

# Biochar Effects on Soil Nutrient Transformations

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## Introduction

Nutrient transformations are influenced by a myriad of biotic and abiotic factors. However, to date, there have been no attempts to synthesize the literature regarding the influence of biochar on soil nutrient transformations. Although the major focus of this book is to review biochar as a soil amendment in agro-ecosystems, the majority of the literature that addresses the effects of biochar on nutrient transformations has originated from studies in natural forest ecosystems. The addition of biochar to forest soils has been found to directly influence nitrogen (N) transformations in phenol-rich acidic forest soils of both temperate (DeLuca et al, 2006; Gundale and DeLuca, 2006; MacKenzie and DeLuca, 2006) and boreal (DeLuca et al, 2002; Berglund et al, 2004) forest ecosystems. Applying biochar to forest soils along with natural or synthetic fertilizers has been found to increase the bioavailability and plant uptake of phosphorus (P), alkaline metals and some trace metals (Glaser et al, 2002; Lehmann et al, 2003; Steiner et al, 2007), but the mechanisms for these increases are still a

matter of speculation. Biochar additions to soil have been found to stimulate mycorrhizal infection (Saito, 1990; Ishii and Kadoya, 1994) and influence P solubility in forest soils (Gundale and DeLuca, 2007), which may be responsible for observed increases in P uptake. The influence of biochar on sulphur (S) transformations has received little or no attention and has not stood out as a dominant effect of adding biochar to natural soil environments. However, biochar applications to mineral soils may have a noted effect on P and S transformations in manure-enriched agro-ecosystems. The mediation of nutrient turnover by biochar has significant implications for organic agricultural systems where biochar may increase stabilization of organic nutrient sources (Glaser et al, 2001) and reduce nutrient leaching losses (Lehmann et al, 2003).

The purpose of this chapter is to provide a state-of-knowledge review of the influences of biochar on N, P and S transformations in soil ecosystems and to provide an overview of the known and potential mechanisms driving

these processes. This chapter provides a discussion of the nutrient content of biochar; the potential mechanisms by which biochar

modifies nutrient transformations; and the direct and indirect influences of biochar on soil nutrient transformations.

## Nutrient content of biochar

Prior to considering the influence of biochar on nutrient transformations, the nutrient capital associated with biochar additions must be considered. In other words, does biochar serve as a significant source of nutrients irrespective of other inputs? The nutrient content of biochar is discussed in depth in Chapter 5. It is important to note that biochar is somewhat depleted in N and slightly depleted in S relative to more thermally stable nutrients. During the pyrolysis or oxidation process that generates biochar, heating causes some nutrients to volatilize, especially at the surface of the material, while other nutrients become concentrated in the remaining biochar (see Chapter 5).

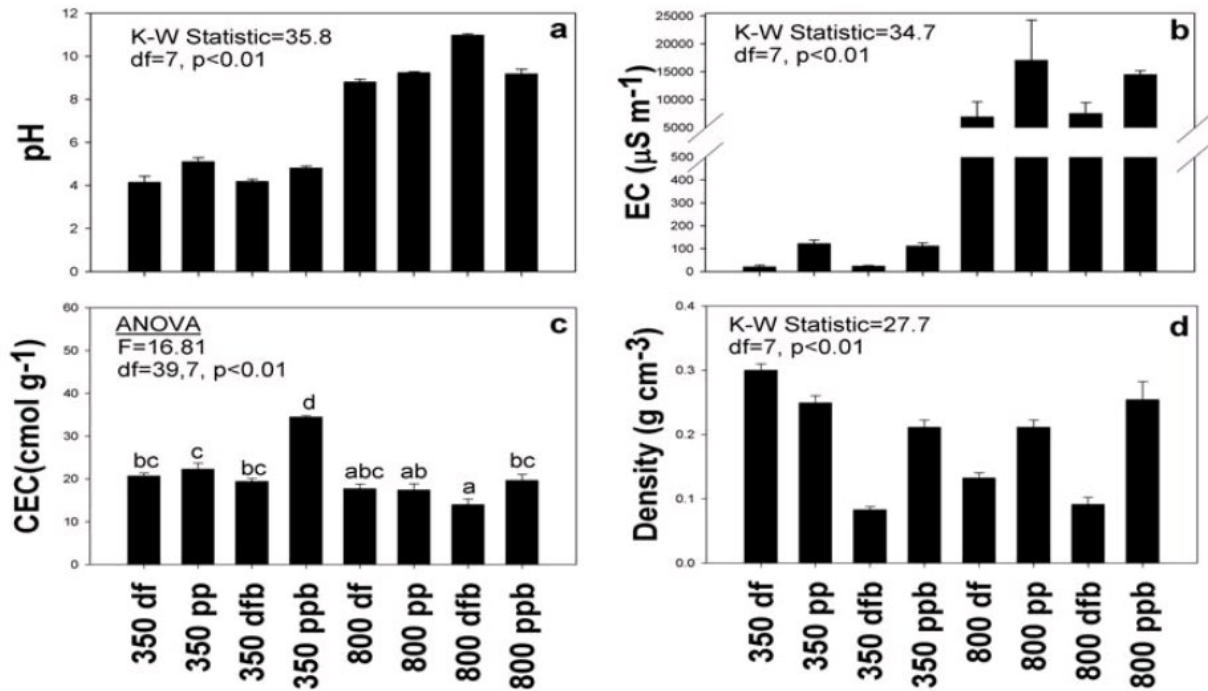
Temperature, the time a material is held at a given temperature and the heating rate directly influence the chemical properties of biochar. Individual elements are potentially lost to the atmosphere, fixed into recalcitrant forms or liberated as soluble oxides during the heating process. In the case of wood-based biochar formed under natural conditions, carbon (C) begins to volatilize around 100°C, N above 200°C, S above 375°C, and potassium (K) and P between 700°C and 800°C. The volatilization of magnesium (Mg), calcium (Ca) and manganese (Mn) occurs at temperatures above 1000°C (Neary et al, 1999; Knoepp et al, 2005). Biochar produced from sewage sludge pyrolysed (heated in the absence of oxygen) at 450°C contains over 50 per cent of the original N (although not in a readily bioavailable form) and all of the original P (Bridle and Pritchard, 2004). The relative concentration and molecular speciation of these elements during heating generates

substantial variability in the chemical composition of the resulting biochar and is discussed in greater detail in Chapter 5.

Nitrogen is the most sensitive of all macronutrients to heating; thus, the N content of high-temperature biochar is extremely low (Tyron, 1948). Pyrolysis conditions during the production of wheat straw biochar resulted in the loss of about 50 per cent of the S at temperatures of 500°C and about 85 per cent of the S was lost in 950°C pyrolysis (Knudsen et al, 2004), greatly reducing the S content of the resulting biochar. Accordingly, extractable concentrations of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  generally decrease with increasing pyrolysis temperature during biochar generation, with a portion of  $\text{NH}_4^+$  being oxidized to a small exchangeable  $\text{NO}_3^-$  pool at higher temperatures (Gundale and DeLuca, 2006).

