of the organo-mineral complexes by biotic mechanisms occurs rather than stabilization by formation of Ca-humate or OM-polyvalent cation-soil particle linkages. Therefore, SOC is protected from further decomposition and the production of casts may contribute to the formation of a rather active but physically protected SOC pool in the soil (Martin, 1991; Lavelle and Martin, 1992; Guggenberger et al., 1996). The presence of a cortex in these structures contributes to the structural stability of casts, creating an anaerobic condition that reduces OM mineralization inside casts (Elliot et al., 1990). All these aspects are not included in most models of SOM dynamics. The balance between the production and destruction of these structures shows that there is an active regulation of soil structure by the activities of soil organisms. For example, in the savannas of Colombia it has been observed that only one earthworm species is able to transform between 2-11% of the total 0-10 cm soil layer into macroaggregates (Decaëns, 2000), and that in less than 10 years this layer has passed through the digestive tract of the earthworm (Jiménez et al., 1998). The figures would be higher if the activities of the whole earthworm community (i.e., 7 species) are considered. Even in the absence of the organisms that produced the aggregates their effects may last longer than the lifespan of these organisms in soil, because important soil processes continue in the biogenic structures produced.

The impact of these processes on SOC losses due to soil erosion by water run-off needs to be further quantified, as well as the proportion of SOC that is dissolved and flows through the soil. In tropical ecosystems, it may constitute a large amount of SOC loss that can be transported by water flows to streams.

C. Modeling Aggregate Formation

The binding of mineral particles into microaggregates and then into macroaggregates has been conceptualized by Tisdall and Oades (1982). Clay polyvalent metal-humified SOM complexes cement free primary particles together into microaggregates. This constitutes the more recalcitrant and persistent SOM. The more transient (polysaccharides) and temporary binding

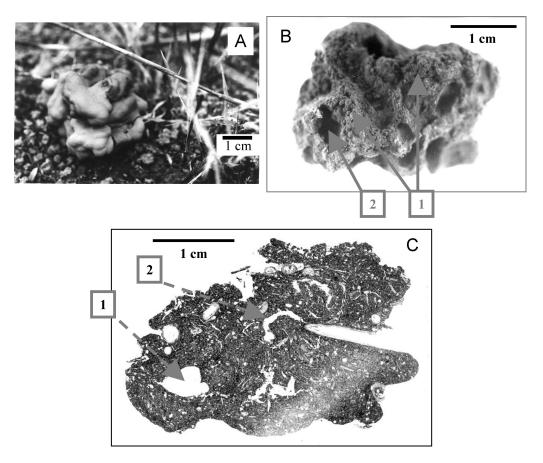


FIG. 3. A) Fresh surface cast of *Martiodrilus* sp. in the native savanna of the Colombian "Llanos." B) External view of a 5-month old earthworm surface cast; 1 - cast covered by facees, 2 - cast perforated by termite galleries. C) Thin section (subaxial horizontal cut) of a 5-month-old surface earthworm casts collected in the intensive pasture. 1 = termite burrow, 2 = retraction crack (reprinted from: *Biology and Fertility of Soils*, Vol 32(2); 2000, pp. 149–156; T. Decaëns; figures 2, 9 and 11, respectively; © Springer-Verlag. With kind permission of Springer Science and Business Media).

TABLE 4AAggregation processes in soil

Aggregate	Cementing			
size (μ m)	Abiotic	Biotic	Process	
0.2	Clay plates, Oxides, Amorphous alluminosillicates	Organic polymers sorbed onto clay surfaces	Electrostatic bonding; flocculation	
2-20	Clay particles (packages)	Microbial, fungal and plant debris	Encrustation	
200	Particles or aggregates	Roots, hyphae	Binding	
2,000	Aggregates	Soil fauna	Selection of particles Formation of biogenic structures	

agents (roots and fungal hyphae) stick microaggregates together into macroaggregates (Table 4a). These are considered the more labile or decomposable SOM fraction (Oades, 1984; Beare et al., 1994). Later this model was slightly changed by Oades (1984) by assuming that microaggregates are principally formed within macroaggregates (Beare et al., 1994; Gale et al., 2000, Six et al., 2000). In the model proposed by Six et al. (2000) macroaggregates $(250 - 2000 \,\mu\text{m})$ are formed around fresh residues, but how they are formed is not well understood. Biological, physical and chemical interactions occur in the inner part of the residue that is in contact with the soil. However, there are also factors that link the residue with the soil, apart from abiotic. The contribution of soil organisms to the process is also an important factor. In this process, only soil microorganisms (bacteria and fungi) are considered, and not larger organisms like earthworms (Guggenberger et al., 1996; Decaëns, 2000) or litter arthropods. Some examples of the physical protection of OM in the biogenic structures created by large soil organisms and the mechanisms involved in this process are presented in Table 4b.

Paustian *et al.* (2000) proposed a model for aggregate turnover and CO_2 release from the mineralization of OM in

TABLE 4B Physical protection of C in forming-aggregates and mechanisms of disagregation in biogenic structures produced by soil invertebrates

		Aggregate	Mechanism and J	processes	Free aggregates in
Organism	Туре	size ¹ (mm)	Biotic	Abiotic	the soil surface
Earthworm	Globular cast	7–10 (high C content)	Hydrosoluble carbohydrates?; fungi, algae growth in the surface; colonizing termites; root growth	Dry rewetting cycles	Transport by surface run off
Earthworm	Granular cast	<2 (high C content)		Rainfall	
Termite	Paste-board like	(very high C content)	Faeces + salivary excretions; Microbial activation and inhibition	Fire	Seedling germination
Termite BS	Cemented soil	8–9	Faeces + salivary excretions; Microbial activation and inhibition	Disaggregation	Incorporation into the soil matrix
Ant mounds	Loose aggregates	<1.5	Transportation,no binding agents	Cattle trampling	

 1 > 50% of aggregates

which again the role of larger soil organisms in the process was not included. Here we propose a new model that includes these activities (Figure 4). According to our model, fresh plant residues provide the coarse particulate organic matter (POM), which acts as a nucleation site for the growth of fungi and bacteria (Puget et al., 1995; Angers and Giroux, 1996; Jastrow, 1996) as long as they are in contact with the resource (Lavelle, 1996). The process starts when the residue (resource) is in intimate contact with these microorganisms which produce extracellular polysaccharides that help bind organic debris and soil particles. Following the incorporation of fresh residue or mulch by tillage practices, or by natural means through the action of invertebrates that live and/or feed in the litter and incorporate to the soil, microorganisms continue to use the more easily decomposable carbohydrates. In this process, more recalcitrant intra-aggregate particulate organic matter (iPOM) with a higher proportion of alkyl-C is yielded (Golchin et al., 1994a, 1995). This iPOM is further decomposed and this finely fragmented iPOM becomes encrusted with clay particles and microbial byproducts, leading to increased physical protection of the iPOM within more stabilized microaggregates ($<250 \,\mu m \,\emptyset$) (Oades, 1984; Elliott and Coleman, 1988; Beare et al., 1994; Golchin et al., 1995; Jastrow, 1996). As decomposition occurs, the binding agents in the macroaggregate are eventually lost releasing the highly recalcitrant residual POM and stabilizing microaggregates $(\langle 250 \, \mu m \, \emptyset)$. These materials may subsequently be incorporated into new aggregates. A model of aggregate formation and stability for $20 - 250 \,\mu\text{m}$ Ø aggregates is also provided by Golchin *et al.* (1994b). In general this process is taken for granted but the mechanisms involved need to be assessed. Further studies should attempt to quantify the percentage of macroaggregates that are formed through this process.

D. Compact Aggregate's Induced Soil Degradation from the Amazon Basin

In the Brazilian Amazon, near Manaus, 95% of the deforested area is converted into pastures, and of these, about 50%can be considered degraded due to mismanagement, phytosanitary problems, poor soil fertility, and soil structural modification (linked to faunal activity). When the forest is converted to pasture, the mechanized practices, and later the cattle trampling, cause severe soil compaction, particularly in the 5-10 cm layer, impeding root development and hence SOC accumulation (Chauvel et al., 1999), (Figure 5). The reason is that the active regulation of soil structure by native populations of soil macro-faunal communities is radically altered, and an opportunistic invading earthworm (Pontoscolex corethrurus), occupies the empty niches after deforestation (nearly 90% of the total soil faunal biomass). This species produces more than 100 Mg castings ha⁻¹, dramatically decreasing soil macroporosity down to a level equivalent to that produced by the action of

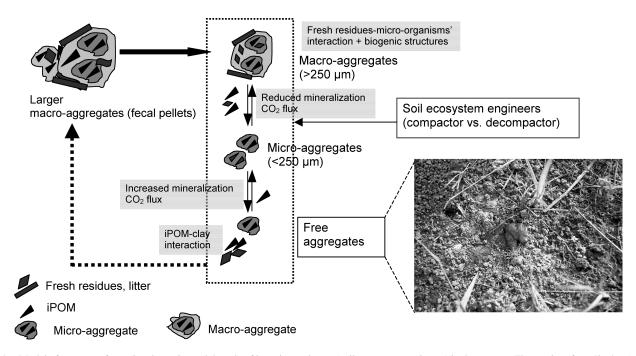


FIG. 4. Model of aggregate formation dynamics and the role of large invertebrates (soil ecosystem engineers) in the process. The caption (from Jiménez) shows the soil surface under savanna vegetation fully covered with earthworm casts and free aggregates once these structures are destroyed by both abiotic and biotic processes. In the original model proposed by Paustian *et al.* (2000) the role of soil organisms in the process, dotted line, is not included.

heavy machinery on the soil $(2.7 \text{ cm}^3 100\text{g}^{-1})$. Chauvel and colleagues observed that soil aggregation is strongly affected by compaction in the first 5 cm of topsoil and, subsequently, the system collapses and the pasture degrades, decreasing the proportion of NPP allocated to plant roots. During the rainy

season these casts plug up the soil surface thus saturating the soil and producing a thick muddy layer, where anaerobic conditions prevail (increasing CH_4 emission and denitrification). In the dry season, desiccation cracks the surface and the inability of roots to extract water from the soil causes the plants to wilt and

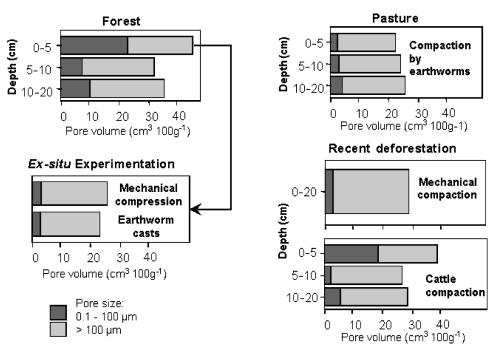


FIG. 5. Soil degradation in Amazonian pastures (redrawn from Chauvel et al., 1999).

die, leaving bare patches in the field (Figure 5). This earthworm species has many positive effects but the management of the system in this specific case makes the high presence of this species a problem.

