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16

## Priming effects in biochar-amended soils: implications of biochar-soil organic matter interactions for carbon storage

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### Introduction to biochar – soil organic matter cycling interactions

While understanding of biochar persistence in soil has improved in recent years, the ways in which biochar interacts with non-biochar (naïve) soil organic matter (SOM) are only beginning to be understood. Research within the last decade has revealed that biochar additions to soil can affect the mineralization of soil organic carbon (SOC). Conversely, the mineralization of biochar in the environment has also been shown to vary with soil type, likely due to the effect of native SOM and other soil properties on the mineralization of biochar. It is important to recognize and study biochar-SOM interactions for a number of reasons. First, these interactions must be understood and quantified so that biochar users or land managers can accurately predict future soil C stocks following biochar amendments, which is particularly important in scenarios where the C impact of biochar application must be properly determined for climate change mitigation purposes. Second,

many important properties of soil depend upon the quantity of organic matter (OM) present, including fertility, water holding capacity and aggregation. Third, any changes in SOC cycling following the addition of biochar will have effects on the cycling of other nutrients associated with SOM, including nitrogen (N) and phosphorus (P), possibly altering nutrient availability to soil microbes or plants, nutrient leaching or gaseous emission rates. Thus, the interactions between biochar and SOM could have a critical effect on most or all of the very benefits one hopes to gain through the application of biochar to soil. Research on biochar-SOM interactions is still growing (e.g., this chapter and its subject are a new addition to the first, 2009, edition of this book). This chapter reviews what is known about biochar-SOM interactions, theorizes possible mechanisms for these interactions and suggests future research directions and approaches.

## Trends and mechanisms for changes in native SOC mineralization with biochar additions

C and have a baseline, no-biochar control treatment. The studies that found the greatest increases in SOC mineralization with biochar additions usually detected these increases during short laboratory incubation periods or during early portions of longer term studies (Luo et al, 2011; Zimmerman et al, 2011; Singh and Cowie, 2014; Farrell et al, 2013) (Figure 16.3).

Some studies have found that increases in native SOC mineralization observed initially diminish with time (Keith et al, 2011; Zimmerman et al, 2011; Singh and Cowie, 2014). Still other studies have observed decreases in SOC mineralization with biochar additions (Kuznyakov et al, 2009; Dempster et al, 2011; Keith et al, 2011; Jones et al, 2012; Stewart et al, 2012; Prayogo et al, 2013; Whitman et al, 2014b), and there are some studies that have found that biochar additions decreased SOC mineralization immediately (Cross and Sohi, 2011; Whitman et al, 2014a). These immediate decreases may be transient effects, due to a number of possible mechanisms that decrease SOC mineralization discussed below, such as substrate switching or the dilution effect (Singh and Cowie, 2014; Whitman et al, 2014a). Finally, many studies have found no significant effect of biochar additions on native SOC mineralization (Kuznyakov et al, 2009; Cross and Sohi, 2011; Dempster et al, 2011; Mukome et al, 2013; Prayogo et al, 2013). The widely ranging results of these previous studies are not necessarily surprising, given the diversity of systems which have been studied. These differences may be due to variations in the proportion of labile C in biochars (Luo et al, 2011), amount and type of labile OM in soil (Keith et al, 2011), the extent of biochar aging in soil (Liang et al, 2010; Cross and Sohi,

There are diverse mechanisms that may account for increased or decreased mineralization of native SOC following biochar additions. Before discussing these and other effects, the phenomenon known as 'apparent priming' should be understood. Blagodatskaya and Kuznyakov (2008) describe apparent priming as an increase in CO<sub>2</sub> evolution from soils due to acceleration of microbial metabolism (or 'maintenance respiration'), such as that which might be caused by the addition of nutrients or organic substrates to a system (Figure 16.4). Thus, while microbial C turnover may increase, non-microbial biomass SOC mineralization does not. However, they note that this increased microbial activity may still be accompanied by greater SOC mineralization through increased enzyme production and sustained co-metabolic effects, which would be defined as a 'true' priming effect. A coarse indicator of the presence of true priming is that the amount of CO<sub>2</sub> respired is greater than the amount of C present as microbial biomass (Kuznyakov, 2010). By measuring the effect of a substrate on microbial biomass and its contribution to the microbial C pool, apparent priming can be distinguished from true priming (Paterson and Sim, 2013).

Due to the still limited number of studies and the wide range of systems in terms of soil and biochar types and experimental conditions, it is difficult to conduct a meaningful meta-analysis on the effects of biochar on native SOC mineralization at this point. However, it is possible to point to some broad trends in the results of studies conducted to date. The final timepoint data from 13 biochar-SOM interaction studies were combined to produce Figures 16.2 and 16.3, with the criteria for inclusion being that studies conclusively partition SOM and biochar-derived

## 'Priming': biochar interactions with SOM

SOM in a soil receiving an organic amendment as compared to the turnover of SOM in an untreated soil, in recent years, the term has been applied to extremely diverse phenomena. For example, Kuznyakov et al (2000) defined priming effects as, 'strong short-term changes in the turnover of soil organic matter caused by comparatively moderate treatments of the soil. Such treatments might be input of organic or mineral fertilizer to the soil, exudation of organic substances by roots, mere mechanical treatment of soil, or its drying and rewetting.' Clearly, under such a broad definition, priming almost becomes a synonym for any change in SOM turnover rate induced by an external forcing.

In systems that include biochar, it is now recognized that priming can be interactive – i.e., each C source – biochar and SOM – affects the mineralization of the other (Keith et al, 2011; Zimmerman et al, 2011). Furthermore, both positive and negative priming can occur simultaneously, but may change in relative importance over time (Zimmerman and Gao, 2013), as observed in laboratory incubation studies (Keith et al, 2011; Zimmerman et al, 2011; Singh and Cowie, 2014). While all the systems discussed in this chapter include native SOM and biochar, systems with other OM inputs, such as fresh plant residues, root exudates or root litter, will also be discussed. Because of the broad and varied meanings assigned to the term 'priming' across the literature, for clarity, the terms 'increased or decreased decomposition or mineralization' (of SOM or SOC relative to a no-biochar treatment) will be used preferentially.

The term 'priming' is commonly used to describe an increase or decrease in mineralization of one source of OM (e.g., native SOM) due to the addition of a new OM source (e.g., biochar, Figure 16.1).

The 'priming' phenomenon was first identified by Löhnis in 1926, who observed that additions of fresh organic matter, or 'green manure', to soils resulted in the stimulation of N mineralization in existing SOM (Löhnis, 1926). About 30 years later, Bingham et al (1953) introduced the idea that priming effects could be both positive (mineralization increases) or negative (mineralization decreases). While positive (or negative) priming is most commonly used to refer to the faster (or slower) turnover of

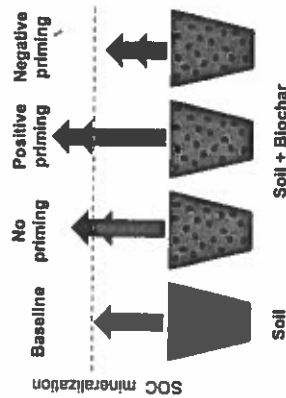


Figure 16.1 Schematic of positive and negative priming of soil organic matter (SOM) by biochar. The size of the arrows represents the magnitude of C mineralized from SOM (grey) and biochar (black) in soils without (far left) and with (three scenarios on right) biochar additions

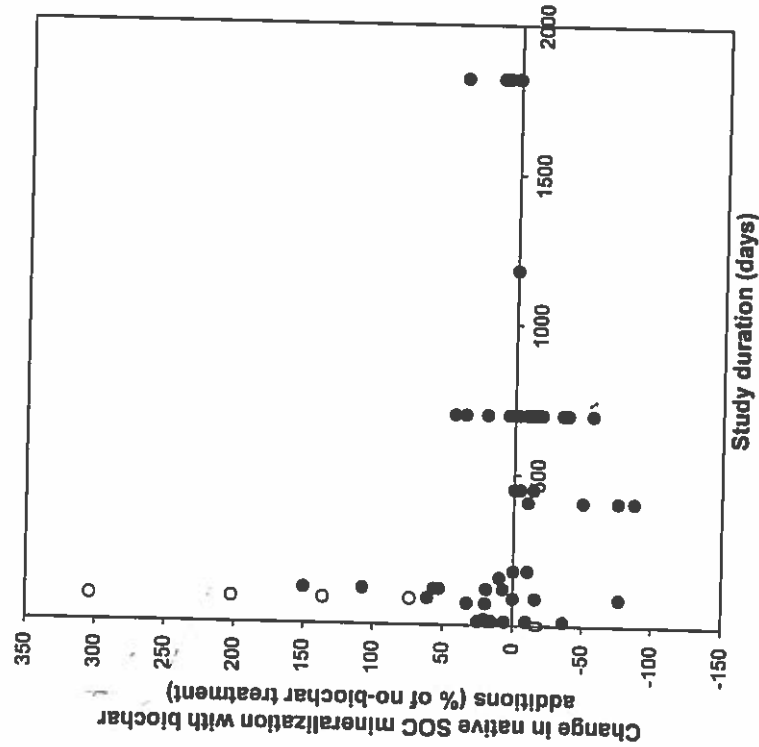


Figure 16.2 Net biochar effect on native SOC mineralization (relative to the no-biochar control) vs. total duration of study. Data from 13 studies (Kuzaykov et al. 2009; Steinbeiss et al. 2009; Cross and Sohi, 2011; Jones et al. 2011; Keith et al. 2011; Luo et al. 2011; Zimmermann et al. 2011; Bruun and El-Zehery 2012; Santos et al. 2012; Stewart et al. 2012; Farrell et al. 2013; Maestrini et al. 2014; Singh and Cowie, 2014). Open circles indicate data from Luo et al (2011)

2011; Zimmermann et al. 2011), and soil type, among other factors. This chapter covers the mechanisms that may be driving these diverse effects, with more details from specific studies summarized in Table 16.1. The following discussion of mechanisms of biochar-SOM interactions is organized by the overarching

effect of biochar additions (increased vs. decreased SOC mineralization) and whether the added biochar is metabolized by microbes (direct effects) or simply affects microbial activity by altering chemical or physical properties of the soil (indirect effects).

