

Stability of Biochar in the Soil

Johannes Lehmann, Claudia Czimczik, David Laird and Saran Sohi

Introduction

The stability of biochar is of fundamental importance in the framework of biochar use for environmental management. There are two reasons why stability is important; first, stability determines how long C applied to soil as biochar will remain sequestered in soil and how long it may influence emissions of greenhouse gas from the pedosphere and contribute to the mitigation of climate change. Second, stability will determine how long biochar can provide benefits to soil and water quality.

Conversion of biomass to biochar followed by application of biochar to the soil increases the residence time of carbon (C) in the soil relative to the application of the same biomass directly to the soil, and therefore can be considered over particular timescales to result in a net withdrawal of atmospheric CO₂ (Lehmann, 2007a). In addition, biochar applied to soil may directly reduce emissions of other greenhouse gases, such as direct emissions of nitrous oxide or methane from soil (Yanai et al, 2007; see Chapter 13). Greenhouse gas emissions associated with

fertilizer or lime production may also be reduced through higher fertilizer-use efficiency and the liming effect of biochar (Lehmann et al, 2003; see Chapter 15). The long-term benefits of biochar additions to soil and water quality can be manifold and include improved nutrient retention and nutrient availability (see Chapter 5), reduced leaching of nutrients (see Chapter 15) and other contaminants (see Chapter 16), potentially increased water availability to plants, improved mycorrhizal activity (Warnock et al, 2007), and possible benefits to other groups of microorganisms and their function in soil (see Chapter 6).

If biochar decomposes rapidly, these benefits would be affected in extent and duration. Therefore, biochar must be of significantly greater stability in the environment than other organic matter in order to extend the duration of these benefits. This chapter explores the extent of biochar stability in soils, the mechanisms controlling its decay and stability, and implications of physical export for biochar stability.

Extent of biochar decay

Estimation of long-term stability of biochar

Ample evidence suggests that biochar is very stable in the environment. In soil, it typically has the greatest average age of any C fraction (Pessenda et al, 2001) but is not always the only form of very old C (Krull et al, 2006). Biochar as residues from forest fires is frequently found to be more than 10,000 years old in various soil ecosystems (reviewed by Preston and Schmidt, 2006). Biochar found in high proportions in the so-called 'Terra Preta' soils of the Amazon region (Glaser et al, 2001; Liang et al, 2008) have been radiocarbon dated and found to originate from 500 up to 7000 years BP (Neves et al, 2003). They provide a visually compelling proof for the longevity of biochar. Unfortunately, radiocarbon dates alone do not provide quantitative information about the decomposition rate of biochar, but rather establish the average time that has lapsed since photosynthesis formed the biomass that was pyrolysed to create the biochar currently remaining in the soil. In addition to the uncertainty around the time lag between carbon dioxide (CO₂) fixation into plant biomass, pyrolysis and deposition to soil – which can extend to a few hundred years and is already well acknowledged in research on the turnover of plant litter – decay of a one-time input of biochar cannot be quantified on the basis of its average age alone. A quantitative description of biochar decomposition can, in these cases, only be obtained if additional information about the amount of biochar at deposition is available. But since the period for which information is sought in most cases exceeds the availability of archived samples or historical records, very few opportunities may ever exist to conduct a straightforward mass balance (Hammes et al, 2008). However, the great age of biochar

found in soil studies and many archaeological sites is proof of stability even with the mentioned constraints for obtaining decay rates.

Regional or global C budgeting of biochar (commonly referred to as biomass-derived black C in the scientific literature dealing with this aspect) suggests that biochar has a much greater average stability than plant litter. Global biochar production of only 0.05Gt C yr⁻¹ to 0.3Gt C yr⁻¹ (Forbes et al, 2006) is less than 0.5 per cent of the 60Gt C yr⁻¹ estimated for global net primary productivity (Sabine et al, 2004), yet biochar concentrations are often above 10 per cent of total organic C in soils (Skjemstad et al, 1996, 2002). These data suggest a difference in decomposition rates of at least one order of magnitude. On the other hand, these global calculations also make clear that biochar is eventually mineralized to CO₂ (Schmidt, 2004), and microorganisms have been unmistakably shown to decompose biochar (Czimczik and Masiello, 2007). Future efforts in assessing the controls over sources and sinks of biochar, along with a broader effort to quantify biochar in soils on a regional to global scale, will enable calculation of decomposition rates in a more rigorous fashion.

On the spatial scale of individual sites, some estimates of turnover time of biochar is already possible if steady-state conditions of natural char production and disappearance occurred over long periods of time. By matching annual production of char by savannah fires to measured char stocks for various soils in Northern Australian woodlands, mean residence times of 718 to 9259 years were obtained (Lehmann et al, 2008). These estimates strongly depended upon the assumptions made for the proportion of char produced per unit biomass burned and the extent and frequency of biomass burning as

Box 11.1 Terminology for quantification of decay

Mineralization of soil organic carbon (SOC) to CO₂ is commonly modelled by assuming an exponential decay, with the resultant dynamic expressed as decay rate, mean residence time (equivalent to mean life time), half-life or turnover time, which can also be applied to biochar. These are not synonymous but are mathematically related. A decay rate is the exponent (k , as a function of environmental conditions) in the exponential decay function and has a unit of 1/time:

$$\text{biochar}_{(\text{at time } t)} = \text{biochar}_{(\text{at time } 0)} e^{-kt} \quad [1]$$

Mean residence time (MRT) is then the inverse of the decay rate ($1/k$) and is the average time that biochar is present. The half-life is the time that elapses before half of the biochar decomposes and can be obtained by multiplying the mean residence time by the natural logarithm of 2. For computing the turnover time, information about the stock of biochar is required. It is calculated by dividing the stock at equilibrium by the loss per unit time.

Heterogeneous composite materials such as biochar and other natural organic matter are typically composed of a mixture of individual compounds or groups of compounds, here called 'fractions', each with different rates of decay. This may necessitate assigning multiple exponential functions to describe the overall decay process, using distinct (although usually conceptual) 'pools'. For biochar, since more recalcitrant fractions seem to predominate, simplification may be possible when considering long timescales. Such equations can be solved mathematically to yield an estimate for ' k ', provided that the assumption of no interaction and no transfer of decomposition products to other pools can be made. Although this assumption cannot hold for all soil components, it may be argued for biochar. The alternate approach is multi-pool modelling typified by soil organic C models such as Century and RothC, in which material entering a pool as the product of one or more other pools is accounted for, and the status of each pool is reassessed at each successive calculation 'time step' (dynamic simulation). Thus, in this chapter 'mineralization' refers to the process by which CO₂ is emitted from a particular soil pool and which can be modelled relatively simply, and 'decomposition' refers to that which leads to both CO₂ emission and the transfers of organic by-products (such as microbial metabolites), and which demands pool-based modelling approaches.

well as biomass production. The most likely and conservative scenarios suggested mean residence times of 1300 to 2600 years under the dryland conditions of Northern Australia (Lehmann et al, 2008).

Measurements of biochar stocks in a time series or so-called chronosequence (set of sites with a common history of contrasting duration) from coastal temperate rainforest of western Vancouver suggest an average half-life of 6623 years (from Preston and Schmidt, 2006, calculated after Gavin et al,

2003). In contrast, Hammes et al (2008) calculated a turnover time of biochar from fires in a Russian steppe ecosystem of only 293 years. This study made use of an archived soil monolith taken in 1900 and proven fire suppression after 1900. In both types of studies, some uncertainty remained as to whether spatial variability affected the calculation.

Interpreting the difference of biochar stocks over time as decomposition or mineralization to CO₂, however, can lead to

erroneous conclusions. Losses of biochar over time are potentially not only a result of mineralization, but also of leaching or erosion (see the following section), as well as reburning of biochar by subsequent fires (Czimczik et al, 2005). It is also conceivable that biochar is deposited by subsequent nearby fires or through sheet erosion, leading to an underestimate of decay. Losses other than mineralization may partly explain the rapid decrease in biochar stocks found after savannah burning in Zimbabwe, with calculated mean residence times of several decades (Bird et al, 1999) or after forest clearing by fire in Kenya with a calculated mean residence time of eight years (Nguyen et al, 2008).

Even during long-term decomposition, the remaining biochar still shows similar chemical characteristics and recalcitrance against microbial decay observed initially. Liang et al (2008) found no changes in aromaticity determined by X-ray techniques for biochar particles with ages ranging from 700 to 7000 years obtained from Amazonian Dark Earths. Concurrently, mineralization of biogenic organic matter in the biochar-rich dark earths (with generally more than 70 per cent biochar as a fraction of soil organic C) were identical irrespective of the age of the biochar (Liang et al, 2008). Similar results were reported over the first 100 years of biochar exposure to soil in Kenya (Nguyen et al, 2008). Surfaces of biochar particles oxidized rapidly within less than five years, while below an approximately 10nm thick surface layer the O/C ratio remained unchanged. It appears from these examples that although biochar certainly decomposes, the stability of the remaining biochar remains high over long periods of time, even though some indications exist that aging may decrease stability (Krull et al, 2006).

Short-term decomposition of biochar

Although information about short-term

decay generally does not inform about long-term stability of biochar, quantification of the easily decomposable fraction of biochar is important for estimating the total amount of biochar ultimately remaining in soil, and to establish good estimates for mean residence time and prediction of long-term decay (see 'A biochar stability framework' at the end of the chapter).

In laboratory experiments, Hamer et al (2004) found a CO₂-C loss to the amount of 0.3 and 0.8 per cent of initial C for biochar produced from either oak wood or a maize/rye straw mixture at 800°C and 350°C, respectively, during a 60-day incubation at 20°C. Baldock and Smernik (2002) reported a C loss of less than 2 per cent from biochar made from *Pinus resinosa* Aiton sapwood (heated without restricting airflow at 250°C to 350°C) over 120 days (see Figure 11.1). Mineralization was even lower for aged biochars retrieved from various 130-year-old charcoal storage sites and amounted to 0.05 per cent to 0.4 per cent of initial C after 50 days (at 30°C) (Cheng et al, 2008). The average mean residence time of these biochars was estimated as 1335 years at a 10°C mean annual temperature (Cheng et al, 2008). Using a similar calculation approach with biochar from Amazonian Dark Earths (500–7000 years; Liang et al, 2008) results in a mean residence time of 4035 years for the stable pool of these very old biochars projected for a mean annual temperature of 10°C (using the Q₁₀ of Cheng et al, 2008). Wardle et al (2008) found no mass loss at all after ten years of monitoring biochar decay in a boreal forest using buried mesh bags. These very low decomposition rates compared to uncharred organic matter (Baldock and Smernik, 2002) contrast with findings by Brodowski (2004), who reported 16 to 51 per cent loss of biochar (made from maize and rye residues at 350°C) during the first two years.