Gundale and DeLuca (2006) evaluated the effect of temperature on biochar formation from several woody substrates collected from a Montana ponderosa pine/Douglas-fir forest. High-temperature (800°C) biochar demonstrated higher pH, electrical conductivity (EC) and extractable  $\text{NO}_3^-$  relative to low-temperature (350°C) biochar (see Figure 14.1). In contrast, density, extractable  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$  and soluble and total phenols were lower in high-temperature biochars relative to low-temperature biochars (see Figure 14.2). These data suggest that substantial variation can occur in the chemical properties of biochar due to the temperature that the plant material reaches during charring.

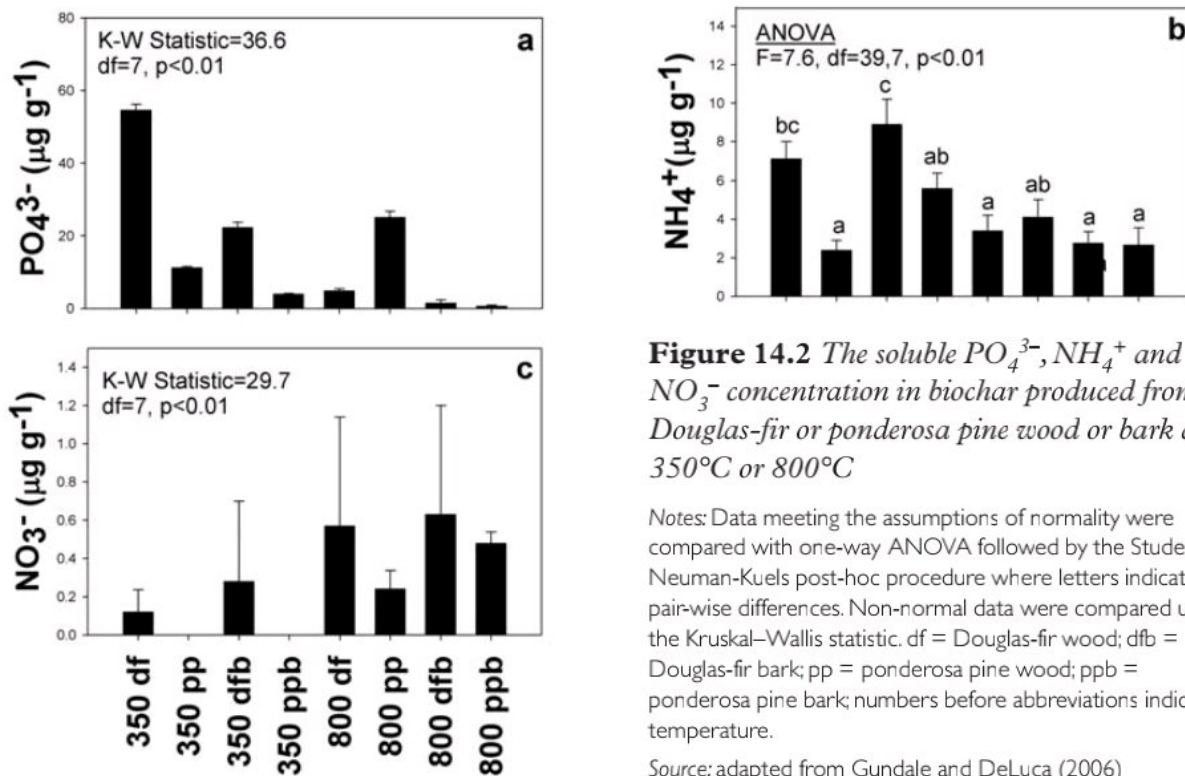
Biochar additions to soil provide a modest contribution of nutrients depending, in part, upon the nature of the feedstock



**Figure 14.1** The pH, electrical conductivity (EC), cation exchange capacity (CEC) and density of biochar produced from Douglas-fir or ponderosa pine wood or bark at 350°C or 800°C

Notes: Data meeting the assumptions of normality were compared with one-way ANOVA followed by the Student-Neuman-Kuels post-hoc procedure where letters indicate pair-wise differences. Non-normal data were compared using the Kruskal–Wallis (K–W) statistic. df = Douglas-fir wood; dfb = Douglas-fir bark; pp = ponderosa pine wood; ppb = ponderosa pine bark; numbers before abbreviations indicate temperature.

Source: adapted from Gundale and DeLuca (2006)



**Figure 14.2** The soluble PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> concentration in biochar produced from Douglas-fir or ponderosa pine wood or bark at 350°C or 800°C

Notes: Data meeting the assumptions of normality were compared with one-way ANOVA followed by the Student-Neuman-Kuels post-hoc procedure where letters indicate pair-wise differences. Non-normal data were compared using the Kruskal–Wallis statistic. df = Douglas-fir wood; dfb = Douglas-fir bark; pp = ponderosa pine wood; ppb = ponderosa pine bark; numbers before abbreviations indicate temperature.

Source: adapted from Gundale and DeLuca (2006)

(wood versus manure) and upon the temperature under which the material is formed (Bridle and Pritchard, 2004; Gundale and DeLuca, 2006). However, biochar is probably more important as a soil conditioner and driver of nutrient transformations and less so

as a primary source of nutrients (Glaser et al, 2002; Lehmann et al, 2003). Therefore, the following discussion is focused on biochar as a modifier of N, P and S transformations in mineral soils.

## Potential mechanisms for how biochar modifies nutrient transformations

Biochar is a high surface-area, highly porous, variable-charge organic material that has the potential to increase soil water-holding capacity, cation exchange capacity (CEC), surface sorption capacity and base saturation when added to soil (Glaser et al, 2002; Bélanger et al, 2004; Keech et al, 2005; Liang et al, 2006). The surface area, porosity, nutrient content and charge density all change in relation to the temperature of biochar formation (Gundale and DeLuca, 2006; Bornermann et al, 2007). Biochar additions to soil also have the potential to alter soil microbial populations and to shift functional groups (Pietikäinen et al, 2000) and have the potential to reduce soil bulk density (Gundale and DeLuca, 2006). The broad array of beneficial properties associated with biochar additions to soil may function alone or in combination in order to influence nutrient transformations, described below. The physical characteristics of biochar are discussed in Chapter 2, pH and nutrient contents in Chapter 5, and biotic influences in Chapter 6. Here, we extend this discussion by exploring the known and potential effects of these bio-physico-chemical changes on nutrient transformations.

It is well understood that autotrophic nitrifying bacteria are favoured by less acidic soil conditions (Stevenson and Cole, 1999). Thus, biochar additions to mineral soil that increase soil pH are likely to favourably influence nitrification. However, activated biochar and glycine added to acid boreal forest soils was found to have no influence on pH, but

significantly increased net nitrification (Berglund et al, 2004). Furthermore, the addition of natural field-collected biochar – a soil-neutral phosphate buffer slurry – immediately stimulated nitrification potential with no shift in the pH of the suspension (DeLuca et al, 2006). This puts into question the assumption that pH is the major driver of the nitrification response to biochar additions to soil. It is possible that archaeal ammonia oxidizers (*Crenarchaeota*), which have the capacity to nitrify under low pH conditions (Leininger et al, 2006), are the primary drivers of nitrification in coniferous forest soils.