Table 16.1 Summary of studies of biochar-soil organic carbon mineralization interactions. Modified from Zimmermann and Gao (2013)

Source	Biochar feedstock and production conditions	Soil	Incubation duration (days)	Biochar C mineralized (% of total added)	Soil C mineralized (% change from no-biochar control)	Initial SOC-C (m)
Kuzaykov et al (2009)	<sup>14</sup> C-labeled ryegrass, 400°C, 13h	Haplic Luvisol	1181	4.0	0.0	0.1
Steinbeiss et al (2009)	<sup>13</sup> C-labeled glucose, hydrothermal pyrolysis	Arable Eutric Fluvisol	120	8.0	53.0	0.3
Steinbeiss et al (2009)	<sup>13</sup> C-labeled yeast, hydrothermal pyrolysis	Arable Eutric Fluvisol	120	9.0	150.0	0.3
"	<sup>13</sup> C-labeled glucose, hydrothermal pyrolysis	Forest Cambisol	120	3.0	57.0	0.3
"	<sup>13</sup> C-labeled yeast, hydrothermal pyrolysis	Forest Cambisol	120	6.0	108.0	0.3
Major et al (2010)	Mango prunings charred in kiln, 400–600°C, 48h	Oxisol	730	2.2	38.5	~5 in top 0.1m
Zimmermann et al (2011)	Grass, 250°C under N <sub>2</sub>	Forest Alfisol	90	2.9	61.3	3.8
"	Grass, 650°C under N <sub>2</sub>	Forest Alfisol	90	0.9	-15.6	4.7
"	Grass, 250°C under N <sub>2</sub>	Wetland Mollisol	90	6.8	0.1	1.0
"	Grass, 650°C under N <sub>2</sub>	Wetland Mollisol	90	0.2	-76.4	1.2
"	Grass, 250°C under N <sub>2</sub>	Forest Alfisol	90–500	1.9	-75.1	3.8
"	Grass, 650°C under N <sub>2</sub>	Forest Alfisol	90–500	0.1	-87.1	4.7
"	Grass, 250°C under N <sub>2</sub>	Wetland Mollisol	90–500	3.8	-9.9	1.0
"	Grass, 650°C under N <sub>2</sub>	Wetland Mollisol	90–500	2.6	-49.8	1.2

Table 16.1 continued

Source Biochar feedstock and production conditions Soil Incubation duration (days) Biochar C mineralized (% of total added) Soil C mineralized (% change from initial 50C-C/I no-biochar control) Initial BC-C/I

Gross and Sohli (2011)	Sugarcane bagasse, 350°C, 40min	14	1.1	15.1	1.7
"	Sugarcane bagasse, 550°C, 40min	14	0.2	18.0	1.8
"	Fallow silty-day loam	14	0.7	25.1	0.9
"	Sugarcane bagasse, 350°C, 40min	14	0.0	6.1	1.0
"	Sugarcane bagasse, 550°C, 40min	14	0.4	-9.3	0.5
"	Sugarcane bagasse, 350°C, 40min	14	0.0	-36.0	0.5
Kethi et al (2011)	<sup>13</sup> C-depleted eucalyptus, 450°C, 40min	120	0.8	7.4	3.0
"	<sup>13</sup> C-depleted eucalyptus, 550°C, 40min	120	0.4	19.4	3.3
Luo et al (2011)	Straw, 350°C, 30min under Ar	87	0.6	304.0	5.7
"	low pH	87	0.8	202.0	5.1
"	high pH	87	0.1	136.0	5.7
"	Straw 700°C, 30min under Ar	87	0.2	74.0	5.1
"	low pH	87	0.2	74.0	5.1
"	high pH	87	0.2	74.0	5.1
Jones et al (2011)	Mixed hardwood, 450°C, 48h	21	-0.045	21 average	2.2
Brun and El-Zehery (2012)	Barley straw, 400°C	451	1.7	0	0.06
"	Luvistol	451	1.7	-4.5	0.28
Santos et al (2012)	<sup>12</sup> C-enriched pine, 450°C, 5h under N <sub>2</sub>	180	0.4	-10.0	0.1
"	Forest - andesitic parent material	180	0.4	-10.0	0.1
"	<sup>13</sup> C-enriched pine, 450°C, 5h under N <sub>2</sub>	180	0.4	0.0	0.1
"	Forest - granitic parent material	180	0.4	0.0	0.1
Stewart et al (2012)	Oak 550°C fast pyrolysis	699	4.9	-18.8	0.8
"	Arctic Argyustoll	699	2.5	-16.7	4.1
"	Oak 550°C fast pyrolysis	699	1.7	-8.3	8.2
"	Arctic Argyustoll	699	2.8	-56.3	16.5
"	Oak 550°C fast pyrolysis	699	7.6	0.0	0.5
"	Arctic Haplustoll	699	4.7	20.0	2.5
"	Oak 550°C fast pyrolysis	699	6.0	35.4	4.9
"	Arctic Haplustoll	699	7.9	43.1	9.8
"	Oak 550°C fast pyrolysis	699	6.9	-3.0	0.4
"	Arctic Haplaquept	699	3.7	4.5	1.9
"	Oak 550°C fast pyrolysis	699	4.4	4.5	3.8
"	Arctic Haplaquept	699	7.7	-34.3	7.6
"	Oak 550°C fast pyrolysis	699	2.1	-11.5	0.3
"	Oxyaquic Halpudalf	699	0.7	-19.2	1.4
"	Oxyaquic Halpudalf	699	0.7	-19.2	1.4

### Mechanisms by which biochar additions may increase SOC mineralization

#### Direct effects

**INCREASED MICROBIAL ACTIVITY AND ENZYME PRODUCTION STIMULATED BY LABILE C ADDITIONS**  
 Biochar may provide energy-rich organic compounds that stimulate microbial growth and activity (Luo et al, 2013; Singh and Cowie, 2014), leading to increased degradation of all OM types, including SOM. Evidence for this mechanism has been found in the greater increases in native SOC mineralization observed both earlier in incubation experiments and with the addition of biochars that are relatively rich in labile compounds (Zimmerman et al, 2011; Singh and Cowie, 2014). This could possibly sustain increased SOC mineralization over several years (Singh and Cowie, 2014). For example, Luo et al (2011) observed greater short-term SOC mineralization following biochar addition to soil for a low-temperature (350°C) *Miscanthus* biochar, which had higher levels of water-

extractable (and thus likely microbially available) biochar-C, compared to a high-temperature (700°C) *Miscanthus* biochar. Similarly, Singh and Cowie (2014) showed that the increased mineralization of native SOC, relative to a control, was greater in the presence of manure-based or 400°C biochars than that of plant-based or 550°C biochars and this pattern was consistent with the lability of the tested biochars (Singh et al, 2012). Finally, Zimmerman et al (2011) found a greater increase in SOC mineralization during the early period of soil-biochar incubations (first 3 months), and in biochars made from grass (*vs.* oak) and those made at 250 and 400°C (*vs.* 535 and 650°C). Again, this pattern mirrored the lability of the tested biochars (Box 16.1).

Those biochars associated with greater increases in native SOC mineralization corresponded to those with greater volatile matter content (Zimmerman et al, 2011), and those yielding greater dissolved C leachate (Mukherjee and Zimmerman, 2013). The release of a portion of this water-soluble fraction from biochar surfaces may occur immediately, followed by a slower diffusion-limited

### Box 16.1 Notes on the properties of biochars

Certain properties of biochar are key to understanding the potential mechanisms of biochar-SOM interactions. As discussed in Chapter 10, biochar possesses a continuum of OM forms, from easily mineralizable to relatively persistent (Hilscher et al, 2009; Nguyen et al, 2010). While much of the C in biochar is predominantly aromatic (MacBeath and Smerik, 2009; Singh et al, 2012), it contains a small organic fraction that is water-extractable and relatively easily mineralizable (Farrell et al, 2013; Whitman et al, 2013; Lin et al, 2012; Zimmerman and Gao, 2013). There is a rich body of literature describing research on the effects of labile organic matter additions to soil (e.g. in the form of simple sugars (Dalenberg and Jager, 1981), root exudates (Zhu and Cheng, 2010), or fresh organic matter (Fontaine et al, 2004)), which might mirror the effects induced by the labile organic fractions in biochar. In addition, there are effects of biochar on SOM cycling that may be specific to biochar as compared with other organic soil amendments – particularly those associated with its more persistent organic fraction or its ash content – but distinguishing the effects of different forms of organic fractions or the ash fraction on SOC mineralization requires careful experimental design (Singh and Cowie, 2014).