These differences may, to some extent, be explained by different feedstock proper-

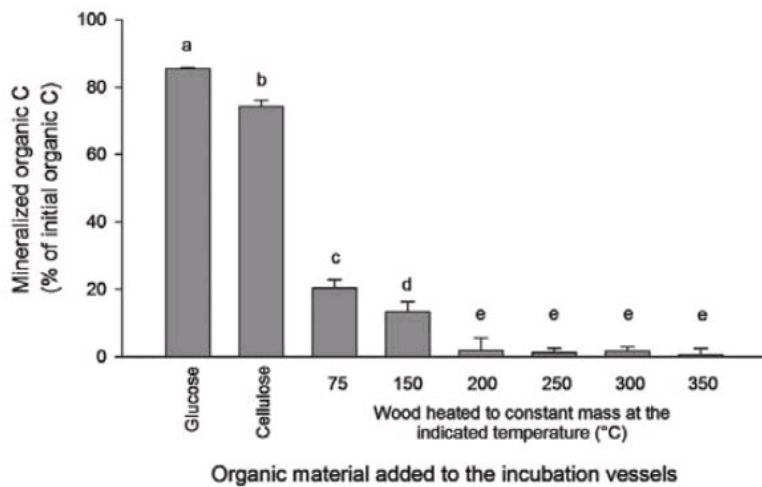


Figure 11.1 Mineralization of organic C in glucose, cellulose and *Pinus resinosa* sapwood heated to equilibrium at increasing temperatures: bars with different letters are significantly different at $P < 0.05$

Source: Baldock and Smernik (2002), with permission from the publisher

ties and charring conditions used in the experiments. Another explanation may also be the different analytical approaches employed. For example, Hamer et al (2004) and Cheng et al (2008) determined the evolved $\text{CO}_2\text{-C}$, which should be equivalent to the C remaining in the incubation as measured by Baldock and Smernik (2002). These methods are not able to capture a decomposition of biochar if it did not lead to $\text{CO}_2\text{-C}$ loss but only to the formation of non-biochar C such as microbial metabolites. The litterbag method used by Wardle et al (2008) may even have underestimated biochar decay due to adsorption of dissolved organic matter from the forest floor to biochar surfaces, which led to a slight increase in mass over time. On the other hand, the molecular marker method used by Brodowski (2004) would not only classify a transformation of biochar to microbial metabolites as a loss of biochar, but also surface oxidation. While surface oxidation may, indeed, initiate mineralization to CO_2 (see the following section) it may for the most part be an overestimate of C loss. Since surface oxidation of fresh biochar can be significant and very rapid (Cheng et al, 2006)

and since biochars can possess large surface areas (see Chapter 2), this overestimate of biochar decomposition could potentially be very high. One way of improving estimates of long-term stability by relatively short-term incubation experiments is to use aged biochars (Cheng et al, 2008; Liang et al, 2008). These differences have to be recognized in order to correctly interpret the results of such experiments. From a C accounting viewpoint as related to C sequestration and trading, it may be less relevant in what form the biochar is present in soil as long as it is not mineralized to CO_2 .

It is also important to note that many of the incubation experiments reported in the literature were conducted in a sand medium (e.g. Baldock and Smernik, 2002; Hamer et al, 2004; some incubations from Brodowski, 2004). Exclusion of aggregation and clay-biochar interactions (see the following sections) may lead to significant overestimates of decay rates. Potentially important interactions between biochar properties and those of soil minerals are missed that could significantly affect biochar stabilization in soil, similar to uncharred organic matter.

Biochar properties and decay

The physical and chemical properties of biochar can, as outlined in detail in Chapters 2 to 5, vary considerably. Indeed, different biochar products decompose to greatly contrasting extents, as highlighted above (Brodowski, 2004; Hamer et al, 2004). In this respect, not only will the organic molecular structure differ between biochars (Czimczik et al, 2002; Bourke et al, 2007), but their mineral content and chemical composition

will vary as well. Differences in mineral content and ramifications for biochar stability have rarely been assessed (and are therefore insufficiently captured in this chapter). Nevertheless, they deserve greater attention in future research. Since biochar properties may have differential effects on processes that control biochar decomposition, these properties are discussed in the individual sections below.

Mechanisms of biochar decay

Biological decomposition

The organo-chemical (see Chapter 4) and physical (Harris, 2005; Paris et al, 2005; Bourke et al, 2007; see Chapters 2 and 3) structure of biochar are the main reasons for the high stability of biochar (Schmidt and Noack, 2000) (see Figure 11.2). The diversity of cross-links in refractory macromolecules, in addition to steric protection, appears to be an important feature in the resistance of black C such as biochar to hydrolytic enzymes (Derenne and Largeau, 2001). However, biochar can be metabolized by microorganisms, and heterotrophic decomposition is the most important mechanism of biochar decay (Shneour, 1966; Baldock and Smernik, 2002; Brodowski, 2004), which is schematically presented in Figure 11.2. When microbial activity is suppressed, biochar mineralization does not occur to a significant extent (Schneour, 1966; Brodowski, 2004). The relative contribution of fungi or bacteria to the decomposition process is currently unknown (see Chapter 6). Both bacteria and fungi have been found to be located on surfaces and in the pores of biochar (see Chapter 6; Laird et al, 2008), but conclusions from mere presence to metabolization may not be

valid. Fungi are more likely to metabolize biochar and the ability of, for example, white-rot fungi to metabolize coal and wood (Hofrichter et al, 1999) may suggest their importance in biochar decomposition. Extracellular enzymes such as laccase (abundant in white-rot fungi) have been shown to yield degradation products when added to biochar (Hockaday, 2006). Additions of inoculum consisting of the basidiomycete fungus *Schizophyllum commune* to biochar produced from a mixture of beech and oak wood also significantly increased decomposition, leading to an 11 per cent increase in dissolved organic C originating from biochar (Wengel et al, 2006).

Co-metabolism and priming

Numerous other organic compounds are present in soils apart from biochar and may influence its decomposition. Willmann and Fakoussa (1997) suggested that co-metabolism may be the major mechanism for the degradation of complex C forms such as brown coal. Therefore, microbial utilization of readily available sources of organic C may also promote concomitant decomposition of biochar. In laboratory experiments, additions of glucose (Hamer et al, 2004) or glucose

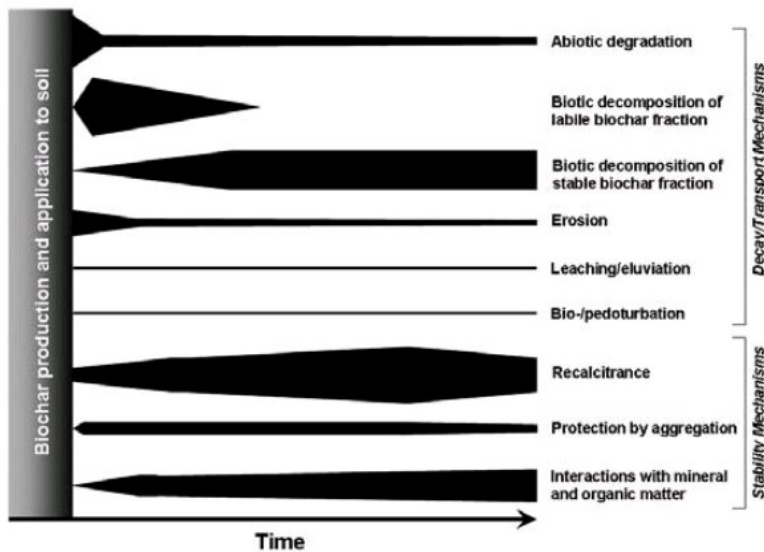


Figure 11.2

Schematic representation of the factors that may influence stability or decay and transport of biochar, and their proposed importance over time (as indicated by the thickness of the bars)

Source: chapter authors

together with nutrients (Brodowski, 2004) were, indeed, found to approximately double short-term decomposition of biochars made from oak wood, rye and maize residues. Whether the presence of easily degradable organic C is required for the decomposition of biochar is not proven but is possible.

This co-metabolism does not, however, necessarily mean that biochar decomposition is enhanced by the addition of labile organic matter, a process that is called ‘priming’ (Bingemann et al, 1953). Without direct evidence, it cannot be assumed that priming of biochar decay occurs to a significant extent in soils because:

- Added organic matter such as manures or crop residues are still much more recalcitrant and chemically complex than glucose and could have a different effect on biochar.
- A range of recalcitrant organic compounds beside biochar are present in soil and may be co-metabolized first if they are less resistant to decay than biochar.
- Aged biochar may behave very differently than fresh biochar, which may still have large amounts of aliphatic and aromatic surface groups.

- Interactions with both labile organic matter and mineral particles may change the behaviour of biochar in soils.

In fact, a greater increase in mineralization of uncharred soil organic matter (SOM) was found by additions of organic C (in this case, sugar cane residue) than mineralization of biochar over a period of 550 days (Liang, 2008). Nevertheless, priming of biochar decay by added labile C may exist, to some extent, in soils, and needs to be quantified. However, it may be small and possibly more important for the less aromatic fraction of biochar.

Labile compounds that cause co-metabolism may not only be found in soil but may also be intrinsic to the biochar. During pyrolysis, a range of different aliphatic materials remain in biochar (see Chapters 4 and 8). These compounds can be decomposed very rapidly within the first months of exposure to soil (Cheng et al, 2006) (see Figure 11.2). It is possible that this non-aromatic fraction of biochar accelerates the decomposition of the more aromatic fraction by co-metabolism. Proof of the existence and quantification of the extent of such a process appears to be difficult as changes in pyrolysis conditions to manipulate the quantity of the aliphatic frac-

tion by, for example different, pyrolysis temperatures to test this hypothesis will also change the nature of the aromatic C.

