

Changes of Biochar in Soil

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Introduction

Until recently, the paradigm has been that naturally occurring char (similar to certain forms of biochar) deposited in the soil is relatively inert and stable for millennia and can serve as a sink for atmospheric C (Schmidt and Noack, 2000; Forbes et al, 2006; Preston and Schmidt, 2006; Czimczik and Masiello, 2007). If char deposited by vegetation fires were inert, the Earth's carbon (C) reservoirs would be entirely converted to biochar in less than 100,000 years (Goldberg, 1985; Druffel, 2004). Although biochar pieces are still present in the dark-coloured, fertile Terra Preta soils of the Amazon thousands of years after slash-and-burn practices have ceased in the region, the majority of the highly aromatic biochar particles present in these soils are no longer recognizable as physical pieces (Glaser et al, 2001, 2002). The majority of the biochar applied and incorporated within the soil in this region of the Amazon over centuries underwent various changes and became macroscopically unrecognizable, while enriching the soil with nutrients and

changing soil properties. Changes in soil properties have been recorded for different soils to which biochar was added and include increasing the cation exchange capacity and pH of the soil (Liang et al, 2006; Cheng et al, 2008), creating hydrophobic sites (Rumpel et al, 2006), and increasing adsorption sites for microbes (Baldock and Smernik, 2002; Hamer et al, 2004; Hockaday et al, 2006, 2007), minerals (Brodowski et al, 2005) or pesticides (Smernik et al, 2006).

Knowing the extent and implications of the changes that added biochar in the soil undergoes is vital for understanding the contribution that biochar can make to soil amelioration and sustainable soil management in the future. Ideally, biochar in the soil should be stable enough (i.e. change physically, chemically and biologically at a slow enough pace to provide long-term benefits to the environment, such as the biochar-rich Terra Preta soils). The topic of biochar stability is discussed extensively in Chapter 11.

The changes that biochar can undergo also depend upon its production conditions. These conditions are of great importance to achieve long-term soil enhancement – for example, its sorption properties are initially strongly influenced by the production temperature (Lehmann, 2007) and atmosphere, which determine the surface area of the particles (Brown et al, 2006). This is discussed in detail in Chapter 8. This chapter specifically looks at the mechanisms of

change which biochar undergoes that are brought about by the environment to which it is added or in which it occurs. Many examples in this chapter relate to char from natural or anthropogenic burning, or char specifically produced for an experiment relating to changes in soil properties; but the changes that these char particles undergo can be applied to biochar in soil that is specifically produced and applied as a soil amendment.

Mechanisms of incorporation and movement of biochar in soil

As deliberate soil amendment (as apposed to char from vegetation fires), biochar is, in most cases, incorporated within the soil, rather than just being added on the surface where wind or water erosion can transport biochar particles (Glaser et al, 2002). Biochar has some unique properties that make it particularly susceptible to movement in the soil. Biochar can be mobilized at different scales in the landscape, ranging from fractions of metres in the soil profile that mainly involve tillage, turbation and dissolution, up to hundreds of metres through erosion of biochar from the soil.

Soil tillage

Little has been published about the application of biochar in soil (see Chapter 12). Specifically, the incorporation of biochar within the soil and its associated mobility in the soil profile is important to study since different locations in the soil's profile provide different environments for microbial activity, oxygen (O) supply and oxidation of biochar (Leifeld et al, 2007). We can gain some insight into how biochar can be incorporated and moves within the soil profile from studies where biochar, from natural or anthropogenic burning, already present in the soil

was further incorporated in the soil profile. In soil that remained under sugar cane cultivation in Australia for more than 35 years, a large proportion of biochar was found in the subsoil (Skjemstad et al, 1999). There was evidence that some of this subsoil biochar had been relocated from shallower horizons via tillage. Most of this biochar pre-dated cane farming through a common historical practice to clear land under savannahs and open woodland in Australia and Southern Africa (Bird et al, 1999; Skjemstad et al, 1999). However, in some of the light-textured soils analysed in this study (Skjemstad et al, 1999), recent burning of cane could have contributed to the accumulation of biochar at depth, also by means of tillage.

Turbation

Physical mixing is not only restricted to management practices. Bioturbation is common in soils such as Alfisols and Mollisols, with high activity from earthworms and burrowing rodents, which can relocate biochar deeper in the soil (Eckmeier et al, 2007). In Vertisols, the extreme shrink–swell capacity of the soils physically mixes biochar to depth (Czimczik and Masiello, 2007).