Source	Biochar feedstock and production conditions	Soil	Incubation duration (days)	Biochar C mineralized (% of total added)	Soil C mineralized (% change from initial SOC-C)	Initial SOC-C / no-biochar control (mm)
"	Oak 550°C fast pyrolysis	Oxyaquic Hapudalf	699	0.7	-15.4	2.8
"	Oak 550°C fast pyrolysis	Oxyaquic Hapudalf	699	1.0	-38.5	5.7
Farrell et al (2013)	<sup>13</sup> C-labelled wheat, 450°C, 40min under N <sub>2</sub>	Andic Arenosol	74	0.3	20.0	0.2
"	<sup>13</sup> C labelled blue gum, 450°C, 40min under N <sub>2</sub>	Andic Arenosol	74	0.2	33.0	0.3
Mastrini et al (2014)	<sup>13</sup> C-labelled ryegrass, 450°C, 4h under N <sub>2</sub>	Cambisol	158	4.3	10.1	0.1
Singh and Cowie (2014)	Eucalyptus 400°C, 40min	Grassland Vertisol	1820	2.0	8.3	1.4
"	Eucalyptus leaves 400°C, steam activated	Grassland Vertisol	1820	2.5	12.4	1.3
"	Poultry Litter 400°C, 40min	Grassland Vertisol	1820	6.9	38.2	0.8
"	Cow Manure 400°C, 40min	Grassland Vertisol	1820	7.3	10.3	0.3
"	Eucalyptus 550°C, 40min	Grassland Vertisol	1820	0.5	2.1	1.6
"	Eucalyptus leaves 550°C, steam activated	Grassland Vertisol	1820	1.2	9.3	1.4
"	Poultry Litter 550°C, 40min, steam activated	Grassland Vertisol	1820	2.1	8.3	0.8
"	Cow Manure 550°C, 40min	Grassland Vertisol	1820	2.2	1.0	0.3

Table 16.1 continued

release of water-soluble C fraction held within biochar pores (Jones et al., 2011), determining to some extent the timescale over which this process might occur. Because this explanation is based on the premise that the soil is limited in energy-rich organic compounds, it could be predicted that its effects would be predominantly found in soils with less labile SOM or added OM, which is consistent with the findings of a number of studies (e.g., Keith et al., 2011; Zimmerman et al., 2011). Similarly, the amount of labile biochar-C present could be expected to predict the duration and magnitude of this effect. This expecta-

tion is supported by a significant correlation between the increase in native SOC mineralization with biochar additions and the fraction of biochar C mineralized during each experiment (Figure 16.3). Possible reasons the data points from Luo et al. (2011) have comparatively large increases in SOC mineralization with biochar additions may include a relatively short incubation duration (87 d) with a majority of the increases in native SOC mineralization observed in the first three days, and/or a pH effect in the acidic soil resulting in the release of any inorganic C in biochar (Farrell et al., 2013).

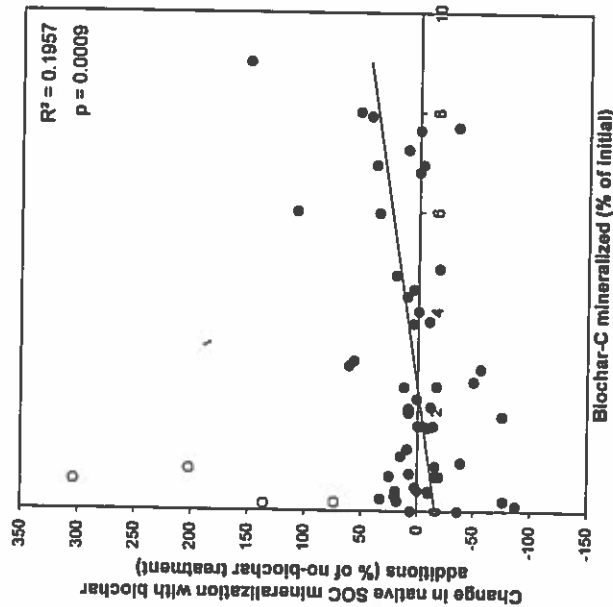


Figure 16.3 Net (end-of-study) biochar effect on native SOC mineralization (relative to the no-biochar control) vs. total fraction of added biochar mineralized. Line indicates linear regression,  $R^2=0.19$ ,  $p=0.0009$ . Data from 13 studies listed in the caption of Figure 16.2. Open circles indicate data points from Luo et al. (2011), which were not included in the regression analysis

The term 'co-metabolism' is used to refer to the situations in which the addition of more labile compounds are explicitly required for the production of enzymes to cause decomposition of more complex SOM compounds, rather than just causing increased microbial activity (Figure 16.4), that is, the decomposition of these complex compounds is not energetically favourable or possible without the presence of an additional organic substrate. The small amounts of low molecular weight organic compounds found in biochars (Lin et al., 2012) could provide the labile compounds that drive this mechanism. However, more targeted experiments are needed to distinguish between the occurrence of co-metabolism and more general microbial stimulation, under different biochar and soil combinations and experimental conditions.

#### SOM 'MINING' FOR N OR P

Nutrient mining refers to the effect when OM is decomposed by microbes in search of nutrients, resulting in the incidental mineralization of C. Although biochar is rich in relatively stable organic C, it also contains some soluble and relatively easily decomposable organic substrates that could induce microbial scavenging of soil N or P, as they are needed for microbial growth and activity. These changes could then drive microbial 'mining' of SOM for its N (Ramirez et al., 2012) or P. This could result in increased C mineralization as N- or P-limited microbes decompose SOM through the release of OM-degrading enzymes. Simultaneously, biochar may directly and temporarily stabilize N or P species through SOM or mineral N or P sorption on surfaces and within pore spaces of biochar particles, further reducing N or P availability. This mechanism has not been investigated in detail and could be easily conflated with increased microbial activity due to labile substrate addition. Designing experiments with varying levels and types of available N or P in soil and

varying levels of mineralizable C in biochar could help to distinguish these mechanisms.

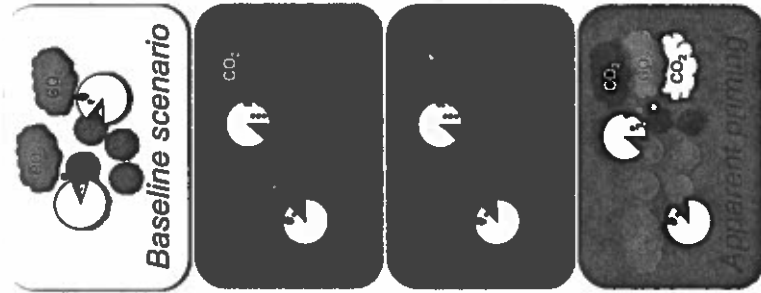


Figure 16.4 Illustration of two ways by which biochar additions could increase SOC mineralization or induce 'apparent priming'. White 'Pac-men' represent microbes, circles represent SOC (grey) and biochar (black), and bubbles represent  $CO_2$  emissions from microbial mineralization of SOC (grey), biochar (black), and maintenance respiration or 'apparent priming' (white)

### Indirect effects

#### pH EFFECTS

Biochar additions may change soil pH (Chapter 7) favourably for microbes and enzymes, increasing their activity. For example, Luo et al (2011) attributed a greater relative increase in SOC mineralization from a lower pH soil (3.7) than from a higher pH soil (7.6), with both 350°C and 700°C *Miscanthus giganteus* biochar additions to a limiting effect. It is important to distinguish between the effects of mechanisms related to changes in soil pH and the simple release of inorganic C from (usually alkaline) biochar when it is mixed into an acidic soil (Demppster et al, 2011; Jones et al, 2011; Farrell et al, 2013; Bruun et al, 2014) or upon dissolution of carbonates (e.g., in a sludge biochar), possibly caused by the acidity generated during biochar oxidation even in a higher pH soil (Singh et al, 2012). Stewart et al (2012) observed predominantly increased native SOC mineralization relative to a soil-only, control with 550°C fast pyrolysis oak pellet biochar additions only in an acidic soil (which became more basic with biochar additions), while the already basic soils experienced decreased native SOC mineralization.

#### ALLEVIATION OF NUTRIENT CONSTRAINTS

Biochar can contain significant levels of nutrients and a proportion of the total nutrients in biochar may be present in readily bioavailable forms (Chapter 7). The addition of these nutrients could relieve constraints, increasing microbial activity. Cumulative losses during successive batch extractions of grass and oak biochar accounted for about 0.5–8 and 5–100 per cent of the total N and P initially present, respectively (Mukherjee and Zimmermann, 2013). In this study, ammonium was usually the most abundant N form in leachates, but nitrate was also released by some biochars, while organic N and P represented as much

as 61 per cent and 93 per cent of the total N and P lost, respectively. In another study, 15–20 per cent of Ca, 10–60 per cent of P and about 2 per cent of N in mallee wood biochar was readily leachable (Wu et al, 2011). Because many of these nutrient forms were released very quickly, while others were leached gradually over longer time periods (Mukherjee and Zimmermann, 2013), they may also play a role in the variation in the extent and direction of biochar's effects on native SOC mineralization over time.