Abiotic processes

Surfaces of fresh biochar are hydrophobic and have relatively low surface charge but can be rapidly transformed in soil environments (see Chapter 10). Hydrolysis and oxidation of biochar surfaces creates negatively charged carboxylate and phenolate groups after a few months of incubation (Cheng et al, 2006). During the initial stages of biochar aging in soil, this change is mainly abiotic (Cheng et al, 2006) (see Figure 11.2), although some enzymatic reactions may take place (Hockaday, 2006).

Degradation of biochar appears to also change the crystal structure of biochar (see the following section) first by oxidation of the ordered phases via a pathway to non-ordered

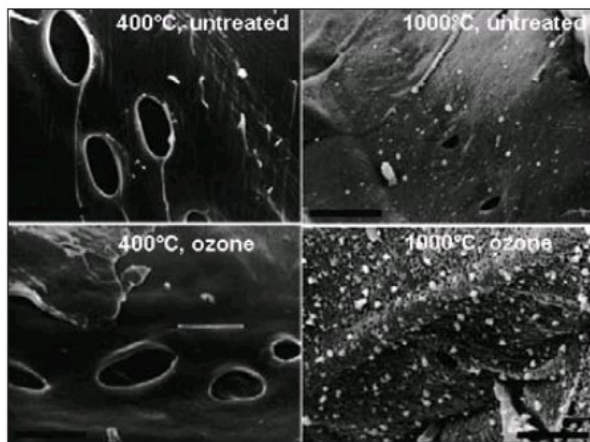


Figure 11.3 Scanning electron micrographs of biochar samples produced from *Fagus crenata* Blume sawdust with and without ozone treatment for two hours

Note: Biochars were produced at a heating rate of $5^{\circ}\text{C min}^{-1}$ either to 400°C (maintained for 24 hours) and treated with 7.3 per cent ozone or 1000°C (maintained at 500°C for 6 hours and at 1000°C for 6 hours) and treated with 3.8 per cent ozone. Bars are $5\mu\text{m}$. Biochar produced at 1000°C showed signs of oxidation in the form of small carbonaceous deposits and pores as a result of ozone exposure.

Source: Kawamoto et al (2005), with permission from the publisher

phases (Cohen-Ofri et al, 2007). Abiotic oxidation may not be associated with a significant loss in C, but can result in the formation of polycarboxylic compounds (Decesari et al, 2002) and possibly even in a weight increase. However, such abiotic oxidation may facilitate the microbial metabolization of the otherwise highly recalcitrant aromatic ring structures and hydrophobic biochar surfaces. Abiotic oxidation tests using ozone revealed that the biochar with the greater polyaromatic structure (produced at higher temperature) oxidized on surfaces more vigorously than biochar with greater aliphatic C contents (produced at lower temperature), as shown by changes in surface morphology in Figure 11.3. It is plausible that abiotic oxidation is a necessary step towards microbial mineralization of highly aromatic biochar.

Physical breakdown of biochar

The size of biochar particles may have a significant effect on achieving microbial decay by increasing the accessible surface area and facilitating surface reactions necessary to initiate decomposition. Over time, biochar particles do become reduced in size, and 30 years after deposition to an Oxisol in Kenya, biochar particles larger than $50\mu\text{m}$ had disappeared (Nguyen et al, 2008). At the moment, it can only be speculated upon whether tillage accelerates the physical breakdown of biochar. Uncharred plant litter is typically broken down by litter transformers among the soil fauna (Brussaard, 1998), but similar observations have not been reported for biochar. In contrast, processing of biochar by soil fauna has, rather, been found to aid in its stabilization than promote its decay (see the following section).

In cold regions, seasonal freeze-thaw dynamics are conceivably of greater importance than faunal activity since biochar has a large proportion of fine pores and great internal pore space (see Chapter 2) that, once aged and hydrophilic, may be water filled.

Freezing would probably fragment biochars and render them more susceptible to transport and mineralization. In drylands, breakage during swell–shrinking dynamics of clay-rich Vertisols may occur (Gouveia and Pessenda, 2000). Whether these processes actually lead to a greater decomposition of

biochar has not been demonstrated and will depend upon the extent to which stabilization mechanisms promoted by physical breakdown counteract the effect: several of the processes that stabilize organic matter and biochar rely on a small particle size and large exposed surface area (see following sections).

Stabilization of biochar in soil

Several principle mechanisms operate in soils through which organic matter entering the soil is stabilized and that significantly increase its residence time in soil. These involve its intrinsic recalcitrance, spatial separation of decomposers and substrate, and formation of interactions between mineral surfaces and organic matter (Sollins et al, 1996). The relatively stable nature of organic matter protected within aggregates or through the formation of organo-mineral interactions may also be of relevance to the stability and longevity of biochar in soil.

Recalcitrance

The conversion of organic matter to biochar by pyrolysis significantly increases the recalcitrance of C in the biomass. The composition changes through a complete destruction of cellulose and lignin and the appearance of aromatic structures (Paris et al, 2005) with furan-like compounds (Baldock and Smernik, 2002). Some differences in pyrolysis products are documented for thermal decomposition of different individual organic molecules (Knicker, 2007). Even though the clusters of condensed aromatic C remained relatively small with further heating of wood to 450°C (Czimczik et al, 2002), the mineralization rates of sapwood of *Pinus resinosa* decreased by one order of magnitude due to conversion to biochar (Baldock and Smernik, 2002). These changes in the composition of organic bonds by pyrolysis have a significant effect on the

stability of biochar. Less information is available on the relevance of the crystal structure of biochar for its recalcitrance. Biochar is mainly characterized by amorphous structures and turbostratic crystallites (unordered graphene layers; see Figure 11.4b and c) that may contain defect structures in the graphene sheets with oxygen (O) groups and free radicals (Bourke et al, 2007). Ordered graphene sheets (see Figure 11.4a) were found to increase only at a carbonization temperature above 600°C (Kercher and Nagle, 2003). Carbonization temperatures for low-temperature pyrolysis would typically remain below such values (see Chapter 8). Because of their unordered structure, amorphous and turbostratic crystallites have a high stability (Paris et al, 2005), which could be one reason for the stability of biochar produced at relatively low temperatures of less than 600°C. In comparison, layers of graphene in graphite (see Figure 11.4a) are held together by comparatively weak van der Waals forces. Rounded structures may be even more stable than turbostratic structures in biochar (Cohen-Ofri et al, 2007). For cedar wood pyrolysed at 700°C, onion-like graphitic particles have been observed that are probably formed from lignin (Hata et al, 2000), but it is not clear whether these are a common feature in biochar (Shibuya et al, 1999). Round structures are known as fullerenes, molecular-scale spherical structures that include both hexagonal and pentagonal rings that have great stability

(Harris, 2005). Fullerene-related structures are probably present in biochars as folded or curved domains (see Figure 11.4d) that could contribute to its recalcitrance. Simulations of the development of fused aromatic ring structures during charring show the appearance of heptagons and, with increasing temperature, heptagons in conjunction with folding of the graphene sheets (Acharya et al, 1999; Kumar et al., 2005). Rounded features were also reported in biochars from German Chernozems with ages of 1160 to 5040 years using high-resolution transmission electron microscopy (Schmidt et al, 2002). The differences in crystal structures, their changes in soil and the importance for recalcitrance and reactions with soil material are not well documented and warrant further research.

Likewise, the effects of the mineral content on the stability of biochar have received little attention. Some biochars, such as those produced from poultry manure or rice husks, contain a large proportion of minerals. For example, poultry biochar was found to contain 45 per cent minerals (Koutcheiko et al, 2007). Knowledge about the interaction of high mineral contents with C structures in biochars is only evolving (see Chapter 3), and the implications on stability are not well understood at present.

Spatial separation

Biochar has been preferentially found in fractions of SOM that reside in aggregates rather than as free organic matter (Brodowski et al, 2006; Liang et al, 2008), which is considered to reduce its accessibility to decomposers. Biochar particles are, indeed, abundant within stable micro-aggregates (see Figure 11.5). However, Liang et al (2008) found no difference in mineralization between biochar-rich soils with 27, 10 and 0.3 per cent clay, suggesting that greater aggregation in the finer-textured soils had no influence on biochar mineralization. As shown in Chapter

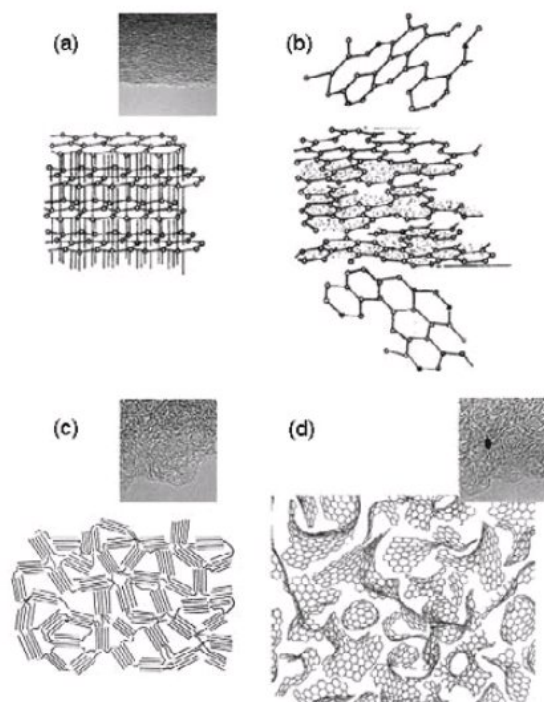


Figure 11.4 Schematic of the structure of (a) crystalline graphite; (b) turbostratic C; (c) turbostratic crystallites (or non-graphitizing C); and (d) fullerene-type structures

Source: Cahn and Harris (1969): turbostratic C; Franklin (1951): turbostratic crystallites; Harris (2005): fullerene-type structures. Insets are high-resolution electron micrographs from Harris et al (2000), which demonstrate the experimental evidence for the different schematics, with permission from the publishers

6 and by Laird et al (2008), microorganisms can be spatially associated with biochar in soils. Reducing accessibility by aggregation is therefore proposed to be significant in controlling biochar decomposition, but of less importance than chemical recalcitrance (see Figure 11.2).