III. INTERACTION OF C WITH CLAY FRACTIONS

The relationship between clay type and content and SOM accumulation and stabilization is complex. Clay content is usually correlated with factors that result in SOM production, like plant nutrients and water regime, and also to the formation of aggregates. The type of clay and associated cations also exert an influence on the stabilization of SOM. The fulvic and humic acids and their polymers are adsorbed on to mineral surfaces by the functional groups, of which the most important ones are carboxyl (-COOH), carbonyl (-C=O), hydroxyl (-OH), amino (=NH), and amine (-NH₂). Large uncharged polymers (e.g. polysaccharides) can be adsorbed by hydrogen-bonding and by van der Waals' forces, and also serve as binding agents between mineral particles.

The importance of clay in retaining SOC across soils is influenced by mineralogical composition. Residence times of SOC in clay minerals can exceed a hundred years (Laird, 2001), compared to several months for partially mineralized SOC. The SOM associated to silt- and clay-size fractions has a strong link to mineral particles, so that an OM-mineral complex is formed. The majority of the research on SOM linkages with particle-size fractions is from 2:1 clay temperate soils [see review in Feller and Beare (1997)]. In these studies, 10-30% of total SOC pool is associated with the sandsize fraction (>50 μ m), 20–40% with the silt-size fraction $(20-50\,\mu\text{m})$ and 35–70% with the clay-size fraction $(0-20\,\mu\text{m})$ (Feller and Beare, 1997). The fine-clay fraction contains less stable SOM than the coarser fine silt and coarse clay fractions (Tiessen and Stewart, 1983). In contrast, some studies have shown that the stability of OM increase with decrease in the particle-size fraction (Zhang et al., 1988; Christensen, 1992).

The interaction between clay and SOC concentration is determined by the molecular structure of clay and requires a review of the different clay minerals that are normally found in tropical soils. A classification scheme for phyllosilicates related to clay materials is presented in Table 5. The three major clay groups found in soils of Latin America are kaolinite, montmorillonite and illite.

A. Structure of Clay and Cation-Polyvalent Humic Complexes

Three main groups of tropical soils have been distinguished based on their mineralogy: i) kaolinitic/halloysitic, or low activity clay (LAC) soils, mainly Oxisols and Ultisols, which cover almost 70% of tropical soils; ii) the smectitic or high-activity clay (HAC) soils, like Vertisols; and iii) allophane soils, for example, volcanic soils (Andisols). The SOC concentrations do not differ among these groups (Feller and Beare, 1997). In LAC soils clay and silt fractions are important in the amount of SOC pool (Feller *et al.*, 1991; Lepsch *et al.*, 1994). However, few data are available for HAC soils (smectitic) of the Neotropics.

Clay mineralogy determines the mechanisms of formation and stabilization of clay-humic complexes. Humic substances coat, partially or totally, mineral particles such as clay, often protecting the coated particles from weathering. Polyvalent cations (e.g., Ca²⁺, Mg²⁺, Fe³⁺, Al³⁺) play a major role in the stabilization of organic and inorganic colloids-when in abundance limiting their ability to shrink and swell-favoring a flocculated (stable) condition. Polyvalent cations serve as bridges between negatively charged clays (inorganic colloids) and negatively charged organic colloids, which enhances structural stability. Organic anions of SOC-rich humic colloids and polysaccharides are adsorbed by clay particles through those polyvalent metals $(Ca^{2+}, Al^{3+}, and Fe^{3+})$ following the basic microstructure as clay particle-polyvalent metal-organic matter (Greenland, 1965; 1971). One positive charge of the di- or trivalent cation bonds the negative charge of the organic anion and the other charge bonds the negatively charged clay plate, thereby serving as a bridging mechanism. The relation of these anion-cation-anion complexes occurs within clay domains forming clusters of microaggregates (Wild, 1988; Oades, 1984). In acid soils, clay minerals retain few cations compared to humic substances that have a considerable retention capacity even at a pH as low as 2.5 (Bonneau and Souchier, 1979).

Clay minerals exhibit different morphologies that determine the different packing characteristics. The microstructure of clays has been analyzed with SEM by Oades and Waters (1991) for some Australian Oxisols (Figure 6). They observed clusters of fine kaolin crystals held together by oxides. Alluminosillicate is the basic unit and its organization is controlled by the particle morphology. Oades and Waters (1991) described the degree of ordering the particles within the first stage clay aggregates ranging from:

Clay minerals and some associated physico-chemical properties							
Clay mineralParticle size (mm)Surface area $(m^2 g^{-1})$ CEC (Cmol + Kg^{-1})Formula							
Kaolinite	0.1-5.0	5-20	3–15	$Al_2(OH)_4Si_2O_5$			
Illite Montmorillonite	0.1–2.0 0.01–1.0	100–200 700–800	15–40 80–100	$\begin{array}{l} K_{00-2}Al_4(Si_{8-6}Al_{0-25})\ O_{20}(OH)_4\\ Al_2(OH)_2Si_4O_{10} \end{array}$			

 TABLE 5

 Clay minerals and some associated physico-chemical properties

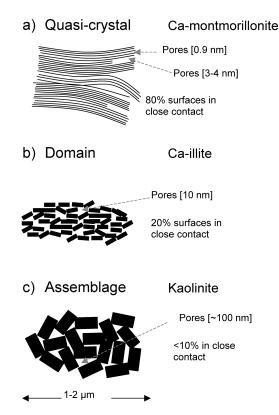


FIG. 6. Schematic diagram on the structure of clays. Clay aggregates (a) quasicrystals, (b) domain and (c) assemblage of kaolinite crystals (after Oades, 1987).

- 1. minimal: large blocky rigid particles with low width-tothickness ratios as found in many kaolins, to
- 2. a rather parallel stacking of platy particles with width-tothickness ratios of less than 10, as in illites, to
- 3. parallel configuration: where thin flexible plates with widthto-thickness ratios exceeding 100 as shown by smectites.

B. Stabilization of Soil Organic Matter with Clay

The interaction of C with clay particles is a primary factor in the stabilization of OM in aggregates, especially the highactivity expandable clays. In kaolinitic soils, clay and silt contents are determinants of C levels for both natural and humaninduced agricultural ecosystems (Figure 7). The clay fractions of many highly weathered soils of tropical humid regions are dominated by these minerals. The cations Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe³⁺, and silica are removed from the topsoil by leaching. Secondary minerals are formed in an oxidizing environment with a low pH where acidic compounds are formed and silica is dispersed.

Stabilization of organic molecules may occur between quasicrystals (a packet of several layers) and within interlayers of 2:1 swelling clays such as montmorillonite. This mechanism has been inferred from examination of high resolution transmission electron micrographs that show presence of organic molecules within $\sim 1.0 \,\mu$ m diameter pores between clay crystals. It is assumed that these domains provide considerable protection

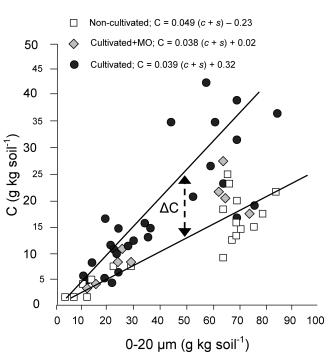


FIG. 7. Relationship between C content (g kg⁻¹) and clay + silt content ($c + s < 20 \,\mu$ m) in low-activity clay (LAC) and high-activity clay (HAC) soils under different land use management strategies: uncultivated, annual cropping with organic amendments and continuous cropping system; all regressions are significant at P < 0.001. Δ C indicates the maximum variation between noncultivated and cultivated situation (redrawn from Feller and Beare, 1997).

against microbial attack. Laird *et al.* (2001) reported that these organomineral complexes sequester SOC by means of three critical physical and biochemical functions:

- 1. organic materials react with clay particles through adsorption,
- 2. clay surfaces polymerize humic substances, and
- polymerized organic compounds are physically and chemically sequestered by clay crystals inaccessible to decomposition by soil microorganisms.

Clay minerals may limit decomposition by coating organic molecules (substrates) and microorganisms. This may occur through the adsorption of organic molecules (e.g., on allophanes) or by the sequestering of SOC between the layers of phyllosilicate clays, especially in smectites. Clear inverse relationships have been observed between the mineralization rates of some soils and the type of clays (Kobus and Pacewiczowa, 1966; Darici *et al.*, 1986).

Mineralogy is important to the storage of SOC in soils. With tropical soils, there is considerable lack of information on how SOC storage in smectitic soils differs from kaolinitic-oxidic soils. In natural and non-disturbed soils the positive relationship observed between SOC and clay content relates to the presence of POM (plant debris; >50 or 20 μ m), and amorphous SOM associated with silt and clay fractions, while in cultivated soils the differences observed in SOC are associated to the clay fraction.