#### IMPROVED MICROBIAL HABITAT AND SOIL FAUNAL STIMULATION

As a highly porous material, biochar may provide a preferred site for microbial colonization (Pietikäinen et al, 2000), enhancing microbial activity and thus, C utilization. Possible reasons for microbial colonization of biochar include: i) protection of microbes from predation within pores; and ii) presence of sorbed OM and nutrients that are relatively more available to surface-colonizing microbes. For example, Wright et al (1995) found that small (<6µm neck diameter) soil pore sizes afforded protection to *Pseudomonas fluorescens* from the soil ciliate *Colpoda steinii*. Hamer et al (2004) suggested that the increased mineralization of glucose in a sand incubation with additions of 350°C maize (*Zea mays* L.) and rye (*Secale cereale* L.) straw biochar could be due to the provision of more surfaces for microbial growth, although they did not test for this directly. However, this mechanism, if important, likely acts simultaneously with other mechanisms, because while biochars produced at lower temperatures tend to have lower surface area and pore volume than those made at higher temperatures, they tend to result in greater increases in SOC mineralization than high temperature biochars (Zimmermann, 2010; Singh and Cowie, 2014). Further, Quilliam et al (2013) reported limited microbial colonization of a

mixed hardwood 450°C biochar after three years of burial in a Eurric Cambisol (although they did not compare colonization rates to that of adjacent soil).

Besides being inhabited directly by microbes, biochar may also affect microbial habitat by changing soil physical conditions. For example, biochar additions to soil could change soil temperature (due to an albedo effect) or water holding capacity (Chapter 19). This could, of course, increase microbial activity if the changes result in a more optimal moisture regime for microbes. Just as biochar additions to soil may affect the soil's water-holding capacity, its porous structure may increase soil aeration, which could increase soil oxygen levels, promoting aerobic respiration. While Jones et al (2011) determined improved soil aeration was likely not the cause of increased native SOC mineralization with biochar additions in their incubation study using 450°C hardwood biochar and a grassland soil, they suggest this was because their soil already had relatively good structure, and do not rule it out for other biochar-tolerant systems. Whether and how soil physical factors, such as the ratio of soil air-to-water pore space, water-holding capacity or water potential, are controlled in experimental studies is challenging and could have an important impact on soil microbial biomass and activity and, consequently, on biochar-SOM interactions. For example, should water content be normalized by gravimetric water content, water-filled pore space or water pressure potential across different soil-biochar mixtures? Each choice might produce different results.

Other, non-labile, components of biochar may also stimulate microbial activity. During oxidative aging, biochar surfaces gain substituted aromatic functional groups including phenols and quinones and lactones (Cheng and Lehmann, 2009; Cheng et al, 2008; Mukherjee et al, 2014), which have

been found to increase numbers of active soil microbes (Visser, 1985). In addition, these compounds can act as electron shuttles, serving as electron acceptors during microbial respiration (Scott et al, 1998).

Soil fauna tend to promote SOM decomposition, commonly ascribed to their comminution of organic matter, increasing its surface area for microbial attack, but also, perhaps, through a number of other mechanisms, such as faunal grazing effects on fungal decomposers (Bradford et al, 2002) or soil fauna-driven N mineralization (Osler and Sommerkorn, 2007). Thus, if biochar additions stimulate soil fauna activity or populations (Chapter 13), SOM decomposition could be accelerated. There are few studies on the effects of biochar on soil fauna to date (Lehmann et al, 2011), but, for example, earthworms have been found to prefer some biochar-soil combinations (Chan et al, 2008).

### Mechanisms by which biochar additions may decrease SOC mineralization

#### Direct effects

##### SUBSTRATE SWITCHING

According to this phenomenon (described generally by Kuzyakov et al (2000) and in the context of biochar additions to soil by Singh and Cowie (2014)), the most labile organic fraction of biochar may be preferentially used by microbes to temporarily replace the use of native SOC, thus decreasing native SOC mineralization (Figure 16.5). This phenomenon may be of relatively greater importance in C-poor soils that receive an external supply of labile organic matter. Both Gontikaki et al (2013) and Guenet et al (2010) suggested this mechanism to explain their findings in systems with labile OM additions to soils. Because it is dependent on the presence of



very labile biochar components, it may be expected to persist only until these compounds are used up by microbes (Whitman et al., 2014a).

#### DILUTION EFFECT

The dilution effect (Figure 16.5) is similar to substrate switching, except that labile biochar is not used preferentially by microbes – rather, there is just temporarily more total labile C in soil (from both biochar and native SOC) following biochar amendment than microbes can use, resulting in a temporary decrease in SOC mineralization. A combination of this effect and substrate switching may be responsible for the short-term (< 1 week) decrease in native SOC mineralization following 350°C sugar maple (*Acer saccharum*) biochar additions to a Typic Fragiucept (Whitman et al., 2014a).

#### Indirect effects

##### SORPTION OF LABILE SOC

Pyrogenic materials have demonstrated a high sorption affinity for a wide range of natural organic compounds including recalcitrant OM (Kaszo et al., 2010; Li et al., 2002) and labile and water-soluble fractions of SOM, making them less available to microbes. This could take the form of encapsulation – SOM is absorbed within pores in biochar particles and becomes physically unavailable to microbes – or sorptive protection – SOM is sorbed on biochar surfaces and becomes less easily accessible to microbes (Figure 16.6). Both of these mechanisms have been found to be operative for organic compounds of a range of molecular sizes on mineral surfaces (Zimmerman et al., 2004). In support of this mechanism, biochars with greater sorptive capacities (higher temperature biochars and hardwood biochars) have generally been found to result in the greatest long-term decreases in SOC mineralization

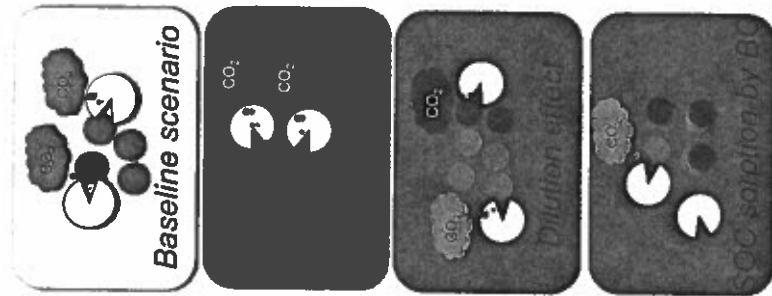


Figure 16.5 Illustration of three mechanisms by which biochar additions may decrease SOC mineralization. White 'Pac-men' represent microbes, circles represent SOC (grey) and biochar (black), and bubbles represent CO<sub>2</sub> emissions from microbial mineralization of SOC (grey) and biochar (black)

(Zimmerman et al., 2011). Cross and Sohi (2011) found that the highest temperature sugarcane bagasse biochar that they studied provoked the greatest decrease in grassland

soil respiration in an incubation study. Kuzaykov et al (2009) also postulated this may partly explain the decreased SOC mineralization that they observed in a loess soil with 400°C ryegrass (*Lolium perenne*) biochar additions in an incubation trial. This sorption may be kinetically limited by the slow speed of diffusion into biochar pores (Kaszo et al., 2010), delaying the onset of the effects of this mechanism. Furthermore, the surfaces and pore networks of biochar may get clogged by high molecular weight organic substances in soil (Pignatello et al., 2006), which could limit biochar's sorption capacity for dissolved organic matter over time. It might be predicted that decreased SOC mineralization due to the sorptive properties of biochar would be associated with its more recalcitrant fractions. This is suggested by the positive linear relationship between increased SOC mineralization and BC mineralization shown in Figure 16.3.

##### SORPTION OF MICROBIAL ENZYMES OR SIGNALING MOLECULES

Like other organic compounds, enzymes likely have a high affinity for biochar surfaces. Enzymes sorbed by biochar particles may be deactivated or inhibited, due to changes in pH or ionic strength at or near the biochar surface, conformational changes to the enzyme upon sorption, or steric hindrance, as can occur with enzyme-mineral interactions (Quiquampoix and Burns, 2007; Zimmerman and Ahn, 2010). When the enzyme laccase was sorbed to grass and oak biochars pyrolysed at 650°C, its activity was reduced by 60–99 per cent. However, the enzyme retained greater than 80 per cent of its activity when sorbed to oak and grass biochars produced at 250 and 400°C (Zimmerman and Gao, 2013). Possible reasons for these variations include differences in the morphology and the chemistry of different biochar surfaces. Recent work by Masiello et al (2013)

indicates that biochar can also sorb microbial quorum-sensing signal compounds. Removal or inactivation of these compounds by biochar could interfere with processes such as biofilm formation, nitrogen fixation symbioses and pest attack of root crops.