Bioavailable C may be adsorbed to biochar surfaces, thereby reducing the potential for immobilization of nitrate formed under biochar stimulation of nitrification. Biochar added to soil with an organic N source yielded an increase in net nitrification; however, the addition of organic N with or without biochar resulted in high rates of  $\text{NH}_4^+$  production that were not immobilized (DeLuca et al, 2006), reducing the likelihood of this explanation.

Biochar may act as a habitat or safe site for soil microorganisms (Pietikäinen et al, 2000) involved in N, P or S transformations. Biochar certainly has the capacity to support the presence of adsorbed bacteria (Pietikäinen et al, 2000; Rivera-Utrilla et al, 2001) from which the organisms may influence soil processes. Both saprophytic and mycorrhizal fungi have been observed to colonize soil biochar; but the significance of their presence has not been clarified (Saito,

1990; Zackrisson et al, 1996). Some researchers have suggested that the small pore sizes of biochar might exclude grazing protozoa and nematodes, allowing for the proliferation of fungi and bacteria (Warnock et al, 2007). However, recent studies suggest that bacteria and fungi primarily colonize the surface of biochar, but that limited oxygen availability may limit growth inside the small internal pores (Yoshizawa et al, 2005).

The high surface area, porous and often hydrophobic nature of biochar makes it an ideal surface for the sorption of hydrophobic organic compounds (Cornelissen et al, 2004; Bornermann et al, 2007). Numerous papers have reported a reduction in soluble or free phenolic compounds when activated carbon is added to soils (DeLuca et al, 2002; Wallstedt et al, 2002; Berglund et al, 2004; Gundale and DeLuca, 2006). Additional

studies have demonstrated that biochar formed during wildfires or agricultural residue burning also functions to adsorb phenolic and various aromatic and hydrophobic organic compounds (Yaning and Sheng, 2003; Brimmer, 2006; DeLuca et al, 2006; Gundale and DeLuca, 2006; MacKenzie and DeLuca, 2006; Bornermann et al, 2007). Through these sorption reactions, biochar may reduce the activity of compounds that may be either inhibitory to nutrient transformation specialists, such as nitrifying bacteria (White, 1991; Ward et al, 1997; Paavolainen et al, 1998), or reduce the concentration of phenolic compounds in the soil solution that would otherwise enhance the immobilization of inorganic N, P or S (Schimel et al, 1996; Stevenson and Cole, 1999).

## **Direct and indirect influences of biochar on soil nutrient transformations**

### **Nitrogen**

Nitrogen is the single most limiting plant nutrient in most cold or temperate terrestrial ecosystems (Vitousek and Howarth, 1991). In soils, the majority of N exists in complex organic forms that must be ammonified to  $\text{NH}_4^+$  and then nitrified to  $\text{NO}_3^-$  prior to uptake by most agricultural plants (Stevenson and Cole, 1999). Recent studies have demonstrated that the addition of biochar to surface mineral soils may directly influence N transformations. Here we review the evidence for the direct and indirect influences of biochar on ammonification, nitrification, denitrification and  $\text{N}_2$  fixation, and provide potential mechanisms that may be driving these relationships.

#### ***Ammonification and nitrification***

Nitrogen mineralization is the process whereby organic N is converted to inorganic

N through the methods of ammonification (where  $\text{NH}_4^+$  is formed) and nitrification (where  $\text{NO}_3^-$  is formed). Ammonification is a biotic process driven primarily by heterotrophic bacteria and a variety of fungi (Stevenson and Cole, 1999). Nitrification is considered to be a strictly biotic process that is most commonly mediated by autotrophic organisms, including bacteria and archaea, in agricultural, grassland and forest soils (Stevenson and Cole, 1999; Grenon et al, 2004; Leininger et al, 2006; Islam et al, 2007). Biochar has been found to increase net nitrification rates in temperate and boreal forest soils that otherwise demonstrate no net nitrification (Berglund et al, 2004; DeLuca et al, 2006). There is no evidence for such an effect in grassland (DeLuca et al, 2006) or agricultural soils (Lehmann et al, 2003; Rondon et al, 2007), which may already accommodate an active nitrifying community. Results from the studies cited above are

**Table 14.1** Effect of biochar (natural biochar, lab-generated biochar or activated carbon) on nitrogen mineralization and nitrification from studies performed in different forest ecosystems

Ecosystem	Biochar type	Nutrient source and incubation	Control NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>+</sup> -N	Biochar addition NO <sub>3</sub> <sup>-</sup> -N	Statistical difference	Reference
Ponderosa pine, western Montana	Wildfire biochar, ponderosa pine wood	Glycine in greenhouse, resin collected, 30 days	150 ± 200 (µg N cap <sup>-1</sup> ) <sup>1</sup>	200 ± 100 (µg N cap <sup>-1</sup> )	700 ± 400 (µg N cap <sup>-1</sup> )	1200 ± 500 (µg N cap <sup>-1</sup> )	No NH <sub>4</sub> <sup>+</sup> Yes NO <sub>3</sub> <sup>-</sup>	Mackenzie and DeLuca (2006)
Ponderosa pine, western Montana	Lab biochar, ponderosa pine wood	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> and KH <sub>2</sub> PO <sub>4</sub> in lab, aerobic incubation, 15 days	NA	40 ± 5 (µg N g soil <sup>-1</sup> )	NA	70 ± 3 (µg N g soil <sup>-1</sup> )	Yes NO <sub>3</sub> <sup>-</sup>	DeLuca et al (2006)
Ponderosa pine, western Montana	Lab biochar, ponderosa pine (wood and bark), Douglas-fir (wood and bark)	Glycine in lab, aerobic incubation, 14 days	47 ± 4 (µg N g soil <sup>-1</sup> )	5 ± 1 (µg N cap <sup>-1</sup> )	ppw <sup>2</sup> 20 ± 5 ppb 25 ± 6 dfw 32 ± 8	ppw 21 ± 4 ppb 20 ± 8 dfw 11 ± 8	Yes NH <sub>4</sub> <sup>+</sup> Yes NO <sub>3</sub> <sup>-</sup> Yes NH <sub>4</sub> <sup>+</sup> Yes NO <sub>3</sub> <sup>-</sup> No NH <sub>4</sub> <sup>+</sup> No NO <sub>3</sub> <sup>-</sup> No NH <sub>4</sub> <sup>+</sup> Yes NO <sub>3</sub> <sup>-</sup>	Gundale and DeLuca (2006)
Scots pine, Sweden	Activated carbon	Glycine in field, resin collected, 30 days	20 ± 13 (µg N cap <sup>-1</sup> )	0.06 ± 0.02 (µg N cap <sup>-1</sup> )	low <sup>3</sup> 410 ± 99 high 780 ± 302	low 0.12 ± 0.03 high 1.89 ± 1.1	Yes NH <sub>4</sub> <sup>+</sup> Yes NO <sub>3</sub> <sup>-</sup> No NO <sub>3</sub> <sup>-</sup> Yes NH <sub>4</sub> <sup>+</sup> Yes NO <sub>3</sub> <sup>-</sup>	DeLuca et al (2002)
Scots pine, Sweden	Activated carbon	Glycine in lab, aerobic incubation, 60 days	46 ± 6 (µg N g soil <sup>-1</sup> )	2.8 ± 0.4 (µg N g soil <sup>-1</sup> )	1350 ± 50 (µg N g soil <sup>-1</sup> )	(µg N cap <sup>-1</sup> ) 5.5 ± 0.6 (µg N g soil <sup>-1</sup> )	Yes NO <sub>3</sub> <sup>-</sup> Yes NH <sub>4</sub> <sup>+</sup> Yes NO <sub>3</sub> <sup>-</sup>	Berglund et al (2004)
Scots pine, Sweden	Activated carbon	Glycine in field, resin collected, 75 days	20 ± 3 (µg N cap <sup>-1</sup> )	0.20 ± 0.20 (µg N cap <sup>-1</sup> )	146 ± 42 (µg N cap <sup>-1</sup> )	0.6 ± 0.1 (µg N cap <sup>-1</sup> )	Yes NH <sub>4</sub> <sup>+</sup> No NO <sub>3</sub> <sup>-</sup>	Berglund et al (2004)

