

# Biochar: Nutrient Properties and Their Enhancement

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## Introduction

Despite the recent interest in the use of biochar in agriculture, its current use is still limited. In terms of market development, if biochar can be used as a soil amendment to improve soil quality and to increase crop production, this will increase its appeal (Day et al, 2004). In this regard, an obvious positive attribute of biochar is its nutrient value, supplied either directly by providing nutrients to plants or indirectly by improving soil quality, with consequent improvement in the efficiency of fertilizer use. As a measure of the direct nutrient value of biochars, it is not the total content but, rather, the availability of the nutrient that is an important consideration. The total content of nutrients is not an appropriate indicator of the availability of nutrients as only a fraction of the total content is immediately available or is readily converted to available forms for uptake by plants (Keeney, 1982).

An example of the indirect nutrient value of biochar is its ability to retain nutrients in the soil and, therefore, to reduce leaching losses, resulting in increased nutrient uptake

by plants and higher production. According to Glaser et al (2001), one reason for the ability of Amazonian Terra Preta soils, which are characterized by their high content of biochar-like pyrogenic carbon (C), to maintain high fertility (compared to adjacent infertile soils) is their ability to retain nutrients. Another example of the indirect nutrient value of biochars is the removal of soil constraints limiting plant growth and production (e.g. the use of lime to overcome soil acidity, with resulting improvement in fertilizer-use efficiency and increases in plant production).

In this chapter, we review the existing information on the direct, as well as indirect, nutrient properties of biochars and their effect on crop yield and production. Factors controlling nutrient properties, both composition and the availability of nutrients during pyrolysis, are examined, and in the light of existing knowledge and information, research opportunities to improve the nutrient properties of biochars are identified.

## Nutrient properties of biochars and crop production responses

### Nutrient contents of biochars

Since biochars are manufactured from biomass, it is expected that they are high in C and contain a range of plant macro- and micro-nutrients. The composition of biochars depends upon the nature of the feedstocks and the operating conditions of pyrolysis. A review of the literature has revealed that only scant information is available on the nutrient properties of biochars. Most of the research on pyrolysis of biomass has focused on energy and fuel quality (Horne and Williams, 1996; Tsai et al, 2006) rather than on biochar as a soil amendment. Often, biochar is looked upon as a fuel for further energy production or as a by-product to be upgraded to activated carbon and used in purification processes (Horne and Williams, 1996). Furthermore, information on the nutrient content and properties of biochars used in agronomic studies has not always been included in the reporting of experimental results, making it difficult to assess the agronomic values of biochars used in previous research. Table 5.1 summarizes total elemental composition – C, nitrogen (N), phosphorus (P) and potassium (K), available P and mineral N – as well as the pH of biochars as recorded in the literature by various studies.

From this limited and, unfortunately, incomplete data set, the most striking feature is the high variability of all parameters, with the exception of pH. In the case of pH, the data show that biochars used as a soil amendment in prior research are usually alkaline in nature (pH > 7.0). However, biochars can be produced at almost any pH between 4 and 12 (Lehmann, 2007) and can decrease to a pH value of 2.5 after short-term incubation of four months at 70°C (Cheng et al, 2006). Carbon contents range between 172g kg<sup>-1</sup> and 905g kg<sup>-1</sup> (coefficient of variation, CV =

106.5 per cent). The ranges are even larger in the case of total N (1.8g kg<sup>-1</sup> to 56.4g kg<sup>-1</sup>), total P (2.7g kg<sup>-1</sup> to 480g kg<sup>-1</sup>) and total K (1.0g kg<sup>-1</sup> to 58g kg<sup>-1</sup>), all with CV ≥ 100 per cent (see Table 5.1). The variability can be attributed to different feedstocks and different conditions under which the various biochars were manufactured. The influence of feedstocks is particularly evident in the case of total P where higher contents were found in biochars produced from feedstocks of animal origin – namely, sewage sludge and broiler litter – than those from plants (e.g. wood). Similarly, total N contents of biochars from sewage sludge (64g kg<sup>-1</sup>; Bridle and Pritchard, 2004) and soybean cake (78.2g kg<sup>-1</sup>; Uzun et al, 2006) were much higher than those from pure plant origins (e.g. green wastes) (1.7g kg<sup>-1</sup>; Chan et al, 2007b). Compared to other forms of organic amendments commonly used in agriculture (see Table 5.2), both total N and P contents of biochars cover ranges that are wider than those reported for the whole spectrum of typical organic fertilizers. It is important to note that the same type of feedstock can produce very different biochars. For example, Chan et al (2007b) reported total N contents of 20g kg<sup>-1</sup> for biochar produced from poultry litter compared to 7.5g kg<sup>-1</sup> and 6.0g kg<sup>-1</sup> for two biochars made from different poultry litter reported by Lima and Marshall (2005). Such large differences in total N are a result of either different poultry litter qualities or different pyrolysis conditions. This cannot be ascertained as information is typically not given to the extent that allows such conclusions to be drawn. A much higher temperature (700°C) was used by Lima and Marshall (2005) compared to the 450°C reported by Chan et al (2007b). This information may suggest that operating conditions during pyrolysis