Transport in solution (dissolution)

Over time, biochar particles can degrade to such a degree that dissolved organic carbon (DOC) of aromatic nature can be measured in soil pore water. One hundred years after char was deposited in a forest soil after a fire, Hockaday et al (2006, 2007) detected condensed aromatic ring structures with high functionality (O-containing functional groups), originating from the degradation of these char pieces, in soil pore waters. This type of finding has also been made in other places in North and South America: coastal waters off the East Coast of the US (Chesapeake Bay) (Mannino and Harvey, 2004), the Rio Negro or a black water stream from the New Jersey Pine Barrens (Kim et al, 2004). In drained peatland soils in Switzerland where wood and coal char residues were previously disposed, Leifeld et al (2007) found substantial amounts of biochar (up to 51g kg⁻¹ soil) below 0.3m (ploughing depth of the soil). The large pore volume and water saturation of the soil could have led to the transport of soluble biochar down the profile (Leifeld et al, 2007). Hammes et al (2008) also found an increasing proportion of highly condensed black C (mellitic acid) in the subsoil (below 0.3m) of a recently sampled biochar-rich Chernozem soil compared to the same soil sampled 100 years earlier. Highly condensed biochar molecules are not easily degraded and are, instead, transported down the profile over time, whereas less condensed biochar is more easily broken down (Hammes et al, 2008). In another study, a mixture of biochar produced from two types of wood at 400°C was incubated with *Schizophyllum commune*, a typical wood-rotting fungus-producing exoenzyme. After 84 days, the transformation of biochar by the fungus was clearly demonstrated by the release of DOC that was rich in aromatic compounds (Wengel et al, 2006). In what

way biochar-derived DOC differs in its adsorption to minerals (Kaiser and Guggenberger, 2000) is not known.

Erosion as a means of mobility in the landscape

On agricultural land subjected to slash-and-burn, with steep slopes that are prone to erosion, such as the tropical regions of northern Laos, biochar particles from burning of agricultural residues have been found to preferentially erode from the soil compared to bulk soil organic matter or mineral-bound C (Rumpel et al, 2006). Reasons for this include:

- the low density of biochar particles (Glaser et al, 2000), which even allows larger particles to float; and
- the small colloidal size of the smallest biochar particles compared to other soil components, allowing them to stay suspended for a longer period of time.

On the other hand, biochar particles bound to mineral matter are much harder to detach from the soil by splashing or to transport by discontinuous runoff (Rumpel et al, 2006). A similar set of rules apply in cold climate regions, such as northern Siberia, where permafrost stores large amounts of organic C, which includes biochar from biomass burning. The biochar in permafrost is usually protected from alteration and loss; but during snowmelt periods and concurrent surface water flow, biochar has been calculated at almost 4 per cent of the exported organic C in the stream water (Guggenberger et al, 2008). Similar to results from tropical regions, biochar was found to be mobilized in a dissolved and colloidal phase and exported from the soil. However, compared to the tropical soil and the permafrost, the mineral soil (with no permafrost) in the Siberian region did not store as much biochar as the

mineral soil in the tropics, where biochar can be bound to minerals (Guggenberger et al, 2008). This could be due to a combination of unfavourable climatic conditions, reburning

of biochar in organic layers and a different mineralogy in the cold climate mineral soil compared to the tropics.

Physical changes of biochar in soil

Particle fragmentation

When large biochar pieces are fragmented into smaller particles by physical means, they expose more surfaces that are accessible to further chemical and biological processes acting on these particles in the soil (Carcaillet, 2001; Cheng et al, 2006). Several processes have been identified to cause fragmentation of biochar particles in soil and are discussed below.

Freeze–thaw cycles

In places with steep temperature gradients and frequent freeze–thaw cycles (such as areas at high elevations), large biochar particles can be fragmented into smaller particles when water penetrates the pores and swell during freezing, forcing the bigger biochar particles to break (Carcaillet, 2001).

Rain and wind

Raindrops or wind may reduce the particle size of biochar from certain types of biomass (Skjemstad and Graetz, 2003). Biochar from grassland and understorey vegetation in savannahs and woodlands is more sensitive to physical impact than wood biochar (Skjemstad and Graetz, 2003). This type of fragmentation could be minimized by the incorporation of biochar amendments within the soil; but further research is needed to determine the extent of this type of fragmentation.