In general, POM is highly susceptible to depletion during cultivation, especially in tropical soils where about 10-30% of SOC pool is associated with the sand-size fraction (Feller and Beare, 1997).

Surface area is an important factor in SOC sequestration. Differences in specific surface area may regulate clay dynamics for sequestering SOC. Laird (2001) observed that when clay was dominated by smectitic minerals larger SOC storage occurred than in kaolinite- and chlorite-dominated clay minerals. Smectitic soils not only protect more SOC inside the clay crystals but the SOC turnover rates and residence times inside were longer than in other clay minerals due to increased surface area and retention locations (interstitial layers) of smectites (Saggar *et al.*, 1996).

The nature and amount of clay minerals may greatly influence the effects mentioned above. Minerals with low specific surface areas and low charge densities have relatively low overall electrostatic charge levels and are thus less effective in forming structural aggregates. This is the case for many soils where kaolinite is the dominant clay-type mineral (Uehara, 1982) as in many Oxisols and Ultisols, which occupy about 60% of tropical soils. Thus, bioturbation by roots and soil macrofauna (e.g., termites, earthworms, and ants) that produce biological structures are important factors in the formation of aggregates.

Feller et al. (1991) assessed the SOC contents of different particle-size aggregates following physical fractionation methods. These authors reported that the fraction $>20 \,\mu\text{m}$ was composed of plant debris at different stages of decomposition; the $2-20\,\mu m$ fraction was termed the "organo-silt complex" and was the result of highly humified plant and fungal debris associated with organomineral microaggregates (not easily disrupted by fractionation), and the fraction $<2\,\mu m$ was termed the "organo-clay complex," with a predominance of amorphous OM acting as coating in the clay matrix (Feller and Beare, 1997). These authors also showed that under forest or savanna ecosystems, plant cell walls were detected only in the coarse clay fraction, and never in the fine clay fraction. Similar findings were reported by Golchin et al. (1994). They found that the proportion of total SOC occluded is high in soils with high clay content. The important role of clays in stabilizing SOM was emphasized by Jenkinson and Rayner (1977), Sørensen (1981), and Paul (1984). Organic materials contained in this fraction are adsorbed to the surfaces of inorganic colloids to form clay-organic complexes, and hence protect SOM from further decomposition. The low C/N ratio and the absence of lignin and other plant components bearing phenolic C suggest a microbial origin for this C, probably from aminoacids.

There are both chemical (at the molecular level) and physical (at the aggregate level) mechanisms of protection of OM retaining C in organomineral complexes.

C. Physical Determinants of Clay Adsorption

Porosity exerts a strong influence on the fate of residues added to the soil because it defines the domains in which microorganisms can function and those smaller domains into which organic molecules can migrate and become physically isolated from microbial attack. Kilbertus (1980) observed that bacteria function only in pores, which are at least 3 times their own diameter. Thus, bacteria are excluded from much of the pore space in soils, an effect that becomes more pronounced with increasing clay content. Thus, in clay-rich soils the physical separation between microorganisms and organic molecules can be extensive and account in part for their tendency to have larger accumulations than coarser-textured soils formed under otherwise comparable conditions.

In Latin American soils there are differences in the type of clays found in different areas. Tropical acid soils are composed of residual primary minerals, mainly quartz grains (SiO₂) and newly generated secondary minerals, mainly kaolinite, which is the most predominant secondary mineral in the topsoil and smaller quantities of gibbsite, hematite (Fe₂O₃), and goethite (FeOOH) (Lucas et al., 1993). Top horizons of the highly weathered tropical soils have been explained by the deposition of alloctonous kaolinitic material after the formation of the lower layers. However, this alloctony is more restricted than previously thought (Lucas et al., 1993). The observed vertical succession is the opposite of what is predicted by most geochemical soil formation models (Fritz and Tardy, 1973; Lasaga, 1984). Most soils of the tropics are formed in situ (Lecomte, 1988) with contribution of outsource material by dust deposition (Brimhall et al., 1992). This siliceous topsoil is explained by several factors like the transportation of deep material by soil fauna (Nye, 1955), especially in areas where the dry season is long, or a rapid percolation of the rainwater through the kaolinitic horizons, or decreased activity of water in the topsoil during the dry seasons, displacing the kaolinite-gibssite equilibrium (Lucas, 2001).

Physical fractionation methods have been used to study the factors involved in the associations between soil mineralogy and SOM differing in composition, structure and function (Christensen, 1992, 2001; Cambardella and Elliot, 1994). The interaction of clay minerals with SOM and the interaction of clay minerals with Fe and Al ions, Fe- and Al-oxides (sesquioxides) is especially relevant in tropical Oxisols an Ultisols with loamy and clay-loam textures. In a study conducted in a sandy clay loam Ultisol from Brazil, Bayer et al. (2001) identified the relationship of Fe oxides and kaolinite concentrations with mineral-associated SOM stability. They found that the mineralassociated SOM had five to nine times more SOC than POM and was responsible for 69% (38 Mg ha^{-1}) to 80% (51 Mg ha^{-1}) of total atmospheric CO₂ sequestered by soil in two cropping systems. The higher SOC and SON pools were associated with greater recalcitrance of mineral associated SOM to biological decomposition, resulting from its interaction with variable charge minerals. The negative relationship between decay rates of SOM and the concentrations of Fe oxides and kaolinite demonstrated the physical stability of SOM caused by interaction with variable charge minerals (Bayer et al., 2001).

Highly weathered conditions in tropical soils have led to the presence of sesquioxides (Fe and Al oxides and hydroxides)

resulting in a high Al saturation (>90% in some cases) with important chemical constraints in these soils. For example, P is retained in highly stable Al compounds thus limiting its availability. These minerals display surface electrical charge, caused by protonation and deprotonation of hydroxyl (-OH) groups. Clay minerals with this type of charge are termed variable-charge clays and are greatly affected by environmental conditions, being negative or positive depending on pH and ionic strength of electrolytes in solution in contact with organic polymers (like carboxylic, phenolic and enolic groups, SOM and allophone groups) (Oades et al., 1989). The zero point charge (ZPC) is a function of the mineral and organic particles in the soil and the pH. There is a point where the net charge equals zero and represents the same number of protonated and deprotonated sites on the soil (Van Raij and Peech, 1972). The SOM can affect this ZPC and thus the ability to retain cations against leaching (Oades et al., 1989), which is probably an important factor in the amounts and fluxes of dissolved organic C (DOC) in soils. A pioneering study on how the ZPC changes through the production of biogenic structures by a tropical earthworm was reported by Rangel et al. (1999).

The SOC content is strongly determined by the amount of clay. Desjardins et al. (2004) observed more SOC contents in clayey Ferralsols (more than 80% of kaolinite) near Manaus in the Central Amazonia $(5.5-6.1 \text{ kg C m}^{-2})$ than in sandy-clayey Acrisols from the Eastern Amazonia, in the region of Pará (2.9-3.4 kg C m⁻²). Other studies in the region have also reported similar values for clayey Oxisols (Choné et al., 1991; Koutika et al., 1997) and sandy Ultisols (Desjardins et al., 1994; Neill et al., 1997). The amount of SOC in the forest was lower compared to the older pastures (Brachiaria humidicola), and the increase in SOC content in the topsoil horizon after conversion of the native vegetation has been often documented (Choné et al., 1991; Trumbore et al., 1995). However, other studies have documented an opposite trend (Desjardins et al., 1994), or even no effect at all (Serrão et al., 1979; Hetch, 1982). Pasture management has an important effect as seen in the example of Chauvel et al. (1999) but few studies have addressed the role of management practices on SOC pool in the Amazon basin. The contribution of the vegetation to the different particle-size fractions was characterized by higher inputs of C derived from the pasture (Desjardins et al., 2004). These results are in accord with those obtained by Choné et al. (1991) who observed higher inputs of pasture-derived C in SOC stock of the 0-3 cm upper layer in Manaus, i.e., 30% and 68% after 2 and 8 years, respectively. Desjardins et al. (1994) observed that 10 years after deforestation in soils of the Eastern Amazonia, 49% of the total SOC stock of the 0-10 cm upper layer was derived from pasture. Neill et al. (1998) reported a similar pattern in sandy loam soils in Western Amazonia, with contributions of 42 and 44% of the C of the top 10 cm derived from 9- and 13-year-old pastures, respectively. In older pastures, Trumbore et al. (1995) observed that only 21% of the SOC content of the 0-10 cm layer was derived from pasture.

D. The Case of Charcoal

In the Brazilian Amazon, black C may play a key role as is the case of Terra preta do Índio soils, also known as Amazonian dark earths (ADE). These areas range in size from less than a hectare to many km² and include both sand- and clay-dominated soil profiles. Charcoal resulting from burning through lightning or early Amerindian occupation is common in Amazonian soils under natural rainforest (Sanford et al., 1985). These soils were enriched by these populations with OM from the surrounding environment and also with phosphates as a result of their hunting and fishing activities. The deposition of residues (garbage) by humans was important in the formation of these soils but not as a main contributor of the bulk mass soil, but rather as a stimulator of biological processes in those soils (McCann et al., 2001). A stable complex of the OM and Kaolinite, together with the added phosphorus and, possibly, silica is responsible for the double content of OM in the upper 50-100 cm. The CO₂ emissions from these soils are comparatively lower than in adjacent soils as a result of the stabilization of OM in silt and clay fractions. The contribution of black C in the clay fraction increases with depth, as a result of transport by illuviation (Glaser et al., 2001).

IV. TRANSPORT OF DISSOLVED ORGANIC CARBON INTO SUBSOIL HORIZONS

The dissolved organic carbon (DOC) is defined as all C of plant, animal, fungi and/or bacteria origin that is dissolved in a given volume of water at a particular temperature and pressure. These DOC compounds are comprised of soluble carbohydrates, and amino acids to more complex high-molecular weight molecules. The chemical structure of DOC molecules can be recognizable and easily defined, such as fats, carbohydrates, and proteins. However, most have nonidentifiable structure and are lumped under the term humic or tannin substances. Recent studies indicate that the oceanic DOC reservoir may be comparable in size to the terrestrial C reservoir.

