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Controls on black carbon storage in soils

Claudia I. Czimczik¹ and Caroline A. Masiello²

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[1] Fire-derived black carbon (BC: charcoal and soot) has been thought to be a passive player in soils, contributing to the refractory soil organic carbon (SOC) pool, but playing no role in pedogenesis and regional short-term carbon cycling. This model, however, is at odds with recent results on the role of charcoal in soil fertility and its detection in the dissolved organic carbon (DOC) pool. For example, if BC simply accumulated passively in soils, its pattern of accumulation should match a simple model correlating fire frequency to BC storage. Instead, soil type, climate, biota, and land use practices all appear to play roles in controlling whether BC accumulates or is lost from soils. We summarize current knowledge of BC-soil interactions and construct a new paradigm describing the controls on BC storage in soils. We reconcile the refractory-labile BC paradox by proposing a model where BC storage is controlled by (1) fire frequency, (2) ecosystem presence or absence of aromatic precursor carbon and appropriate combustion conditions, (3) biological or physical mixing to remove BC from the soil surface, where it is vulnerable to combustion in future fires, (4) the presence or absence of soil mineral fractions able to sorb BC into the long-term stable carbon pool, and (5) the presence of microbial communities capable of degrading aromatic carbon. We also recognize that soil BC/SOC ratios are strongly influenced by land-use practices and add (6) human activities as a final control.

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1. Introduction: The Paradox of Refractory-Labile BC

[2] One remainder of fire in the Earth's soils is burned biomass, also called 'black carbon' or BC. This material is best represented as a physical and chemical 'combustion continuum' [Masiello, 2004]. BC can account for up to 45% of SOC in frequently burned agricultural soils [Skjemstad *et al.*, 2002]. BC is ubiquitously present in the Earth System, and its existence in long-term carbon cycle reservoirs, including sedimentary rocks, has led to the assumption that BC is inherently refractory. However, increasing evidence suggests this perspective is imperfect.

[3] Existing BC literature reveals both refractory and dynamic roles for BC in soils. Its refractory behavior in soils has been well documented via radiocarbon (¹⁴C) analysis, ¹³C NMR and electron microscopic examinations of refractory soil fractions (see below). Conversely, its ability to act as a labile, dynamic part of the soil system has been demonstrated by incubation experiments, field measurements of loss rates, and its presence in the soil DOC pool. We argue that the refractory-labile BC paradox can be resolved via a model of BC in soils which takes into

account the physical, chemical, and biological capabilities of soils to interact with BC. Specifically, we hypothesize that the storage of BC in soils is controlled by (1) fire frequency (production), (2) precursor carbon aromaticity and combustion conditions, (3) soil turbation, (4) soil mineral reactivity, and (5) the presence of microbial communities capable of degrading aromatic carbon. We also recognize that soil BC/SOC ratios are strongly influenced by land-use practices, making (6) human activities an additional system control.

1.1. Refractory BC: A Long-Term Carbon Sink in Soils

[4] The soil literature is rich with data showing that at least under some conditions, BC can be very difficult to decompose. ¹⁴C measurements are frequently used to assess SOC refractivity, and ¹⁴C measurements of charcoal in soils routinely reach thousands and sometimes tens of thousands of years [Gavin *et al.*, 2003; Gouveia *et al.*, 2002; Pessenda *et al.*, 2001]. When bulk SOC ¹⁴C data is available to complement BC ¹⁴C data, charcoal ages significantly exceed the ages of the carbon in the host soil horizon, confirming that BC is more difficult to decompose than non-fire-altered organic matter, both in the case where macroscopic charcoal particles were hand-picked prior to isotopic measurement [Pessenda *et al.*, 2001], and in the case where the BC fraction was separated via UV oxidation prior to ¹⁴C measurement [Schmidt *et al.*, 2002].

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[5] BC has been observed to be a major component of the most chemically refractory (and presumably stable) components of SOC. For example, high-resolution transmission electron microscopy (HRTEM) on the refractory organic fraction of two soils (the 0- to 30-cm horizon of an acid, loamy forest soil from SW France, and the 300- to 310-cm horizon of a ferralic Arenosol from Congo) showed a substantial, but unquantitated contribution from two types of BC molecules, potentially distinguishing between nano-scale charcoal and soot [Poirier et al., 2000, 2002]. BC has also been observed via ^{13}C NMR and scanning electron microscopy (SEM) to be a major component of the chemically resistant fractions of fire-prone soils [Skjemstad et al., 2001; Krull et al., 2006].