Notes: 1 Ionic resin analysis used approximately 1 g mixed bed resin in nylon mesh capsules approximately 25.4 mm in diameter.

2 ppw = ponderosa pine wood; ppb = ponderosa pine bark; dfw = Douglas-fir wood; dfb = Douglas-fir bark biochar produced at 350°C.

3 Low biochar application rate of 1000 kg ha<sup>-1</sup>; high application rate was 10,000 kg ha<sup>-1</sup>.

NA = not available.

summarized in Table 14.1, specifically focusing on ammonification and nitrification in biochar or activated carbon-amended soil samples, field plots or mesocosms in comparison to unamended controls. Both activated carbon (DeLuca et al, 2002; Berglund et al, 2004) and biochar collected from recently burned forests (DeLuca et al, 2006; MacKenzie and DeLuca, 2006) or generated in laboratories by heating biomass in a muffle furnace (Gundale and DeLuca, 2006) were found to stimulate net nitrification in forest soils.

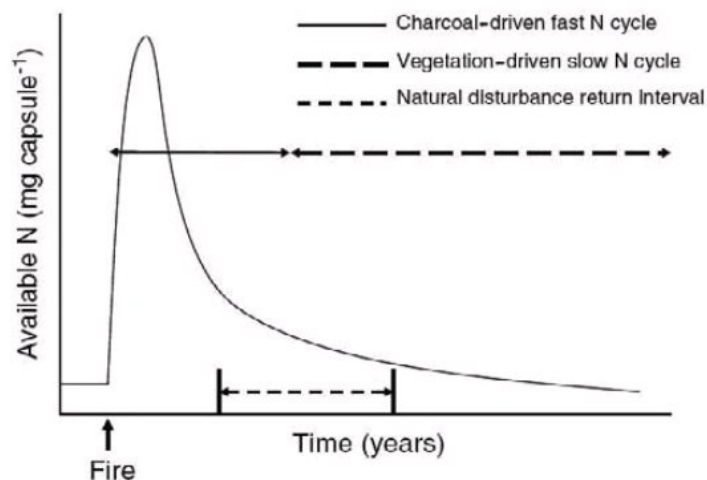
Nitrification was found to be below the detection limit in the acidic phenol-rich, late succession forest soils of northern Sweden, whereas forest sites recently exposed to fire were found to have measurable levels of nitrification (DeLuca et al, 2002). The injection of glycine (a labile organic N source) into these late succession soils readily stimulated ammonification, but failed to stimulate any nitrification. The injection of activated carbon into the humus layer induced a slight stimulation of nitrification (see Table 14.1), but the injection of glycine with activated carbon consistently stimulated nitrification, demonstrating that ammonification in these soils was substrate limited, whereas nitrification was being inhibited by a factor that could be mitigated by adding activated carbon (DeLuca et al, 2002; Berglund et al, 2004). In all soils treated with activated carbon, a significant reduction in soluble phenols was recorded (DeLuca et al, 2002; Berglund et al, 2004). It is possible that the activated carbon adsorbed organic compounds that either inhibited net nitrification (White, 1991; Ward et al, 1997; Paavolainen et al, 1998) or caused immobilization of the accumulated  $\text{NO}_3^-$  (McCarty and Bremner, 1986; Schimel et al, 1996).

Biochar collected from forests that had been exposed to recent forest fires was found to stimulate net nitrification in soils from low-elevation ponderosa pine forests that otherwise demonstrated little or no nitrifica-

tion (DeLuca et al, 2006). Nitrifier activity, as measured using an aerated slurry method (Hart et al, 1994), was found to be extremely low in soils collected from sites that had not been exposed to fire for approximately 100 years and relatively high in soils exposed to recurrent fire (DeLuca and Sala, 2006). The addition of field-collected biochar to soils expressing no net nitrification readily stimulated nitrifier activity in a 24-hour aerated soil slurry assay (DeLuca and Sala, 2006; DeLuca et al, 2006). The addition of biochar to grassland soils that already demonstrated relatively high levels of nitrification had no measurable effect on nitrifier activity (DeLuca et al, 2006). A small increase in nitrification was observed in sterile control samples amended with sterile biochar, suggesting that the oxide surfaces on biochar may stimulate some quantity of auto-oxidation of  $\text{NH}_4^+$  (DeLuca et al, 2006). Wood ash commonly contains high concentrations of metal oxides, including CaO, MgO,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and CrO (Koukouzas et al, 2007). Exposure of biochar to solubilized ash may result in the retention of these potentially catalytic oxides on active surfaces of the biochar (Le Leuch and Bandosz, 2007). These oxide surfaces may, in turn, effectively adsorb  $\text{NH}_4^+$  or  $\text{NH}_3$  and potentially catalyse the photo-oxidation of  $\text{NH}_4^+$  (Lee et al, 2005).

The rapid response of the nitrifier community to biochar additions in soils with low nitrification activity and the lack of a stimulatory effect on actively nitrifying communities suggest that biochar may be adsorbing inhibitory compounds in the soil environment (Zackrisson et al, 1996), which then allows nitrification to proceed. Fire induces a short-term influence on N availability; but biochar may act to maintain that effect for years to decades after a fire (see Figure 14.3).