A. Flux of Carbon Trough the Soil Profile

Despite its importance the flux of DOC through the soil profile has not been included in the global budgets of C sequestration until recently. Vertical transport of DOC may contribute to increasing the SOC pool in the subsoil. The fluxes of DOC through this internal system can be several times larger than the stream fluxes. In tropical areas there is a lack of studies on DOC fluxes (Table 6). In fire-prone savanna ecosystems from Ethiopia, Michelsen *et al.* (2004) reported that DOC increased seasonally with depth, mainly because of microbial metabolism, even though there is important C loss due to fire.

The boundaries of ecosystems are not considered in the DOC studies, as may be the case for terrestrial C sequestration, since the borders around the sites under study constitute pathways for the flow of C between sites and through the landscape. The DOC then is important in the flux of C from terrestrial to aquatic ecosystems, and this process can be either in the surface or

TABLE 6
Fluxes of DOC in subsurface soil (20-100 cm) from several
tropical sites (data from Neff and Asner, 2001)

-			. ,
Site	Ecosystem	DOC flux (g C m^{-2} y r^{-1})	Reference
Central Amazon, Brazil	Tropical evergreen forest	2	McClain <i>et al.</i> (1997)
Central Amazon, Brazil	Tropical flooded forest	40	McClain <i>et al.</i> (1997)
Luquillo, Puerto Rico ¹	Tropical evergreen forest	4–9	McDowell (1998)

¹ stream fluxes were 3 g C m^{-2} yr⁻¹.

through the soil solums. The export of DOC to surface waters is positively correlated with the soil C:N ratio (Aitkenhead and McDowell, 2000). Ecosystem export of DOC increases linearly from <5 to ~ 100 kg C ha⁻¹ yr⁻¹ over a soil C:N ratio of ~ 13 to 30 (Hessen *et al.*, 2004).

The Amazon River Basin transports the highest amount of C to the Atlantic Ocean than any other river in the world (Spitzy and Ittekkot, 1991), e.g. 36 Pg C yr⁻¹ (Richey et al., 1990). Mc-Clain et al. (1997) studied two watersheds in Central Amazonia and observed that the contribution of DOC to water streams was very low, from 2 to 40 g C m⁻² yr⁻¹, representing only 0.2 and 8% of the total turnover in the forest, 92.0 to 99.8% of C being mineralized. This means that upland areas where Oxisols and Ultisols are the most extended soil types (more than 72% of the total area in the Amazon) are effective barriers against SOM transfer to water streams. The contribution of riparian zones to DOM in water streams is by far the main factor in the amount of DOM in the Amazon River (McClain et al., 1997). In another study conducted in a Peruvian Andean region, Townsend-Small et al. (2005) documented DOC fluxes ranging from 0.6 to 6.1 mg C L^{-1} with the highest rates obtained during storm events, but there was no relationship between the DOC content in water streams and altitude. Previous studies found DOC concentrations in the Andes to range from 1 to 2 mg C L^{-1} (Guyot and Wasson, 1994). Lastly, at larger spatial and temporal scales the continuous loss of DOC, together with other limiting nutrients, like P for instance, can reduce the capacity of ecosystems to support NPP (Vitousek et al., 1998).

The flux of DOC decreases from the litter layer to deeper mineral soil horizons by 50–90% in soils with high clay contents (Cronan and Aiken, 1985; Dalva and Moore, 1991; Dosskey and Bertsch, 1997). Surface soil fluxes of DOC range from 10 to 85 g C m⁻² yr⁻¹ and from 2 to 40 g C m⁻² yr⁻¹ in subsurface horizons (Neff and Asner, 2001; Hagedorn *et al.*, 2002; mainly data from temperate zones). The concentrations of DOC in deep soil horizons and the contribution to DOC fluxes (exports) are relatively small (Guggenberger and Zech, 1992), with a range from 4 to 37 g DOC m⁻² yr⁻¹ retained in the mineral subsoil (Currie *et al.*, 1996; Guggenberger and Kaiser, 2003).

Litter layer fluxes can account for 1 to 19% of total litter C flux, and 1 to 5% of NPP (Gosz *et al.*, 1973; Qualls *et al.*, 1991). These values, however, are from temperate forest sites. There exists a relationship between temperature and losses of DOC from litter, due to activation of microbial populations. Goedde *et al.* (1996) observed a relationship between the overall microbial activity and DOC production from the litter layer.

The movement and flow of DOC through soils represents an important mechanism by which a set of processes are affected. Some of these processes include the distribution and stabilization of C in soils, or the control it exerts in the activation of soil micro-organisms at certain soil depth (Trumbore, 1993). As much as 20 to 50% of the DOC from litter-fall is biologically available or labile, although there are seasonal differences, while in the litter leachate the labile fraction of DOC ranges between 5 to 16% (Qualls and Haines, 1992). As DOC moves deeper in the subsoil, its biological availability decreases reflecting either the transport of residual, recalcitrant components of the DOC or a physical desorption/dissolution flux of C from SOM to dissolved organic matter (DOM) (Qualls and Haines, 1992). Nevertheless, this reduction in the bioavailability of labile fractions is not always observed. For example, in agricultural soils a continuous available fraction of 55% at different soil depths is observed (Zsolnay and Steindl, 1991).

The DOC plays an important role as a substrate for the activation of soil micro-organisms. They may use a substantial fraction of the labile soluble compounds for their own growth (Jandl and Sollins, 1997). Soluble root exudates and microbial byproducts, even microbial structures may contribute substantially to the amount of DOC in soils (Guggenberger and Zech, 1992). Quantitative estimations are difficult (Moller et al., 1999). Biondini et al. (1998) estimated the flow of soluble C through root exudates as high as 17% of total plant C fixation in a grassland ecosystem. However, other studies have reported values of less than 2% in croplands (wheat), with 15-25% of the added ¹⁴C pulse labeling respired by roots and the rhizosphere (Gregory and Atwell, 1991). Solution of DOC in soils is composed by degraded plant and microbial byproducts (Guggenberger, 1994), and the origin can be tracked by looking at the Gluccose + Mannose / Arabidose + Xylose ratio. However, the controls on plant exudates release and their use by micro-organisms are not fully understood, partly because of the lack of precise tools and techniques to evaluate these fluxes, although improved assessment tools have recently started to be used.

B. Controls of Dissolved Organic Carbon Fluxes

There is a lack of comprehensive knowledge regarding the processes that control DOC fluxes in soils (Neff and Asner, 2001). The origin, function and fate of DOC are not fully understood, with most estimates based on low river fluxes of DOC (i.e., from 1 to $10 \text{ g C m}^{-2} \text{ yr}^{-1}$) in most ecosystems (Hope *et al.*, 1994). These fluxes are low compared to C fluxes associated to NPP or heterotrophic respirations (Schimel, 1995). Most of the

studies on DOC have been addressed at small scales under laboratory conditions, or through modeling at larger scales (Boyer *et al.*, 1996; Currie and Aber, 1997; Kalbitz *et al.*, 2000). Neff and Asner (2001) addressed this issue under a different perspective, by trying to link DOC to both physical and biological processes of SOM cycling. This model also highlights some of the uncertainties attributed to the role of DOC in the C cycle in the soil and ecosystem dynamics (Neff and Asner, 2001). Laboratory studies have shown that hydrophobic DOM of aromatic nature sorbs strongly to iron oxides. The hydrophilic fraction of DOM, which contains more labile polysaccharide material, is weakly absorbed (Kaiser and Guggenberger, 2000).

Abiotic factors moderate mostly DOC losses from terrestrial ecosystems, although the interactions between hydrology and microbial DOC-relationships are important in determining the fluxes of DOC in the litter and surface horizons (Neff and Asner, 2001). The DOC fluxes to deeper soil layers can support microbial activity (up to 30%) below 40 cm depth (Neff and Asner, 2001), together with the activities of soil macrofauna (Lavelle and Spain, 2001). Hydraulic conductivity also plays an important role in the flow of DOC through the soil profile. However, this property has been generally overlooked, despite its important role in fluxes of inorganic elements in solution (Prendergast, 1995). Water flow rate affects the reactivity of DOC. For example, under controlled conditions in the laboratory, a 50% increase in pore water velocity led to 18% decrease in the slope of the adsorption isotherm and 83% increase in the desorption coefficient (Weigan and Totsche, 1998).

Field experiments on fine particle size fractions that contain SOM stabilized by interaction with soil minerals have shown that lignin, which is the most important aromatic compound in soil is not stabilized. However, polysaccharides are preserved in soils (Kiem and Kögel-Knabner, 2003; Schmidt et al., 2000). β -glucosidase and phenol-oxidase are important C-cycling enzymes. There is a strong correlation between the β -glucosidase and DOC (Fenner et al., 2005). The activity of these enzymes is crucial in mobilising DOC from the peat matrix, with implications for C exports to the receiving waters. Models developed to explain the DOC fluxes do not address the contribution of biotic processes other than microbial activity. The fate of SOC can be determined by studying its distribution and composition through the soil profile with ¹³C CPMAS NRM (Cross Polarization Magnetic Angle-Spinning Nuclear Magnetic Resonance) spectroscopy (Guggenberger et al., 1995), isotope analysis (Staddon, 2004), and Near Infrared spectroscopy (Joffre et al., 2001) in order to see which components are forming the stabilized SOM in the different soil horizons.

