

Soil carbon sequestration in a changing global environment

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Abstract Throughout its long history the Earth has undergone warm periods with high atmospheric concentrations of greenhouse gases (GHG), and has responded with different buffering mechanisms whereby atmospheric C has been transferred to other geochemical compartments. Strategies for the mitigation and adaptation to the current climatic forcing may thus be generated by the acceleration of such natural mechanisms, especially those involved in short cycles, mainly in the biosphere and the pedosphere. Although these contain smaller C stocks than other compartments (< 0.01% of the total C), they circulate large amounts of C from the atmosphere through photosynthesis and mineral weathering (e.g., 120 Pg C are circulated through terrestrial ecosystems and total C in the atmospheric compartment is 805 Pg C). Increased C sequestration can thus be achieved in terrestrial ecosystems, by: (1) favouring growth of biomass; (2) promoting and facilitating carbonation processes; (3) reducing erosion and favouring pedogenesis; (4) developing organic matter-rich horizons; (5) recovering degraded or contaminated soils, and/or (6) managing waste by use of systems that minimize emissions of GHG. Within the latter option, the following actions are considered here in more detail: 1) production of Technosols, and 2) production of biochar. All of the above options should form part of a strategy for the mitigation and adaptation to global climate change. In this review, we analyze those focused on promoting soil conservation, soil restoration and soil formation.

Keywords Carbonization · Carbonation · Carbon sequestration · Soils · Organic matter · Technosols · Biochar

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1 Geochemical carbon compartments and fluxes

Like the other light elements (except H and He), the C existing in the Earth was formed by fusion within stars and was thereafter concentrated at the Earth's surface as a result of different biogeochemical processes. The total amount of C present in the Earth is almost constant, except for (1) the small gains and losses produced by falling meteorites, and (2) the losses of low molecular weight C compounds to space. The global C budget can therefore be considered constant, and C conservation follows the first law of thermodynamics (Houghton 2007).

Nonetheless, the forms and amounts of C present in the different geochemical compartments (atmosphere, biosphere, pedosphere, hydrosphere and lithosphere) are not constant, and transfers take place as a consequence of natural cycles or anthropogenic activities. The amount of C present in the atmosphere is relatively small compared with amounts in the other compartments (except the biosphere), where the C species predominantly occur in non-gaseous forms, and thus do not contribute to climatic forcing (Table 1). However, the total concentration of atmospheric CO₂ has increased greatly since 1750 (from ~ 280 to 385 ppmv) as a result of human activities, and now far exceeds pre-industrial values (IPCC 2007). Global increases in concentrations of CO₂ (37.5% since the preindustrial era) are mainly due to the burning of fossil fuels, although land use changes account for other smaller but significant contributions. Lal (2004a) estimated that, since the industrial revolution, total global emissions of C to the atmosphere from fossil fuel combustion have been 270±30 Pg (1 Pg=10¹⁵g) and those resulting from changes in land use and soil cultivation, 136±55 Pg. Emissions from terrestrial ecosystems during the preindustrial era (throughout 7,800 years) have been estimated to be about 320 Pg (Lal 2004a).

There is a well established relationship between the concentration of CO₂ (and of other gases, such as CH₄ and N₂O) and the greenhouse effect in the Earth (IPCC 2007). These gases selectively absorb a fraction of the outgoing radiation and re-radiate it both downward and upward. This process is essential for maintaining the current temperature of the Earth, as otherwise the planet would be so cold as to be uninhabitable. However, at present, there is an urgent need to stabilize and even decrease (Hansen et al. 2008) the concentrations of greenhouse gases (GHG) in the atmosphere to mitigate dangerous anthropogenic interference with the climate system. Hansen et al. (2008) proposed a target atmospheric concentration of CO₂ of 350 ppmv to be pursued on a decadal timescale if catastrophic effects of climate change are to be avoided. This therefore entails a net reduction in anthropogenic GHG

Table 1 Capacity of biogeochemical compartments (Falkowski et al. 2000; Houghton 2007; Hansen et al. 2008) and relevant forms of C (In Pg C; 1 Pg=10¹⁵g)

Compartment	Inorganic C		Organic C		Total C Quantity (Pg)	% total C
	Quantity (Pg)	Forms	Quantity (Pg)	Forms		
Atmosphere	805	CO ₂ , CO, CH ₄	–	–	805	0.001
Biosphere	–	–	550	Biomass C	550	0.001
Pedosphere	1 700	Ca, Mg, Na ₂ , Fe (CO ₃)	1 500	Litter, soil organic matter	3 200	0.004
Hydrosphere	37 400	HCO ₃ ⁻ , CO ₃ ²⁻ , CO ₂ (aq)	1675	Dissolved organic C	39 075	0.052
Lithosphere	>60 000 000	Ca, Mg, Na ₂ , Fe (CO ₃)	15 000 000	Kerogens, Fossil fuelss	75 000 000	99.942

emissions. In addition, any processes able to sequester C into compartments other than the atmosphere—thus not interfering with the global climate—are of fundamental relevance.

Changes in annual C fluxes between the atmosphere, the hydrosphere and the terrestrial compartment (which includes the biosphere, pedosphere and lithosphere) in relation to increasing anthropogenic emissions of CO₂ from 1850 until present have been schematically represented by Houghton (2007), as shown in Fig. 1. The increase in atmospheric concentrations of CO₂ during this period has been smaller than expected—on the basis of total anthropogenic emissions—owing to the existence of mechanisms that have acted as sinks (Ciais et al. 1995; Schindler 1999). These sinks are located in both oceanic and terrestrial compartments and are basically of natural origin. The terrestrial compartment sink—calculated by difference, assuming a constant global C budget—is often referred to as “the residual C sink”. Inverse modelling predicts that most of this sink is allocated in temperate and boreal latitudes of the Northern Hemisphere (Bousquet et al. 1999), although recent studies suggest that tropical forests absorb much of the human-generated C present in terrestrial ecosystems (Stephens et al. 2007). The oceanic uptake of CO₂ may decrease if the temperature continues to increase following Henry’s law, although under current conditions, changes in ocean temperature will probably make a small contribution, as fluxes may be dominated by the greater changes in CO₂ concentrations. The role of the terrestrial ecosystem is even more uncertain (Reay et al. 2007).