The temperature of biochar formation and the type of plant material from which the biochar is generated also potentially influence



**Figure 14.3** Hypothetical change in N availability with time since the last fire, where biochar induces a fast turnover of N for years after a fire event

Source: adapted from MacKenzie and DeLuca (2006)

ammonification and nitrification (Gundale and DeLuca, 2006). Gundale and DeLuca (2006) evaluated how biochar produced at two different temperatures (350°C and 800°C) from the bark and wood of two different tree species common to western North America (ponderosa pine and Douglas-fir) influences N mineralization and nitrification. All biochar treatments increased nitrification, except for Douglas-fir wood, which suggests that for some species, bark may create a more effective biochar than wood. In these experiments, biochar addition to soil also caused reduced ammonification compared to the control (Gundale and DeLuca, 2006). This is possibly due to  $\text{NH}_4^+$  adsorption to biochar (Berglund et al, 2004). Results were similar for biochar created at 800°C, except for ponderosa pine bark, which did not significantly increase nitrification. It is clear that the temperature of formation and type of organic material pyrolysed are important factors to consider when assessing the effects of biochar on nutrient-cycling processes in soil, and ones not easily dealt with given the multiplicity of combinations that these two factors represent.

In a study of forest floor/mineral soil mesocosms collected intact from a site not exposed to fire for over 100 years in western Montana, biochar was found to stimulate

nitrification under the ericaceous shrub community, but not under the sedge community (see Table 14.1; MacKenzie and DeLuca, 2006). The shrub mesocosm was found to have high concentrations of free phenolic compounds whose recovery was greatly reduced by adding biochar. The sedge mesocosm had low concentrations of free phenols and measurable levels of net nitrification prior to biochar additions. Nitrification in the sedge mesocosm was stimulated by glycine addition to soil without biochar, suggesting that nitrification under sedge was substrate limited (not inhibited) and thus not affected by adding biochar. In this study, charred material was scraped off of the outside of burned trees, making it similar to the charred bark material described above. It is possible that the wildfire biochar functioned as an inoculant, introducing nitrifying bacteria into the soil system; however, nitrifying bacteria are found in most forest soils, but often induce little net nitrification due to rapid N immobilization rates (Stark and Hart, 1997) or inhibition, as described above.

Biochar additions to agricultural soils of the tropics have been reported to either reduce N availability (Lehmann et al, 2003) or to increase N uptake and export in crops (Steiner et al, 2007). Reduced N availability may be a result of the high C/N ratio of



biochar and, thus, greater potential for N immobilization (see below) or due to biochar adsorption of  $\text{NH}_4^+$  (described above), which in turn reduces the potential for N leaching losses and sustained higher N fertility over time in surface soils (Steiner et al, 2007). It should be noted, however, that immobilization potential associated with biochar additions to soil would be greatly limited by the recalcitrant nature of biochar (DeLuca and Aplet, 2007).

To summarize, biochar additions to acid phenol-rich soils that lack net nitrification have the potential to stimulate nitrification. Biochar additions to agricultural and grassland soils that already demonstrate net nitrification will probably have no effect on nitrification and may express a slight decline in net ammonification due to  $\text{NH}_4^+$  adsorption or enhanced immobilization. Whether adsorption is sustained after biochar weathering in soil or decreases as shown for adsorption of polycyclic aromatic hydrocarbons to biochar (Chapter 18) remains to be investigated.

### *Immobilization, volatilization and denitrification*

Little direct evidence exists to demonstrate the effect of biochar on N immobilization, volatilization or denitrification. The latter is discussed in greater detail in Chapter 13. A few studies have suggested that biochar can adsorb both  $\text{NH}_4^+$  and  $\text{NH}_3^-$  from the soil solution (Lehmann et al, 2006), thus reducing solution inorganic N at least temporarily, but perhaps concentrating it for microbial use. Because biochar residing in soil becomes occluded with organic matter (Zackrisson et al, 1996; Wardle et al, 1998), or aggregates both mineral and organic matter fractions together into physically protected pools (Brodowski et al, 2006), the N in those organic matter pools may remain unavailable for some period of time.

As discussed above, biochar is an N-depleted material having a uniquely high C/N ratio. Some decomposition occurs when fresh

biochar is added to soil (Schneour, 1966; Liang et al, 2006), which could induce net immobilization of inorganic N already present in the soil solution or applied as fertilizer. Low-temperature biochar, in particular, would probably induce net immobilization when applied to mineral soils as microbes degrade residual bio-oils (Steiner et al, 2007) or surface functional groups (Liang et al, 2006). This immobilization process could create a temporary reservoir of organic N, which would reduce the potential for leaching of inorganic N in highly leached soils (Steiner et al, 2007).

There have been no studies that have directly evaluated the influence of biochar on  $\text{NH}_3$  volatilization. Ammonia volatilization in agricultural soils is favoured at alkaline pH and when high concentrations of  $\text{NH}_4^+$  are present (Stevenson and Cole, 1999). Biochar and biochar mixed with ash have the potential to raise the pH of acid soils (Glaser et al, 2002), but not to a level that would increase volatilization (Stevenson and Cole, 1999). Biochar additions to agricultural soils, as well as acid forest soils, have been found to reduce  $\text{NH}_4^+$  concentrations, which could be a result of volatilization; but it is more likely that surface adsorption of  $\text{NH}_4^+$  (Le Leuch and Bandosz, 2007) reduces soil  $\text{NH}_4^+$  concentrations and reduces the potential for  $\text{NH}_3$  volatilization.

Denitrification is a biotic dissimilatory process in which  $\text{NO}_3^-$  is reduced to  $\text{N}_2$  (g) in the absence of  $\text{O}_2$ . Several intermediates (including NO and  $\text{N}_2\text{O}$ ) are formed during this reductive process and are potentially released into the soil atmosphere when conditions are not favourable for complete reduction of  $\text{NO}_3^-$  to  $\text{N}_2$ . The influence of biochar on denitrification is partially covered in Chapter 13, where it is demonstrated that biochar has the potential to catalyse the reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$ , potentially reducing the emission of this important greenhouse gas to the atmosphere.

To date, there have been few studies that directly address the influence of biochar on

denitrification. Our evaluation of the fire effects literature suggests that biochar could directly or indirectly influence denitrification. The process of denitrification requires the presence of substrate (available C) and a terminal electron acceptor, such as  $\text{NO}_3^-$  (Stevenson and Cole, 1999). An increase in net nitrification in acid forest soils when biochar is added (e.g. DeLuca et al, 2006) would increase the potential for denitrification under anaerobic conditions where available C is high. Adding manure with biochar (e.g. Lehmann et al, 2003; Steiner et al, 2007) would potentially increase bioavailable C in the soil solution. The combination of these two factors could increase denitrification potential in mineral soils amended with a mixture of biochar and manure.

Drawing from the fire effects literature, Castaldi and Aragosa (2002) found that fire treatments caused co-variation between moisture content,  $\text{NH}_4^+$  concentrations and denitrification enzyme activity (DEA); but the trends were only evident during the wettest time of the year, which was September to November in the studied Mediterranean climate. In a 'light fire treatment', DEA varied with  $\text{NH}_4^+$  concentration, and in the 'intense fire treatment', DEA varied with soil moisture content (Castaldi and Aragosa, 2002). It is not clear whether the high-intensity fire treatment yielded a greater amount of biochar or not, as higher-intensity fires generally result in greater volatilization of C and a greater potential to deposit ash rather than biochar (Neary et al, 1999). However, the fact that DEA varied with moisture content and not pH suggests that ash production was minimal (Castaldi and Aragosa, 2002).