Penetration by plant roots and fungal hyphae

In an incubation study where biochar was

mixed with soil and planted with cowpeas, biochar particles between 1mm and 20mm in size were covered with fine plant roots and sometimes even penetrated by plant roots after 45 days (Lehmann et al, 2003). This could be a possible mechanism whereby biochar particles are fragmented into smaller particles for further chemical and microbial reactions, while also directly delivering nutrients to the plant. Money (1995) describes the significant force that fungal hyphae can exert on solid materials to penetrate them, and ascribes it to increased cell turgor. Some fungi, such as *Magnaporthe*, can exert a pressure of up to 8.0MPa to penetrate a cell wall (Money, 1995, and references therein). This mechanism probably also occurs in soil when colonizing fungi penetrate and fragment biochar pieces.

Bioturbation

Small rodents and insects can actively incorporate biochar into the soil. In a slash-and-burn experiment, it was suggested that mice probably mixed biochar particles lying on the forest floor with the uppermost part of the soil (Eckmeier et al, 2007). Earthworms ingested these particles (>2mm) (but did not digest them) and redistributed them in the profile (concentrated at 0.8m depth) by excretion, as shown by thin sections of soil with small biochar particles present in earthworm casts (Eckmeier et al, 2007). In tropical organic-poor soils it was found that the earthworms do not ingest the particles, but push them aside as they burrow, or when they are ingested they are excreted in a muddy paste, transporting biochar deeper

into the soil (Glaser et al, 2000; Topoliantz and Ponge, 2003; Ponge et al, 2006). Bioturbation does not necessarily contribute to biotic transformation of biochar in soil, although it can be a first essential step, facilitating any further alteration of biochar, where particles are often ground to silt-size fractions (Ponge et al, 2006).

Pore size change with adsorption of organic matter

Biochar has a fine pore structure (depending upon the production temperature and atmosphere), which allows the trapping of different compounds physically within the pores (see

Figure 10.1) (Nguyen et al, 2004; Yu et al, 2006). Biochar adsorbs organic C that is rich in functional groups (Kaiser and Guggenberger, 2000), a process which is made possible by the presence of oxidized functional groups (carboxylic and phenolic functionalities) on the surface of biochar particles (Glaser et al, 2002; Lehmann et al, 2005). Using nuclear magnetic resonance (NMR), Hockaday et al (2007) showed that biochar in soil originating from a forest fire over 100 years ago had acquired non-aromatic and O-containing functional groups during oxidation, compared to biochar from a recent fire.