2 Terrestrial ecosystem responses to changes in GHG concentrations and climate on a geological scale

Global temperatures may fluctuate (1) through internally-generated variability in the climate system, (2) through variability in natural forces (tectonics, relative position of continents, degree of continentality, volcanic aerosols, natural changes in GHG concentrations), and (3) as a result of human-induced changes (Juckes et al. 2007), with mineral weathering being the most effective mechanism for controlling atmospheric CO₂ and the Earth’s climate in the long term (Berner and Kothavala 2001; Gislason et al. 2008; Hansen et al. 2008). Climate simulations and empirical paleoclimate reconstruction can greatly increase our understanding of factors governing past climate change. On the basis of such reconstructions, we can infer that volcanism may explain a substantial fraction of temperature variability on decadal and

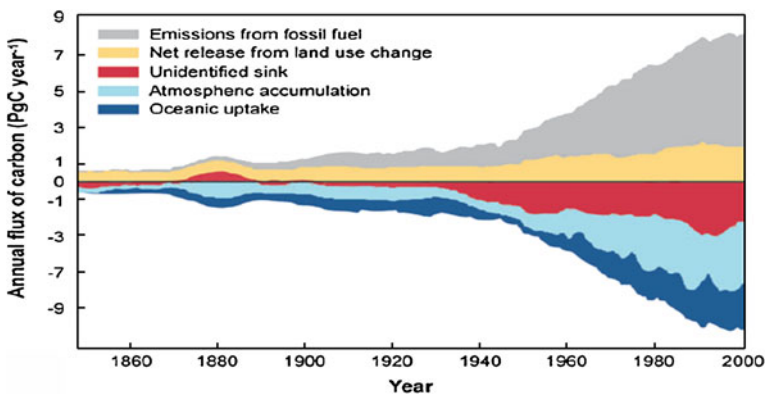


Fig. 1 Annual sources and sinks of C from 1850 to 2000 for a balanced C budget (total sources are balanced by total sinks). The unidentified sink is the residual terrestrial sink (Houghton 2007)

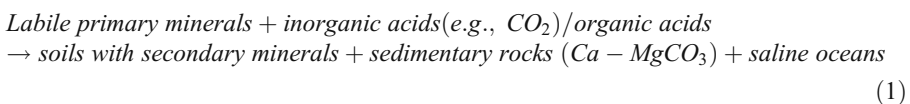
centennial timescales (Hegerl et al. 2006). The role of solar forcing is found to be larger for longer timescales (Zachos et al. 2001), whereas internal variability dominates anomalies on local and regional scales (Dima and Lohmann 2007; Zhang et al. 2007).

Analysis of gases trapped in ice cores from the last 600,000 years (IPCC 2007) confirms what was already demonstrated by Berner et al. (1983) for previous periods, showing a remarkably consistent periodicity between high concentrations of CO₂ during interglacial periods and low concentrations during glacial events. Major glacial-interglacial climate changes are induced by slow changes in the Earth's orbit, which mainly affect the distribution and amount of incident solar energy (Zachos et al. 2001; Hansen et al. 2008). The most effective feedback is the increase in atmospheric CO₂ as the climate warms up, with the CO₂ transfer mainly from oceans—partly due to the dependence of the solubility of CO₂ on temperature (Henry's law), and partly to oceanic mixing processes (Köhler and Fisher 2006). On longer time scales, however, changes in the total amounts of atmospheric CO₂ are mainly controlled by exchange with the solid Earth reservoirs, with orbital processes having only a minor effect on larger climate fluctuations (Zachos et al. 2001; Hansen et al. 2008). These exchanges mainly occur via (1) weathering of silicate rocks and pedological processes, leading to formation of carbonates and bicarbonate ions, and (2) burial of organic matter (France-Lanord et al. 1998; Berner 1999; Berner and Kothavala 2001), with the former predominating.

Changes in deep ocean temperatures during the Cenozoic era (the past 65.5 My) have been estimated from the oxygen isotopic composition of benthic foraminifera shells (Zachos et al. 2001; Hansen et al. 2008). The Earth has undergone periods with warmer temperatures than in the present interglacial period—such as in the late Paleocene (55 My), and the Oligocene-Miocene periods (30–20 My), with high CO₂ concentrations—estimated to reach values above 1,000 ppm in some cases (Zachos et al. 2001). High temperatures and high concentrations of CO₂ have also been estimated for previous periods, such as the Cretaceous (145 to 65 My). Moreover, the Earth has undergone extremely severe glacial periods, such as that referred to as “snowball Earth” (790 to 630 My), during which the Earth was mostly covered by ice. Under such circumstances, concentrations of atmospheric CO₂ may have decreased to values as low as 80 ppm, as estimated by modelling methods (Goddéris et al. 2007).

2.1 Mineral weathering and carbonation processes

During continental weathering [1], Ca and Mg carbonates form within bottom sediments via the reaction of atmospheric CO₂ with Ca and Mg silicates. This takes place after many intermediate processes including: (1) fixation of CO₂ via photosynthesis, (2) release of CO₂ from soil organic matter decomposition and microbial respiration, (3) reaction of carbonic and organic acids with primary silicate minerals, (4) conversion of CO₂ to HCO₃⁻ in the soil solution, (5) transport of HCO₃⁻ as counter ion from rivers to the ocean, and (6) precipitation of oceanic HCO₃⁻ as Ca-Mg carbonates on the ocean floor (Berner 1999). Under xeric or aridic conditions, carbonate ions can precipitate in soils to form secondary carbonates with Ca, Mg and, under the most alkaline conditions, with Na.