### **Biological nitrogen fixation**

Biological  $\text{N}_2$  fixation is uniquely important in low-input agro-ecosystems where external N inputs are minimal. Therefore, it is important to know whether biochar applications have the capacity to alter symbiotic or free-

living  $\text{N}_2$ -fixing organisms. Rondon et al (2007) tested the effect of adding different amounts of biochar to nodulating and non-nodulating varieties of the common bean, *Phaseolus vulgaris*, inoculated with *Rhizobium* strains, and measured changes in N uptake using an isotope pool dilution technique. Biochar significantly increased  $\text{N}_2$  fixation compared to a control; but the highest application rate, 90g biochar  $\text{kg}^{-1}$  soil, did not produce the highest soil N concentration or plant biomass (Rondon et al, 2007). The study further indicates that biochar may stimulate  $\text{N}_2$  fixation as the result of increased availability of trace metals such as nickel (Ni), iron (Fe), boron (B), titanium (Ti) and molybdenum (Mo). The highest rates of biochar application decreased the magnitude of the effect and, if taken to the extreme, might interfere with  $\text{N}_2$  fixation. Legume nodulation might also be affected if added biochar interfered with signalling compounds in the soil environment (Warnock et al, 2007). The formation of root nodules in leguminous plants is initiated by their release of flavonoids, which are polyphenolic signalling compounds (Jain and Nainawatee, 2002). Biochar is highly effective in the sorption of phenolic compounds, including flavonoids (Gundale and DeLuca, 2006). Therefore, high biochar applications may interfere with signal reception and initiation of the legume root infection process.

Free-living  $\text{N}_2$ -fixing bacteria are ubiquitous in the soil environment. Agro-ecosystems that enhance the presence of these organisms may reduce the need for external inputs. Unfortunately, to date, there are no studies that directly demonstrate an influence of biochar on free-living  $\text{N}_2$ -fixing bacteria. In forest restoration studies involving prescribed fire, Burgoyne (2007) found no effect of fire treatments on the activity of free-living N-fixing bacteria, although these same plots revealed a significant increase in biochar in both the forest floor and surface mineral soil (DeLuca, unpublished data). It is

well understood that excess soluble N in the soil solution reduces  $N_2$ -fixation rates in free-living  $N_2$ -fixing bacteria (Kitoh and Shiomi, 1991; DeLuca et al, 1996) and available soil P stimulates  $N_2$  fixation (Vitousek et al, 2002). Therefore, it is possible that the activity of these  $N_2$ -fixing bacteria could be increased in an environment where applied biochar functions to increase P solubility (Lehmann et al, 2003; Steiner et al, 2007) and reduce soluble soil N concentrations (due to immobilization or surface adsorption of  $NH_4^+$ ). Conversely, biochar additions to forest soils that stimulate nitrification (e.g. DeLuca et al, 2006) may ultimately down-regulate  $N_2$  fixation by free-living  $N_2$ -fixing bacteria.

## Phosphorus

Similar to N cycling, microbial turnover and decomposition regulate P mineralization and, thus, influence how much P is available for plant uptake. In contrast to N cycling, however, P availability is also greatly affected by a series of pH-dependent abiotic reactions that influence the ratio of soluble-to-insoluble P pools in the soil. Several studies have demonstrated enhanced P uptake in the presence of biochar; but very little work has focused on the variety of mechanisms through which biochar may directly or indirectly influence the biotic and abiotic components of the P cycle. In this section we discuss a few of these mechanisms, including:

- biochar as a direct source of soluble P salts and exchangeable P;
- biochar as a modifier of soil pH and ameliorator of P complexing metals ( $Al^{3+}$ ,  $Fe^{3+2+}$ ,  $Ca^{2+}$ ); and
- biochar as a promoter of microbial activity and P mineralization.

### *Soluble P salts and exchangeable P*

Altered P availability associated with biochar is probably due, in part, to:

- the release of P salts from woody tissues during charring;
- biochar interference with P sorption to Al and Fe oxides;
- biochar-induced changes in the soil ion exchange capacity; and
- biochar sorption of plant and microbial chelates.

The release of P from biochar has long been recognized (Tyron, 1948), and the mechanism for direct P release from biochar is not complex. The concentration of P in plant tissues is small relative to the large concentration of C, and a significant portion of plant P is incorporated within organic molecules through ester or pyrophosphate bonds (Stevenson and Cole, 1999). This organic P in dead plant tissues is not available for plant uptake without microbial cleavage of these bonds. When plant tissue is heated, organic C begins to volatilize at approximately 100°C, whereas P does not volatilize until approximately 700°C (Knoepp et al, 2005). Combustion or charring of organic materials can greatly enhance P availability from plant tissue by disproportionately volatilizing C and by cleaving organic P bonds, resulting in a residue of soluble P salts associated with the charred material. Gundale and DeLuca (2006) demonstrated this as an increased extractable  $PO_4^{3-}$  from biochar made from bark and bole samples of Douglas-fir and ponderosa pine trees from a Montana pine forest. Furthermore, it was found that charring at both low and high temperatures (350°C and 800°C) resulted in a significant extractable  $PO_4^{3-}$  pool from all substrates, but that extractable P declined in biochar produced at high relative to low temperatures, where the volatilization threshold for P had been reached. Increased extractable P in soils amended with a variety of charred materials has also been observed for tropical soils (Glaser et al, 2002; Lehmann et al, 2003).

In addition to directly releasing soluble P, biochar can have a high ion exchange capac-

ity (Liang et al, 2006), and may alter P availability by providing anion exchange capacity or by influencing the activity of cations that interact with P. It has been demonstrated that fresh biochar has an abundance of anion exchange capacity in the acid pH range (Cheng et al, 2008), which can initially be in excess of the total cation exchange capacity of the biochar. It is possible that these positive exchange sites compete with Al and Fe oxides (e.g. gibbsite and goethite) for sorption of soluble P, similar to that observed for humic and fulvic acids (Sibanda and Young, 1986; Hunt et al, 2007). To date, however, there is a noted lack of studies evaluating the effect of short-term anion exchange capacity on P cycling and availability.