C. Bioturbation

Bioturbation is also a factor of some importance in indirectly affecting the release of DOC, through the formation of biologically-created soil aggregates that may change the surface area for desorption. For example, biogenic structures produced

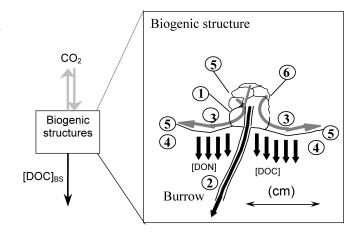


FIG. 8. Processes and determinants affecting the availability and quantity of dissolved organic C and N in biogenic structures (BS) produced by soil macrofauna (earthworm). 1. Production of NH_4^+ and NO_3^λ in fresh turricules. 2. Vertical illuviation of NO_3^λ through the earthworm burrow; 3. Lateral migration of NO_3^λ through the BS and soil surface where bacteria are stimulated with the substrate; 4. Vertical leaching of [DOC] and [DON] through the soil profile; 5. Denitrification plus assimilation by roots (plant-uptake) and micro-organisms. 6. Cessation of mineralization in dry turricules (adapted and modified from Decaëns *et al.*, 1999).

by some soil invertebrates, like earthworms, have been shown to contain important quantities of C (Decaëns et al., 1999) and Ccycling enzymes (Mora et al., 2005). The amount of C that can be stored in these structures can be relatively high and ranges from 2 to 30% of the total SOC in the 0 to 10 cm. In regions with strong rainfall events, these structures and the free aggregates in the soil surface can be washed away to lowlying areas and waterways, as observed in Oxisols of the Neotropical savannas (Decaëns and Jiménez, personal observation). Each precipitation event constitutes an abiotic mechanism by which fluxes of soluble compounds go through the soil surface and into the soil. Also, the washing of more resistant biogenic structures results in the transport of C and N (Figure 8; Decaëns et al., 1999). This model is applicable to other surface structures that are normally observed in any ecosystem bearing in mind the physicochemical properties of any of these structures, since C contents vary from one type to another. For instance, ant deposits are constituted by loose aggregates with low contents in C, whereas termite mounds may have greater values of C and extraordinary high values of N in some cases (Decaëns et al., 2001; Jiménez and Decaëns, 2006). All these processes need to be studied and included in the global budgets of C fluxes through ecosystems including the contribution of soil macrofauna to the indirect and direct effects as a result of their activities in the incorporation of C into the soil (Figure 9).

D. Sorption and Desorption

The stabilization and production of DOC in soils are determined by two important processes, i.e., sorption and desorption. Organic materials form a variety of bonds with



FIG. 9. Earthworm burrow filled with casts in the Colombian "Llanos" where other smaller earthworm species and soil macrofauna groups feed upon (several months), producing tiny faecal pellets that can, in turn, release C which become available for plant uptake (see the rather ramified grass-root attached to one of the sides of the earthworm burrow. The role and implications of this phenomenon in C sequestration have not been yet quantified (original picture by P. Lavelle, used with permission).

mineral surfaces, ranging from strong to weaker ligand exchanges (McBride, 1994). The type of organomineral associations are quite complex and highly variable, making the development of conceptual models for this process difficult. Sorption isotherms are normally and commonly used to explore the links between the concentration of solution and the soil surface association.

The DOC sorption reactions are best represented with the Initial Mass (IM) linear isotherm (Nodvin *et al.*, 1986):

$$RE \bullet mX_i \,\lambda b \tag{1}$$

where RE is the amount of DOC released from soil solution, *m* is the regression coefficient (partition), X_i is the initial DOC concentration (mg g soil⁻¹), and *b* is the intercept (when $X_i = 0$, mg DOC g soil⁻¹). The IM isotherm can also be used to estimate the size of the reactive soil pool:

$$RSP \bullet \frac{b}{(1\,\lambda m)}$$
[2]

that is the soil C pool that can be lost through leaching.

There are differences in the sorption affinity (m) for DOC regarding soil types. This affinity is closely related to certain physical soil properties; for example, a number of studies have reported positive relationships between m and clay content, dithionite extractable iron (Fe_d) and oxalate extractable aluminum (Al_o) (Table 7) (Moore et al., 1992; Donald et al., 1993; Kaiser and Zech, 1998). These physical properties correlated strongly with DOC sorption because they are indicators of the surface area available for reaction through ionic and physical associations. Prediction of m variation according to soil types is difficult since there are positive and negative relationships between m and SOM. Some studies have shown that SOC is inversely correlated with m (Jardine et al., 1989; Kaiser et al., 1996), and positive correlations have been observed in other studies (Moore *et al.*, 1992). Although at a broader scale there seems to be a clear relationship (Neff and Asner, 2001), sometimes the graphs plotted with m values against soil C content show weak correlations, indicating that a more precise assessment of the underlying differences is needed, together with new studies, especially in the tropics.

Desorption of OM from soils and sediments may increase the rates of SOM mineralization up to five orders of magnitude (Keil et al., 1994; Nelson et al., 1994). Precipitation of DOM may contribute to the formation of stable OM but this process has not been widely studied. Recent studies on budget calculations of DOC fluxes and available sorption capacity in forest mineral soils have challenged the paradigm of sorptive OM stabilization in the mineral soil, at least in temperate forest soils. Sorptive stabilization of DOC is likely the main process for the retention in the mineral soil (Kalbitz et al., 2000). For example, Guggenberger and Kaiser (2003) hypothesized that sorptive stabilization is restricted to juvenile mineral surfaces, while the degradation of DOM sorbed onto surfaces already occupied with OM should be large. This hypothesis implies that the contribution of DOM to the formation of stable OM in the mineral soil is related to the availability of mineral sorption sites.

Sorption on mineral phases is a very important control on the DOC concentrations. The relationship between the effects of soil properties on the sorption of DOC is not always straightforward. Some researchers have identified Fe and Al oxides-hydroxides and the edge sites of layer silicates as potential sorbents of soluble SOM (Tipping, 1981; Schultness and Huang, 1991). The sorption of DOC as influenced by SOC, sesquioxides (oxides and hydroxides of iron and aluminum), and extractable $SO_4^{2\lambda}$ was investigated by Kaiser and Zech (1998). They found that the sorption of total DOC was reduced when increasing content of SOC, in particular, the sorption of hydrophilic DOC, while the effect of SOC on the sorption of hydrophobic DOC was rather weak, indicating that there is a competitive sorption of both fractions (Kaiser and Zech, 1998). Preferential sorption for hydrophobic DOC has been reported in several studies (Jardine et al., 1989; Vance and David, 1992), which show that hydrophobic interactions determine the binding of DOC with the mineral soil. The ligand exchange between carboxyl and

Soil type	Soil type Regression equation		
Sorption affinity (m) Spodosols, Inceptisols, Alfisols, Entisols, Mollisols	$m = 0.64 + 0.15 \log Fe_d + 0.19 \log Al_o - 0.26 \log OC$	0.75	Kaiser et al. (1996)
Inceptisols, Spodosols, Mollisols	$m = 0.451 + 0.02 \log Fe_d + 0.032\sqrt{A1} + 0.064 \log OC$	0.39	Moore <i>et al.</i> (1992)
Ultisols, Spodosols, Inceptisols, Oxisols	$m = 0.15 \ln \% \ soil \ C \ 0.51$	0.41	Qualls and Haines (1992)
Desorption parameter (b) Spodosols, Inceptisols, Alfisols, Entisols, Mollisols with carbonates	$\log b = 0.32 + 0.72 \log OC$	0.76	Kaiser et al. (1996)
Spodosols, Inceptisols, Alfisols, Entisols, Mollisols without carbonates	$\log b = 0.02 + 0.88 \log OC$	0.82	Kaiser <i>et al.</i> (1996)
Inceptisols, Spodosols, Mollisols	$b = 0.145 + 0.103 \log OC \ 0.055 \sqrt{A1} \ 0.045 \log Fe_d$	0.72	Moore <i>et al.</i> (1992)
Ultisols, Spodosols,	b = 0.05% soil $C + 0.09$	0.48	Neff (1999);

 TABLE 7

 Mineral and organic control on DOC sorption (m) and desorption (b) in a range of soil types (from Neff and Asner, 2001)

hydroxyl groups of SOM and OH and OH_2 groups at the surfaces of mineral phases is the sorption mechanism widely accepted by researchers.

Oxisols and Ultisols. When the content of Al(OH)₃, ferrihydrite

 (Fe_{o}) and goethite (Fe_{c}) increase the sorption of total DOC, both

hydrophilic and hydrophobic is increased. The release of total

DOC is reduced by coating the soil material with sesquioxides

in the following order $Al_o > Fe_o > Fe_c$ (Kaiser and Zech, 1998). Sorption of DOM to the mineral soil is a selective pro-

cess for hydrophobic and aromatic compounds (Kaiser et al.,

1996; McKnight et al., 1997). Therefore, it must also be selec-

tive with respect to the biodegradability of sorbed OM, because

aromatic, complex and hydrophobic compounds are the most

stable DOM components (Kalbitz et al., 2003a, b). Sorption of

DOM to the mineral soil results in its stabilization. Kalbitz *et al.* (2005) proposed that the main mechanisms for DOM stabiliza-

tion are the selective sorption of intrinsically stable compounds and strong chemical bonds to the mineral soil and/or a physi-

cal inaccessibility of OM to microorganisms. They reported that

from a pool of 110 Mg C ha⁻¹ stored in the mineral soil, about

22% originated from DOM, despite being unable to determine

whether this pool was being stabilized or was already stabilized.

In conclusion, a "sorption front" moves downwards through the

soil profile as a pedogenesis process towards a horizon where a

large number of sorption sites are available (Guggenberger and

Kaiser, 2003; Ussiri and Johnson, 2004).

The same mechanistic process may occur in tropical

Inceptisols, Oxisols

E. Modeling

In the models used the simplest representation of the DOC pool is a combination of labile and recalcitrant fractions. Parton *et al.* (1987, 1994) modeled the SOM dynamics using the Century model. They divided the C pool into three separate pools: active, slow and passive, which are differentiated by their different turnover rates, from months to decades and centuries, and correspond to:

Moore et al. (1992)

- 1. Active pool: microorganisms and microbial byproducts (several months to 1 year);
- Slow pool: recalcitrant but moderately decomposable material (10–100 yr);
- 3. Passive pool: physically and chemically protected pool of C highly resistant to decomposition (1,000 to 10,000 yr).