**Table 5.1** Nutrient contents, pH and carbonate contents of biochars

Biochar feedstocks	pH	C (g kg <sup>-1</sup> )	N (g kg <sup>-1</sup> )	C/N	P (g kg <sup>-1</sup> )	K (g kg <sup>-1</sup> )	P <sup>a</sup> (mg kg <sup>-1</sup> )	Nmin <sup>b</sup> (mg kg <sup>-1</sup> )	CO <sub>3</sub> <sup>c</sup> (%)	Production conditions	References
Wood	– <sup>d</sup>	708	10.9	65	6.8	0.9	–	–	–	By local farmers	Lehmann et al (2003b)
Green wastes	6.2 <sup>e</sup>	680	1.7	400	0.2	1.0	15	<2	<0.5	450°C	Chan et al (2007b)
Poultry litter	9.9 <sup>e</sup>	380	20	19	25.2	22.1	11,600	2	15	450°C	Chan et al (2007b)
Sewage sludge	–	470	64	7	56	–	–	–	–	450°C	Bridle and Pritchard (2004)
Unknown	9.6 <sup>f</sup>	905	56.4	16	2.7	51	–	–	–	Unknown	Topoliantz et al (2005)
Broiler litter	–	258	7.5	34	48	30	–	–	–	700°C and steam activated	Lima and Marshall (2005)
Broiler cake	–	172	6.0	29	73	58	–	–	–	700°C and steam activated	Lima and Marshall (2005)
Bark of <i>Acacia mangium</i>	7.4 <sup>f</sup>	398	10.4	38	–	–	31	–	–	260°C–360°C	Yamato et al (2006)
Rice straw	–	490	13.2	37	–	–	–	–	–	500°C	Tsai et al (2006)
Sugar cane bagasse	–	710	17.7	40	–	–	–	–	–	500°C	Tsai et al (2006)
Coconut shell	–	690	9.4	73	–	–	–	–	–	500°C	Tsai et al (2006)
Oil mallee tree after oil extraction	8.4	340	12	28	1.2	7.0	–	–	–	'Moki' method	Blackwell et al (2007)
Soybean cake	–	590	78.2	7.5	–	–	–	–	–	550°C	Uzun et al (2006)
<i>Eucalyptus deglupta</i>	7.0 <sup>g</sup>	824	5.73	144	0.6	–	49.5	–	–	350°C	Rondon et al (2007)
Range from	6.2	172	1.7	7	0.2	1.0	15	0	<0.5		
to	9.6	905	78.2	400	73	58	11,600	2	15		
Mean	8.1	543	22.3	67	23.7	24.3	–	–	–		
Percentage CV <sup>h</sup>	18	40	110	152	118	96	–	–	–		

Notes: a Plant available P.

b Mineral N (extractable nitrate plus ammonium).

c Carbonate content as a percentage of oven dry weight of biochar.

d Data not available.

 e pH measured in 0.01 M CaCl<sub>2</sub>.

f pH measured in 1 M KCl.

g pH measured in de-ionized water.

h CV = coefficient of variation

**Table 5.2** Typical N, P and K contents of common organic fertilizers

Organic fertilizer/compost	N (%)	P (%)	K (%)	N <sub>min</sub> <sup>1</sup> (mg kg <sup>-1</sup> )	References
Poultry manure	3.1	2.5	1.6	– <sup>2</sup>	Burgess (1993)
Cow manure	1.5	0.5	1.2	–	Burgess (1993)
Blood and bone	5.3	5.2	1.6	–	Burgess (1993)
Green waste compost – unblended	1.0	0.16	–	16	Chan et al (2007a)
Green waste compost – blended	1.2	0.38	–	202	Chan et al (2007a)
Biosolids	2–8	1.5–3.0	0.1–0.6	–	Cogger et al (2006)

Notes: 1 Mineral N (extractable nitrate plus ammonium).