##### INCREASED ORGANOMINERAL INTERACTIONS AND STABLE AGGREGATE FORMATION

Biochar may mediate organomineral interactions between native or added organic matter and soil minerals, possibly through ligand exchange or cation bridging mechanisms (Liang et al., 2010; Keith et al., 2011; Fang et al., 2014). Dissolved OM released by biochar, as well as colloidal biochar particles, may facilitate the formation of stable soil aggregates in which SOC is less accessible to microbes (Brodowski et al., 2006; Liang et al., 2010). Supporting this, Liang et al (2010) found that labile OM amendments were incorporated into physically protected soil fractions more quickly in a highly aged biochar-rich Anthrosol as compared to biochar-poor adjacent soils. Singh and Cowie (2014) hypothesized that increased organomineral interactions during biochar ageing was a possible reason for the reduced native SOC mineralization in a biochar-amended clayey soil (relative to the non-amended control) in the later stages of their 5-year long incubation study. Although Mukherjee et al (2014) found no significant change in water stable aggregates or the geometric mean diameter of aggregates in a Crosby silt-loam soil incubated over a growing season with additions of 650°C oak biochar, this may indicate that aggregate formation takes longer than a single growing season, or requires interactions with plants and soil fauna. These biochar-mediated organomineral interactions may be enhanced when additional labile organic matter is supplied (e.g., Keith et al., 2011) or by increased plant root activity and exudation in the presence of biochar (Major et al., 2010;



Slavich et al, 2013). Keith et al (2011) found rapid stabilization of labile OM (sugarcane residue) applied to a clayey soil in the presence of relatively young wood biochar. Thus, it could be hypothesized that higher organic matter content in a biochar-amended mineral soil would favour increased microbial biomass and activity, facilitating stable aggregate formation and soil structure development, possibly through organomineral interactions enhanced by microbiota (Young et al, 1998). Similarly, Herath et al (2014) found greater formation of stable aggregates in an OM rich mineral soil (Andisol) amended with a 350°C corn stover biochar than in an Alfisol containing relatively low native SOM, but opposite trends for stable aggregate formation in the Andisol vs. the Alfisol were observed for the 550°C biochar.

#### DECREASED NUTRIENT AVAILABILITY

Biochar may decrease nutrient availability in soil through direct sorption (Mukherjee and Zimmerman, 2013; Chintala et al, 2014). Kuzyakov et al (2009) postulated that sorption of nutrients by biochar may partly explain the decreased C mineralization they observed in a nutrient-poor loess soil with 400°C ryegrass (*Lolium perenne*) biochar, although they did not explicitly measure nutrient availability. Biochar addition may also cause the precipitation of nutrients, converting them into unavailable forms (due to pH shifts (Chapter 15) or interactions with biochar-derived mineral nutrients (Chapter 7)), thus decreasing availability of native nutrients in soil. Furthermore, biochar presence may increase immobilization of mineral nutrients by microbes, particularly when they are promoted in their growth and activity in the presence of biochar, thus resulting in the incorporation of mineral nutrients into microbial biomass, making the nutrients less readily accessible, decreasing native SOM mineralization (Novak et al, 2010; Chapter 15).

Additionally, Prommer et al (2014) showed in a field study that wood biochar addition slows the cycling of soil organic N, possibly through the sorption of various forms of soil organic N and enzymes on biochar surfaces and in pore network, and hypothesized that this phenomenon may enhance soil C sequestration due to increases in non-biochar derived SOM.

#### NUTRIENT 'MINING' INHIBITION

If substantial levels of available nutrients, such as available N or P, are added with biochar, this could result in decreased 'mining' of older SOM for nutrients by microbes (Ramirez et al, 2012; Chintala et al, 2014). This would, in turn, reduce the SOC mineralization associated with microbial decomposition of SOM. However, although 'black N' may play an important role in SOM cycling (Knicker, 2007), biochar does tend to have low available N (Chapter 7), particularly when produced at higher temperatures (>500°C) or from woody, low-N feedstocks. Thus, the inhibition of nutrient mining due to the addition of available nutrients in biochar is not expected to be a common mechanism for decreased SOC mineralization for most biochars, although lower-temperature biochars produced from high N or P feedstocks such as manure or biosolids could be an exception. For example, a significant proportion of P in biochar may be present in readily available forms, depending on biochar type (Singh et al, 2010; Chapter 7), which could have implications for reduced P mining of SOM following the addition of biochar.

#### MICROBIAL OR SOIL FAUNA INHIBITION DUE TO pH EFFECTS, TOXICITY, OR OXYGEN LIMITATION

Biochar additions could also change soil pH (Chapter 15) unfavourably for microbes, decreasing their activity. This would depend heavily on the specific soil and biochar combination and their individual characteristics

(Enders et al, 2013). Oxidation of biochar occurs both by abiotic and microbially mediated processes (Zimmerman, 2010; Chapter 9). If this consumption of oxygen through oxidation occurs very rapidly, it could inhibit the activity of aerobic microbes and extracellular OM decomposing enzymes that require oxygen such as oxidases. Since biochars are predominantly aromatic and have relatively low levels of labile C, this mechanism might only be likely in soils that are already nearly anaerobic. Additionally, biochar may be asso-

## Mechanisms by which soil organic matter may affect biochar C turnover

Many of the mechanisms discussed in the previous section for explaining biochar effects on SOM decomposition could also apply in the reverse direction. To understand these interactions, it is important to continue to think of biochar as a heterogeneous material, with different sub-components within any single biochar sample, and one biochar being different from the next, depending on its feedstock, production temperature and production conditions. In general, one would expect native SOM to alter the C mineralization of labile components of biochar (e.g., water-extractable, volatile or aliphatic compounds) through different mechanisms than it might alter the C mineralization of recalcitrant components of biochar (e.g., aromatic compounds).

### Increased biochar C mineralization by labile SOM

Zimmerman et al (2011) found that soils with greater labile SOM had increased rates of biochar C mineralization. In addition, adding a source of labile OM to biochar-soil or biochar-sand mixtures has been found to increase biochar C mineralization (Hammer et

ciated with toxic compounds, such as polycyclic aromatic hydrocarbons (Chapter 21) or ethylene (Spokas et al, 2010), which could inhibit microbial activity. The presence of these compounds varies widely from one biochar to the next and depends on the production mechanism, conditions and feedstock used (Hale et al, 2012). If these or other changes inhibit soil fauna (Chapter 13), their stimulation of SOM decomposition (Bradford et al, 2002) could be inhibited.

al, 2004; Nocentini et al, 2010; Keith et al, 2011; Luo et al, 2011). One of the most likely explanations for this finding is that the presence of or additions of labile OM increases microbial activity and enzyme production, which stimulate the decomposition of biochar through co-metabolic effects. This is analogous to the increased activity mechanism for biochar's effects on SOC mineralization.

Most studies have not been designed to explicitly differentiate between mechanisms that may lead to an increase in biochar C mineralization, but the form and quantity of SOC or OM additions is likely important. For example, Hamer et al (2004) found an increase in 350°C wood and maize biochar C mineralization with (highly labile) glucose additions in a sand incubation study. However, Nocentini et al (2010) observed that while mineralization of 350°C pine needle and wood biochar was stimulated by additions of glucose, it was not stimulated by cellulose (a sugar polymer), in a sand incubation medium. Keith et al (2011) found that 450°C and 550°C *Eucalyptus saligna* biochar mineralization increased with increasing additions of relatively labile sugar cane residues in a soil incubation trial, although this

effect decreased over time. This suggests that biochar mineralization is stimulated by easily available organic C added to the soil and the subsequent increase in microbial activity. Once this added C source is depleted, the effects on biochar C may also disappear. Similarly to the findings of Hamer et al (2004), Kuznyakov et al (2009) observed an increase in biochar mineralization with glucose additions in an incubation study, but they also noted that while glucose additions increased mineralization of 400°C perennial ryegrass (*Lolium perenne*) biochar in two soil types, there was a greater effect of glucose addition on biochar C mineralization in the low-C loess soil than the higher-C soil of the same parent material. This may indicate that the native soil C also interacts with the added organic matter, with different effects depending on the level of native soil C and the relative mineralizability of the added OM, SOM and biochar.

### Decreased biochar C mineralization by labile SOM

Labile OM additions or higher SOC contents may not always lead to higher biochar C mineralization. Liang et al (2010) did not find evidence for any stimulation of CO<sub>2</sub> emissions from biochar-rich Anthrosols with additions of organic matter (sugar cane leaves) as compared to low-biochar adjacent soils, in an incubation study. However, these soils had received biochar additions centuries ago, and thus any effects driven by easily mineralizable components in biochar would likely no longer be active, as these components would disappear over time. Fang et al (2014) found the greatest mineralization of 450 and 550°C *Eucalyptus saligna* biochar C when mixed with a low-C, quartz-rich Inceptisol, less when mixed with a medium-C, smectite-rich Vertisol, and even less in a high-C, sesquioxide-rich Oxisol. In addition to the possible

effects of soil mineralogy or organomineral interactions on decreasing biochar C mineralization (see below), a mechanism similar to substrate switching might also explain why increasing native SOM or labile OM additions could result in decreased biochar C mineralization. This could explain the observation that mineralization of sugarcane bagasse biochar produced at a range of temperatures was greater in a soil previously kept fallow than in high-C agricultural or grassland soils (Cross and Sohi, 2011). In this study, labile C in biochar may have been a more readily available substrate than the native SOC in the fallow soil, which had the lowest CO<sub>2</sub> emissions on its own of all the soils. Zavalloni et al (2011) observed lower total CO<sub>2</sub> emissions from a mixture of 500°C hardwood biochar and wheat straw in a Cambisol than when the biochar and straw were added individually to soil, which could be partially explained by a substrate switching or a dilution effect. However it was not possible to tell whether the biochar 'replaced' wheat straw mineralization or vice-versa, or how SOC mineralization changed.