Slow cycling of C can be modeled as occurring through reaction of organic ligands with Al^{3+} and Fe^{3+} cations in the upper horizons, followed by sorption to amorphous inorganic Al compounds at depth (Masiello *et al.*, 2005). Organic ligands stabilized by this process traverse the soil profile as DOC (both from surface horizons and root exudates). This chelation and transport process is highly correlated with the storage and long-term stabilization of SOC, and not only in Spodols but also in other soil orders like Alfisols, Inceptisols and Mollisols (Masiello *et al.*, 2005). A model for DOC is precisely described in Neff and Asner (2001).

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	SIC content	Central America	South America		
FAO soil group	$(\text{kg C m}^{-2} \text{ up to 1 m})$				
Xerosols, Yermosols	33.9	12.0	36.5		
Calcaric Fluvisols, Calcaric regosols, Calcaric Gleysols	11.4	0.6	0.8		
Chemozems, Kastanozems	16.0	4.7	7.0		
Calcic Luvisols, Calcic Cambisols	17.7	0.4	0.4		
Vertisols	6.5	0.9	1.7		
Total (Pg)		18.6	46.4		

 TABLE 8

 SIC pools up to 1 m depth in Latin American soils according to FAO soil group classification (From Sombroek *et al.*, 1993)

V. FORMATION OF SECONDARY (PEDOGENIC) CARBONATES

The SIC is important in soils of the arid and semi-arid regions since it is part of the constituent of subsurface soils, and it may contain two to five times more SIC than SOC in the top one meter. The SIC pool consists of primary (lithogenic) and secondary (pedogenic) carbonates. The former are typically found in desert soils, are derived from the weathering of parent material, and remain in these arid environments where Ca^{+2} and Mg^{+2} are not removed by leaching, unless these dry environments become wetter. In deserts, a large fraction of total C is contained in inorganic form, primarily as CaCO₃.

Despite the dominant role that calcium carbonate plays in modifying the physical, chemical and biological properties and behaviour of plant nutrients in the soil, its role in C sequestration in calcareous soils is not widely documented (Lal, 2002). The role of SIC is important for sequestering C, but the mechanisms involved are not well understood. The rate of SIC sequestration as secondary carbonates is low (2 to 5 kg C ha⁻¹ yr⁻¹) and is accentuated by biogenic processes and leaching of carbonates into the groundwater (Nordt *et al.*, 2001), especially in soils irrigated with water containing low carbonates.

The SIC occurs in carbonate minerals in two forms, i.e., calcium carbonate (CaCO₃) and dolomite (MgCO₃). In tropical highly weathered acid-soils the amount of SIC is not considerable because most of the carbonates present in the parent material have been dissolved. The total carbonate pool in world soils ranges from 222 to 245 Pg C (0–30 cm), and from 695 to 748 Pg C for the upper 100 cm (Batjes, 1996), values similar to those obtained by Schlesinger (1982) and Sombroek *et al.* (1993). Values of SIC for different soil types in Latin America are indicated in Table 8.

The formation of secondary carbonates occurs through the reaction of carbonic acid (H_2CO_3) with Ca^{2+} and Mg^{2+} (Lal and Kimble, 2000; Raymond and Cole, 2003). Most of the carbonate that precipitates in soils and forms calcic or pretrocalcic horizons is the result of aerosolic deposits of carbonate through dusts, or primary carbonates in the rock or sediment that are dissolved and

re-deposited. Some studies have reported that much of the Ca^{2+} is originated from carbonate in dry dust or from Ca^{2+} dissolved precipitation that came from carbonate dust, thus indicating that direct involvement of atmospheric CO₂ is negligible (Gile and Grossman, 1979; Chadwick and Capo, 1993).

The SIC sequestration may constitute a significant pathway of C sequestration in arid and semi-arid regions (Lal *et al.*, 2000). The formation of secondary carbonates also occurs in soils of the humid regions. The rate of sequestration is very low as to have a considerable effect in climate change mitigation. For example, Schlesinger (1997) estimated that the magnitude of SIC flux with the atmosphere is low at about 0.023 Pg C yr⁻¹. However, the process can be important at larger temporal scales. Monger and Gallegos (2000) and Nordt *et al.* (2000) argue that the formation of secondary carbonates is an important mechanism of SIC sequestration to mitigate climate change. How to distinguish primary from secondary carbonates is rather complicated (Rabenhorst *et al.*, 1984).

There is not only a lack of studies on the role of SIC in C sequestration but also the mechanisms are the least understood in the global process (Lal, 2003). Leaching of bicarbonates into the groundwater is a major mechanism of SIC sequestration. The rate of C sequestration by this mechanism may be 0.25 to 1.0 Mg C ha⁻¹ yr⁻¹. There is no agreement on the rate of C sequestration through formation of secondary carbonates and it is still a matter of discussion. Some argue that the rate is slow (3 to 5 g C m^{-2} yr⁻¹) and of little significance (Schlesinger, 1997). Others, however, support the idea that rate of sequestration of atmospheric C may be much higher with a maximum rate of 0.114 to 0.124 Mg C ha-1 yr-1 (Table 9) (Monger and Gallegos, 2000; Nordt et al., 2000). For example, the formation of secondary carbonates can be accentuated by biotic activity because of high concentration of CO_2 in the soil air (e.g., root growth, termites) (Monger and Gallegos, 2000). An important mechanism of SIC sequestration is through leaching of carbonates in irrigated soils, if the irrigation water is not already saturated (Nordt et al. 2000). Reconstruction of carbonate fluxes in soil formed in strongly calcareous parent material over

Ecoregion	P/PET ¹	Land area (Bha)	Potential rate of C sequestration (kg $ha^{-1} yr^{-1}$)	Total sequestration potential(Pg C yr ⁻¹)
Arid ²	0.05-0.20	2.55	0–1	0-0.0026
Semiarid ³	0.20-0.50	2.31	3–114	0.0069-0.2633
Sub-humid ⁴	0.50-0.65	1.30	1–124	0.0013-0.1599
Total		6.16		0.0082-0.4258

 TABLE 9

 Estimates of C sequestration through formation of secondary carbonates (from Lal, 2001)

¹ P = Precipitation; PET = Potential evapotranspiration

² annually <200 mm in winter and <400 mm in summer

³ annually 200–500 mm in winter and 400–600 mm in summer

⁴ annually 500–700 mm in winter and 600–800 mm in summer

geological time periods suggests that this mechanism could account for upward of 1 Mg ha⁻¹ yr⁻¹ of SIC.

In Latin America, drylands occupy nearly 28% of total area (Table 10). Most soils under drylands include Aridisols and Entisols, but Alfisols, Mollisols and Vertisols are also normally found (FAO, 2001). The predominant land use system in dry areas includes pastoralism and rangeland linked to a subsistence food production. In Argentina, for example, the Pampa region (steppe) receives between 250 and 500 mm of precipitation annually, i.e., more than twice the quantity that falls in true desert areas where rainfall is insufficient to support vegetation that could protect the land from erosion (FAO, 2001).

Dryland estimates on the amount of C that can potentially be sequestered by adoption of several land management practices are still sparse. These drylands are less prone to lose SOC pool, since lack of water reduces the rates of mineralization of SOM and thus the contribution to formation of secondary carbonates through leaching. Assuming the low rate of formation of secondary carbonates of 0.03 to 0.05 Mg ha⁻¹ yr⁻¹, the potential of SIC sequestration in 682 Tha (Tha = 10^3 ha) of drylands, including arid, semi-arid and dry subhumid lands in Latin America ranges from 20.5 to 34.1 Gg C yr⁻¹.

The role of specific bacterial outer structures (such as glycocalix and parietal polymers) on calcium carbonate crystallization in terrestrial environments has been addressed by Braissant *et al.* (2003) in order to show implications of exo-polysaccharides and amino acids in the mineralogy and morphology of CaCO₃ crys-

TABLE 10Drylands in Latin America (FAOSTAT, 2002)

Ecoregion	Land area (Bha)	Land area (%)	Food crops (FAO)
Arid	5.97	7.1	Marginal pasture, spare vegetation
Semiarid	122.43	14.54	Millet and sorghum
Sub-humid	250.21	5.97	Maize, bean, groundnut peats, barley, wheat, lentils
Total	378.6	27.6	

tals produced by living bacteria. They showed the influence of bacterial outer structure composition on the morphology and mineralogy of bacterially induced CaCO₃. This point emphasizes the role of micro-organisms on carbonate accumulations in terrestrial environments.

VI. SOIL ORGANIC CARBON STOCKS IN LATIN AMERICA UNDER DIFFERENT LAND MANAGEMENT OPTIONS

In Latin America all the biomes and soil types are present. In only one country, Colombia, one transect from the west to the east yields the whole range of soils. This gives an idea of the high diversity of sites and places present in Latin America. However, we will try to provide data on the amount of C stocks in different soils of under different land use management options. Some authors have provided some data in review articles but there are still places where studies need to be conducted that consider the large heterogeneity of soils. We will start with the most common biomes found in Latin America.

A. The Colombian "Llanos" and Brazilian "Cerrados"

Tropical savannas form one of the most predominant ecosystems in South America occupying around 250 millions ha (Cole, 1986). The Eastern Plains of Colombia (locally called "Llanos") are covered with acid savannas that are traditionally used for extensive grazing systems. In the absence of such interventions as sowing of introduced grasses and application of fertilizers, these lands are usually managed in extensive holdings of low productivity (Fisher et al., 1995). The Brazilian "Cerrados" occupy an area of about 204 millions ha (\sim 82% of the total). The mechanisms by which C is accumulated in Oxisols of the Colombian Llanos are given in Fisher et al. (1994). These authors provided evidence that deep-rooted grasses were responsible for increasing SOC content to certain depth in the soil at an annual rate of 0.1 to 0.5 Pg C. Tiessen et al. (1998) provided data under different land use systems in tropical savannas and dry forests of Brazil.