2 Data not available.

determine to a significant extent the N contents through greater N loss at higher pyrolysis temperatures, as will be discussed later in this chapter.

It is important to point out that the total elemental contents of many nutrients, especially organically bound nutrients such as N and sulphur (S), do not necessarily reflect the actual availability of these nutrients to plants. Very few data on the available nutrient contents of biochar are found in the literature. From the limited data available, mineral N is very low and available P is highly variable (see Table 5.1). Despite a high total N content of 6.4 per cent, biochar produced from sewage sludge was found to have negligible mineral N (ammonium-N + nitrate-N) even after 56 days of incubation (Bridle and Pritchard, 2004). Similarly, mineral N was found to be <2mg kg<sup>-1</sup> for a green waste and poultry manure char with total N of 1.7g kg<sup>-1</sup> and 20g kg<sup>-1</sup>, respectively (see Table 5.1; Chan et al, 2007b). In contrast, available K in biochars are typically high and increased K uptake as a result of biochar application has been frequently reported (Lehmann et al, 2003b; Chan et al, 2007c).

The C/N ratios of biochars vary widely between 7 to 400, with a mean of 67 (see Table 5.1). This ratio is often used as an indicator of the ability of organic substrates to mineralize and release inorganic N when applied to soils. Generally, a C/N ratio of 20

of organic substrates is used as a critical limit above which immobilization of N by microorganisms occurs; therefore, the N applied with the substrate is not available to plants (Leeper and Uren, 1993). Sullivan and Miller (2001) suggested that composts with C/N ratios above 25 to 30 immobilize inorganic N. Based on these values, given their very high C/N ratios, most of the biochars are expected to cause N immobilization and possibly induce N deficiency of plants when applied to soils alone. However, there is a degree of uncertainty if the same criterion is directly applicable to biochars. C/N ratios of Terra Preta soils are usually higher than the adjacent Ferralsol; but they tend to have higher available N (Lehmann et al, 2003a). As the bulk of biochars is made up of biologically very recalcitrant organic C, which is not easily mineralized, it is expected that N immobilization is negligible or transient despite the high C/N ratios. Application of biochar may, indeed, lead to lower N uptake, as shown in several studies (e.g. Lehmann et al, 2003b; Rondon et al, 2007). It is likely that this is due to the presence of only a small portion of the freshly produced biochar that is relatively easily mineralizable, but may cause N immobilization because of its high C/N ratio. However, the bulk of the remaining organic C (with even higher C/N) does not cause mineralization-immobilization reactions because of its high degree of biological recalcitrance.



For 16 biochars made from different plant biomass as well as poultry litter, bicarbonate extractable available P (Colwell, 1963) was found to range between  $15\text{mg kg}^{-1}$  and  $11,600\text{mg kg}^{-1}$  (Chan et al, 2007b). Significantly higher levels of available P were found in biochars produced from poultry litter than those from plant biomass.

Few data are available on the content of trace elements in biochars. However, high contents of heavy metals have been reported in biochars produced from a range of feedstocks (e.g. sewage sludge and tannery wastes) (Muralidhara, 1982; Bridle and Pritchard, 2004). Bridle and Pritchard (2004) reported high concentrations of copper (Cu), zinc (Zn), chromium (Cr) and nickel (Ni) in a biochar produced from sewage sludge. Biochar produced from tannery wastes can be very high in Cr (Muralidhara, 1982) as this metal can make up 2 per cent of total dry weight of the wastes. The Cr was found to bind to the organic material in biochar in a trivalent complex form and can be recovered by leaching with dilute sulphuric acid (Muralidhar, 1982). Little is known about the availability of these potentially toxic metals.

Some of the biochars have fairly high concentrations of carbonates (see Table 5.1), which can be valuable as a liming material for overcoming soil acidity (Van Zwiiten et al, 2007). Chan et al (2007b) reported carbonate contents of less than 0.5 to 33 per cent for a range of biochars produced from different feedstocks and conditions. There was no direct relationship between liming value and the pH of the biochars.

Biochars are therefore variable materials in terms of total nutrient content and availability, and given the very large variability in contents of different nutrients, we would expect varying plant and soil responses from direct nutrient additions of biochars. From the available data, no optimum rate of application for biochars can be obtained because of the stated large variability in biochar prop-

erties. In fact, both Glaser et al (2002) and FFTC (2007) concluded that the optimal application rate of biochars may have to be determined for each soil type and plant species.