In some soils, biochar may promote aggregation by initially forming a nucleus of biological activity and organic matter forms similar to the process described for plant litter (Tiessen and Stewart, 1988), which may lead to coatings of biochar particles with minerals (Lehmann, 2007b). If biochar, indeed, fosters proliferation of mycorrhizal fungi, as discussed by Warnock et al (2007),

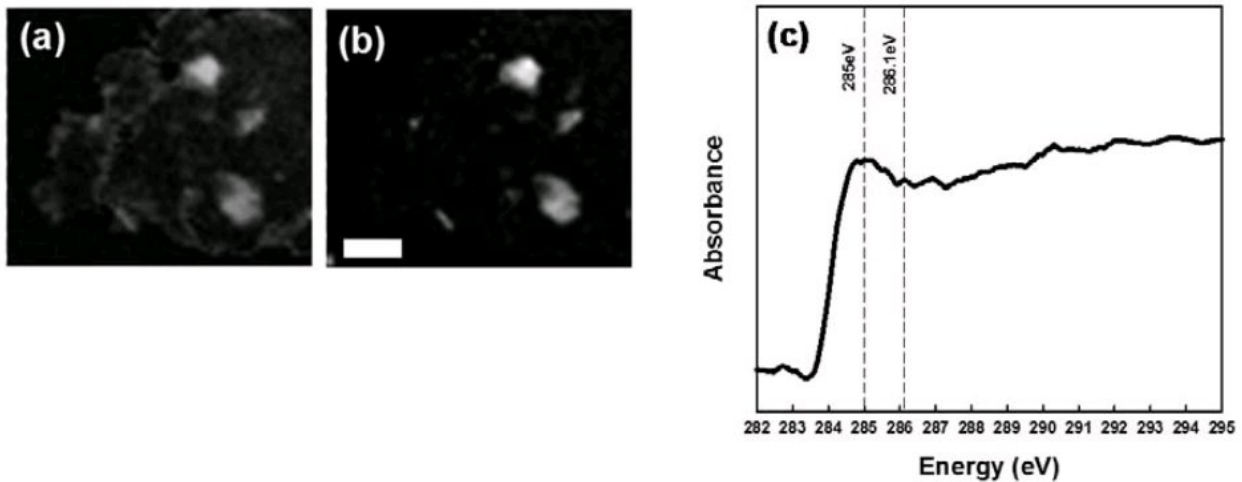


Figure 11.5 Particulate and finely divided biochar embedded within micrometre-size aggregates from a biochar-rich Anthrosol of the central Amazon region: near-edge X-ray absorption fine structure (NEXAFS) spectroscopy coupled with scanning transmission X-ray microscopy (STXM) of (a) total C and (b) biochar-type C characterized by (c) dominance of aromatic C at 285 eV and a characteristic peak at 286.1 eV

Note: Areas in white are regions rich in C. Bar is 6 µm.

Source: for method see Lehmann et al (2005)

then aggregation may increase by greater abundance of fungal hyphae. The connection between mycorrhizal hyphae and aggregate abundance and stability is well established (Tisdall and Oades, 1982; Miller and Jastrow, 1990; Rillig et al, 2002). To what extent this process influences the stability of biochar is not known, and in the absence of experimental evidence, it may be considered limited (see Figure 11.2).

Ingestion and excretion of biochar by earthworms may be an important mechanism by which biochar is mixed with the soil and forms stable aggregates (Topoliantz et al, 2006). In some instances, earthworms may even preferentially ingest biochar (Topoliantz and Ponge, 2005). Such a process may prove to be useful for managing the stability of biochar. Similar information for other groups of soil fauna is not available.

The particulate form may have an important role in decreasing decomposition rates of biochar. Oxidation of biochar particles starts at its surfaces (Cheng et al, 2006) and typi-

cally remains restricted to the near-surface regions even for several millennia (Lehmann et al, 2005; Liang et al, 2006; Cohen-Ofri et al, 2007). Therefore, its particulate nature may lend stability to biochar, where the outer regions of a biochar particle protect the inner regions from access by microorganisms and their enzymes. This is considered a very important property that is responsible for much of the recalcitrance of biochar (see Figure 11.2).

Interactions with mineral surfaces

A significant portion of biochar was found in the organo-mineral fraction of soil (Brodowski et al, 2006; Laird et al, 2008; Liang et al, 2008), suggesting that biochar forms interactions with minerals. Direct spectroscopic evidence for large particles showed biochar to be embedded within the mineral matrix (Glaser et al, 2000; Brodowski et al, 2005), but can also be present as very

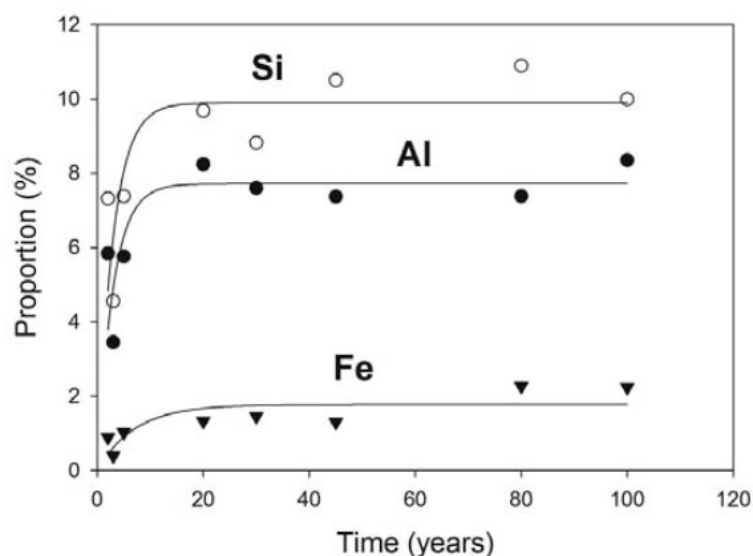


Figure 11.6 Long-term dynamics of Si, Al and Fe on biochar surfaces originating from forest clearing in western Kenya: relative elemental proportions (percentage of total C, O, Si, Al and Fe) were obtained by wide-scan X-ray photoelectron spectroscopy (XPS) on intact particles, probing the surface properties to a depth of approximately 10nm

Source: data from Nguyen et al (2008)

fine, yet distinguishably particulate, material within aggregates (see Figure 11.5). Therefore, finely divided biochar may indeed be able to form interactions with mineral surfaces, and vice versa.

Rapid association of biochar surfaces with Al and Si and, to a lesser extent, with Fe was found during the first decade after addition of biochar to soil (see Figure 11.6), which increased more slowly within biochar structures (Nguyen et al, 2008). It is not clear whether these associations are complexation with free Al^{3+} and Fe^{3+} or interaction with their oxides, and whether one or the other process is lending more stability to the biochar. Coating of biochar particles with mineral domains is frequently visible in soils (Lehmann, 2007b) and suggests interactions between negatively charged biochar surfaces and either positive charges of variable-charge oxides by ligand exchange and anion exchange, or positive charges of phyllosilicates by cation bridging. Concurrent increases of Si on biochar surfaces in the example shown in Figure 11.6 support the interpretation of interactions with phyllosilicates. Similarly, Ca was shown to increase biochar stability, most likely by enhancing interactions with mineral surfaces (reviewed by Czimczik and Masiello, 2007).

The relevance of electrochemical phenomena on biochar surfaces has not been sufficiently explored, but could be of importance for its interaction with mineral surfaces. Biochars carbonized at 1000°C have shown high electric conductivity (Bourke et al, 2007). The behaviour of high-mineral biochars in comparison to wood biochars that have been more commonly investigated is also a matter of ongoing research.

On the other hand, Laird et al (2008) found particulate biochar could be physically separated from an Iowa Mollisol in the coarse clay fraction ($0.2\ \mu\text{m}$ to $2\ \mu\text{m}$) along with quartz, feldspars, and discrete kaolinite and illite particles, whereas the finer fractions dominated by smectites were low in biochar, yet rich in biogenic organic matter (see Figure 11.7). Short-term mineralization normalized by organic C content was 48 to 78 per cent lower in coarse- than fine-clay fractions. This evidence suggests that either stabilization by the particulate nature or chemical recalcitrance of biochar is more important than by interaction with clay (as also concluded by Liang et al, 2008), or that there is a lower size limit of biochar for it to persist.

Large amounts of ionic Fe and Al were also found in biochar-type humic fractions (Nakamura et al, 2007), which may indicate

that complexation between biochar surfaces and polyvalent metal ions could increase biochar stability. Decreases in mineralization rates by additions of free Al^{3+} to organic matter have been widely documented (Sollins et al, 1996). Adsorption of relatively large amounts of metals is a plausible mechanism for reducing bioavailability and, hence, stabilizing biochar.

In addition to interactions with mineral matter, biochar particles also interact with organic matter in soil, which may render biochar more stable. Surfaces of biochar were found to be coated by organic matter (Lehmann et al, 2005), mixed with biogenic organic material in soil fractions (Laird et al, 2008) and associated with microbial matter (Hockaday et al, 2007; Laird et al, 2008). Hydrophobic molecules produced from the microbial decomposition of plant cell walls may be involved in the protection of fresh biochar (Knicker and Skjemstad, 2000). In addition, 42 per cent of dissolved organic C from litter extracts were removed from solution by biochar produced from crowberry twigs (Pietikäinen et al, 2000). The reversibility of these adsorption processes and the quantitative significance for the soil C cycle is less clear, but must impact not only upon the stability of biochar but also upon that of the adsorbed organic matter (which is not the focus of this chapter).