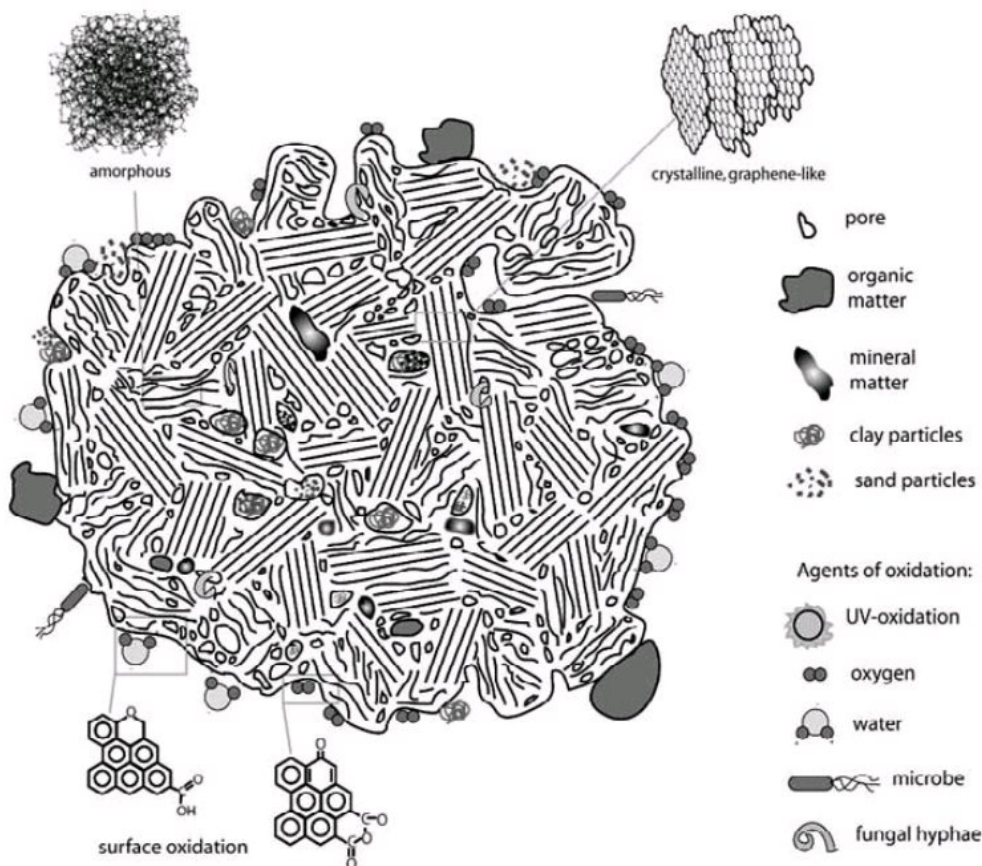


Figure 10.1 A basic model of a complex biochar particle in the soil, containing two main distinguished structures of biochar: crystalline graphene-like sheets surrounded by randomly ordered amorphous aromatic structures and pores of various sizes

Note: Biochar particles are subjected to surface oxidation by various agents and adsorption of non-biochar organic matter in the soil. The most important surface oxidation products, including phenol, carbonyl and carboxylic acid groups, are shown (amorphous carbon with permission under free document licence).

However, an aspect of this adsorption property that has not been investigated much is the fact that biochar pores may be blocked by the substances it is adsorbing, rendering inner pores inaccessible as further adsorption sites (Zackrisson et al, 1996; Kwon and Pignatello, 2005; Warnock et al, 2007). After 90 days of incubating maple biochar in a soil–water suspension, the total surface area reduced tenfold, probably due to the adsorption of organic matter (Kwon and Pignatello, 2005). In a complementary study, Pignatello et al (2006) determined that high molecular weight humic substances on the external surfaces of powdered wood biochar with pores smaller than 2nm blocked access to sorption sites deep within the pores and acted as competitive adsorbates. In a study on the ability of biochar to adsorb phenolic compounds, relatively fresh biochar (<100 years) could adsorb significantly more phenolic compounds than biochar from fires more than 100 years ago (Zackrisson et al, 1996). The authors suggest that, over time, biochar becomes deactivated as its pores become clogged and its sorption capacity decreases. Biochar pores from woody species

are generally <20µm, which allows the entry of bacteria, fungi and certain nematodes that aid in the decomposition of the adsorbed phenols. This relationship leads to the reactivation of biochar particles (Zackrisson et al, 1996).

Another interesting phenomenon regarding polycyclic aromatic hydrocarbon (PAH) sorption to biochar was observed by Hockaday (2006). In soil rich with natural organic matter (NOM), the pyrene sorption capacity of biochar seems to decrease over a 100-year period in soil. The surface area of entire biochar particles produced in a fire in 1900 was at least half of that of recently produced biochar in 1998. However, this was not due to pore blockage by the NOM, but rather explained by the ability of NOM associated with the biochar surface to displace pyrene that would otherwise sorb to the biochar surface by multilayer stacking in the absence of NOM (Hockaday, 2006). How NOM interferes with PAH sorption to biochar particles has not been fully explained and this phenomenon requires further research.

Chemical changes of biochar in soil

An increasing number of long-term field studies give evidence that the chemical state of biochar is altered with residence time in the soil.

Non-aromatic functionality increases with residence time in soil

Fresh biochar mainly consists of a crystalline phase with graphene-like sheets and an amorphous phase of aromatic structures (see Figure 10.1 and Chapter 11; Lehmann et al,