[6] It is clear that the lifetime of BC in soils can be much longer than that of other forms of organic matter [Forbes et al., 2006]. Thus in ecosystem or soil C models, BC is usually represented as a inert pool [Skjemstad et al., 2004].

1.2. Dynamic BC

[7] Although ample evidence exists that BC can be a refractory component of soils, it is also becoming clear that BC degrades in the natural environment. We know this directly via measurements of biological, chemical and physical BC degradation. We also know this indirectly from mass balance calculations, which point to the creation of implausibly large BC soil pools without a natural sink mechanism [Masiello and Druffel, 2003; Schmidt et al., 2003].

1.2.1. Degradation of BC

[8] The potential for biological degradation of BC has been documented by multiple studies. Graphite is degraded by microorganisms isolated from soil and wood in the presence of other nutrients [Shneour, 1966]. More recently, Baldock and Smernik [2002] observed BC decomposition in lab-produced charcoals exposed to a microbial inoculum, showing BC decomposition decreased as a function of increasing charring temperature. Hamer et al. [2004] incubated BC in the presence and absence of glucose for 60 days, and showed that the addition of glucose caused an increase in 800°C charred wood decomposition rates from 0.3% to 0.6%. A similar glucose addition increased the decomposition rate of 350°C charred corn from 0.6% to 1.2%. Giving further evidence of a microbial mechanism for charcoal degradation, Hockaday [2006] showed that when fresh charcoal is exposed to microbial enzymes, copious humic acids are produced (70% more humics than enzymatically untreated charcoal). Then, using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) Hockaday et al. [2006] identified condensed aromatic ring structures (CARS) within the DOC released from charcoal-rich soils. Charcoal within the Hockaday et al. [2006, 2007] soils were thoroughly penetrated with fungal hyphae, suggesting a fungal role in BC degradation.

[9] BC is also degraded chemically in the natural environment. Laboratory studies of the atmospheric behavior of soot show rapid surface hydroxylation followed by solubilization when exposed to low levels of ozone [Chughtai et al., 1991; Smith and Chughtai, 1996]. This process has been

shown to create aromatic polyacids [Decesari et al., 2002], which have been detected in the atmosphere [Graham et al., 2002]. It is not a stretch to assume that the aromatic backbone of charcoal will experience similar environmental chemical oxidation.

[10] In addition, combustion during recurring fires has been suggested as a BC loss mechanism, especially in the boreal forest region [Czimczik et al., 2005; Ohlson and Tryterud, 2000]. In high-light and arid environments such as savannas, UV-oxidation plays an important role in organic matter degradation [Gallo et al., 2006] and may also contribute to BC loss.

[11] Besides microbial and chemical loss processes, BC can also be removed from soils physically via pulverization by soil processes followed by erosive and hydrologic transport. In some Vertisols, pulverization of BC particles by shrink-swell dynamics has been observed [Gouveia and Pessenda, 2000]. Like SOC, BC concentrations were found to reach a maximum in (sombrio) Bt horizons [Gouveia et al., 2002]. In other Vertisols, however, BC was either uniformly distributed within the mineral soil and well stored, or only existed on the soil surface in smaller quantities [Skjemstad et al., 2001]. Vertical redistribution of BC in soil, together with degradation, could also explain the rapid loss (<50 years) of BC from the surface soils of savanna systems [Bird et al., 1999; Dai et al., 2005].

[12] Recent work suggests that BC is mobilized from soils via erosion [Rumpel et al., 2006a] and in at least some cases, can be preferentially mobilized relative to bulk organic matter [Rumpel et al., 2006b]. These data on BC mobilization point to the delivery of BC to rivers.

[13] Although no measurements of BC in fluvial sediments yet exist, evidence does point to, first, the presence of BC in river sediments, and second, the preferential transport of BC by hydrologic processes. Guo et al. [2004] measured BC in sediments collected from the mouths of a range of Arctic rivers and found BC to be $9 \pm 4\%$ of total organic carbon. They measured BC via a thermal technique which has been shown to measure about 50% of soot and to exclude almost all forms of charcoal [Nguyen et al., 2004; Hammes et al., 2007], making their 9% value likely a significant underestimate. Evidence also points to the hydrologic mobilization of BC. Rumpel et al. [2006b] have shown that BC is enriched relative to total SOC throughout the process of erosion in a tropical mountain ecosystem subjected to slash-and-burn agriculture. In this system, BC moves more efficiently than other forms of SOC to topographic lows. This strongly implies that BC will also be efficiently moved into water bodies, perhaps even at a higher rate than other forms of SOC.