Since aged biochar is highly oxidized and contains large amounts of negatively charged functional groups (Cheng et al, 2006; Liang et al, 2006), adsorption of hydrophilic organic matter by mechanisms similar to those applying to mineral matter would be the most likely process. Aged biochar was shown to be less prone to enzymatic degradation than relatively recently deposited biochar (Hockaday, 2006), which could be the result of either biochar–organic or biochar–mineral interactions. However, it is difficult to quantify the relative importance of such protection mechanisms in comparison to the effect of a relatively rapid decomposition of a

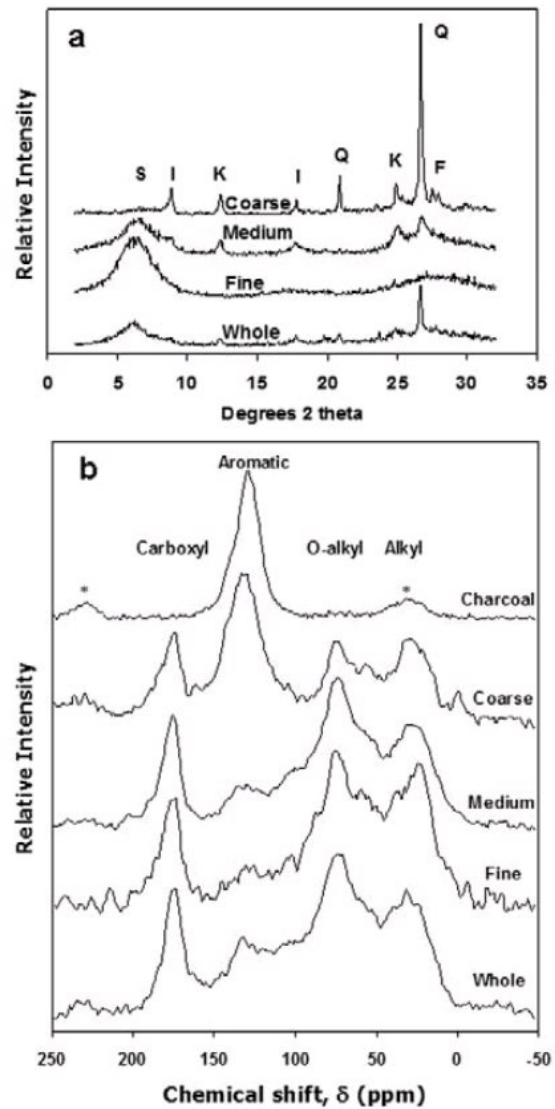


Figure 11.7 (a) Mineralogy and (b) relative proportion of aromatic C forms as an indicator of biochar in coarse ($0.2\text{--}2\mu\text{m}$), medium ($0.02\text{--}0.2\mu\text{m}$) and fine ($<0.02\mu\text{m}$) clay fractions of a *Typic Endoaquoll* from Iowa, US

Source: Laird et al (2008), with permission from the publisher

labile fraction of biochar that leaves more recalcitrant fractions characterized by lower mineralization rates (see Figure 11.1).

These interactions with mineral material and organic matter are most likely initiated soon after application to soil and gain importance over time (see Figure 11.2).

Environmental conditions affecting biochar stability and decay

Temperature sensitivity of biochar decomposition

Mineralization of organic matter generally increases with rising temperature, and biochar is no exception to this rule. Since one concern over future climate change is rising temperatures, the temperature sensitivity of biochar decay is an important question to resolve, specifically in the light of using biochar as a means of mitigating global warming (Lehmann et al, 2006). The increase in decomposition rate resulting from a 10°C rise in temperature is commonly referred to as the Q_{10} . This Q_{10} is expected to increase with greater chemical recalcitrance of an organic material (Davidson and Janssens, 2006). Since biochar is a very recalcitrant form of organic matter, the Q_{10} may be significantly greater than for uncharred organic matter. Cheng et al (2008) calculated a Q_{10} of 3.4 between 5°C and 15°C, using a climosequence of sites in eastern North America where biochar accumulated during the 1800s as a result of the pig iron production process. This value is at the upper range of temperature sensitivity observed for different plant residues (Fierer et al, 2005). Given the much lower decomposition of biochar than uncharred litter, this calculated Q_{10} appears to be low. Litter decomposition may have very different and, most likely, greater temperature sensitivity than SOM that is in close contact and protected by mineral matter. If the mechanism of organic matter stability is physical inaccessibility to decomposition rather than chemical recalcitrance, as is often the case when organic matter is located within stable micro-aggregates or interacts with mineral surfaces, decomposition hardly increases with temperature (Davidson and Janssens, 2006). Therefore, some experimental evidence shows limited

increase in mineralization of the more stable forms of SOM (Czimczik and Trumbore, 2007). If biochar shows strong interactions with the mineral matrix as described above, thereby decreasing its accessibility to enzymatic decay, temperature sensitivity may be less than what decomposition studies of isolated biochar suggest.

Transport and burial

In many field experiments, decreases in biochar content must not only be attributed to decomposition, but are, in most cases, also due to erosion, eluviation and leaching. Significant amounts of biochar at depth in various ecosystems (Skjemstad et al, 1999; Dai et al, 2005; Rodionov et al, 2006; Brodowski et al, 2007; Leifeld et al, 2007) suggest that biochar can be transported downwards in soil (Preston and Schmidt, 2006). In some cases, however, biochar distribution in a soil profile may not be the result of transport by water but of either deposition during times when the respective depth was at the surface, as in many anthropogenic soils, or of redistribution by soil faunal activity (Gouveia and Pessenda, 2000), mixing through root uplift during tree fall (Bormann et al, 1995) and through pedoturbation (Ping et al, 2005).

Direct evidence for leaching of biochar in the dissolved phase was provided by identification of aromatic structures in leachates from biochar particles, soil pore, and ground and river water (Kim et al, 2004; Hockaday et al, 2007). Direct quantification of the condensed aromatic portion of biochars derived from forest fires demonstrated a slightly preferential export of biochar from a Siberian watershed in comparison to other organic matter (Guggenberger et al, 2008). Initially, leachates from biochar appear to be

aromatic and change towards a more aliphatic nature over the course of days (Bennett et al, 2004). After several years, intermediately oxidized biochar-type dissolved organic matter appears to be preferentially transported, with O/C ratios between 0.2 to 0.55, while both highly aromatic and highly oxidized biochar may be retained within the watershed (Hockaday et al, 2007). Oxidation of biochar may therefore not only be connected with gaseous losses of biochar as CO₂, but also with increases in transport by leaching and lateral export within stream networks.

Less information is available about transport of particulate biochar. Since subsoils are typically enriched in biochar (Czimczik et al, 2005; Dai et al, 2005; Brodowski et al, 2007), a likely mechanism is a transport in dissolved form. In peatlands with very large porosity of up to 91 per cent, a very rapid transport of at least 6mm yr⁻¹ to 12mm yr⁻¹ was estimated over 50 years for both dissolved and particulate black C of various sources, including biochar and coal char or soot (Leifeld et al, 2007).

Erosion of biochar can be a significant pathway of export from a watershed (Rumpel et al, 2006). Erosion is probably more important than leaching, especially initially after application to soil (see Figure 11.2), but direct evidence is still sparse. Biochar is then either accumulating in depressions (Bassini and Becker, 1990) or transported within aqueous systems (Guggenberger et al, 2008) and eventually deposited in fluvial or oceanic sediments (Masiello and Druffel, 1998). The extent of mineralization of biochar during transport in water is not known. However, the contribution of biochar to total C along the transport pathway from soils to sediments appears to increase rather than decrease, suggesting a decreasing turnover rate. Using a quantification method that only captures the most aromatic portion in the black C continuum, Mitra et al (2002) found up to 28 per cent of

the C transported in the Mississippi River to be composed of combustion-derived C. Using a method that fully includes biochar will most likely result in a much greater proportion. In estuary sediments in Eastern Australia, biochar made up a large proportion of the total organic C (Golding et al, 2004), underpinning the slow turnover and enrichment in sediments.

The oldest black C that invariably contains biochar was found in ocean sediments up to 13,900 years older than the age of other organic C (Masiello and Druffel, 1998), and it has been identified in sediments that are several million years old with little trend in sizes with age, indicating low decomposition over time (Herring, 1985). Black C makes up a significant portion of 15 to 31 per cent of total organic C in these sediments (Masiello and Druffel, 1998; Middelburg et al, 1999). With an increase of O₂, decomposition of uncharred organic matter in ocean sediments was found to be 83 per cent over a period of 10,000 to 20,000 years in comparison to only 64 per cent for black C (Middelburg et al, 1999). Without O₂, the biochar probably remains virtually unchanged in deep ocean sediments over geological timescales.

These results indicate that once biochar is buried in sediments under low O₂ or even anoxic conditions, the turnover time probably significantly increases compared to terrestrial environments, even though the biochar will be of less use for soil improvement. It is not clear to what degree transport within the water column of fluvial or marine environments affects overall losses of biochar.

Soil cultivation and biochar stability

Even though cultivation typically increases decomposition of SOM, this has not been found to significantly increase biochar decay. In fact, long-term cultivation of two Australian Vertisols was shown to leave the

size of the UV-unoxidizable fraction of SOM, which mainly consists of biochar, largely unaffected (Skjemstad et al, 2001). As a result, the proportion of this biochar-dominated C as a fraction of total SOM increased from native savannah at 33 and 7 per cent during 50 and 45 years of cropping mainly wheat and sorghum to 53 and 27 per cent. The chemical composition of this fraction that was isolated by UV oxidation gradually changed towards a greater proportion of aryl C determined by nuclear magnetic resonance (NMR) spectroscopy, indicative of biochar (Skjemstad et al, 2001). This observation suggests that biochar was the most refractory portion of the stable C fraction during cultivation.

High proportions of biochar in SOM after long-term cultivation were also

observed in the US (Skjemstad et al, 2002), Germany (Schmidt et al, 2001), Russia (Rodionov et al, 2006) and Kenya (Nguyen et al, 2008).

Nutrient management during cultivation may also affect biochar stability. Application of nutrients that limit decomposition, such as nitrogen (N) added to organic material with a high C/N ratio, typically increase its mineralization (Hobbie, 2003). Since biochar shows high C/N ratios (see Chapter 5), N fertilization could conceivably increase decomposition of applied biochar. Experimental evidence does, at present, not support this mechanism. On the contrary, an application of commercial fertilizers was not found to affect the contents of biochar-type organic matter (Brodowski et al, 2007).

A biochar stability framework

The available scientific evidence clearly demonstrates that biochar is the most stable form of organic matter that can be added to soil, even though residues of uncharred plant biopolymers also show great ages in some instances (Krull et al, 2006). However, some types of biochar can be mineralized to a significant extent in the short term and all types of biochar eventually decompose, with a complex interplay of stabilization, destabilization and transport processes that change over time (see Figure 11.2). It is therefore important to quantify the extent of short-term decomposition both for the calculation of C credits as well as for its effects on soil.

Assessing biochar decay in soil

The generally slow decay of biochar poses challenges to quantifying its longevity. Decomposition rates of plant litter have often been established experimentally by adding litter to soil and measuring its disappearance (Melillo et al, 1982). Since the turnover time

of litter ranges between weeks and years, the organizational and financial commitment to such efforts is feasible. In contrast, direct measures of turnover times for biochar may require centuries to millennia, and are therefore not experimentally accessible by such an approach. For example, Wardle et al (2008) used a litterbag experiment for assessing biochar decay in the organic horizon of a boreal forest and found no mass loss after ten years.