At present there are 50 million ha of pastures, mainly introduced African Brachiaria grasses in the "Cerrado" region that are degraded due to mismanagement in fertilization rates and grazing stocking rates. Da Silva et al. (2004) provided data on soil carbon storage under six different introduced pastures and compared to the native grassland (Panicum maximum grass). They observed that soil C accumulation in degraded pastures or in those under an ongoing degradation process does not contribute significantly to the sinking of atmospheric CO_2 as well as to the reduction of greenhouse gases concentration in the atmosphere. The SOC under degraded cultivated pastures was, in general, lower compared to the stock obtained under the native pasture, which overall represents a loss of C. Only significant increases were obtained in two pastures aimed at seed production, indicating that management and soil fertility status is a key component in C sequestration. Da Silva et al. (2004) observed SOC accumulation values in the soil up to 1-m depth in the range of 100 Mg ha⁻¹. This is half the value obtained by Fisher *et al*. (1994) for the Colombian savannas. It is therefore improbable that the Brazilian "Cerrados" constitutes part of the missing sink for the unbalanced CO₂ budget (Da Silva *et al.*, 2004).

B. Amazon Basin

Oxisols and Ultisols are the most common soil types found in Brazil. Oxisols cover almost 40% of the total land area in Brazil. Soils of the Amazon basin store 47 Pg C up to 1 m of which 45% is stored in the first 20 cm (Moraes *et al.*, 1995). Bernoux *et al.* (2002) reported values of SOC pools of 22.7 \pm 2.3 Pg (0–30 cm). The closed forest Amazon had high values of SOC compared to the open Amazon forest and in the "Cerrado" type savanna region, SOC content was determined strongly by soil type.

Bernoux *et al.* (2002) provided a very reliable estimation of the SOC pool in Brazil, according to different soil types under different vegetation types (soil-vegetation associations = SVA). Calculations (0–30 cm) were done according to the classical way of calculating SOC pool (C mass per area) for a given depth, by summing C pool of the successive horizons in the respective profile. Carbon pool in a soil horizon was determined as a product of bulk density, C concentration and horizon thickness. The SOC pool ranged from 15 Mg C ha⁻¹ in sandy soils of the Northeast Steppe to 418 Mg C ha⁻¹ in the Atlantic Forest. More than three fourth of all the soil-vegetation types had mean values of SOC that ranged from 30 to 60 Mg C ha⁻¹ (with 41% of the extent covered by SVA showing values from 40 to 50 Mg C ha⁻¹).

The potential C sequestration in Brazilian soils under native vegetation for the 0- to 30-cm layer was obtained by combining the table of the RCS with the SVA map. Bernoux *et al.* (2002) calculated a total of 36.4 ± 3.4 Pg C stored in 8,257,846 km² of the SVA. This represents about 5% of the total SOC in the first 30 cm in soils of the world. Cerri *et al.* (2000) estimated a C sequestration potential of 41 Pg C for the 0 to 100 cm, with 23.4 Pg C (57% stored in the top 0.3 m) including

an estimated error associated to bulk density estimation of about 10%.

The regions with the highest C sequestration are characterized by the presence of wet soils, i.e., the Pantanal in the Western region (near the border with Bolivia), Bananal in the Central region and in the Northwestern Amazon Basin. On the other hand, the southern part of Brazil had high SOC sequestration mainly because of the colder climatic influence that directly affects the vegetation and the soil organic matter decomposition. The northeastern region (known as "Sertão") showed an important climatic influence (semiarid) and was characterized by low C sequestration (Bernoux *et al.*, 2002).

C. Forest Regrowth in the Amazon Basin

There is little known about the effects of forest conversion to tree plantations on SOC pool in the Amazon. Slash-and-burn agriculture leads to above-ground C losses in the range of 20 to 47 Mg ha⁻¹ (Hughes et al., 2000). Secondary forests acts as frequent source and undetectable sinks for C and, therefore, cannot offset for the continuous slash-and-burn of the primary forests across the Brazilian Amazon, unless there is a shift from current land use practices to regrowth areas for forest that can act as C sinks (Hughes et al., 2000). However, such prolonged periods of regeneration have not been considered in the patterns of land use in the Brazilian Amazon in the past years. The current land use pattern for regrowth forest acts as either sinks or sources of C in the Brazilian Amazon. Hughes et al. (2000) concluded that secondary forests have the capacity to accumulate and store substantial amounts of C but only when they are allowed to regenerate for long periods. They set a threshold limit of 19% of the C lost during burning for annual C accumulation rates at the plot level. In other words, when less than 19% of the total area accounted for by secondary forests within a given region in the Brazilian Amazon are cut and burned, those forests will be net accumulators (sink) of C during that given year. The contrary will occur when more than 19% of regenerating forests are burned within a region during a given year (source of C).

In the Eastern Amazon of Brazil Smith *et al.* (2000) showed that plantations that were established in the 1960s and 70s in Oxisols had an average SOC pool ranging from 72 to 114 Mg C ha^{-1} compared to the 98 Mg C ha^{-1} of the natural rainforest. The natural forest had not been disturbed recently, but charcoal was found at 5 to 100 cm depth, indicating that they were influenced by fire in the past (Smith *et al.*, 2000). C pool in the 0 to 20 cm depth at this site was close to the maximum values reported for the first 30 cm in Oxisols of the Amazon region (Cerri *et al.*, 2000).

D. Brachiaria Pastures

The effects of the conversion of tropical forest to pasture on total SOC pool has been addressed by several authors. Cerri *et al.* (2004) reported average SOC values in forest soils about

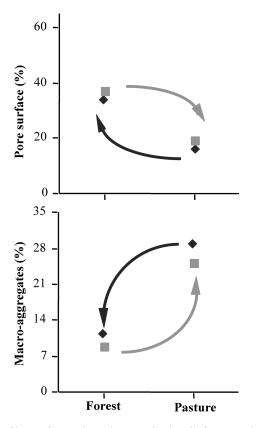


FIG. 10. Changes in porosity and aggregation in soils from a tropical forest from Brazil and the introduced pasture; degradation of soil structure can be reversed in 12 months (adapted from Chauvel *et al.*, 1999).

25 Mg C ha⁻¹. Pastures have the potential to introduce large amounts of SOM (Fisher et al., 1994). But pastures can act either as sinks or sources of C depending on management (see review by Fearnside and Barbosa, 1998). Overgrazing leads to SOC losses in the Amazon region (Trumbore et al., 1995). High stocking rates may have a very negative influence on the ability of pastures to accumulate SOC in soil, especially if it is associated with soil compaction due to the loss of native soil fauna that help maintain and active soil structure regulation (Chauvel et al., 1999). For example, important changes in soil structure have been observed in a relatively short period of time when soil monoliths were transferred from degraded pasture to forest and vice versa (Figure 10). This may be the reason why degraded pastures with little grass cover are less likely to accumulate SOC because inputs of C from pasture roots are reduced (Neill et al., 1997). The avoidance of these bad management practices must be accompanied by policy support in order to reduce the rates of soil degradation in this part of the world.

In a study conducted across the state of Rondônia in the southwestern Brazilian Amazon Basin, Neill *et al.* (1997) reported changes in SOC pool to a depth of 30 cm under pasture ranged from a loss of 0.72 kg m⁻² to an increase of 1.77 kg m⁻². SOC pool increased in 14 of 18 pastures, but these increases were significant in only 4 pastures. Besides, SOC accumulation increased with pasture age but was independent of soil texture. These authors concluded that site history and management may be more important than soil type as determinants of the direction and magnitude of changes in soil C pools. These authors found that pasture-derived C inputs approximately balanced or slightly exceeded losses of original forest-derived C. A similar dynamic also occurs in pastures planted in former Neotropical savanna (Fisher *et al.*, 1994).

SOC pool ranged from 29.7 Mg C ha⁻¹ in sandy soils under regrowth forest (8-yr-old) to 50.4 Mg C ha⁻¹ in more clayey soils under forest (7-yr-old). On average, 53% of the total SOC pool up to 30 cm was found in the first 10 cm (data recalculated from Neill *et al.*, 1997). In 13 out of 18 pastures analyzed, SOC concentration in 0–10 cm depth increased generally in comparison with forest (Neill *et al.*, 1997). Nonetheless, these increases were significant only in the 81-yr-old pasture (the oldest). SOC accumulation ranged from 1.23 to 1.77 kg m⁻² (0–30 cm) in those pastures where significant statistical differences were observed. This potential of C storage represents from 45 to 56% increase in total SOC, and comprises 3–12% of the C stock of the original forest vegetation (Neill *et al.*, 1997).

Because the highest rates of C accumulation occurred in young pastures, the total future gains of soil C are limited by a lower annual rate of C sequestration in older pastures. From 40 to 93% of forest derived C remained in 7- to 9-yr-old pastures in seven locations, and in 20-yr-old pastures from four sequences, 65–92% remained. Similar results have been reported from Oxisols in Amazonas and Pará by other authors (Bonde *et al.* 1992, Desjardins *et al.* 1994) or in Central America from cleared humid forest in Costa Rica (Veldkamp, 1994).

E. No-till Systems

Studies on the amounts of SOC and C sequestration rates in agricultural cropping systems under no-tillage are not abundant to date. During the last years some work has been conducted in Brazil where 27% of cropland (about 13.4 million hectares) are no-tillage systems with almost 71% (i.e., 9.43 million hectares) located in the southern part of the country (Paraná, Santa Catarina, and Rio Grande do Sul State). For example, Freixo et al. (2002) studied the differences in the SOC pools under different cropping systems under no-till or conventional tillage practices in Oxisols of Rio Grande do Sul (Southern Brazil). They observed that soil C decreased 47% in conventional tillage (CT) soils and 23-29% in no-till (NT) soils (0-5 cm layer) in those areas under long-term cultivation. Changes induced by land management in C pools were best detected by the free light fraction of OM, especially in the first 5 cm depth because that is where the plant material is accumulated. Most of the SOC was associated to the silt and clay fractions as it is normally observed in other studies mentioned in this review.