1.2.2. BC as a Component of the Earth's DOC Pools

[14] BC is solid when produced, so its detection in the Earth's DOC pools is also evidence of its dynamic role in the soil system. We now know that BC is present in some, but not all, soil and river DOC pools. The first implicit evidence for the presence of BC within DOC came from ^{14}C measurements of marine sediment samples [Masiello and Druffel, 1998]. Evidence for BC's reactivity is becoming clearer with the detection of combustion-derived, soluble compounds in riverine DOC via FT-ICR mass spectrometry

[Kim *et al.*, 2004; Kramer *et al.*, 2004; Hockaday *et al.*, 2006]. The position of these soluble aromatics on a van Krevelen diagram rule out noncombustion sources [Kim *et al.*, 2003] making possible a compelling argument that some rivers have a significant 'black' DOC pool. Black DOC has also been detected in soil DOC [Hockaday *et al.*, 2006]. Hockaday *et al.* [2006, 2007] shows that over ~100 years, charcoal BC leaches aromatic, carboxylated fragments, leaving behind an increasingly aromatic molecular frame closely associated with the soil mineral matrix.

1.2.3. BC is Pedogenically Active

[15] Several studies indicate that BC can play an important role in the fertility of soils when present in large quantities [Glaser *et al.*, 2001]. BC has been identified as a major component of the SOC pool of the most fertile and heavily farmed soils on earth, such as temperate grassland soils [Glaser and Amelung, 2003; Golchin *et al.*, 1997a, 1997b] and the Terra preta de Indio soils of the Amazon region [Glaser *et al.*, 2001]. This fertility enhancement occurs both because of the physical benefits of incorporating a low-density, porous material within a clay matrix, and also because of the chemical effects of adding a material with both nonpolar and charge-active regions.

[16] BC strongly sorbs many other compounds. It has been shown that the distribution of heavy metals (e.g., Pb [Hiller and Brümmer, 1997]) or organic pollutants (such as polycyclic aromatic hydrocarbons (PAHs) [Gustafsson and Gschwend, 1998; Yu *et al.*, 2006]) in soils and sediments correlates more strongly with the distribution of BC than SOC. The layer of BC produced in fires has an adsorbing capacity resembling activated carbon, allowing the trapping of compounds physically within BC's fine pores [Yu *et al.*, 2006]. BC also absorbs organic carbon rich in functional groups [Kaiser *et al.*, 2000], a process which is made possible by the presence of oxidized functional groups (carboxylic and phenolic functionalities) on the surface of BC particles [Glaser *et al.*, 2002; Lehmann *et al.*, 2005].

[17] Together, sorption of ions and organic carbon and the presence of oxidized functional groups have been shown to improve soil fertility, for example, by lowering Al toxicity and increasing cation exchange capacity [Glaser *et al.*, 2001; Liang *et al.*, 2006]. BC clearly interacts with both soil organic and inorganic constituents and, like other organic carbon forms, shapes the pedogenic development of its host soil matrix.

2. Controls on the Formation of BC-Rich Soils

[18] Fires leave behind about 3% of initial ecosystem carbon as BC, regardless of the type of vegetation burned [Forbes *et al.*, 2006]. However, the accumulation of BC in soils does not appear to be only a function of BC production. Soils for which high amounts of BC are reported are Mollisols under prairie/steppe vegetation and Terra Preta under tropical rain forest. These systems do burn, but fires are also (or more) frequent in boreal forests and savannas; no soils with high BC contents have been reported from these systems.

[19] We propose that the paradox of refractory-labile BC can be resolved via a conceptual model of BC production,

storage, and loss. We hypothesize that the creation of BC-rich soils requires (1) fire to produce BC; (2) aromatic precursor carbon and appropriate combustion conditions; (3) biological or physical mixing to remove BC from the soil surface, where it is vulnerable to combustion in future fires; (4) a chemical protection mechanism within mineral soil horizons to prevent loss of BC within the soil DOC fraction; and (5) the absence of efficient BC decomposers. We summarize this concept for soils of different climatic regions in Figure 1. Additionally, soil BC/SOC ratios are affected by land use and management practices. Because of this, (6) human behavior is a final control on the production of soils with high aromaticity.