### Effects of soil texture, mineralogy and structure on biochar mineralization

Soil texture and mineralogy have been shown to directly affect biochar C dynamics. For example, Bruun et al (2014) found a small but significant effect of soil clay content on biochar mineralization, with slightly lower biochar C mineralization in soils with higher clay contents. This is consistent with our understanding of clay content and clay minerals often being associated with increased SOC stabilization (Six et al, 2002). Clay may also have an indirect effect on biochar mineralization, through interactions between SOC, added labile OM and biochar C mineralization (Fang et al, 2014; Zavalloni et al, 2011). For exam-

ple, the decrease in biochar C mineralization with increasing levels of added labile OM in a clayey soil observed by Keith et al (2011) may suggest that the labile OM additions increased organomineral interactions between biochar and soil particles, protecting biochar C from mineralization. Soil structure could also play a role in biochar-SOC interactions. For example, Kuznyakov et al (2009) observed that soil mixing increased the mineralization of biochar, which could simply indicate disruption of physical protection of biochar by soil, but could also be due to stimulation by labile organic matter released during soil mixing.

### Effect of plant roots on SOC-biochar interactions

There is a large body of research showing that the presence of roots and their relatively labile exudates often results in increased SOC mineralization (Cheng et al, 2003; Kuznyakov, 2010). However, little study has been done on biochar-SOC interactions in systems with plants. This is problematic, both because many systems – natural and managed – contain plants, and also because it is to be expected that biochar-SOC interactions will differ in planted systems. Biochar additions could drive changes to below-ground C inputs via roots, root exudates and mycorrhizae (Chapter 14). In turn, the presence of roots and these changes in root C input dynamics could alter SOC and biochar C cycling. Many questions remain – would root-derived C add to the general stimulation of the microbial community, increasing SOC and biochar mineralization, or would this C source be used preferentially over the other two sources, decreasing SOC and biochar mineralization (Figure 16.6)? These effects are largely uncharacterized, as there have been very few studies of biochar-SOC interactions that include plants.

Ventura et al (2014) found that a 500°C biochar made from fruit tree prunings did not change total soil CO<sub>2</sub> emission rates in an apple orchard on a Haplic Calcisol, but did increase total soil CO<sub>2</sub> emission rates when the tree roots were excluded by trenching. This may indicate that biochar applications decreased root respiration, that the presence

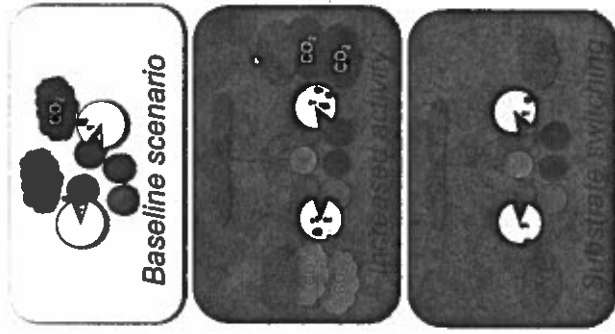


Figure 16.6 Illustration of two possible effects of root-derived C on SOC and biochar-C mineralization. White 'Pac-men' represent microbes; circles represent SOC (light grey), biochar (black), and root-derived C (dark grey) and bubbles represent CO<sub>2</sub> emissions from microbial mineralization of SOC (light grey), biochar (black), and root-derived C (dark grey)

of roots inhibited biochar and/or SOC mineralization, or some combination of interactions between the three CO<sub>2</sub> sources. However, trenching introduces a number of complicating factors, particularly, a high one-time input of C from roots killed during trenching. In a field study, Major et al. (2010) found increases in soil CO<sub>2</sub> emissions with additions of mango wood biochar to a savannah soil, with this effect decreasing in the second year of the trial. They also observed increased above-ground biomass in the plots with biochar additions, leading them to suggest that these increases in CO<sub>2</sub> emissions could be attributed to greater below-ground growth and activity by plants. Slavich et al. (2013) found that 550°C feedlot manure and green-waste biochar applications to a Ferralsol that was planted with a forage peanut (*Arachis pintoi* cv. Amarillo) and ryegrass (*Lolium*

*multiflorum*) rotation increased total soil C more than could be explained by biochar C additions alone. Whitman et al. (2014a) found that 350°C sugar maple (*Acer saccharum*) biochar additions to soil counteracted increased SOC mineralization induced by corn (*Zea mays* L.) plants. This counteractive effect may be due to an increased contribution of roots to total below-ground C that decreased or offset the SOC losses induced by roots. It could also be caused by increased stabilization of SOC or root-derived C by biochar and possibly by enhanced organomineral interactions in the presence of roots and biochar. While the effects of including plants in the system are largely uncharacterized, they are likely important, making greenhouse, field and laboratory experiments with plants a key area for future research.

### Multiple mechanisms likely act simultaneously and may affect microbial communities

Many of the mechanisms discussed in this chapter, both those enhancing and also those inhibiting SOM or biochar decomposition or mineralization, could, and most likely would, act simultaneously. For example, though net increased SOC mineralization may be observed, some stabilization of SOC may be taking place, and vice versa. This highlights the need to use diverse approaches and carefully designed experiments testing hypotheses and evaluating which mechanisms dominate, under which conditions, and during different stages of an experiment. Additionally, most or all of these effects will depend on the rates of biochar application to soils, which could vary widely in practice. Interestingly, many of these mechanisms would be expected to induce shifts in the soil microbial community. For example, biochar additions may initially shift the community toward r-strategists

(copiotrophs) due to the addition of a labile fraction of biochar-C. Then, over time, a shift toward k-strategists (oligotrophs) could be expected as the labile biochar-C fraction is consumed, leaving more persistent OM (see discussion in Zimmerman et al., 2011). Farrell et al. (2013) observed increased SOC mineralization with 450°C wheat (*Triticum aestivum* L. var. Ypsi) and blue gum eucalypt (*Eucalyptus globulus* Labill. ssp. *globulus*) biochars, and determined that biochar C was rapidly used by copiotrophic gram-positive bacteria initially, using compound specific isotopic analysis of phospholipid fatty acids. Fungal uptake of biochar C increased with time, and some of the biochar C was detected in actinomycetes by the end of 74-day incubation, which is consistent with our understanding of these organisms as being situated more to the oligotrophic end of the spectrum.

Biochar has been shown to change soil microbial communities (Anderson et al., 2011; Watzinger et al., 2014) and such shifts in soil microbial communities could further entrench the induced changes in decomposition

### Methods and approaches to studying biochar-SOM interactions

In order to detect biochar-induced changes in the mineralization of C in SOM, it is necessary not only to measure C mineralization rates following a biochar addition, but also to distinguish C derived from each different C source (biochar and native SOM or other amended organic materials). An 'additive' approach compares C mineralization of soil alone and biochar alone to soil amended with biochar. The weighted sum of C mineralization rates of soil and biochar incubated separately are then compared to the C mineralization rate of the mixture of the two. This was the approach used by Wardle et al. (2008), in their litterbag study with organic surface horizon materials, biochar produced from *Empetrum hermaphroditum* at 450°C and mixtures of the two. Likewise, Zimmerman et al. (2011) examined a range of biochars incubated, *in vitro*, separately and mixed with a number of soils. While useful as an indication of interactive effects, there are two limitations to the additive approach. The first is that it is not possible to determine whether the change in total C mineralization is due to changes in SOC mineralization, biochar C mineralization, or both. The second limitation is that the additive approach requires a baseline C mineralization rate for soil and biochar separately. While this is not an issue when incubating soil alone, biochar does not usually exist in isolation from the soil, and so this approach requires decisions such as whether and how to inoculate it with microbes, amend it with nutrients, control or

dynamics or could alter soil microbial activity in other ways, through inter-specific interactions, such as competition, adding another layer of complexity to the mechanisms described here.

account for pH effects, and/or mix it into some inert substrate, such as sand, and how to maintain 'equivalent' moisture. Additionally, there are some issues with litterbag studies – particularly that they cannot distinguish losses due to comminution of organic matter, leaching and mineralization.