There are few comparisons between CT and NT systems for SOC dynamics in Oxisols that consider soil under natural vegetation as a base line representing the steady-state level. Bayer et al. (2000) reported a SOC sequestration rate of 1.33 Mg C $ha^{-1} yr^{-1}$ conducted in southern Brazil. In another study Sa *et al*. (2001) assessed the amount of C from an Oxisol under a CT and NT chrono-sequence located in Paraná State (southern Brazil). The NT system led to the highest increases in SOC storage, with mostly 60% of the total in the first 10 cm, and especially in the finer particle-size fractions ($<20\mu$ m). The authors argue that long-term NT with high crop residues input improved the protection and concentration of SOC through the formation of silt-sized mineral-organo complexes, probably due to the presence of fungal hyphae debris. Crop residues had an important effect on the amount of C stored in soils where a significant relationship was found ($r^2 = 0.74$) and most of the crop residues entered into the coarse particle-size fraction. The C sequestration rate for NT was 0.81 Mg C ha⁻¹ yr⁻¹ in the 0–20 cm depth and 0.99 Mg C ha⁻¹ yr⁻¹ in the 0.4 m depth. The NT C sequestration potential for South Brazil was estimated at 9.4 Tg C yr⁻¹. Only after 40 years of the adoption of NT agricultural practices with high inputs of crop residues a new steady-state level is achieved (Sa et al., 2001).

F. Andean Ecosystems

There is a lack of studies dealing with SOC dynamics in Andean ecosystems. In Ecuador, for example, Zehetner *et al.* (2003) assessed the amount of C in volcanic soils and they observed a correlation between SOC content and altitude. The SOC sequestration rates seem to be higher in high elevation pedons compared to those located in low altitude areas. In the "páramo" they reported that SOC was correlated well with Al pyrophosphate. The additions of OM from the "páramo" vegetation together with low rates of decomposition due to lower temperatures in high altitude areas resulted in higher amounts of C in these Andeans ecosystems (Zehetner *et al.*, 2003). This process is probably extended to other parts of the Andean mountains in other South American countries.

VII. FINAL REMARKS AND CONCLUSIONS

There are important gaps in knowledge about the main mechanisms addressed in this review, especially for the last two: the role of DOC and the formation of secondary carbonates. In Latin America, although substantial research has been done under different ecosystems and land use systems in some countries, like Brazil, Colombia, Argentina, there is a need to conduct more studies in natural ecosystems and agricultural systems, and in some areas like in Central America few studies have been undertaken to date. Moreover, it is important to conduct more field studies with agreed standard methodologies so data can be comparable between sites, biomes and regions.

In the Neotropical savannas, most of the SOC pool is concentrated in the top 25 cm of soil and the rates of C loss by cultivation is higher than in temperate soils. The rates of SOC sequestration are, in general, lower in the tropics (especially soils with low activity clays like kaolinite) than in temperate soils because of high temperatures, although the factors of SOC sequestration are similar in soils from both regions.

Processes that influence and determine terrestrial soil C sequestration are expressed at different spatial and temporal scales. Even at the shortest scales important mechanisms and controls may have an impact on the process at larger scales. The binding of C with clay particles occurs at atomic scales (nanometers). The physical protection of C in biogenic structures produced by soil invertebrates is expressed at larger scales, sometimes, several tens of cm due to the three- dimensional structure of soil. Different and opposite processes may occur at very short scales, e.g., mineralization can be reduced or enhanced due to the presence of microbial population that are in intimate contact with the organic resources.

Although an aggregate hierarchy was suggested by Oades and Waters (1991), this may not be applied to all soil types, like Oxisols, where oxides and hydroxides are the dominant agents of aggregates. It is not well understood yet how macroaggregates form from a group of microaggregates before being stabilized. Biotic processes determined by the activities of soil organisms, including, bacteria, fungi, plant roots and large invertebrates are key elements in an active regulation of soil structure, and they probably interact in more than one mechanism of C stabilization within aggregates. Most models do not consider the formation, stabilization and lifespan of the aggregates that have been formed by the action of soil organisms. The overlooking of soil organisms' role in this process must be avoided and be included in future studies (Jiménez and Thomas, 2001).

Soil organisms may regulate important soil processes at the scale of the structures they produce, where macroaggregates of certain size, bulk density and with different organic debris may last for some time, preventing OM to be mineralized until the structure has been degraded and the constituting aggregates spread over the soil surface. At a larger spatial scale, together with the high production of these structures under certain ecosystems and land management, this process may lead to important and significant effects on soil structure, C accumulation or C losses to low-lying areas due to run-off events. A considerable effort in research is still needed to quantify this process. In some cases, the huge activity carried out by some organisms together with mismanagement options may lead to severe soil compaction problems, impeding root development and hence C accumulation in soil (Chauvel *et al.*, 1999).

The importance of clay in retaining SOC depends on the mineralogical composition with residence times exceeding 100 years in some cases (Laird, 2001). SOC associated to silt- and clay-size fractions is strongly linked to mineral particles. Clay mineralogy determines the mechanisms of formation and stabilization of clay-humic complexes. The interaction of C with clay particles is a primary factor in the stabilization of SOC in aggregates. Organic anions of SOC rich humic colloids and polysaccharides are adsorbed by clay particles through polyvalent metals like Ca^{2+} , Al^{3+} and Fe^{3+} so participating in the formation of clusters of microaggregates (Oades, 1984). The

organomineral complexes formed sequester SOC by three different mechanisms: adsorption, polymerization of humic substances and protection of C in aggregates.

The SOC content is generally determined by the amount of clay, although some studies conducted in tropical sites indicate an opposite trend or no effect at all. In tropical soils there is still a considerable lack of information about how SOC storage in smectitic soils differs from kaolinitic-oxidic soils. Under natural ecosystems the positive relationship between SOC and clay relates to the presence of POM (plant debris) with amorphous OM associated to silt and clay fractions. In cultivated soils, however, POM is generally highly susceptible to depletion as 20 to 40% of the SOC is associated with the sand-size fraction (Feller and Beare, 1997). Under forest or savanna, plant cell walls are detected in the coarse clay fraction only, and never in the fine clay fraction. The organiomineral complexes may contain from 5 to 9 times more SOC than POM, and it can be responsible for 69 to 80% of the total CO_2 sequestered in the soil (Bayer *et al.*, 2001).

Ecosystem C stocks in the humid tropics vary in size, being the highest in natural ecosystems like soils under forest or savanna, and then decreasing in the order secondary forests > fallows > agroforestry plantations > annual crops. The age of the pasture and its management have an important effect on SOC in the Amazon Basin and the effect of the vegetation ranges between 40 and 50% of the total SOC pool of the first 10 cm of soil is derived from pasture 10 years after deforestation. In older pastures only 20% of the C content of the 0-10 cm soil layer is derived from pasture. This means that as pasture age increases the incorporation of C into the different soil fractions is not occurring and a large proportion of the C is lost. The mechanisms involved in this process require further assessment.

The flow of DOC is an important process in the transport of SOC through the soil profile. The boundaries of the ecosystems are not considered since the limits around the sites under study are pathways for the flow of C between sites and throughout the landscape. The fluxes of DOC through this internal system can be several times larger than the stream fluxes which can constitute an important component of the ecosystem C balance. Ecosystem export of DOC increases linearly from <5 to ~100 kg C ha⁻¹ yr⁻¹ over a soil C:N ratio of 13-30 (Hessen *et al.*, 2004).

The flux of DOC decreases with depth up to 50–90% in the deeper mineral layer in soils with high clay contents. In the surface layer fluxes of DOC range from 10 to 85 g C m⁻² yr⁻¹ and from 2 to 40 g C m⁻² yr⁻¹ in subsurface horizons. The concentration of DOC in deep soil horizons and the flow of DOC are relatively small. The sorptive stabilization of DOC is the main mechanism involved in this retention (Kalbitz *et al.*, 2000). However, there is still a lack of comprehensive knowledge regarding the processes that control DOC fluxes in soils (Neff and Asner, 2001), as the origin, function and fate of DOC are not fully understood since most studies have been conducted

under laboratory conditions. Abiotic factors moderate most of the DOC losses in terrestrial ecosystems. Bioturbation can be a factor of importance in controlling indirectly the release of C in terrestrial ecosystems (Jiménez and Thomas, 2001; Jiménez and Decaëns, 2004). For example, the amount of C stored in the surface biogenic structures produced by earthworms can be relatively high and ranges from 2 to 30% of the total SOC in the 0-10 cm. In regions with strong rainfall events these structures and the free aggregates that are in the soil surface can be washed away to low-lying areas.

The highest amount of C transported by any river is in the Amazon basin, but even in the largest river of the world the contribution of DOC to water streams is very low, i.e., 2 g C $m^{-2} yr^{-1}$, representing 0.2 and 8% of the total turnover in the forest, and the rest is mineralized.

Finally, the formation of secondary carbonates needs to be further addressed and quantified, even if the rate of SIC formation is low and apparently with not an important role in the global C cycle. However, SIC formation may constitute an important and significant pathway of C sequestration in semi-arid and arid regions. Besides, the formation of secondary carbonates can be accentuated by biotic activity because of high concentration of CO_2 in the soil air (e.g., roots and termites). Moreover, the composition of the bacterial outer structure influences the morphology and mineralogy of bacterially induced $CaCO_3$. This also emphasizes the role of microorganisms on carbonate accumulations in terrestrial environments.

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