2.1. BC Accumulation Requires Frequent Fires, Aromatic Carbon Precursor Biomass, and/or Appropriate Combustion Conditions

[20] BC storage in soils is a function of combustion conditions which act to control BC production rates. Important combustion variables include fire frequency, fuel type, fire type, and fuel source chemistry. High fire frequencies can increase BC concentrations in the mineral soil [Czimczik *et al.*, 2005; Dai *et al.*, 2005]. Production rates of BC are also a function of fuel type: Fuels with high lignin-to-cellulose ratios yield more BC than fuels high in cellulose [Czimczik *et al.*, 2003, 2002]. From this, we expect that in forest ecosystems crown fires produce more BC than ground fires. BC production is also higher in high-energy fires (flaming combustion: 300°–500°C, > 15 vol.-% O₂) than under low-oxygen conditions (smoldering combustion: <300°C, 5–15% O₂) [Gleixner *et al.*, 2001]. High-energy grassland fires produce relatively large amounts of BC, although the fuel is lower in aromatic precursors than wood [Kuhlbusch *et al.*, 1996]. Combustion in forest fires, on the other hand, can also be dominated by fuel low in aromatic precursors (bryophytes) rather than by wood, resulting in low BC yields [Czimczik *et al.*, 2003].

2.2. BC Accumulation Requires Mixing to Depth to Protect From Future Fires

[21] Production of BC via fire is necessary to cause BC accumulation in soils, but this criterion is not sufficient. To protect BC from oxidation in future fires and dispersion via erosion, newly produced BC must be moved to depth in soils. We hypothesize that this occurs in soils such as Alfisols and Mollisols via bioturbation (earthworms and burrowing rodents). In Vertisols, the extreme shrink-swell capacity of the soils physically turbates BC to depth.

[22] The clearest example of fire-prone systems which do not store BC are boreal forest soils [Czimczik *et al.*, 2005; Preston and Schmidt, 2006]. Boreal forest soils lack either burrowing organisms and/or the physical mixing mechanisms needed to move BC into the mineral soil and protect it from oxidation by the next fire. Boreal soils are also biologically poor candidates for BC storage. Saprophytic, potentially BC-degrading fungi have been shown to dominate boreal forests over mycorrhizal fungi following fire (K. Treseder, personal communication, 2005), opening a second BC loss valve within this system.