Plants accelerate mineral weathering—and therefore the removal of CO₂ from the atmosphere—through the secretion of organic acids by roots (Berner and Kothavala 2001).

Plant growth may also be hastened by an increase in atmospheric CO₂, thereby accelerating mineral weathering, although this may be restrained by nutrient availability (Reay et al. 2007). The latter may be particularly evident when the soils reach the residual system (Chesworth 1973), after complete weathering of the primary labile minerals (ferrallitic soils with geric properties, IUSS Working Group WRB 2006) (Fig. 2). Overall, warm conditions and high concentrations of CO₂ promote mineral weathering, soil formation, plant growth and root activity, if not limited by water or nutrient availability.

Mineral weathering was probably more accentuated in the young planet Earth, as basic and ultrabasic volcanic materials (komatiites) were much more abundant in the Earth's crust than at present, and these rocks are very rich in readily weatherable minerals. It is estimated that during the Pre-Cambrian period these materials were at least 30% more abundant than at present, mainly because of the greater internal heat of planet Earth (Veizer 1976). In general, the rock weathering and soil formation that occurred after the dominant rifting processes (e.g., the breaking up of Rodinia, Pangea I and II) have played a crucial role in mitigating CO₂ concentrations in the atmosphere on a geological timescale.

2.2 Photosynthesis, soil organic matter accumulation and carbonization

Paleoclimate evidence also indicates that during warm periods with high rainfall, water tended to accumulate in poorly drained, low lying areas, creating hydromorphic soils (Gleysols, Histosols) predominated by aquatic vegetation. In such ecosystems, huge amounts of necromass (organic detritus) accumulated under suboxic conditions (0–300 mV), and became buried beneath alluvial loadings of mineral sediments following heavy rains. This gave rise to alternate periods of biostaxia and resistaxia. The former coincided with periods of high rainfall and formation of organic matter-rich soils under hydromorphic conditions. The latter occurred under xeric or arid climatic conditions, with episodes of torrential rain that favoured the formation of large alluvial fans and caused fossilization of the former organic matter-rich soils and eventually—after processes of subsidence—the formation of coal. On top of the fresh sedimentary deposits, new processes of soil formation occurred in news cycles of biostaxia. Formation of coal has thus played an important role in controlling atmospheric concentrations of CO₂ on a geological timescale. Evidence of these cycles has been found in open coal mines, such as in As Pontes (NW Spain), where lignite deposits formed during the Oligocene-Miocene period as a result of

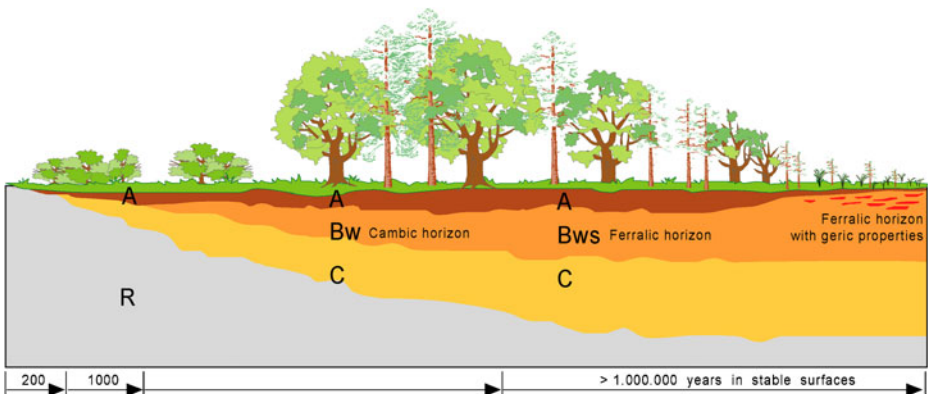


Fig. 2 Evolution of plants and soils towards equilibrium conditions in open systems

consecutive cycles of biostaxia-resistaxia produced by continuous fossilization of organic-rich hydromorphous soils beneath new alluvial sediments (Fig. 3a). Formation of siderite (FeCO_3) was favoured (Fig. 3b) within the mineral horizons of Gleysols (e.g., in the rhizosphere under high pCO_2), thus further promoting C sequestration.

3 Soil organic matter and C sequestration in natural ecosystems

3.1 Soil organic C and redox conditions

Soil organic matter ultimately originates from photosynthesis. The latter process takes place within chloroplasts under highly reduced conditions, with an estimated Eh value of ~ -600 mV. Redox conditions in soils fluctuate between -300 and $+900$ mV, most frequently in the range of $+300$ and $+500$ mV under oxic conditions (Fig. 4a). Fresh organic matter is thus the most reduced fraction in soil and hence the most thermodynamically unstable (Fig. 4b), followed by necromass and most of the soil organic matter, with organic quinone molecules being the most resistant to oxidation and metabolism (Bartlett 1999). As SOM decomposes, it acts as an electron pump supplying electrons to more oxidized species (Chesworth 2004). The thermodynamic stability of C forms varies depending on the different Eh-pH conditions (Fig. 4b); gaseous, bicarbonate and carbonate ionic forms, as well as carbonated salts in the solid phase, are the predominant stable forms under the environmental conditions of most soils. However, organic C stabilised by specific mechanisms (e.g., charcoal, mineral-bound OM) can remain as meta-stable forms in soils for hundreds to thousands of years (Kögel-Knabner et al. 2008).