Some studies (Baldock and Smernik, 2002; Brodowski, 2004; Hamer et al, 2004) have determined biochar decay over timescales of months to two years using incubation experiments. However, extrapolations from such short-term incubations to long-term decay are problematic because of the heterogeneity of fresh biochar and its particulate nature, as discussed by Lehmann (2007b). For example, decomposition of biochar produced from rye and maize was found to be 48 per cent of the initial biochar

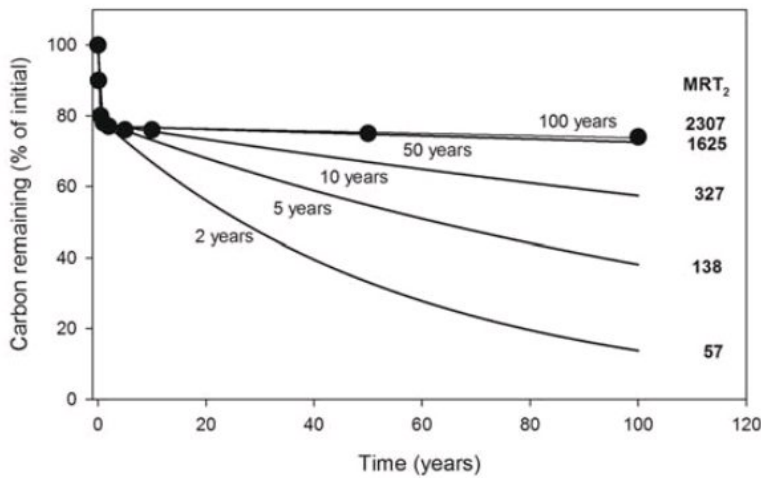


Figure 11.8 Double-exponential model ($C_{\text{remaining}} = C_1 e^{-k_1 t} + C_2 e^{-k_2 t}$, with 1 and 2 being a labile and stable pool, respectively) fitted to hypothetical data of biochar decay after 0.1, 0.5, 2, 5, 10, 50 or 100 years, assuming data availability for either the first 2, 5, 10, 50 or 100 years

Note: MRT₂ is the mean residence time (see Box 11.1) of the stable pool 2, calculated from the rate k_2 , and is given in years.

Source: chapter authors

during the first six months of a laboratory incubation; but was only 3 per cent of initial mass greater during the following 18 months (Brodowski, 2004).

Schematically, this challenge is depicted for a hypothetical data set in Figure 11.8. The calculated MRT increases if data are available for longer periods of time. If data were only available for two years, the MRT obtained by a double-exponential model is merely 57 years for the data shown in Figure 11.8. In this hypothetical example, the MRT of the stable pool of the modelled decay (MRT₂) continued to increase significantly depending upon whether 50 or 100 years of data were available, from 1625 to 2307 years (see Figure 11.8). This example illustrates that long-term decomposition data are necessary to predict biochar decay and that extrapolations from short-term decomposition experiments are likely to fail in many instances. Considering the strongly bi-phasic dynamics of a rapid decay of the labile fraction of biochar (Brodowski, 2004), disregarding the initial mineralization may, in some cases, be a viable strategy. Omitting the first two data points and only using the data between one and ten years in Figure 11.8 resulted in a calculated MRT₂ of 2306 years – similar to the results obtained by using all data for 100 years of observation. This calculation is certainly a simplistic way of handling

a complicated decay process of a mixture of compounds, but illustrates the challenges with respect to extrapolation of short-term decay data. Future modelling efforts should recognize the stabilization of decomposition products from biochar and, thus, the transfer of C from biochar to other pools of soil C.

The long-term decay rates of the more stable fractions of SOM are typically quantified *in situ* by using information about either input or output and stocks. This approach is only valid under equilibrium conditions of C input and output. However, biochar additions to soil under anthropogenic and even natural conditions are rarely continuous over the timescales of thousands of years necessary to perform such simulations as mentioned before. Exceptions may be those savannah grassland and woodland ecosystems that burn almost annually (Lehmann et al, 2008).

Monitoring biochar stability: The way forward

Notwithstanding any significant initial decomposition of biochar, the long-term stability of most biochars appears to be by at least one order of magnitude greater than that of other organic additions under the same environmental conditions (Baldock and Smernik, 2002; Cheng et al, 2008; Liang et al, 2008) and the stable fraction of biochar

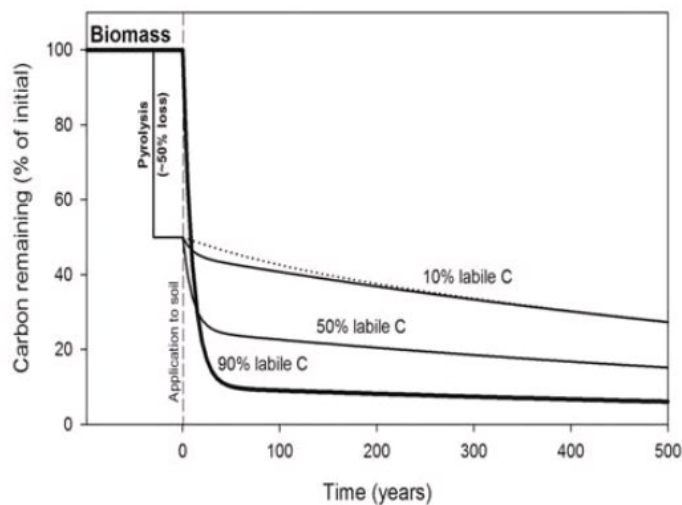


Figure 11.9 Conceptual model of C remaining from biomass using a double-exponential decay model with a mean residence time of 10 years for the labile C pool and 1000 years for the stable C pool, but different proportions of labile C

Note: Thin lines represent of conversion of biomass into biochar; thick line represents decomposition of uncharred biomass. Dotted line shows decomposition with 10 per cent labile C using 100 years as a mean residence time of the labile pool. Carbon losses by pyrolysis average approximately 50 per cent (Lehmann et al, 2003), but can vary significantly depending upon feedstock and production conditions (see Chapter 8).

Source: chapter authors

probably has a mean residence time of greater than 1000 years (see discussion above and Cheng et al, 2008; Lehmann et al, 2008; Liang et al, 2008). In terms of pure C accounting, this greater long-term stability compensates for the C losses during conversion of biomass to biochar by pyrolysis (see Figure 11.9). The MRT of the easily decomposable fraction is of little consequence to the difference in remaining C between a scenario where biomass was pyrolysed before adding it to soil (dashed line in Figure 11.9). For obtaining values for the emission reduction after adding biochar to soil, the decomposition of the stable fraction of biochar has to be estimated. The mean residence time of this stable fraction is estimated to be about several hundred to a few thousand years, given the available information discussed earlier in this chapter. Once this has been established, an assessment of the short-term decay and, specifically, the proportion of the relatively labile fraction may be sufficient and can be used to quantify the proportion of stable C in biochar. Better constraint to the mean residence time of the stable fraction of biochar is therefore desirable, but is of lower importance than an accurate assessment of its proportion (see Figure 11.9). Quantification schemes of the labile fraction then become the basis for classifying the stability of biochars (see Chapter 7).

Even short-term decay will most likely not be part of a routine procedure for quantifying the labile fraction of biochar. Therefore, a more comprehensive approach has to be explored that predicts long-term decay based on easily obtainable characteristics which can be assessed by rapid test methods:

- Establish relationships between biochar properties or rapid stability tests and the proportion of the labile fraction of biochar that will decompose in annual to decadal timescales. This may be achieved by incubation experiments over a few years.
- Establish the decomposition rate of the stable fraction of biochar by a combination of long-term incubation experiments with fresh and aged biochar under elevated temperature, and field experiments that either exclude physical losses or allow their quantification.
- Develop a mechanistic understanding of long-term biochar decay as a function of biochar properties and environmental conditions such as climate and soil.
- Apply the modelling framework recognizing stable and labile fractions of biochar, including decomposition products of biochar, and validate these with long-term field experiments.

References

- Acharya, M., Strano, R. F., Mathews, J. P., Billinge, J. L., Petkov, V., Subramoney, S. and Foley, H. C. (1999) 'Simulation of nanoporous carbons: A chemically constraint structure', *Philosophical Magazine B*, vol 79, pp1499–1518
- Baldock, J. A. and Smernik, R. J. (2002) 'Chemical composition and bioavailability of thermally altered *Pinus resinosa* (red pine) wood', *Organic Geochemistry*, vol 33, pp1093–1109
- Bassini, F. and Becker, P. (1990) 'Charcoal's occurrence in soil depends on topography in *terra firme* forest near Manaus', Brazil. *Biotropica*, vol 22, pp420–422
- Bennett, D., Angove, M. J., Wells, J. D., Johnson, B. B. and Baldwin, D. (2004) 'Characterisation of bushfire residues and their leachates', *SuperSoil 2004: Third Australian New Zealand Soils Conference*, 5–9 December 2004, University of Sydney, Australia, Paper 1549
- Bingemann, C. W., Varner, J. E. and Martin, W. P. (1953) 'The effect of the addition of organic materials on the decomposition of an organic soil', *Soil Science Society of America Proceedings*, vol 17, pp34–38
- Bird, M. I., Moyo, C., Veendaal, E. M., Lloyd, J. and Frost, P. (1999) 'Stability of elemental carbon in a savanna soil', *Global Biogeochemical Cycles*, vol 13, pp923–932
- Bormann, B. T., Spaltenstein, H., McClellan, M. H., Ugolini, F. C., Cromack, K. J. and Nay, S. M. (1995) 'Rapid soil development after windthrow disturbance in pristine forests', *Journal of Ecology*, vol 83, pp747–757
- Bourke, J., Manley-Harris, M., Fushimi, C., Dowaki, K., Nonoura, T. and Antal, M. J. (2007) 'Do all carbonized charcoals have the same chemical structure? 2. A model of the chemical structure of carbonized charcoal', *Industrial and Engineering Chemistry Research*, vol 46, pp5954–5967
- Brodowski, S. B. (2004) *Origin, Function, and Reactivity of Black Carbon in the Arable Soil Environment*, PhD thesis, University of Bayreuth, Bayreuth, Germany
- Brodowski, S., Amelung, W., Haumeier, L., Abetz, C. and Zech, W. (2005) 'Morphological and chemical properties of black carbon in physical soil fractions as revealed by scanning electron microscopy and energy-dispersive X-ray spectroscopy', *Geoderma*, vol 128, pp116–129
- Brodowski, S., John, B., Flessa, H. and Amelung, W. (2006) 'Aggregate-occluded black carbon in soil', *European Journal of Soil Science*, vol 57, pp539–546
- Brodowski, S., Amelung, W., Haumaier, L. and Zech, W. (2007) 'Black carbon contribution to stable humus in German arable soils', *Geoderma*, vol 138, pp220–228
- Brussaard, L. (1998) 'Soil fauna, guilds, functional groups and ecosystem processes', *Applied Soil Ecology*, vol 9, pp123–135
- Cahn, R. W. and Harris, B. (1969) 'Newer forms of carbon and their uses', *Nature*, vol 221, pp132–141
- Cheng, C. H., Lehmann, J., Thies, J. E., Burton, S. D. and Engelhard, M. H. (2006) 'Oxidation of black carbon by biotic and abiotic processes', *Organic Geochemistry*, vol 37, pp1477–1488
- Cheng, C. H., Lehmann, J., Thies, J. E. and Burton, S. D. (2008) 'Stability of black carbon in soils across a climatic gradient', *Journal of Geophysical Research*, vol 113, pG02027
- Cohen-Ofri, I., Popovitz-Niro, R. and Weiner, S. (2007) 'Structural characterization of modern and fossilized charcoal produced in natural fires as determined by using electron energy loss spectroscopy', *Chemistry – A European Journal*, vol 13, pp2306–2310
- Czimczik, C. I. and Masiello, C. A. (2007) 'Controls on black carbon storage in soils', *Global Biogeochemical Cycles*, vol 21, pGB3005
- Czimczik, C. I., and Trumbore, S. E. (2007) 'Short-term controls on the age of microbial carbon sources in boreal forest soils', *Journal of Geophysical Research*, vol 112, pG03001
- Czimczik, C. I., Preston, C. M., Schmidt, M. W. I., Werner, R. A. and Schulze, E.-D. (2002) 'Effects of charring on mass, organic carbon, and stable carbon isotope composition of wood', *Organic Geochemistry*, vol 33, pp1207–1223
- Czimczik, C. I., Schmidt, M. W. I., and Schulze, E.-D. (2005) 'Effects of increasing fire frequency on black carbon and organic matter