Use of stable and radio-isotopes to distinguish CO<sub>2</sub> derived from SOM versus biochar can alleviate some of these limitations. Emitted CO<sub>2</sub> from two substrates can be distinguished if they have different <sup>13</sup>C:<sup>12</sup>C ratios, or <sup>14</sup>C contents. Differences in stable C isotope ratios can occur naturally, as with plants that use C<sub>3</sub> vs. C<sub>4</sub> photosynthetic pathways. For example, Cross and Sohi, (2011), Luo et al. (2011), Zimmerman et al. (2011), and Stewart et al. (2012) all applied such a 'natural abundance' approach in their studies of biochar-SOC interactions by incubating soil from C<sub>3</sub> vegetation systems (e.g., temperate forest) with C<sub>4</sub> vegetation-derived biochar (e.g., corn or sugarcane). Conversely, Singh and Cowie (2014) studied biochar-SOC interactions by incubating a soil from a C<sub>4</sub> vegetation system (treeless grassland dominated by tussock Mitchell grass) with biochars (*Eucalyptus* wood and leaves, poultry litter or cow manure) that have <sup>13</sup>C:<sup>12</sup>C ratios characteristic of C<sub>3</sub>-vegetation. Differences in stable or radio-isotopic C contents can also be artificially generated by growing plants in an environment enriched in <sup>13</sup>CO<sub>2</sub> or <sup>14</sup>CO<sub>2</sub> or depleted in <sup>13</sup>CO<sub>2</sub> (compared to atmospheric CO<sub>2</sub>). For example,

Keith et al (2011), Farrell et al (2013), Fang et al (2014) and Whitman et al (2014a, b) used this approach to distinguish SOC and biochar-C with stable C isotopes, and Hamer et al (2004), Jones et al (2011) and Kuzayakov et al (2009) used this approach with the radioactive C isotope,  $^{14}\text{C}$ . The advantage of using enriched C isotopes over the natural abundance approach is that a larger difference in C isotopic signatures or contents can be generated, allowing for smaller differences in C mineralization to be detected. This is particularly important when measuring biochar-derived  $\text{CO}_2$  fluxes, which can be relatively low, and may fall below detection limits with time as the labile fraction of biochar is mineralized. An enriched C label may also help mitigate the errors created through isotopic fractionation, where biological or chemical processes could discriminate against the heavier C isotope, shifting the signature of, e.g., the respired  $\text{CO}_2$  from the bulk signature of the C substrate.

When using an additive or isotopic approach, all laboratory incubations can be criticized for their inability to truly simulate field conditions with regular plant inputs (Qiao et al, 2014). Furthermore, most laboratory incubations do not account for summative effects on biochar decomposition caused by environmental factors such as UV exposure, rainwater infiltration, bioturbation, variability in climate parameters such as temperature, freeze and thaw cycles and saturation and desaturation, which have been shown to alter microbial activity and OM degradation processes (Sun et al, 2002; Cravo-Laureau et al, 2011). For example, oak biochar was shown to degrade most rapidly under alternating saturated-unsaturated conditions (Nguyen and Lehmann, 2009). Another issue is the possible decrease in microbial biomass over incubation time due to non-ideal conditions, such as nutrient limitation, depletion of labile SOC and buildup of

metabolic products (Spokas, 2010; Singh and Cowie, 2014). Also, laboratory incubations may select for certain groups of microbes (Lehmann et al, 2011) that may not be representative of natural soil communities.

Modelling approaches have also been used to estimate the long-term effects of biochar-SOM interactions on soil C stocks and biochar C persistence in soil (Zimmerman et al, 2011; Woolf and Lehmann, 2012). Although first-order kinetics, single or double pool exponential and power function mineralization models have been used to estimate biochar persistence, a double pool exponential model has most commonly been applied. In this model, organic C is represented as two pools – a relatively quickly cycling component and a relatively slowly cycling component, each mineralized with apparent first-order kinetics. For example, Zimmerman et al (2011) compared the modelled additive mineralization of C in biochar alone and SOC alone with the modelled mineralization of C in biochar and soil mixtures in order to determine the direction and degree of soil-biochar interactions in a laboratory incubation of nearly 2 years. However, it should be understood that these models are constrained by the assumptions of first order kinetics – i.e., that there are no interactions between the mineralization of distinct substrates. A new generation of soil C cycling models may, in the future, provide better abilities to model soil C dynamics in biochar-amended systems and, thus, add to our mechanistic understanding of biochar-SOM interactions. For example, Blagodatsky et al (2010) allowed for the simulation of such interactions by modelling decomposition as a sequential process where OM must be solubilized before it is available to microbes and the mineralization rate of SOC depends on the size of the microbial biomass pool, among other modifications. Bruun et al (2010) proposed developing fractionation methods to isolate

fractions that could be used to parameterize models with continuous quality distributions of organic matter, rather than using fractionation methods and models with discrete pools. Other possible approaches include those of Neill and Guenet (2010), who compared two different models. The 'extended mass action' model generalizes enzyme kinetics at the microbial scale. The 'most probable dynamics' model determines the most probable fluxes of C, given a set of mass and energy constraints, while treating microbes and SOM particles essentially as individual components. Both of these models allowed for interactions between different types of OM to emerge, but Neill and Guenet (2010) found that the most probable dynamics model performed better than the extended mass action model at matching laboratory incubation data.

Future models should enable prediction of long-term (100yr or greater) C persistence in biochar-amended soil using much shorter field or laboratory data (1–8.5yr typically). Woolf and Lehmann (2012) altered the RothC soil turnover model to predict long-term SOC losses under biochar additions in three agroecological zones under maize and with and without yearly biochar additions to the soil. Their model predicted that increases in SOC mineralization induced by biochar would have a negligible long-term effect on SOC stocks (3–4 per cent losses over 100yr), while decreased SOC losses due to increased stabilization of SOC could increase total SOC stocks by 30–60 per cent over 100yr. The main issue with this approach is that the outcomes depend, to some extent, on the assumptions about which mechanisms would drive these changes. Depending on which underlying mechanism is at work, it may be more appropriate to model these changes as a modification to the rate constants (determining how quickly the different pools of SOC

mineralize) or the partitioning constants (determining how relative amounts of SOC are partitioned between more stable or labile pools). For example, Woolf and Lehmann (2012) model increased SOC mineralization with biochar additions by increasing the SOC decomposition rate constant by a factor proportional to the total biochar in the soil, but model decreased SOC mineralization by increasing the proportion of SOC that is transferred to the stable organomineral fraction rather than being mineralized. Thus, the modelling effort is informed or constrained by our understanding of the underlying mechanisms. Another difficulty is that these interactions are likely dynamic, changing in extent or even direction over time (Keith et al, 2011; Zimmerman et al, 2011; Singh and Cowie, 2014) as biochar chemistry evolves with aging over time in the environment (Singh et al, 2013; Kuzayakov et al, 2014). The research community is still a long way from developing models that can incorporate this level of mechanistic complexity.

The majority of biochar-SOC interaction studies to date have been carried out in laboratory settings, with the notable exceptions of Wardle et al (2008), Major et al (2010), Slavich et al (2013) and Ventura et al (2014). Furthermore, there is a dearth of studies examining biochar-SOC interactions that include plants in the system, with the work by Major et al (2010), Slavich et al (2013), Ventura et al (2014) and Whitman et al (2014a) being notable exceptions. All of these studies have relied on either a combined dual C isotope and additive approach (Major et al, 2010; Whitman et al, 2014a) or only an additive approach (Slavich et al, 2013) to distinguish biochar-C, SOC and/or plant-derived C. Part of the reason for this lack of three-part studies is likely the challenges in distinguishing more than two sources of C (see Box 16.2).

### Box 16.2 Using C isotopes to partition three-part systems

One reason that field and greenhouse studies investigating biochar-SOM interactions in the presence of plants are relatively rare is likely that the interactive effect of three-plus part systems (including soil, biochar and plants) makes it challenging to separate soil C or soil CO<sub>2</sub> emissions into their constituent parts using a standard two-pool C isotopic partitioning approach. Using all three C isotopes (stable <sup>12</sup>C and <sup>13</sup>C plus radioactive <sup>14</sup>C) could make this possible. For example, this could take the form of an experiment that distinguishes soil and plants using <sup>13</sup>C abundance levels (e.g. a C<sub>1</sub> soil and C<sub>2</sub> plant, or having one component highly labelled with <sup>13</sup>C), and distinguishes the biochar with a <sup>14</sup>C-enrichment. However, implementing these approaches could be relatively complex and expensive and the use of radioactive C will involve complex regulations, particularly in a field trial.

Alternatively, as a second approach, one could also employ enriched <sup>13</sup>C (instead of enriched <sup>14</sup>C) in two parallel experiments, where first the biochar and then the plants are labelled with <sup>13</sup>C, which could allow separation of root, biochar and soil contributions to total CO<sub>2</sub> evolved with a reasonable certainty. The challenge of using only the two stable isotopes for partitioning is that this approach will result in a range of possible solutions (as illustrated in Figure 16.7). This approach would thus still require the application of a set of assumptions about the interactions between the three components (removing the possibility of conclusively detecting such interactions). However, with a very strong <sup>13</sup>C enrichment, one could make the argument that any shift in the <sup>13</sup>C of the control end members at natural abundance levels (e.g. soil + root system in experiment-1 or soil + biochar system in experiment-2) due to the interactive effects of plant, soil and biochar would be small relative to the <sup>13</sup>C enriched signature from biochar and plant in experiments-1 and -2, respectively. This would require very strong <sup>13</sup>C enrichment beyond natural abundance levels, which can also get relatively expensive.

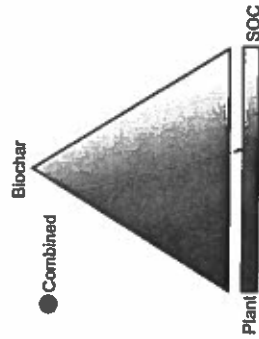


Figure 16.7 Graphic concept of multiple isotopic partitioning solutions to a hypothetical three-part system. Shading represents the <sup>13</sup>C:<sup>12</sup>C ratio of each end-member (biochar, SOC and plant), while the grey circle indicates the combined <sup>13</sup>C:<sup>12</sup>C ratio for a given system. Dashed black lines represent possible partitioning solutions for the combined isotopic ratio. In a two-part system (rectangle between plant and SOC) there is only one solution (e.g., 57% from the plant and 43% from SOC), but for the three-part system (triangle of biochar, SOC and plant), there are multiple solutions

A third approach also allows for the application of just the two stable isotopes, but requires a doubled treatment, where one component is chemically and physically identical in the two treatments, except for having a different isotopic signature in each (e.g. biochar with two levels of <sup>13</sup>C-enrichment) (Kuzayakov and Bol, 2004). It is essential that the component with two different isotopic signatures be otherwise functionally identical. This means biochar or plants are better candidates than soils, because plants could be grown in identical environments, only under different <sup>13</sup>C atmospheres (and then used to produce biochar). It would be challenging to produce two soils with different <sup>13</sup>C values without differences in their SOM content and composition.