Rates of organic matter decomposition in soils and the nature of intermediate compounds formed during this process vary depending on environmental conditions (temperature, water content, nutrient availability, etc.). The rates are fastest under oxidizing conditions, in the presence of free O_2 . In the absence of free O_2 , other electron acceptors enable decomposition of organic matter and release of CO_2 , and under more reduced conditions, release of CH_4 . The sequence of alternative electron acceptors (NO_3^- , MnO_2 , FeOOH , SO_4^{2-} , CO_2) follows the sequence of diminishing production of energy (at pH 7) that is used by the microbial population (Madigan et al. 2006). When CO_2 is used as an electron acceptor, CH_4 is released. As CH_4 is a GHG with a global warming

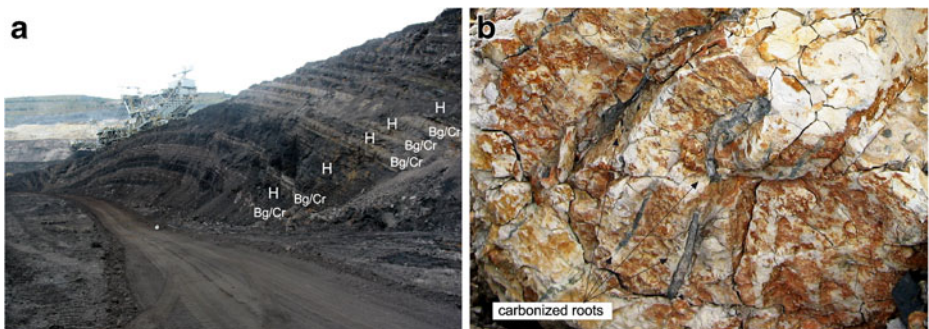


Fig. 3 Several details of As Pontes coal mine. **a** Sequence of Oligocene Paleogleysols and Paleohistolsols. The H horizons gave rise to lignite by diagenetic processes; **b** siderite formed in mineral gleyic horizons (Bg and Cg) close to roots of aquatic plants (*Typhas* sp. and *Juncus* sp.), which are later carbonized and pyritized through diagenetic processes

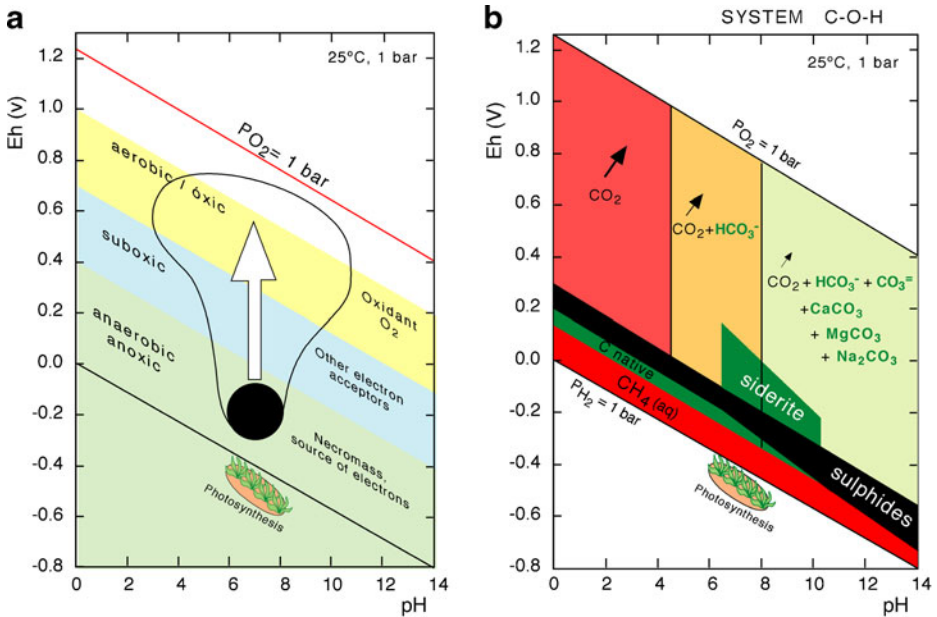


Fig. 4 a Eh-pH conditions: (1) during photosynthesis, (2) in fresh organic detritus, and (3) in soils under different redox conditions (anaerobic, suboxic, aerobic soils). The area included within the mushroom-shaped line corresponds to conditions prevailing in most soils in the planet Earth (modified from Chesworth 2004); b Eh-pH diagram of C species (CH_4 and native C fields; Brookins 1988; siderite field; Chesworth 2004)

potential 23 times greater than CO_2 —within a timescale of 100 years (IPCC 2007)—wetland restoration may not always result in net sequestration of C. In general, when Eh values are between 0 and 300 mV—which is common in most hydromorphic soils (Gleysols and Histosols)—only small amounts of CH_4 are released. Emissions of CH_4 also tend to be low in saltwater marshes, where SO_4^{2-} is abundant (Pelley 2008), as the latter buffers the redox potential. However, release of CH_4 is important at Eh values lower than -100 mV, as in some irrigated soils, i.e. poor in Fe(III), with high contents of OM and dedicated to rice crops, and also in OM-rich thionic sediments in estuarine systems (Otero et al. 2005, 2006).

Formation of siderite ($FeCO_3$) from Fe^{2+} produced by chemical and/or bacterial reduction of Fe(III) may occur at suboxic microsites under neutral/alkaline conditions, thus promoting inorganic C sequestration in reduced, CO_2 -rich environments. However, this process becomes impaired in the presence of excess dissolved H_2S , as formation of FeS and pyrite (FeS_2) prevails. Moreover, under xeric and aridic regimes, formation of secondary Ca, Mg and Na carbonates plays an important role in the sequestration of inorganic C in soils. The latter occurs when cations are supplied from outside the ecosystem (Nordt et al. 2000), via dust, fertilizers, or other soil amendments.