- in Podzols of Siberian Scots pine forests', *European Journal of Soil Science*, vol 56, pp417–428
- Dai, X., Boutton, T. W., Glaser, B., Ansley, R. J. and Zech, W. (2005) 'Black carbon in a temperate mixed-grass savanna', *Soil Biology and Biochemistry*, vol 37, pp1879–1881
- Davidson, E. A. and Janssens, I. A. (2006) 'Temperature sensitivity of soil carbon decomposition and feedbacks to climate change', *Nature*, vol 440, pp165–173
- Decesari, S., Facchinia, M. C., Matta, E., Mirceaa, M., Fuzzia, S., Chughtaib, A. R. and Smith, D. M. (2002) 'Water soluble organic compounds formed by oxidation of soot', *Atmospheric Environment*, vol 36, pp1827–1832
- Derenne, S. and Largeau, C. (2001) 'A review of some important families of refractory macromolecules: Composition, origin, and fate in soils and sediments', *Soil Science*, vol 166, pp833–847
- Fierer, N., Craine, J. M., McLauchlan, K. and Schimel, J. P. (2005) 'Litter quality and the temperature sensitivity of decomposition', *Ecology*, vol 86, pp320–326
- Forbes, M. S., Raison, R. J. and Skjemstad, J. O. (2006) 'Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems', *Science of the Total Environment*, vol 370, pp190–206
- Franklin, R. E. (1951) 'Crystallite growth in graphitizing and non-graphitizing carbons', *Proceedings of the Royal Society of London, Series A, Mathematical and Physical Sciences*, vol 209, pp196–218
- Gavin, D. G., Brubaker, L. B. and Lertzman, K. P. (2003) 'Holocene fire history of a coastal temperate rain forest based on soil charcoal radiocarbon dates', *Ecology*, vol 84, pp186–201
- Glaser, B., Balashov, E., Haumaier, L., Guggenberger, G. and Zech, W. (2000) 'Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region', *Organic Geochemistry*, vol 31, pp669–678
- Glaser, B., Haumaier, L., Guggenberger, G. and Zech, W. (2001) 'The "Terra Preta" phenomenon: A model for sustainable agriculture in the humid tropics', *Naturwissenschaften*, vol 88, pp37–41
- Golding, C. J., Smernik, R. J. and Birch, G. F. (2004) 'Characterisation of sedimentary organic matter from three south-eastern Australian estuaries using solid-state ^{13}C -NMR techniques', *Marine and Freshwater Research*, vol 55, pp285–293
- Gouveia, S. E. M. and Pessenda, L. C. R. (2000) 'Datation par le ^{14}C de charbons inclus dans le sol pour l'étude du rôle de la remontée biologique de matière et du colluvionnement dans la formation de latosols de l'état de Sao Paulo, Brésil', *C. R. Acad. Sci. [Sciences de la Terre et des Planètes]*, vol 330, pp133–138
- Guggenberger, G., Rodionov, A., Shibistova, O., Grabe, M., Kasansky, O. A., Fuchs, H., Mikheyeva, N., Zhazhevskaya, G. and Flessa, H. (2008) 'Storage and mobility of black carbon in permafrost soils in the forest tundra ecotone in northern Siberia', *Global Change Biology*, vol 14, pp1367–1381
- Hamer, U., Marschner, B., Brodowski, S. and Amelung, W. (2004) 'Interactive priming of black carbon and glucose mineralization', *Organic Geochemistry*, vol 35, pp823–830
- Hammes, K., Torn, M. S., Lapenas, A. G. and Schmidt, M. W. I. (2008) 'Centennial black carbon turnover observed in a Russian steppe soil', *Biogeosciences Discussion*, vol 5, pp661–683
- Harris, P. J. F. (2005) 'New perspectives on the structure of graphitic carbons', *Critical Reviews in Solid State and Materials Sciences*, vol 30, pp235–253
- Harris, P. J. F., Burian, A. and Duber, S. (2000) 'High-resolution electron microscopy of a microporous carbon', *Philosophical Magazine Letters*, vol 80, pp381–386
- Hata, T., Imamura, Y., Kobayashi, E., Yamane, K. and Kikuchi, K. (2000) 'Onion-like graphitic particles observed in wood charcoal', *Journal of Wood Science*, vol 46, pp89–92
- Herring, J. R., (1985) 'Charcoal fluxes into sediments of the North Pacific Ocean: The Cenozoic record of burning', in E. T. Sundquist and W. S. Broecker (eds) *The Carbon Cycle and Atmospheric CO_2 : Natural Variations Archean to Present*, Proceedings of the Chapman Conference on Natural Variations in Carbon Dioxide and the Carbon Cycle, Tarpon Springs, FL, 9–13 January 1984 (A86-39426 18-46), AGU, Washington, DC, pp419–442
- Hobbie, S. E. (2003) 'Interactions between litter lignin and soil nitrogen availability during leaf

- litter decomposition in a Hawaiian montane forest', *Ecosystems*, vol 3, pp484–494
- Hockaday, W. (2006) *The Organic Geochemistry of Charcoal Black Carbon in Soils of the University of Michigan Biological Station*, PhD thesis, Ohio State University, Columbus, US
- Hockaday, W. C., Grannas, A. M., Kim, S. and Hatcher, P. G. (2007) 'The transformation and mobility of charcoal in a fire-impacted watershed', *Geochimica et Cosmochimica Acta*, vol 71, pp3432–3445
- Hofrichter, M., Ziegenhagen, D., Sorge, S., Ullrich, R., Bublitz, F. and Fritsche, W. (1999) 'Degradation of lignite (low-rank coal) by lignolytic basidiomycetes and their peroxidase system', *Applied Microbiology and Biotechnology*, vol 52, pp78–84
- Kawamoto, K., Ishimaru, K. and Imamura, Y. (2005) 'Reactivity of wood charcoal with ozone', *Journal of Wood Science*, vol 51, pp66–72
- Kercher, A. K. and Nagle, D. C. (2003) 'Microstructural evolution during charcoal carbonization by X-ray diffraction analysis', *Carbon*, vol 41, pp15–27
- Kim, S., Kaplan, L. A., Benner, R. and Hatcher, P. G. (2004) 'Hydrogen-deficient molecules in natural riverine water samples: Evidence for the existence of black carbon in DOM', *Marine Chemistry*, vol 92, pp225–234
- Knicker, H. (2007) 'How does fire affect the nature and stability of soil organic nitrogen and carbon?', *Biogeochemistry*, vol 85, pp91–118
- Knicker, H. and Skjemstad, J. O. (2000) 'Nature of organic carbon and nitrogen in physically protected organic matter of some Australian soils as revealed by solid-state ^{13}C and ^{15}N NMR spectroscopy', *Australian Journal of Soil Research*, vol 38, pp113–127
- Koutcheiko, S., Monreal, C. M., Kodama, H., McCracken, T. and Kotlyar, L. (2007) 'Preparation and characterization of activated carbon derived from the thermo-chemical conversion of chicken manure', *Bioresource Technology*, vol 98, pp2459–2464
- Krull, E. S., Swanston, C. W., Skjemstad, J. O. and McGowan, J. A. (2006) 'Importance of charcoal in determining the age and chemistry of organic carbon in surface soils', *Journal of Geophysical Research*, vol 111, pG04001
- Kumar, A., Lobo, R. F. and Wagner, N. J. (2005) 'Porous amorphous carbon models from periodic Gaussian chains of amorphous polymers', *Carbon*, vol 43, pp3099–3111
- Laird, D. A., Chappell, M. A., Martens, D. A., Wershaw, R. L. and Thompson, M. (2008) 'Distinguishing black carbon from biogenic humic substances in soil clay fractions', *Geoderma*, vol 143, pp115–122
- Lehmann, J. (2007a) 'A handful of carbon', *Nature*, vol 447, pp143–144
- Lehmann, J. (2007b) 'Bio-energy in the black', *Frontiers in Ecology and the Environment*, vol 5, pp381–387
- Lehmann, J., da Silva Jr., J. P., Steiner, C., Nehls, T., Zech, W. and Glaser, B. (2003) 'Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: Fertilizer, manure and charcoal amendments', *Plant and Soil*, vol 249, pp343–357
- Lehmann, J., Liang, B., Solomon, D., Lerotic, M., Luizão, F., Kinyangi, J., Schäfer, T., Wirick, S., and Jacobsen, C. (2005) 'Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy for mapping nano-scale distribution of organic carbon forms in soil: Application to black carbon particles', *Global Biogeochemical Cycles*, vol 19, pGB1013
- Lehmann, J., Gaunt, J. and Rondon, M. (2006) 'Bio-char sequestration in terrestrial ecosystems – a review', *Mitigation and Adaptation Strategies for Global Change*, vol 11, pp403–427
- Lehmann, J., Skjemstad, J. O., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K., Woodbury, P. and Krull, E. (2008) 'Australian climate-carbon cycle feedback reduced by soil black carbon', *Nature Geoscience*, vol 1, pp832–835
- Leifeld, J., Fenner, S. and Müller, M. (2007) 'Mobility of black carbon in drained peatland soils', *Biogeosciences*, vol 4, pp425–432
- Liang, B. (2008) *Black Carbon Biogeochemistry in Soils*, PhD thesis, Cornell University, Ithaca, NY
- Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J. O., Thies, J., Luizão, F. J., Petersen, J. and Neves, E. G. (2006) 'Black carbon increases cation exchange capacity in soils', *Soil Science Society of America Journal*, vol 70, pp1719–1730