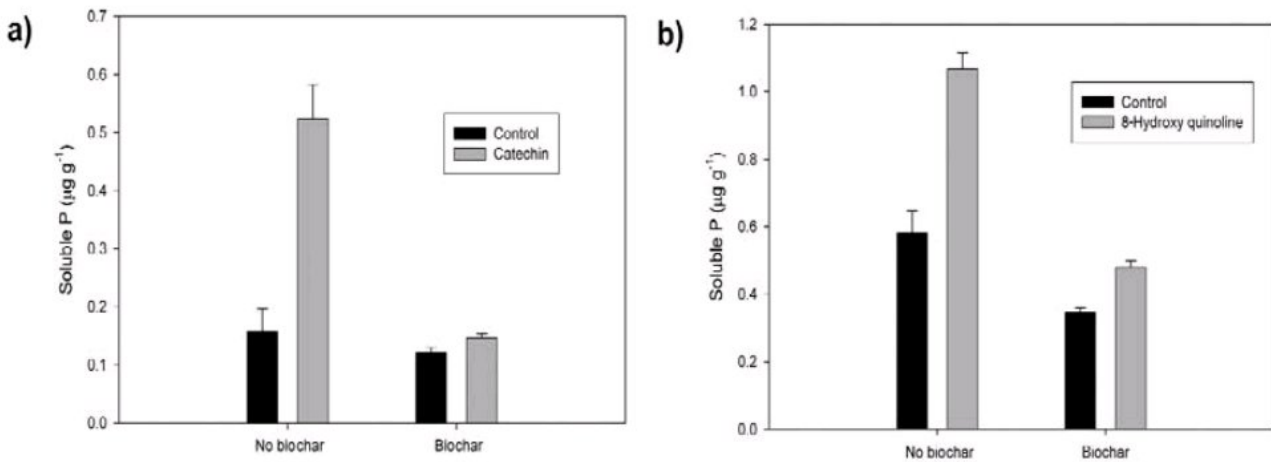
As biochar ages, the positive exchange sites on biochar surfaces decline and negative charge sites develop (Cheng et al, 2008). The biochemical basis for the high CEC is not fully understood, but is probably due to the presence of oxidized functional groups (such as carboxyl groups), whose presence is indicated by high O/C ratios on the surface of charred materials following microbial degradation (Liang et al, 2006; Preston and Schmidt 2006) and is further influenced by the large surface area (Gundale and DeLuca, 2006) and high charge density of biochar (Liang et al, 2006). Phosphorus availability and recycling may be influenced by the biochar CEC over long timescales and in soils that have inherently low exchange capacities. By reducing the presence of free  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  near root surfaces, biochar may promote the formation and recycling of labile P fractions. This is also an area of research that deserves greater attention.

### **Complexation**

A significant component of the P cycle consists of a series of precipitation reactions that influence the solubility of P, ultimately influencing the quantity of P that is available for uptake and actively recycled between plants and microbes. The degree to which

these precipitation reactions occur is strongly influenced by soil pH due to the pH-dependent activities of the ions responsible for precipitation ( $\text{Al}^{3+}$ ,  $\text{Fe}^{2+3+}$  and  $\text{Ca}^{2+}$ ) (Stevenson and Cole, 1999). In alkaline soils, P solubility is primarily regulated by its interaction with  $\text{Ca}^{2+}$ , where a cascading apatite mineral pathway develops. In acid soils, P availability is primarily regulated by its interaction with  $\text{Al}^{3+}$  and  $\text{Fe}^{2+3+}$  ions, where highly insoluble Al- and Fe-phosphates form. Biochar may influence precipitation of P into these insoluble pools by altering the pH and, thus, the strength of ionic P interactions with  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+3+}$  and  $\text{Ca}^{2+}$  (Lehmann et al, 2003; Topoliantz et al, 2005) or by sorbing organic molecules that act as chelates of metal ions that otherwise precipitate P (DeLuca, unpublished data; see below).

Numerous studies have demonstrated that biochar can modify soil pH, normally by increasing pH in acidic soils (Mbagwu 1989; Matsubara et al, 2002; Lehmann et al, 2003). There are few, if any, studies that have demonstrated a reduction in pH with biochar addition in alkaline soils, however, the addition of acid biochar to acidic soils has been observed to reduce soil pH (Cheng et al, 2006). An increase in pH associated with adding biochar to acid soils is due to an increased concentration of alkaline metal ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^{+}$ ) oxides in the biochar and a reduced concentration of soluble soil  $\text{Al}^{3+}$  (Steiner et al, 2007). Adding these alkaline metals, both as soluble salts and associated with biochar exchange sites, is probably the single most significant effect of biochar on P solubility, particularly in acidic soils where subtle changes in pH can result in substantially reduced P precipitation with  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ . In contrast, adding biochar (and associated ash residue) to neutral or alkaline soils may have a limited effect on P availability because adding alkaline metals would only exacerbate Ca-driven P limitations. In support of this, Gundale and DeLuca (2007) found reduced concentra-



**Figure 14.4** Soluble P leached from columns filled with (a) calcareous soil (pH = 8) amended with catechin alone or with biochar; or (b) acid and Al-rich soil (pH = 6) amended with 8-hydroxy quinoline alone or with biochar

Notes: Studies were conducted by placing 30g of soil amended with  $50\text{mg P kg}^{-1}$  soil as rock phosphate into replicated 50mL leaching tubes ( $n = 3$ ). Soils were then treated with chelate, or chelate plus biochar (1 per cent w/w) in comparison to an unamended control, allowed to incubate for 16 hours moist and then leached with three successive rinsings of  $0.01\text{M CaCl}_2$ . Leachates were then analysed for orthophosphate on a segmented flow Auto Analyser III. Data were subject to ANOVA by using SPSS.

Source: DeLuca, unpublished data

tions of resin-sorbed  $\text{PO}_4^{3-}$  in a neutral (pH 6.8) forest soil when the soil was amended with a biochar generated by wildfire containing a high concentration of soluble salts (including  $\text{Ca}^{2+}$ ). However, these biochar amendments did not appear to inhibit the growth of grass seedlings (Gundale and DeLuca, 2007).

In addition to its effect on soil pH, biochar may also influence the bioavailability of P through several other mechanisms associated with P precipitation, such as biochar-induced surface sorption of chelating organic molecules. Biochar is an exceptionally good surface for sorbing polar or non-polar organic molecules across a wide range of molecular mass (Sudhakar and Dikshit, 1999; Schmidt and Noack, 2000; Preston and Schmidt, 2006; Bornemann et al, 2007). Organic molecules involved in chelation of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ca}^{2+}$  ions will potentially be sorbed to hydrophobic or charged biochar surfaces. Examples of such chelates include simple organic acids, pheno-

lic acids, amino acids, and complex proteins or carbohydrates (Stevenson and Cole, 1999).

The sorption of chelates may have a positive or negative influence on P solubility. A clear example of this type of interaction is provided in Figure 14.4. Here, two compounds that have been reported as possible allelopathic compounds released as root exudates (catechin and 8-hydroxy quinoline) (Vivanco et al, 2004; Callaway and Vivanco, 2007) have also been reported to function as potent metal chelates (Stevenson and Cole, 1999; Shen et al, 2001) that may indirectly increase P solubility. Catechin effectively increased P solubility in an alkaline (pH 8.0) calcareous soil and the 8-hydroxy quinoline increased P solubility when added to an acidic (pH 5.0) and Al-rich soil (see Figure 14.4). The addition of biochar to these soils eliminated the presence of soluble chelate in the soil system and, in turn, eliminated the effect of the chelate on P solubility (DeLuca, unpublished data). This interaction may

explain the observed reduction in P sorption by ionic resins with increasing biochar application rates in the presence of actively growing *Koeleria macrantha* (Gundale and DeLuca, 2007). Such indirect effects of biochar on P solubility would vary with soil type and vegetative cover and underscores the complexity of plant–soil interactions.