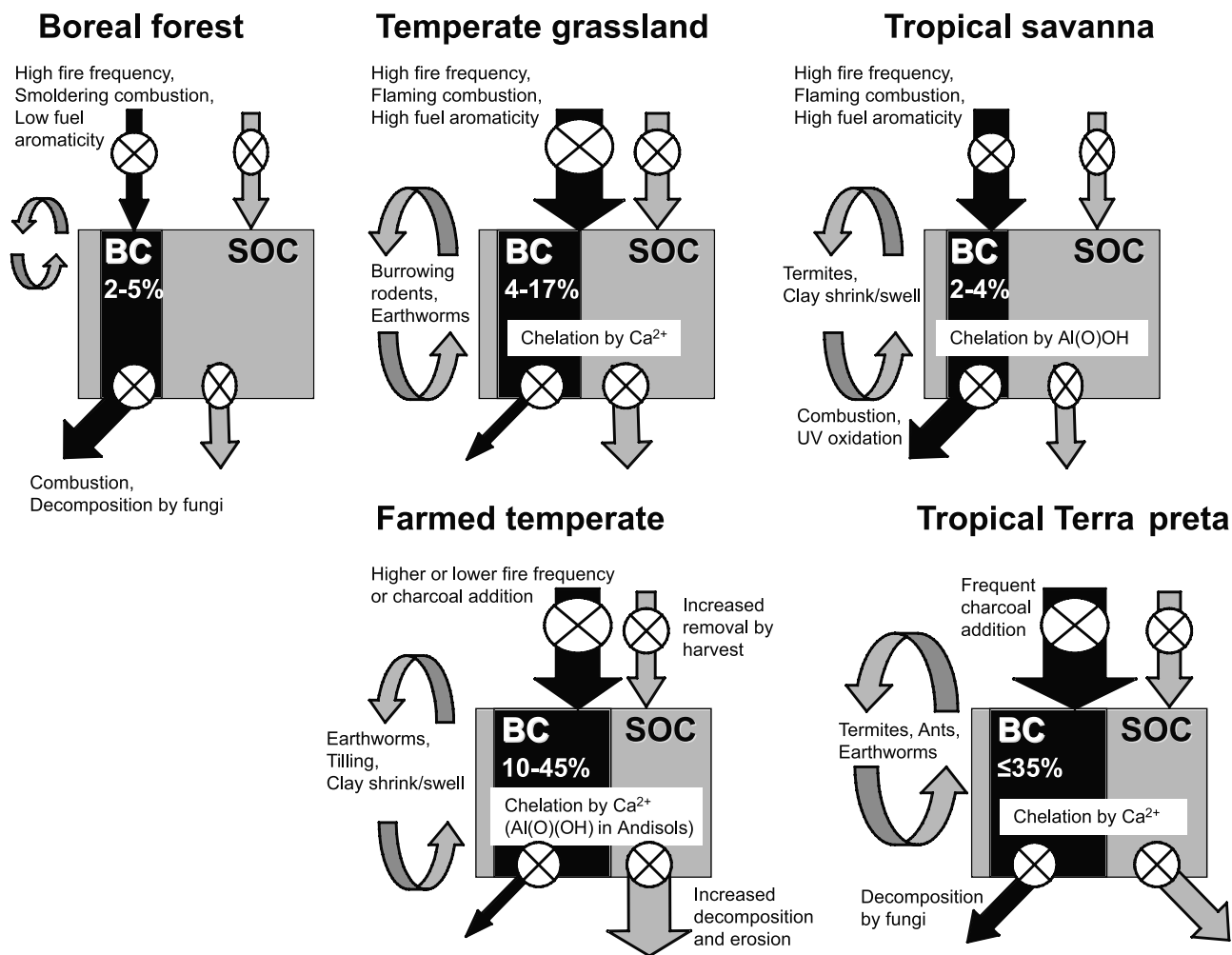


Figure 1. Conceptual model of factors controlling the accumulation of BC in different soils (see text).

2.3. BC Accumulation Requires Reactive Soil Minerals (Ca^{2+} , Al, and Fe Oxyhydroxides)

[23] The distribution of BC in soils with depth is usually highly correlated with that of SOC, indicating that controls on BC storage are not unique; BC is a form of SOC and its interactions with minerals are sometimes similar to those observed for bulk organic matter. That said, BC may be unique in SOC pools in that it is chemically composed of both a refractory aromatic core and reactive carboxyl functionalities on the exterior [Lehmann *et al.*, 2005]. We hypothesize that it is this combination of a refractory core with a reactive exterior that causes BC to be stored so effectively under some mineralogical conditions.

[24] Organic carbon can be chemically stabilized in soils by formation of organo-mineral associations or interactions with the clay mineral matrix [Baldock and Skjemstad, 2000; Hassink, 1995; Six *et al.*, 2002]. In particular, carboxyl and aromatic functionalities have been shown to be more reactive with minerals like goethite [Kaiser, 2003; Kaiser and Guggenberger, 2003; McKnight *et al.*, 1992; Meier *et al.*, 1999]. These studies are all consistent with a ligand-exchange model [Davis, 1982], where an organic ligand

(i.e., COO^-) forms an organo-metal complex with a metal cation on a mineral surface [McKnight *et al.*, 1992]. This ligand exchange reaction appears to be most effective when an organic molecule can deploy multiple carboxyl groups in its interaction with a mineral surface, particularly those present on aromatic rings in ortho positions [Gu *et al.*, 1994]. Scanning electron microscope analyses indicate that partially oxidized BC does indeed interact with the mineral phase of soils [Brodowski *et al.*, 2005a].

[25] This research suggests that BC may be stabilized in soils by interactions with the mineral matrix. However, Möller *et al.* [2000] showed that polyvalent cations may increase the mobility of BC degradation products in soils. Additionally, BC's aromatic core protects bound BC from further decomposition [Lehmann *et al.*, 2005]. This hypothesis is in accord with recent radiocarbon and ^{13}C NMR data [Krull *et al.*, 2006], who have shown that physical protection can extend the turnover time of SOC compounds by decades, but that long-term stabilization is a function of the compounds' chemical nature.