3.2 Organic C and stabilization mechanisms in soils

Conversion of the terrestrial surface to suboxic conditions with the aim of promoting organic C accumulation in soils—such as in Gleysols and Histosols—is, however, not a feasible option in large areas, although it may be a partial solution in certain situations, to the environmental benefit of wetlands. Most terrestrial land on Earth must remain oxidic to

ensure food and fibre supply, and therefore research should be focused on natural mechanisms of organic C stabilization that promote preservation of SOM under oxic conditions. There are numerous mechanisms whereby SOM is stabilized in soils (reviews in Six et al. 2002; Lützwow et al. 2006; Lützwow et al. 2008), although these are generally grouped into three main types: (1) selective preservation of recalcitrant compounds, (2) spatial inaccessibility to decomposer organisms, and (3) interactions between organic matter, minerals and metal ions. A recent study carried out by Marschner et al. (2008) indicated that there is very little evidence that selective preservation is a major mechanism for stabilization of SOM, except for black and fossil C. Long-term SOM preservation is, in fact, mainly due to interactions with mineral surfaces (Kögel-Knabner et al. 2008; Marschner et al. 2008), with turnover times of up to several millennia (Kögel-Knabner et al. 2008).

Three main types of functional surfaces on minerals provide bonding opportunities for SOM (Kögel-Knabner et al. 2008). The first type involves surfaces with single coordinated OH groups (e.g., in Fe and Al oxides, allophane, imogolite). This mechanism is especially important at pH levels at which these surfaces are positively charged—as generally occurs in Ferralsols and Nitisols—and when the degree of crystallinity is low (e.g., Andosols). The second type of surface includes charged siloxane surfaces (e.g., vermiculite, smectite). This mechanism may be particularly important in Vertisols, in which montmorillonite-type clays are abundant. The third type of surface includes uncharged siloxane surfaces (e.g., kaolinite), typical of highly weathered soils, such as Acrisols and Ferralsols.

The increased stability of organo-mineral associations against microbial decomposition is mainly related to the greater amount of chemical energy required for enzymatic cleavage of chemical bonds (Kögel-Knabner et al. 2008). The energy requirements are particularly high for SOM sorbed via ligand exchange mechanisms, while SOM bound by other type of interactions, such as van der Waals forces or cation bridging, is less resistant to mineralization (Mikkuta et al. 2007). Soil organic matter bridged with Ca cations—common in Chernozems, Kastanozems and Calcisols—thus has higher turnover times than SOM directly bound to reactive surface minerals. Aluminum cations, on the other hand, have been reported to bind to SOM through ligand exchange reactions (Scheel et al. 2008) and, therefore have a high chemical energy type of binding, which confers high resistance against microbial attack (Scheel et al. 2007). In addition, organo-Al complexes form flocs that may further contribute to SOM stability through spatial inaccessibility (Macías et al. 1988; Scheel et al. 2008). These organo-Al forms are common in all acid soils, but are especially abundant in Umbrisols, Acrisols, and Ferralsols.

Several mechanisms of SOM stabilization occur within a single soil profile—even within a single soil horizon—so that a sequence of organic C forms of different lability is encountered, in a continuum ranging from readily-mineralizable to recalcitrant forms. However, the potential of a particular soil to stabilize SOM is site and horizon specific (von Lützwow et al. 2008) and is usually related to the ratio between active C and reactive metals, thus favouring flocculation and stabilization as the ratio of C to metal decreases (Macías et al. 1988). In general, in the presence of large amounts of SOM, fewer organic ligands per organic molecule are bound to mineral surfaces, which results in a larger fraction of SOM susceptible to oxidation and microbial decomposition. This explains why the role of organo-mineral interactions in SOM stabilization increases with soil depth (von Lützwow et al. 2008). This can also be explained by the conceptual model of organo-mineral interactions proposed by Kleber et al. (2007). This model assumes a zonal structure for SOM accretions on mineral surfaces, with (1) a contact zone in which strong organo-mineral associations occur, (2) a hydrophobic zone, producing a bilayer model,

which results from the entropically driven shielding of the exposed hydrophobic moieties from sorbed organic compounds with other hydrophobic moieties from other amphiphilic molecules, and (3) a kinetic zone, where SOM is loosely retained by weaker types of bonding (e.g. cation bridging), and is thus more prone to microbial decomposition.

Within each pedoclimatic region, some specific soil types are able to accumulate more organic matter than their surrounding soils. This is the case with (1) humic Latosols in Brazil, (2) “Tierras negras” (Spanish for black soils) and Tirs, i.e. soils with vertic properties, which occur in Southern Spain and North Africa, respectively, (3) Chernozems (Russian for black soils) in the Russian steppes, (4) Andosols in volcanic areas (Ando is Japanese for black soils), and (5) ali-humic Umbrisols (former Atlantic Rankers) and, in general, soils with a predominance of organo-Al complexes (Fig. 5). These organic matter-rich soils differ in terms of the dominant mechanism of organic C stabilization and each represents a reference type of soil to mimic if accelerated C sequestration in soils under similar pedoclimatic conditions is to be achieved. Knowledge of mechanisms of SOM stabilization in “black soils” under different pedoclimatic conditions may thus provide us with the key for accelerating human-induced organic C sequestration in soils.



Fig. 5 Some natural soils with stable C forms and potentially useful as models for the elaboration of Technosols derived from waste. **a** ali-humic Umbrisol (Galicia, NW Spain); **b** alu-Andic Andosol (Galicia; NW Spain); **c** umbric Ferralsol (Minas Gerais, Brasil); **d** rendzic Phaeozem, (Eslovenia), **e** grumic Vertisol (Sevilla, Spain); **f** albic Podzol (Galicia, Spain)

3.3 Losses of SOM in terrestrial ecosystems due to anthropogenic activities

The amount of SOM present in soils is the result of a dynamic equilibrium between inputs and outputs (Lal 2004a). Agricultural and forestry activities (deforestation, intensive tillage, overgrazing, etc.) involve an important level of C transfer from biomass and soils to the atmosphere and have led to the depletion of C stocks in biomass and in soils (Guo and Gifford 2002; Murty et al. 2002). Even in areas under high rainfall ($> 1,500 \text{ mm yr}^{-1}$) and dominated by Andosols, land use change from natural forestry to agriculture has induced a loss of up to 50% organic C (Verde et al. 2005). Losses are even more drastic under dry conditions, such as occur in a large area of the Iberian Peninsula, where organic C losses of more than 60% have been reported (Macías and Camps Arbostain 2009). This, together with other degradative processes common to these xeric and aridic areas (e.g. erosion), explains the almost complete disappearance of mollic horizons in the Mediterranean region. Losses of soil organic C in tropical regions have been reported to reach as high as 75% (Lal 2004a).