2005; Cohen-Ofri et al, 2006). Already shortly after formation and definitely after incorporation in the soil, the outer surfaces of biochar particles undergo oxidation and interactions with various soil constituents (see Figure 10.1). These outer surfaces containing various functional groups (O- and H-containing) are exposed foremost to rapid surface oxidation (Lehmann, 2007). In a detailed study on biochar oxidation by Cheng et al (2006), results indicate that spontaneous abiotic oxidation of biochar particles takes place by chemisorption of O at high temperatures. When biochar was incubated at 70°C

for four months, the acid functional groups significantly increased compared to biochar incubated at 30°C (Cheng et al, 2006). An increase in non-aromatic functionality was also recorded in biochar collected from historical charcoal blast furnaces in the US, and consisted mainly of OH bonds, carboxylic acid groups and phenolic acids (Cheng et al, 2008). Similar findings were made in Australian soils with varying biochar contents that were quantified using ultraviolet (UV) oxidation and NMR (Skjemstad et al, 1999). Apart from being rich in aryl C, these biochar samples also displayed relatively high carbonyl C peaks, which probably resulted from the partial oxidation of fine char particles. This would lead to the production of aryl carboxylic structures (Skjemstad et al, 1999). Additionally, with increasing acid functional groups, biochar can become more hydrophilic and enhance further physical, chemical, and biological weathering, such as fragmentation to smaller particles, leaching down the soil profile, forming DOC, or export from the soil profile (Shindo et al, 1986; Shindo, 1991; Haumaier and Zech, 1995; Bird et al, 1999; Kramer et al, 2004; Cheng et al, 2006).

Elemental composition change with oxidation in soil

Biochar often consists of >70% C, but also contains other elements (O, H, N, S, P, Si, base cations, heavy metals) to varying extents (see Chapter 5; Goldberg, 1985; Preston and Schmidt, 2006). The development of non-aromatic functionality initially takes place on the surface of the biochar with a resulting change in elemental composition of the biochar particles, with increasing proportions of mainly O and H (Cheng et al, 2006, 2008; Hammes et al, 2006; Hockaday et al, 2006, 2007). Apart from surface oxidation, sorption of organic matter to biochar particles can also lead to an increase in functionality, and the two mechanisms are difficult to discern. Figure 10.2 shows the H/C and O/C atomic ratios of different types of wood biochar in a van Krevelen diagram and how the biochar increases in functionality (acquires additional H and O atoms) when incubated for various lengths of time and at different temperatures compared to fresh biochar (Shindo, 1991; Baldock and Smernik, 2002; Cheng et al, 2006, 2008). The inset arrows show the main processes involved in the elemental composition change: oxidation, hydration and de-carboxylation (Hammes et al, 2006).

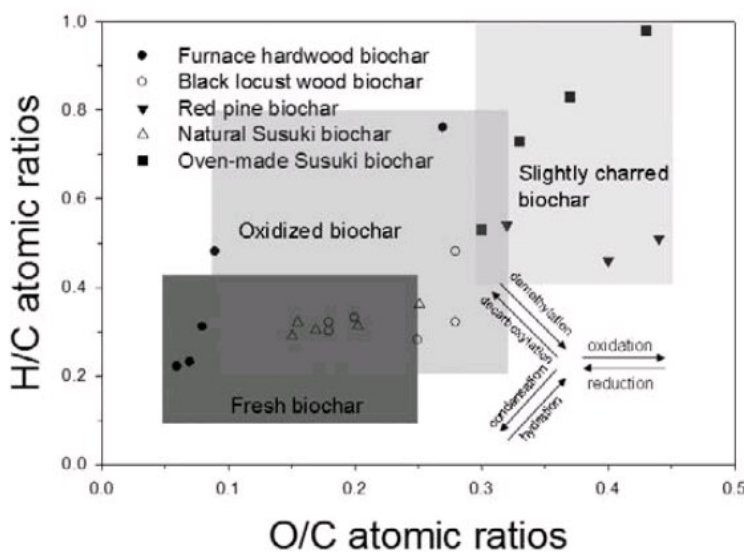


Figure 10.2 Van Krevelen plot of the elemental composition change of five types of biochar with incubation and over time

Note: 'Fresh biochar' implies biochar produced at around 450°C or higher. 'Oxidized biochar' implies biochar that has been subjected to oxidation conditions. 'Slightly charred biochar' implies biochar produced below 450°C. The arrows (lower right) indicate the processes involved in the change in elemental composition of biochar during its residence time in the soil under different circumstances (Hammes et al, 2006).