- Liang, B., Lehmann, J., Solomon, D., Sohi, S., Thies, J. E., Skjemstad, J. O., Luizão, F. J., Engelhard, M. H., Neves, E. G. and Wirrick, S. (2008) 'Stability of biomass-derived black carbon in soils', *Geochimica et Cosmochimica Acta*, vol 72, pp6078–6096
- Masiello, C. A. and Druffel, E. R. M. (1998) 'Black carbon in deep-sea sediments', *Science*, vol 280, pp1911–1913
- Melillo, J. M., Aber, J. D. and Muratore, J. F. (1982) 'Nitrogen and lignin control of hardwood leaf litter decomposition dynamics', *Ecology*, vol 63, pp621–626
- Middelburg, J. J., Nieuwenhuize, J. and Breugel, P. V. (1999) 'Black carbon in marine sediments', *Marine Chemistry*, vol 65, pp245–252
- Miller, R. M. and Jastrow, J. D. (1990) 'Hierarchy of root and mycorrhizal fungal interactions with soil aggregation', *Soil Biology and Biochemistry*, vol 22, pp579–584
- Mitra, A., Bianchi, T. S., McKee, B. A. and Sutula, M. (2002) 'Black carbon from the Mississippi River: Quantities, sources, and potential implications for the global carbon cycle', *Environmental Science and Technology*, vol 36, pp2296–2302
- Nakamura, S., Hiraoka, M., Matsumoto, E., Tamura, K. and Higashi, T. (2007) 'Humus composition of Amazonian Dark Earths in the Middle Amazon, Brazil', *Soil Science and Plant Nutrition*, vol 53, pp229–235
- Neves, E. G., Petersen, J. B., Bartone, R. N. and Silva, C. A. D. (2003) 'Historical and socio-cultural origins of Amazonian Dark Earths', in J. Lehmann, D.C. Kern, B. Glaser and W. I. Woods (eds) *Amazonian Dark Earths: Origin, Properties, Management*, Kluwer Academic Publishers, Dordrecht, The Netherlands, pp29–50
- Nguyen, B., Lehmann, J., Kinyangi, J., Smernik, R. and Engelhard, M. H. (2008) 'Long-term black carbon dynamics in cultivated soil', *Biogeochemistry*, vol 89, pp295–308
- Paris, O., Zollfrank, C. and Zickler, G. A. (2005) 'Decomposition and carbonisation of wood biopolymers – a microstructural study of softwood pyrolysis', *Carbon*, vol 43, pp53–66
- Pessenda, L. C. R., Boulet, R., Aravena, R., Rosolen, V., Gouveia, S. E. M., Ribeiro, A. S. and Lamotte, M. (2001) 'Origin and dynamics of soil organic matter and vegetation changes during the Holocene in a forest-savanna transition zone, Brazilian Amazon region', *Holocene*, vol 11, pp250–254
- Pietikäinen, J., Kiiikkila, O. and Fritze, H. (2000) 'Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus', *Oikos*, vol 89, pp231–242
- Ping, C. L., Michaelson, G. J., Packee, E. C., Stiles, C. A., Swanson, D. K. and Yoshikawa, K. (2005) 'Soil catena sequences and fire ecology in the Boreal forest of Alaska', *Soil Science Society of America Journal*, vol 69, pp1761–1772
- Preston, C. M. and Schmidt, M. W. I. (2006) 'Black (pyrogenic) carbon: A synthesis of current knowledge and uncertainties with special consideration of boreal regions', *Biogeosciences*, vol 3, pp397–420
- Rillig, M. C., Wright, S. F. and Eviner, V. T. (2002) 'The role of arbuscular mycorrhizal fungi and glomalin in soil aggregation: Comparing effects of five plant species', *Plant and Soil*, vol 238, pp325–333
- Rodionov, A., Amelung, W., Haumaier, L., Urusevskaja, I. and Zech, W. (2006) 'Black carbon in the zonal steppe soils of Russia', *Journal of Plant Nutrition and Soil Science*, vol 169, pp363–369
- Rumpel, C., Chaplot, V., Planchon, O., Bernadou, J., Valentin, C. and Mariotti, A. (2006) 'Preferential erosion of black carbon on steep slopes with slash and burn agriculture', *Catena*, vol 54, pp30–40
- Sabine, C. L., Heimann, M., Artaxo, P., Bakker, D. C. E., Chen, C. T. A., Field, C. B., Gruber, N., Quéré, C. le, Prinn, R. G., Richey, J. E., Lankao, P. R., Sathaye, J. A. and Valentini, R. (2004) 'Current status and past trends of the global carbon cycle', in C. B. Field and M. R. Raupach, (eds) *SCOPE 62, The Global Carbon Cycle: Integrating Humans, Climate, and the Natural World*, Island Press, Washington, DC, Chapter 2, pp17–44
- Schmidt, M. W. I. (2004) 'Carbon budget in the black', *Nature*, vol 427, pp305–306
- Schmidt, M. W. I. and Noack, A. G. (2000) 'Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges', *Global Biogeochemical Cycles*, vol 14, pp777–793
- Schmidt, M. W. I., Skjemstad, J. O., Czimeczik,

- C. I., Glaser, B., Prentice, K. M., Gelinas, Y. and Kuhlbusch, T. A. J. (2001) 'Comparative analysis of black carbon in soils', *Global Biogeochemical Cycles*, vol 15, pp777–794
- Schmidt, M. W. I., Skjemstad, J. O. and Jäger, C. (2002) 'Carbon isotope geochemistry and nanomorphology of soil black carbon: Black chernozemic soils in central Europe originate from ancient biomass burning', *Global Biogeochemical Cycles*, vol 16, pGB1123
- Shibuya, M., Kato, M., Ozawa, M., Fang, P. H. and Osawa, E. (1999) 'Detection of buckminsterfullerene in usual soots and commercial charcoals', *Fullerene Science and Technology*, vol 7, pp181–193
- Shneur, E. A. (1966) 'Oxidation of graphite carbon in certain soils', *Science*, vol 151, pp991–992
- Skjemstad, J. O., Clarke, P., Taylor, J. A., Oades, J. M. and McClure, S. G. (1996) 'The chemistry and nature of protected carbon in soil', *Australian Journal of Soil Research*, vol 34, pp251–271
- Skjemstad, J. O., Taylor, J. A., Janik, L. J. and Marvanek, S. P. (1999) 'Soil organic carbon dynamics under long-term sugarcane monoculture', *Australian Journal of Soil Research*, vol 37, pp151–164
- Skjemstad, J. O., Dalal, R. C., Janik, L. J. and McGowan, J. A. (2001) 'Changes in chemical nature of soil organic carbon in Vertisols under wheat in southeastern Queensland', *Australian Journal of Soil Research*, vol 39, pp343–359
- Skjemstad, J. O., Reicosky, D. C., Wilts, A. R. and McGowan, J. A. (2002) 'Charcoal carbon in US agricultural soils', *Soil Science Society of America Journal*, vol 66, pp1249–1255
- Sollins, P., Homann, P. and Caldwell, B. A. (1996) 'Stabilization and destabilization of soil organic matter: Mechanisms and controls', *Geoderma*, vol 74, pp65–105
- Tiessen, H. and Stewart, J. W. B. (1988) 'Light microscopy of stained microaggregates: The role of organic matter and microbes in soil aggregation', *Biogeochemistry*, vol 5, pp312–322
- Tisdall, J. M. and Oades, J. M. (1982) 'Organic matter and water-stable aggregates in soils', *Journal of Soil Science*, vol 33, pp141–163
- Topoliantz, S. and Ponge, J. F. (2005) 'Charcoal consumption and casting activity by *Pontosclex corethrurus* (Glossoscolecidae)', *Applied Soil Ecology*, vol 28, pp217–224
- Topoliantz, S., Ponge, J. F. and Lavelle, P. (2006) 'Humus components and biogenic structures under tropical slash-and-burn agriculture', *European Journal of Soil Science*, vol 57, pp269–278
- Wardle, D. A., Nilsson, M. C. and Zackrisson, O. (2008) 'Fire-derived charcoal causes loss of forest humus', *Science*, vol 320, p629
- Warnock, D. D., Lehmann, J., Kuyper, T. W. and Rillig, M. C. (2007) 'Mycorrhizal responses to biochar in soil – concepts and mechanisms', *Plant and Soil*, vol 300, pp9–20
- Wengel, M., Kothe, E., Schmidt, C. M., Heide, K. and Gleixner, G. (2006) 'Degradation of organic matter from black shales and charcoal by the wood-rotting fungus *Schizophyllum commune* and release of DOC and heavy metals in the aqueous phase', *Science of the Total Environment*, vol 367, pp383–393
- Willmann, G. and Fakoussa, R. M. (1997) 'Extracellular oxidative enzymes of coal-attacking fungi', *Fuel Processing Technology*, vol 52, pp27–41
- Yanai, Y., Toyota, K. and Okazaki, M. (2007) 'Effects of charcoal addition on N₂O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments', *Soil Science and Plant Nutrition*, vol 53, pp181–188