Low organic matter contents in soils favour erosion processes, which further deplete the amount of organic C and soil quality. A study of Spanish soils (Macías and Camps Arbostain 2009) indicates that the amount of organic C stored in the surface horizon per unit cm of soil ranges from 4–8 t C ha⁻¹cm⁻¹ in temperate areas under high annual precipitation ($> 1,200 \text{ mm}$), to 3–4 t C ha⁻¹cm⁻¹ in temperate areas with moderate annual precipitation (800–1,200 mm), and to 1–3 t C ha⁻¹cm⁻¹ in Mediterranean climate areas ($< 600 \text{ mm}$). These values decrease to $< 2 \text{ t C ha}^{-1}\text{cm}^{-1}$ (in moist areas) and to $< 1 \text{ t C ha}^{-1}\text{cm}^{-1}$ (in dry areas) in degraded soils. Therefore, the loss of only one cm of soil represents the loss of huge amounts of organic C if large areas are affected. This does not necessarily mean that all C loss is transferred to the atmospheric compartment, as part of the C may accumulate in downstream sediments (Macías and Calvo de Anta 1988; Page et al. 2004). Nonetheless, the quality of the soils diminishes, as does the capacity of the soils to sustain plant growth and thus, to sustain life. The loss of soil organic C associated with soil loss may be reversed by restoring soils and favouring soil formation. Therefore, any strategy focused on promoting soil conservation, soil restoration and soil formation will not only favour the accumulation of organic C, but will also ameliorate other environmental functions provided by the soils (“win-win strategy”; Robert 2001; Robert and Saugier 2004).

The implementation of soil conservation and soil regeneration strategies must thus be a priority in order to (1) limit soil erosion, (2) accelerate soil formation, and (3) enhance the input of C and nutrients to the soil to improve fertility. Sustainable agricultural and forestry techniques must be focused on fighting climate change. The adoption of restorative land use and recommended management practices for agricultural and forest soils may greatly increase soil C sequestration (Lal 2004b). The latter author lists a series of general recommended practices (Table 2) for improving soil organic carbon sequestration, which should be adapted to site-specific conditions (Lal 2004b).

4 Technologies for mitigating high atmospheric CO₂ concentrations based on natural pedogenic processes

Organic wastes are important sources of GHG to the atmosphere. In recent decades, the amount of waste produced by humans has increased greatly ($> 1,000$ millions of tonnes of exogenous organic waste produced by the EU; van Camp et al. 2004). According to Douglas (1966), “waste is matter out of place”, and therefore for correct reuse and recycling

Table 2 List of traditional methods and alternative management practices intended to increase SOM (modified from Lal 2004b)

Traditional methods	Recommended management practices
1. Biomass burning and residue removal	Residue returned as surface mulch, biochar
2. Conventional tillage and clean cultivation	Conservation tillage, no till and mulch farming
3. Bare/idle fallow	Growing cover crops during the off-season
4. Continuous monoculture	Crop rotations with high diversity
5. Low input subsistence farming and soil fertility mining	Judicious use of off-farm input
6. Intensive use of chemical fertilizers	Integrated nutrient management with compost, high quality biosolids and nutrient cycling, biochar, precision farming
7. Intensive cropping	Integrating trees and livestock with crop production
8. Surface flood irrigation	Drip, furrow or sub-irrigation
9. Indiscriminate use of pesticides	Integrated pest management
10. Cultivating marginal soils	Conservation reserve program, restoration of degraded soils through land use change and the use of Technosols

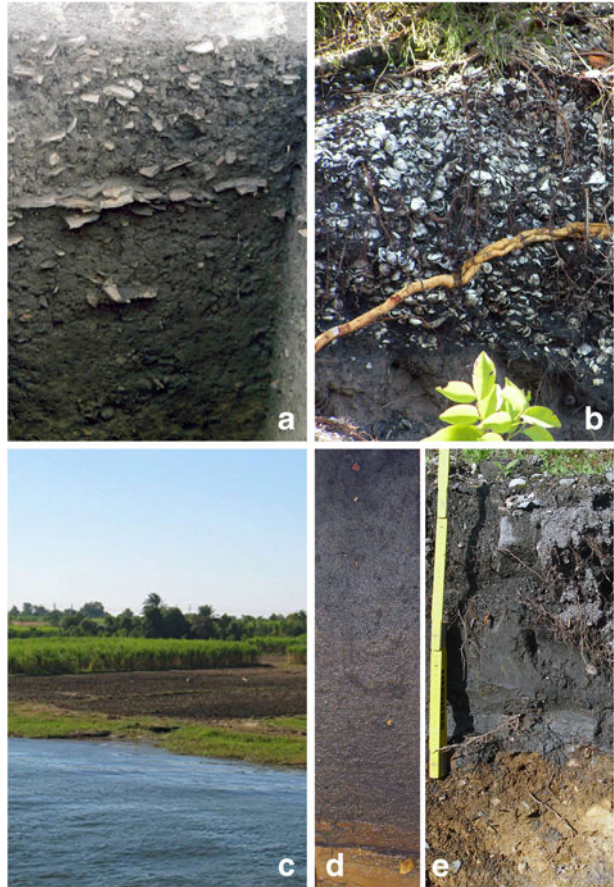
of waste products, waste components should be safely reincorporated into their biogeochemical cycles. New methods and technologies should be developed to allow this to occur in a rapid, sanitary and environmentally-sound manner. Undoubtedly many of these objectives could be attained through soil systems. However, this should be carried out by following a procedure compatible with preservation of the main soil functions and the quality of the terrestrial ecosystems involved.