In a fourth approach, if two of the three components can be ensured to have the same <sup>13</sup>C:<sup>12</sup>C ratio (e.g. C<sub>1</sub> soil and C<sub>2</sub> plants), then the third (e.g. <sup>13</sup>C-labelled biochar) can be distinguished from the first two, but this would not allow for the first two to be distinguished from each other (e.g. we could not distinguish between changes in root respiration or SOC mineralization caused by biochar).

Additionally, we are not aware of any studies that have used imaging approaches to observe *in-situ* biochar-SOC interactions directly. Key soil processes occur at micro- and nanometer scales (Mueller et al, 2013), and may be central to understanding or providing conclusive evidence for specific mechanisms of biochar-SOC interactions,

particularly SOC stabilization on or around biochar surfaces. Techniques such as nanoscale secondary ion mass spectrometry (nanoSIMS), which provide the elemental and isotopic composition of soil aggregates at a sub-micron scale, may prove to be a transformative tool in this area (Heister et al, 2012; Mueller et al, 2013).

## Implications of SOC-biochar interactions for soil C and fertility management

The soil and C management implications of biochar-SOM interactions will depend on: (i) the specific soils and biochars in question; and (ii) soil management practices and objectives. How different biochars may impact different soils is beginning to be better understood, but there remains much to be done before a robust predictive model can be developed. Currently, testing each biochar-soil combination individually, under environmentally relevant conditions, with plants present, is likely necessary to have confidence in predictions of a biochar's many effects on a soil in a real-world situation.

For soil C impacts in particular, the C debt-credit ratio (Whitman et al, 2013), or a

similar metric, could be very useful for predicting the impact of biochar on future C stocks, as our understanding of biochar-soil C interactions improves. The C debt-credit ratio quantifies the net C impact of biochar, including C lost during its production, application to soil and subsequent mineralization, as compared to the addition and mineralization of a mass of fresh, uncharred biomass equivalent to the amount required to produce the biochar (see Box 16.3; Whitman et al, 2013). Herath et al (2014) modified the C debt-credit ratio introduced by Whitman et al (2013) to include the effects of biochar on native SOC mineralization (Box 16.3).

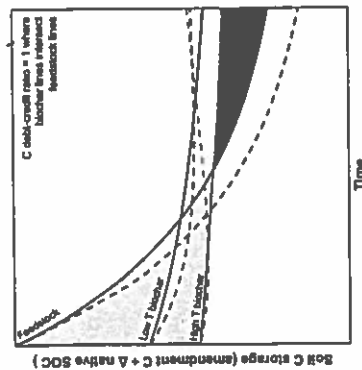
### Box 16.3 C debt-credit ratio in different 'priming' scenarios

The C debt-credit ratio is the ratio of the C remaining in biochar to the C remaining in the original feedstock material (unpyrolysed biomass) after biochar production and the application of both materials (biochar or feedstock) separately to the same soils. A value > 1 indicates that more C remains in the biochar than in the original feedstock, while a value < 1 indicates that less C remains – i.e., C loss during biochar production outweighs the increased stability obtained through charring (Whitman et al. 2013). This ratio will change over time, as the two materials mineralize at different rates.

This ratio was modified by Herath et al. (2014) as the  $C_{net}$  debt-credit ratio, which incorporates the interactive effects of biochar and SOC to indicate the net C impact of biochar production and addition to a soil, including changes in SOC mineralization. This is done by adding or subtracting the change in SOC mineralization that results with the addition of the biochar or the original feedstock material:

$$C_{net} \text{ debt-credit ratio} = \frac{\text{Biochar-C remaining} \pm \text{change in SOC mineralization}}{\text{Feedstock-C remaining} \pm \text{change in SOC mineralization}}$$

The C debt-credit ratio will depend on the characteristics of the original feedstock material and the resulting biochar (Figure 16.8). The timescale over which the various characteristics (initial C loss during biochar production, relative mineralization rate of remaining biochar-C and priming effects) would be important for the C debt-credit ratio would depend on the specific system.



**Figure 16.8** Conceptualization of the comparative effects of biochar characteristics and priming on total C sequestered in the soil over time (amended uncharred biomass, low temperature biochar or high temperature biochar + change in native SOC). Solid and dashed lines indicate C remaining in soil over time without and with priming, respectively, and shaded areas indicate C debt (light grey) and C credit (darker grey) for the high temperature biochar no-priming example. Specific curve trajectories would vary with biomass C mineralization rate, C loss during pyrolysis, biochar C mineralization rate and priming, which may change over time

The cycling of C and nutrients in SOM is a natural and essential part of soil ecology and, thus, it is not necessarily possible to place a value on changes to this cycling. For

perturbations to the cycling of SOM may also have important effects on soil nutrient availability and management. If the primary management goal is to reduce overall SOC mineralization or increase relatively recalcitrant forms of C in soil, using higher-temperature biochars with lower levels of easily degradable C may reduce any interactive effects that are driven by the more labile organic C fractions of biochar. However, the production of higher temperature biochars will result in greater initial losses of C and some other elements, which could potentially reduce C savings and provide fewer available nutrients to the soil (Whitman et al. 2013; Chapter 7). Additionally, slowing down SOM decomposition means that not only is C loss decreased, but also that N, P and other nutrients are released from SOM more slowly. If biochar-induced slowdown of SOM decomposition is sustained in the long term, this could have implications for ecosystem functioning, resulting in nutrient limitations.

Better understanding of mechanisms of biochar-SOM interactions, at a molecular

and microbial community level, will help us to identify and classify specific biochar-soil combinations that are more or less susceptible to increased or decreased SOC losses, and to predict long-term management implications. For example, if the relevant properties of biochar (e.g., per cent labile or stable fraction or ash content) and of soil (e.g., total SOC and its quality, pH, mineralogy or texture) that are responsible for the interactive C cycling responses of soil to biochar additions are determined, it will be possible to measure and use these properties in a modeling framework to predict and subsequently manage biochar-SOM decomposition interactions. This could reduce the need for specific biochar and soil testing for each unique system. Furthermore, this information may be used to predict whether the impacts will be long lasting (as with a persistent pH shift) or short-lived (as with labile fraction-driven interactions). Clearly a better understanding of these interactions is needed to determine the net climate impact of biochar additions to soils.

### Future directions

Over the past few years, substantial progress has been made toward a better understanding of biochar-SOM interactions, but more research is warranted, particularly in planted systems and over longer timescales. Now that interactions between SOM and biochar are known to occur, and a number of strong hypotheses for the causes of these effects have been proposed, the next step is to focus on understanding and quantifying the specific mechanisms at work for each general biochar-soil combination and understanding how these interactions may evolve over time. This will be necessary to determine how biochar-soil(-plant) interactions should be considered in C accounting of biochar-amended

systems. Additionally, there are a number of ways that current research approaches to understanding biochar-SOM interactions could be expanded and improved. These include:

- Controlling studies to isolate and test for specific mechanisms, rather than general phenomena.
- Designing studies to determine how the different mechanisms are impacted by specific environmental conditions, over a range of timescales, and for specific biochar and soil types.
- Profiling microbial communities and activities to identify which taxa are



- responsible for or affected by various biochar-SOM interactions.
  - Using micro-scale investigations (e.g., nanoscale secondary ion mass spectrometry) to provide support for or against various mechanisms, particularly those that elucidate microbiota-biochar interactions and stabilization of SOC on or around biochar surfaces and in aggregates.
  - Addressing the artefacts or confounding factors present in many microcosm studies, particularly the lack of continuous inputs and outputs of C and nutrients. This may include carrying out column flow-through experiments and quantifying all fluxes.
  - Establishing more and longer-term field studies designed to study biochar-soil interactions that include recurring OM or biochar inputs.
  - Investigating dynamics of 3-part systems that include plants and their roots, as well as soil and biochar. Partitioning soil C stocks and fluxes into more than two
- components will require innovative approaches such as three C isotope systems or careful design of two C isotope systems in field or glasshouse settings.
- Developing dynamic models and identifying easily-measurable proxies for predicting soil C dynamics over a 100-year time frame that take into account biochar-soil interactions for modelling and policy applications.
- Understanding biochar-SOC(-plant) interactions is necessary to predict how natural or anthropogenic additions of biochar to soils will change soil C stocks over time. With diverse mechanisms at work, these interactions could result in either increased or decreased SOC storage. A cross-disciplinary effort that will involve soil physics, biogeochemistry, soil microbial ecology, plant physiology, agronomy and mineralogy will be needed to carefully design future studies to determine which mechanisms are important, and when.

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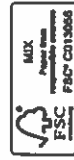
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