### Microorganisms

Biochar may have an indirect effect on P availability and uptake by providing a beneficial environment for microorganisms that, in turn:

- provide greater access to P from organic and insoluble inorganic pools;
- produce and recycle a highly labile pool of organic P; and
- improve plants' direct access to P through improved mycorrhizal activity.

Several studies have demonstrated shifts in microbial activity or community composition with biochar additions to soil (Wardle et al, 1998; Pietikäinen et al, 2000; DeLuca et al, 2006). The mechanisms for increased microbial activity remain unclear because very little research has focused on factors such as how the microbial community size, community structure or specific interactions within soil microbial communities and soil food web change in the presence of biochar (see Chapter 6).

Warnock et al (2007) reviewed several mechanisms through which biochar might affect soil microorganisms, including its effect on sorption of microbial signalling compounds (described above) and the physical structure of biochar, which provides a habitat for microbes within the porous structure of charred material. The physical structure of biochar is inherited from the plant tissue from which it is formed and, thus, can have an extremely high pore density, such as that found in woody xylem tissue. Substantial variability in pore density

and pore size can occur, and this can influence the size of organisms able to enter biochar (Pietikäinen et al, 2000) and the total surface area of biochar that could sorb compounds (Keech et al, 2005). The pore size of wood-derived biochar may range from approximately  $10\mu\text{m}^2$  to approximately  $3000\mu\text{m}^2$ , depending upon the species from which it is derived (Keech et al, 2005). Thus, some biochars may create pore spaces for bacteria and fungi that are safe from even the smallest soil grazers, such as protozoa, whereas, other biochars may only restrict very large soil grazers, such as mites and collembola. The ability of biochar to exclude soil grazers might allow soil microbes to mediate nutrient transformations more efficiently. However, it is possible that microbes primarily colonize the surface of biochar and not the internal pore surface (Yoshizawa et al, 2005).

Very little work has focused on the role of biochar pore spaces within the context of soil food webs. Warnock et al (2007) speculated that the safe pore environment of biochars might enhance activity of mycorrhizal fungi or stimulate mycorrhization helper bacteria. These potential mechanisms may help to explain several studies that have demonstrated higher mycorrhizal colonization in the presence of biochar (Saito, 1990; Ishii and Kadoya, 1994; Ezawa et al, 2002; Matsubara et al, 2002; Yamato et al, 2006).

### Sulphur

Given the similarities between the S and N cycles (Stevenson and Cole, 1999), there is a significant potential for biochar to influence S mineralization and oxidation activity in the soil. Although the majority of soil S originates from the geologic parent material, most soil S exists in an organic state and must be mineralized prior to plant uptake (Stevenson and Cole, 1999). Organic S exists as either ester sulphate or as C-bonded S, the latter having to be oxidized to  $\text{SO}_4^{2-}$  prior to plant uptake.

To date, no studies have directly assessed the influence of biochar on S transformations or S availability in agricultural or forest soils. However, numerous studies involving biochar or biochar additions to soils have recorded changes in the soil environment that suggest that biochar additions could increase soil S bioavailability. Biochar additions to acid agricultural soils have been observed to yield a net increase in soil pH (see Chapter 5), potentially as a function of the alkaline oxides applied along with the biochar or potentially as a result of the influence on free Al/Ca ratios in soils amended with biochar (Glaser et al, 2002; Topoliantz et al, 2005). Sulphur mineralization is favoured at slightly acid to neutral pH. Sulphur mineralization rates have been found to increase following fire in pine forest ecosystems (Binkley et al, 1992), much the same as that observed for N (Smithwick et al, 2005). Separating the effect of fire from the effect of the natural addition of biochar is difficult; but this effect is most likely due to the release of soluble S from litter following partial combustion during fire or heating events at temperatures in excess of 200°C (Gray and Dighton, 2006).

Sulphur oxidation is carried out by both autotrophic (e.g. *Thiobacillus* spp) and heterotrophic organisms. Sulphur oxidation by acidophilic *Thiobacillus* spp would not be favoured by pH increases induced by the

presence of biochar. However, these autotrophic organisms have uniquely high requirements for certain trace elements that are in relatively high concentrations in biochar (see Chapter 5) and are increased in soil when biochar is added (Rondon et al, 2007). Biochar additions to soil that ultimately reduce the surface albedo of mineral soils and result in faster warming of soils in springtime may, in turn, increase S oxidation or mineralization rates (Stevenson and Cole, 1999).

Biochar additions to mineral soils may also directly or indirectly affect S sorption reactions and S reduction. As noted in Chapters 2 and 15, biochar improves soil physical properties through increased specific surface area, increased water-holding capacity and improved surface drainage. Improved soil aeration through these improvements in soil physical condition would, in turn, reduce the potential for dissimilatory S reduction (Stevenson and Cole, 1999). Sulphur is readily adsorbed to mineral surfaces in the soil environment and particularly to exposed Fe and Al oxides. Organic matter additions to soil are known to reduce the extent of  $\text{SO}_4^{2-}$  sorption in acid forest soils (Johnson, 1984); therefore, biochar amendments may act to increase solution concentrations of S in acid iron-rich soils.

## Conclusions

The application of biochar to agricultural soils has the potential to greatly improve soil physical, chemical and biological conditions. In this chapter we reviewed biochar as a modifier of soil nutrient transformations and discussed the known and potential mechanisms that drive these modifications. Biochar clearly has the potential to increase net nitrification in acid forest soils that otherwise demonstrate little or no nitrification. The

mechanisms behind this stimulation of nitrification remains the subject of ongoing debate; however, it is probably due to the sorption of compounds that otherwise lead to the inhibition of nitrification or immobilization of inorganic N. In contrast, biochar has not been found to increase ammonification, and although biochar applications have been found to increase plant uptake of N, there is no evidence for an increase in N availability

following harvest of the crop. This may be a result of the capacity of biochar to adsorb  $\text{NH}_4^+$  once it is formed, thereby leading to no measurable increases in net ammonification.

There is a distinct need for studies directed at explaining mechanisms for increased P uptake with biochar additions to agricultural soils. Although plant P uptake has been found to increase with increasing biochar added in some agro-ecosystems, this has not been directly observed in natural forest soils amended with biochar. It is possible that biochar additions to soils stimulate mycorrhizal colonization, which may increase P uptake; but when applied with P-rich materials, this effect may be lost.

The effect of biochar on soil nutrient transformations has not been adequately studied. Some key areas that require attention include:

- By what mechanisms does biochar affect N mineralization and immobilization in different ecosystems?
- Does  $\text{NH}_4^+$  adsorption by biochar greatly reduce N availability or does it concentrate N for plant and microbial use?
- By what mechanism do biochar additions to mineral soils stimulate P availability?
- How do different plant materials and different temperatures affect the physical character and biochemical potential of biochar?
- How do biochar additions affect S availability and by what mechanism(s)?

The answers to these questions can only be obtained through rigorous investigation of biochar as a natural component of grassland and forest soils, and as a soil conditioner and amendment added to agricultural soils.

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