Within the context of mitigating climate forcing, negative solutions such as waste disposal and incineration should be discounted. Composting is a suitable option for eliminating pathogens and reducing the volume of waste. However, it is not a means of sequestering C and recovering nutrients *per se*, as considerable amounts of C and N—especially the most labile forms—are lost in the composting process, and continue to be lost after addition of compost to soils as an amendment (Macías et al. 2006). Composting and humification are not identical processes. Both are biological processes, but in composting, organic matter is metabolised under dominant oxic conditions, in the absence of mineral components. In contrast, humification occurs in the presence of mineral fractions that are highly heterogeneous in size and surface charge, and within a porous system that induces a wide range of Eh values. Therefore, SOM becomes stabilized through different mechanisms (e.g., interaction with mineral particles), which increase its residence time in soils. For promotion of C and N sequestration, natural mechanisms of SOM stabilization in soils must be imitated to increase the residence time of SOM originating from waste material.

4.1 Preparation of tailor-made Technosols from high quality waste material

Ancient cultures attributed maintenance of the fertility of cultivated soils to the periodic addition of organic and inorganic amendments (anthropogenic materials). In fact, anthropogenic soils have been formed throughout human history and in certain cases, have produced soils that are more fertile, with a higher productive capacity and of better quality than natural soils present under the same pedoclimatic conditions (Sombroek et al. 1993). This is true for many soils defined as “Plaggen soils” in coastal areas of central and northern Europe, and for the soils known as “Terra Preta do Indio”, in Brazil (Fig. 6).

Fig. 6 Some anthropogenic soils with stable C forms, and of potential use as models for elaborating Technosols from waste. **a** Terra Preta (Amazonia, Brazil; courtesy: Wenceslau Gerales Teixeira); **b** Sambaqui (Sao Paulo, Brazil); **c** calcic Fluvisol (Tebas, Egypt); **d** Plaggen soil (The Netherlands); **e** tailor-made alu-andic Technosols in the restored Touro mine (Galicia, Spain)



Anthropogenic materials—also termed anthropogeomorphic materials (FAO 1998) and considered as artifacts (IUSS Working Group WRB 2006)—are defined as those unconsolidated residues derived from anthropogenic activities, with similar characteristics to the geologic and biogenic components of the soils, which may act as fresh parent material, and which under the influence of soil forming factors, may originate new soils (Dudal et al. 2002).

The production of Technosols (soils whose properties and pedogenesis are dominated by their technical origin: IUSS Working Group WRB 2006) from anthropogenic materials may be an economically feasible method of reusing waste products and of returning the elements that they contain to their biogeochemical cycles. Technosols are usually formed as a result of environmentally unsound practices, such as the abandonment of mining or urban waste, but can also be produced rationally with the aim of benefitting the environment. Known natural mechanisms of SOM stabilization can be reproduced when suitable types of anthropogenic materials are mixed to produce tailor-made Technosols (Macías et al. 2007; Yao et al. 2009a,b).

Tailor-made Technosols must fulfill the environmental and productive functions of natural soils. Environmental problems associated with the use of Technosols may be prevented if (1) the characteristics of the materials used, as well as how the constituent

mixtures evolve over time, are well known and suitable for such purposes, and (2) the characteristics of the final products obtained are suited to the pedoclimatic conditions and to uses of the area to be restored (Xunta de Galicia 2008). By producing such soils we aim to (1) simultaneously solve problems associated with waste management and with the restoration of degraded or contaminated soils, in an affordable and environmentally sound manner, (2) eliminate or greatly reduce the impacts of waste products in the most sensitive systems (water, air and biota), and (3) stabilize organic C forms in soils and biomass. Examples of the benefits of the use of tailor-made Technosols in soil restoration are shown in Fig. 7, i.e. the changes in an abandoned Cu mine rich in pyrite (Touro, NW Spain) after the step-wise addition of Technosols (Macías-García et al. 2009a, b). These results show that the management of waste products that mimic mechanisms of organic C stabilization in natural soils and their incorporation in the soils following good practices represents an important means of mitigating atmospheric CO₂ emissions, through stabilization of the organic C present in the waste as well as promotion of plant growth and soil formation.

4.2 Carbonization and biochar

Carbon sequestration via conversion of biomass (short-term biodegradable carbon) into a more durable form (e.g., charcoal) has created a great deal of interest within the framework of global climate change (Seifritz 1993; Lehmann et al. 2006; Lehmann 2007; Titirici et al. 2007, Lehmann and Joseph 2009). Coalification has occurred naturally as a process for



Fig. 7 Use of different Technosols derived from wastes in the recovery of hyperacidic soils and waters in the restored Touro mine (Galicia, NW Spain; Macías-García et al. 2009a, b)

mitigating high concentrations of atmospheric CO₂ in geological terms, while the large-scale use of coal—as well as that of other geological sources of C—from the mid 20th century onwards has produced the inverse effect in a very short period of time. Imitating nature as regards sequestering carbon through the conversion of biomass into recalcitrant carbon forms (e.g., charcoal) in order to reverse the present anthropogenic C flux should therefore not be disregarded.

Much attention is currently being paid to obtaining charcoal from slow-pyrolysis processes, with the final aim of adding the material to soils as a C sink and enhancing soil properties. In this context, the charred material is denoted biochar (Lehmann et al. 2006; Lehmann and Joseph 2009). Carbonization uncouples the atmospheric and terrestrial carbon cycle, as it removes carbon from the cycle in a form that can remain stable for hundreds to thousands of years. However, the recalcitrance of C is highly dependent on the production conditions, as well as on type of feedstock (Krull et al. 2009). Biochars produced above 500°C are predominated by condensed aromatic C—the fraction most recalcitrant to microbial decay—unlike those produced at lower temperatures. Low-temperature pyrolysis, on the other hand, favours the recovery of carbon and also of several nutrients that otherwise are lost when pyrolysed at high temperatures. Biochars produced at low temperature may also have stronger interactions with soil mineral particles and enhanced aggregate formation (Brodowski et al. 2005).