Source: furnace hardwood biochar: Cheng et al (2008); black locust wood biochar: Cheng et al (2006); natural Susuki plant biochar: Shindo (1991); oven-made Susuki biochar: Shindo (1991); red pine biochar: Baldock and Smernik (2002)

Changes in surface charge of biochar in soil

Cohen-Ofri et al (2006) compared the structures of modern and fossil biochar (3000 years' and 40,000 years old) and found that both types contained an inner crystalline phase composed of graphite-like microcrystals and a non-organized phase surrounding it (mainly consisting of aromatic groups). However, there were distinct differences between the modern and fossil biochar. The graphite-like phase of the fossil biochar had a higher electrical resistivity and a markedly altered surface electronic state compared to the modern biochar. This is a clear indication of the extent of surface oxidation that the fossil biochar particles had undergone. With time, the increase in functional groups (including mainly carboxyl groups, but also phenolic, hydroxyl, carbonyl or quinone C forms) leads to an evolution of surface negative charge by replacing the surface positive charge of the particles (Cheng et al, 2006, 2008). These negatively charged particles increase the charge density on the surfaces of biochar particles and are responsible for the high cation exchange capacity (CEC) in the pH range of soil (Liang et al, 2006).

Biochar interaction with different mineral phases

Mineral interactions (formation of 'organo-mineral complexes') can decrease oxidation

and degradation of biochar particles (see Chapter 11; Brodowski et al, 2005) and contribute to the long mean-residence times of biochar in soil (Brodowski et al, 2006). Applying scanning electron microscopy and energy-dispersive X-ray spectrometry, Brodowski et al (2005) observed various associations of biochar particles with mineral particles in an agricultural soil in Germany (see Figure 10.3). Particle size fractionation revealed that the biochar particles occurred either as discrete particles unassociated with minerals, or as particles attached to minerals. Attachment was evident in mainly three forms:

- 1 free biochar particles with embedded and associated clay- and silt-sized minerals (see Figure 10.3);
- 2 small biochar particles bound to minerals; and
- 3 small mineral particles bound to large biochar particles.

In Amazonian Terra Preta soils, most biochar was found in the light soil fraction ($<2.0\text{g cm}^{-3}$), indicating that it was not chemically stabilized, but intrinsically refractory. However, a large part of the biochar was found in the heavy soil fraction ($>2.4\text{g cm}^{-3}$), where it was physically trapped in plaques of Fe or Al on the surface of mineral particles (Gu et al, 1995). The major part of the medium density fraction seemed to be associated with minerals (Glaser et al, 2000).

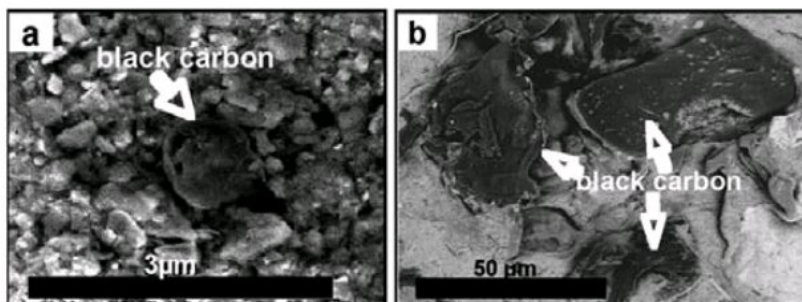


Figure 10.3 Scanning electron micrographs of biochar particles (a) in the clay fraction and (b) in the density fraction $<2.0\text{g cm}^{-3}$

Source: adapted from Brodowski et al (2005), with permission from the authors and the publisher

Biotic changes of biochar in soil

Microorganisms in contact with biochar particles in the soil are able to change the amount and properties of biochar, but due to the long half-life of biochar, this effect is sometimes difficult to measure (Lehmann and Rondon, 2006). Indeed, in a short-term study (four months) of the oxidation of biochar, Cheng et al (2006) recorded significantly more abiotic oxidation on biochar than microbial (biotic) oxidation. The biochar with microbial inoculation showed no or little additional change in pH, CEC or elemental composition compared to the biochar incubated without an inoculum (Cheng et al, 2006). However, an increasing number of studies confirm that significant microbial-induced changes take place in biochar in the long term and that the initial abiotic oxidation could actually facilitate further microbial oxidation.