[26] As is true for bulk SOC, the presence of Ca^{2+} ions can act to increase a soil's ability to hold BC via Ca^{2+}

bridging in Ca-rich soils like Mollisols. The occurrence of unmanaged Mollisols with high BC content have been reported from the North American [Glaser and Amelung, 2003] and South American prairies [Zech *et al.*, 1997]. Also, a causal relationship between BC storage and soil calcium content has been shown via laboratory experiments conducted by Clough and Skjemstad [2000], who manipulated the levels of CaCO₃ in soils prior to gentle UV oxidation and ¹³C-NMR analyses. After laboratory amendment with CaCO₃, the >53 μm soil fraction remained significantly more aromatic following UV oxidation, suggesting that the presence of Ca²⁺ in soils acted to protect charcoal from oxidation (and decomposition).

[27] Mollisols are the prototypical example of soils whose organic matter has been stabilized by reaction with calcium. Given that BC levels in Mollisols have been measured as 10–45% of SOC [Schmidt *et al.*, 2002; Skjemstad *et al.*, 2002], it may be that BC is the majority of carbon stabilized by this mechanism in at least some systems.

[28] The Amazonian Terra Preta Anthrosols are another system where BC stabilization likely occurs dominantly by interaction with calcium ions. Terra Preta soils are black, carbon-rich Anthrosols regionally surrounded by highly weathered, low-carbon Oxisols; typically Terra Preta soils have at least twice as much SOC than their parent Oxisols [Glaser *et al.*, 2002]. The mechanism of formation of these soils is either the intentional or inadvertent simultaneous tillage of charcoal, ash, and fish bones into soils [Lehmann *et al.*, 2006]. Because the initial Oxisol pH was low, the calcium and phosphorus in the bones would have been released and become available to bind BC. Repeated additions of charcoal and cation sources created very highly aromatic soils valued for their high fertility [Glaser *et al.*, 2001; Lehmann *et al.*, 2005, 2006].

[29] Organic carbon can also be stabilized in soils via bridging to Al and Fe oxyhydroxides. This process contributes to the storage of organic carbon in volcanic ash soils (Andisols) which have very high concentrations of oxalate-extractable, poorly crystalline Al and Fe. BC-rich Andisols have been reported from Japan [Golchin *et al.*, 1997b]. These soils, which have been managed as pastures for several hundred years, receive high BC inputs due to annual burning to prevent woody encroachment. Although BC was identified in particulate form in all fractions [Golchin *et al.*, 1997a], bridging of partially oxidized BC with Al³⁺ is also likely: Reports of BC-derived humic acids suggest the presence of partially oxidized BC in these soils [Shindo *et al.*, 1986, 2005].

[30] BC can also be physically protected from enzymatic decomposition by sequestration in micropores (<1 micron, e.g., between platy clays) or stable soil aggregates [Kaiser and Guggenberger, 2003; Oades, 1988; Skjemstad *et al.*, 1998]. Soils with a large proportion clay (and silt) usually have higher SOC than more sandy soils. In nonvolcanic soils, the capacity of clay minerals to bind organic matter decreases from smectite to illite, chlorite, and kaolinite. Skjemstad *et al.* [2001] showed that Vertisols with similar pH (6–9) and Ca₂CO₃ content (1–2%), but a higher proportion of reactive clays (smectite) retained a higher proportion of BC than soils with less reactive clays (kaolinite).

2.4. BC Degradation Requires the Presence of BC-Degrading Microorganisms

[31] The degradation of condensed aromatic carbon compounds such as BC is an energy demanding process. For degradation to occur, the biological capacity for specific degradation pathways must exist in the soil [Baldock *et al.*, 2004]. It is likely that only certain microorganisms can produce the (costly) enzymes required for BC degradation and their presence or absence from soils is thus a crucial control on BC accumulation. Our knowledge of microbial BC degradation processes is slim, but is growing rapidly as ongoing studies release new data pointing toward important relationships between microbes (particularly fungi) and soil BC. Images of fungal hyphae encasing charcoal particles in soils [Hockaday *et al.*, 2007] indicate that in particular, fungi may play a key role in BC biodegradation.

[32] In incubation studies, decomposition of charcoal has been reported by microorganisms obtained from inoculants from decomposing wood [Baldock and Smernik, 2002] or soils containing low-rank coal [Hamer *et al.*, 2004]. The turnover rates for BC were on the same timescale with $4 \times 10^{-4}\%$ C hr⁻¹ (2% loss over 120 days) or $7 \times 10^{-4}\%$ C hr⁻¹ (0.3–1.2% loss over 60 days), respectively.