As in the production of Technosols, carbonization helps reduce waste and return elements to their biogeochemical cycles. The nutrient contents of biochar largely depend on the type of feedstock (Gundale and deLuca 2006; Chan et al. 2008), whereas the availability of nutrients in biochars depends on the elements involved. While N is mostly present as heterocyclic N (Knicker et al. 1996), and thus not considered as readily available, P is mainly found in the ash fraction, with pH-dependent reactions controlling its solubilisation (deLuca et al. 2009), and K is generally available to plants. The surface area and porosity of biochars are generally high (Downie et al. 2009) (Fig. 8), and a large variable surface charge can be generated by pre- or post-processing in the pyrolysis plant and/or weathering once in the soil (Cheng et al. 2006; Liang et al. 2006). All this confers biochars with the potential to increase water retention as well as cation exchange capacity, once they are added to soils.

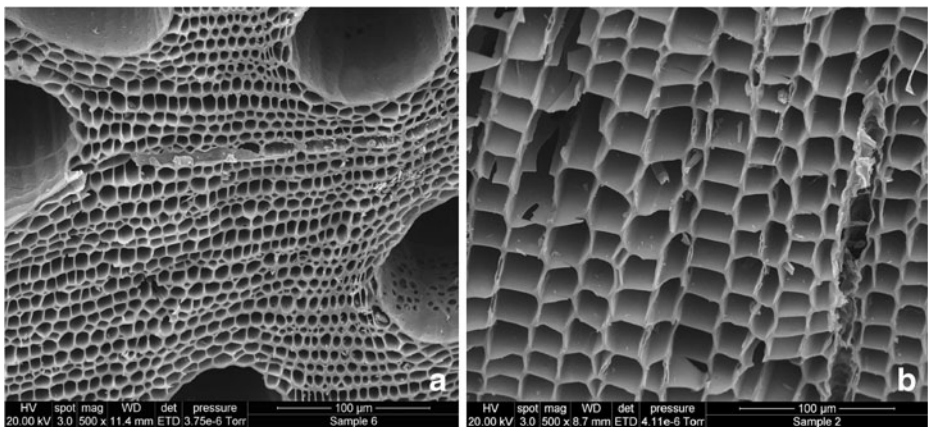


Fig. 8 SEM image of biochar **a** from eucalyptus bark, and **b** from pine bark

The simultaneous addition of biochar and fertilizers to highly weathered soils has been shown to have a synergic effect on crop production (Chan et al. 2007; Steiner et al. 2007; Chan et al. 2008; Novak et al. 2009), further reducing the need for fertilizers. Increasing soil fertility also increases C sequestration by promoting plant and root growth. However, while the positive effects of biochar on soils and plant growth have been shown in unfertile tropical soils—Terra Preta do Indio being the most notorious example—their effects on more fertile temperate soils have still to be demonstrated. The effect of biochar on native organic matter is still unclear, as it may promote microbial growth by providing microorganisms with a highly suitable habitat to colonize (Thies and Rillig 2009), which may induce the decomposition of labile SOM (Wardle et al. 2008). However, because of its high surface area, biochar may promote the stabilization of organic molecules through some of the mechanisms described above.

Each biochar has unique properties and different soils may respond differently to addition of biochar, and thus specific types may have to be created for different soils and crops to ensure that sustained functions of soils and ecosystems are preserved. The role of biochar as a strategy for mitigating climate change may become particularly important if the effects on reducing N₂O emissions are clear (van Zwieten et al. 2009), as the global warming potential of this GHG on a timescale of 100 years is 298 times greater than that of CO₂ (IPCC 2007). Greater efforts are therefore required to understand the role that biochar may play in the future.

5 Conclusions

Faced with the present situation of climate change, actions derived from the Earth's own experience may be taken to sequester C during periods when high atmospheric CO₂ concentrations occur. Understanding the mechanisms that have operated in the Earth under such conditions may enable similar mechanisms to be applied in the fight against climate change. Such natural mechanisms include increased biomass production, rapid weathering of labile minerals and increased speed of soil formation, conversion of CO₂ to bicarbonate and carbonate ions and the formation of carbonate salts in ocean deposits, increased amounts of organic matter and increased residence time in soils through organo-mineral interactions, formation of siderite and coal deposits in buried hydromorphic soils, and precipitation of carbonates in xeric and aridic soils.

As we learn from examining and studying such processes and nature, we can apply this knowledge to reduce C emissions and increase C sequestration in solid, liquid and biotic phases. This can be achieved by favouring the growth of biomass, establishing wetlands under non-methanogenic conditions; promoting and facilitating carbonation processes; reducing erosion and favouring pedogenesis; increasing the concentration of readily-weatherable labile components in surface systems; developing more stable humiferous horizons; recovering degraded or contaminated soils, and managing waste by use of systems that minimize GHG emissions. Amongst the options described, two fulfil many of the desired objectives: production of Technosols and production of biochar, both derived from waste.

The production of Technosols can be tailor-made to imitate those soils with highest C contents and residence times, and the mixtures produced can be used in soil restoration and biomass production. Biochar may be used to promote the fertility and productivity of soils by increasing the cation exchange capacity, water retention, aggregation and porosity, while also maintaining the organic C in the soil during long periods. Biochar may also be one of

the ingredients used to formulate Technosols, by incorporation of such material with suitable characteristics and in appropriate proportions for the type of Technosol desired in each context. All these technologies should be supported by policies that regulate and promote the enhancement of C sinks, in addition to those aimed at reducing GHG emissions.

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