Fungal growth on biochar particles

Fungal hyphae growing on biochar particles in soil could be evidence that fungi may play a key role in changing biochar properties (Hockaday et al, 2007). The authors found filamentous microorganisms that infiltrated biochar particles, which were produced during a fire and deposited in the soil 100 years ago. As discussed above for pore sizes, this could influence the capacity and manner with which these overgrown particles can interact with other soil components such as minerals. The aged biochar also contained more functional groups and oxidized sites compared to fresh biochar in an adjacent soil where the forest was burned recently (Hockaday et al, 2007). On the other hand, Zackrisson et al (1996) propose that biochar particles in soil act as a foci for microbial activity, which decomposes soil organic matter that has adsorbed to the biochar

surface, in this way cleaning and reactivating the surface, and effectively delaying the saturation of the biochar sorption capacity. Data from a boreal forest fire chronosequence suggests that saturation of biochar sorptive capacity for phenolic compounds requires approximately 200 years of residence time in the soil (Zackrisson et al, 1996).

Likely candidates for microbial alteration of biochar are wood-rotting and leaf litter-decaying basidiomycetes. Under oxic conditions, basidiomycetes can cleave C–C bonds in aromatic structures with extracellular enzymes (Mn-peroxidase, lignin-oxidase and laccase) in a co-metabolic process (Czimczik and Masiello, 2007, and references therein).

Other incubation studies also provide evidence for the degradation of biochar by microorganisms:

- a microbial inoculum isolated from a decomposing *Pinus resinosa* log, incubated with biochar for 120 days with partially charred material (Baldock and Smernik, 2002);
- an inoculum of coal-containing agricultural soil, incubated with biochar for 60 days (Hamer et al, 2004); and
- *Schizophyllum commune*, a typical wood-rotting fungus producing exoenzymes, incubated with biochar for 84 days (Wengel et al, 2006).

The authors of these studies did not indicate if microbes had, in fact, infiltrated the biochar particles or only mineralized them with enzymes on the outer surfaces. However, another study specifically looking at the habitation of biochar by microorganisms found that different types of biochar in soil could support various microbial communities (Pietikäinen et al, 2000).

Co-metabolism of biochar with nutrient-rich substrate

The addition of glucose has brought about positive priming effects on soil organic C under various circumstances (Hamer and Marschner, 2002) and changes to biochar properties occur to a greater extent under the addition of a nutrient-rich co-substrate. Biochar mineralization and most likely oxidation in incubated soil were increased with glucose addition by as much as 115 per cent relative to a control soil (Hamer et al, 2004). These observed positive priming effects were probably due to enhanced oxidation of the biochar materials themselves since the addi-

tionally released CO₂-C largely exceeded the amount of microbial C and dissolved organic C introduced with the inoculum (Hamer et al, 2004). Biochar incubated at 30°C for four months with the addition of dairy manure showed a large change in elemental composition (increase in O and decrease in C) compared to biochar incubated alone or with microorganisms (Cheng et al, 2006). In addition, for biochar oxidized in a forest soil over 100 years, it is hypothesized that the oxidation of biochar to water-soluble condensed aromatic ring structures was accelerated by fungal co-metabolism (Hockaday et al, 2006).

Conclusions

Biochar is no longer viewed as an inert material that remains unaltered in the soil where it is deposited. Using the example of the fertile Amazonian Dark Earths, biochar is incorporated in soil with organic or inorganic fertilizer as a soil ameliorant to enhance certain soil properties such as pH, CEC and microbial proliferation. Other chapters in this book discuss the physical and structural properties (Chapter 2), microchemical properties (Chapter 3), organo-chemistry (Chapter 4) and nutrient properties (Chapter 5) of biochar based on its formation conditions. These properties influence the changes that biochar can undergo in soil. After initial physical fragmentation, the most profound changes to biochar in the soil are chemical and microbial, with products including highly functionalized and nega-

tively charged particles associated with clay particles or minerals (among others), as well as aromatic dissolved organic C. Due to the relative longevity of biochar in soil it is difficult to estimate how long it can survive in one form or another (free particles, associated and dissolved) to serve soil fertility and act as a C sink before it is mineralized to CO₂.

Further studies on application rates, mixing and stability of biochar in the soil, under different climatic conditions, are necessary to understand its long-term role in soil fertility management. Moreover, it would be interesting to study whether it is more advantageous to add fresh biochar to the soil as an amendment compared to biochar that has been aged artificially. To this extent, the timescale of biochar change in an agronomic context is not clear yet.

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