[33] The most likely candidates for microbial decomposition of BC are wood-rotting and leaf-litter-decaying basidiomycetes. Under oxic conditions, basidiomycetes can cleave C-C linkages in aromatic structures with extracellular enzymes (Mn-peroxidase, lignin-oxidase, and laccase) in a cometabolic process. These enzymes require H₂O₂ which is generated by the oxidation of nonaromatic carbon sources, for example, glucose. H₂O₂ itself oxidizes high-rank coal only at very low pH values (<1.5) in the presence of metal catalysts such as Fe ('Fenton reaction') [Heard and Senfile, 1984].

[34] In vivo, white rot fungi have been shown to degrade lignin, lignite, and low-rank coals [Hofrichter and Fritsche, 1996, 1997a, 1997b; Hofrichter *et al.*, 1999; Rumpel and Kögel-Knabner, 2002; Temp *et al.*, 1999]. Wengel *et al.* [2006] demonstrated the decomposition of charcoal and black shale by the wood-rotting fungi *Schizophyllum commune* and its conversion to DOC. Here BC turnover rates were higher ($4 \times 10^{-3}\%$ C hr⁻¹ or 7% loss over 84 days).

[35] We also note that one BC method has detected very low concentrations of the combustion markers benzenepolycarboxylic acids (BPCAs) in the biomass of a fungus [Brodowski *et al.*, 2005b], opening up the possibility that fungi also make small aromatic molecules as well as degrading them.

2.5. Humans Can Play a Major Role in Increasing Soil BC/SOC Ratios

[36] Humans can significantly impact BC/SOC ratios by land use practices that either enrich BC or remove nonblack SOC. The most extreme case of BC enrichment is the black 'Terra preta' soils of the Amazon region which are developed from and surrounded by Oxisols [Glaser *et al.*, 2001]. Other examples are European Mollisols ('Chernozems') which have locally developed from what were Alfisols after charcoal additions [Kleber *et al.*, 2003; Schmid *et al.*, 2001, 2002] and Japanese Andisols which have been

converted from forest to grassland by frequent burning [Golchin *et al.*, 1997a, 1997b].

[37] Humans can also increase BC stocks relative to non-BC soil carbon via land use practices which degrade labile carbon. As measured by ^{13}C -CP/MAS NMR, agriculture and pastureland preferentially remove nonaromatic functionalities from surface soils, increasing the BC/OC ratio while decreasing overall carbon inventories [Carter *et al.*, 2002]. Skjemstad *et al.* [2001] compared BC content in Australian Vertisols under varying years of cultivation, measuring BC via UV oxidation followed by ^{13}C CP/MAS NMR. They documented that the BC soil fraction was the least altered over 50 years of cultivation, resulting in a relative enrichment of BC within the SOC pool. Similar results have been shown for north American Mollisols under agriculture [Skjemstad *et al.*, 2002] and European agricultural soils; in one European site, cultivation resulted in the formation of a soil with 30% of SOC represented by BC (based on UV oxidation and ^{13}C -NMR) [Schmidt *et al.*, 2001].

3. Conclusions and Research Needs

[38] Even in its most refractory state, BC is a dynamic component of soils. It interacts with other forms of organic matter and the host mineral matrix. In a partially oxidized state, BC can interact with other organic matter or mineral components via oxidized functional groups on its surfaces.

[39] BC storage in soils is ultimately controlled by its production via fire; however, the dynamic nature of BC adds other layers of control on the system. We hypothesize that the major controls on soil BC storage are (1) fire frequency, (2) ecosystem presence or absence of aromatic precursor carbon and appropriate combustion conditions, (3) biological or physical mixing to remove BC from the soil surface, where it is vulnerable to combustion in future fires, (4) the presence or absence of soil mineral fractions able to sorb BC into the long-term stable carbon pool, (5) microbial community capable of degrading BC, and (6) human land use and management.

[40] A better understanding of the role of BC in the soil system requires both field and lab studies. To validate global inventories and distribution patterns of BC, a global inventory of BC stocks in soils is needed using one or more analytical approaches to cover various types of the BC continuum such as soot and charcoal.

[41] Further, mechanisms of BC degradation (microorganisms, fire, ozone, UV radiation) derived from laboratory experiments need to be tested to understand their relative significance in different soil types under different vegetative covers, land use and climate. Rates of oxidation relative to particles size and degree of condensation need to be addressed. To understand how BC moves through soil vertically and downslope, the importance of mixing and interactions between black DOC and the mineral phase need to be considered at different pH and precipitation regimes.

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