## **Crop responses due to nutrient properties of biochars**

### *Direct nutrient value of biochars*

Positive and, to a lesser extent, negative yield responses as a result of biochar application to soils have been reported for a wide range of crops and plants in different parts of the world (see Table 5.3). Attempts to relate the crop responses to the nutrient contents of the biochar used in the experiments have been limited by the fact that in many of the studies, nutrient contents of the biochar or rate of application were often not provided. Amongst the studies in Table 5.3, only one attributed some of the positive crop response to nutrients supplied directly by the biochar (Lehmann et al, 2003b). The latter reported that using wood biochar at rates of  $68\text{t C ha}^{-1}$  to  $135\text{t C ha}^{-1}$  increased rice biomass by 17 per cent and cowpea by 43 per cent in a pot experiment (in the absence of leaching). The authors attributed the positive growth responses to improved P and K and, possibly, Cu nutrition provided by the biochar applied.

### *Indirect nutrient properties*

A few studies attributed the positive plant responses to other effects of biochar on nutrient availability rather than simply as a direct supplier of nutrients (Iswaran et al, 1980; Wardle et al, 1998; Hoshi, 2001; Lehmann et al, 2003b; Chan et al, 2007c; Van Zwiiten et al, 2007). The positive responses due to biochar application were attributed to either nutrient savings (in term of fertilizers) or improved fertilizer-use efficiency (higher yield per unit of fertilizer applied) and can therefore be regarded as an indirect nutrient value of biochars. Hoshi (2001), Yamato et al

**Table 5.3** Crop yield responses as related to relevant biochar properties

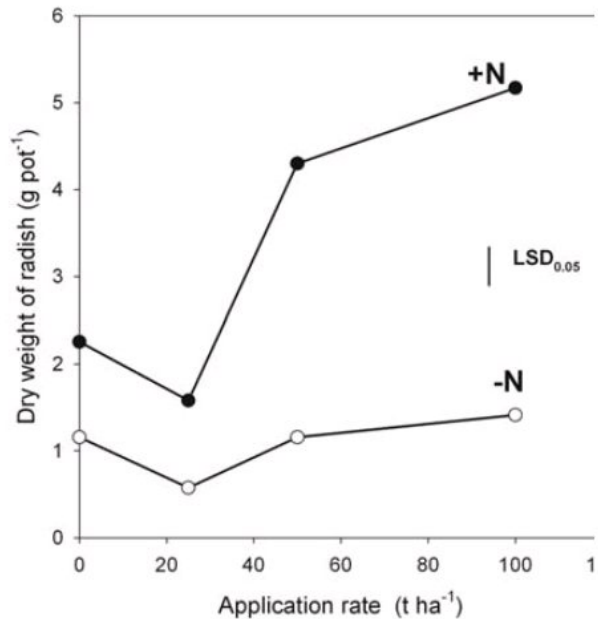
Feedstock for biochar and rate of application	Crops/plants	Responses	Reasons for responses given by authors	References
Unknown wood (0.5t ha <sup>-1</sup> )	Soybean	Biomass increased by 51%	Water-holding capacity and black colour on temperature	Iswaran et al (1980)
Unknown wood (5t ha <sup>-1</sup> and 15t ha <sup>-1</sup> )	Soybean	Yield reduced by 37 and 71%	pH-induced micro-nutrient deficiency	Kishimoto and Sugiura (1985)
Wood for charcoal production, unknown rates	Vegetation in charcoal hearth and non-hearth areas compared after 110 years	Tree density and basal area were reduced by 40%	Negative responses due to changes in soil properties	Mikan and Abrams (1995)
Wood for charcoal production (2t ha <sup>-1</sup> )	Trees ( <i>Betula pendula</i> and <i>Pinus Sylvestris</i> )	Affected only <i>B. pendula</i> and only in substrates high in phenolics	Increased N uptake by countering the effect of phenolics	Wardle et al (1998)
Bamboo, unknown rate	Tea tree	Height and volume increased by 20 and 40%	Retained fertilizer and maintained pH	Hoshi (2001)
Secondary forest wood (68t C ha <sup>-1</sup> –135t C ha <sup>-1</sup> )	Rice, cowpea and oats	Biomass of rice increased by 17%, cowpea by 43%	Improved P, K and possibly Cu nutrition	Lehmann et al (2003b), Glaser et al (2002)
Bark of <i>Acacia mangium</i> (37t ha <sup>-1</sup> )	Maize, cowpea and peanut at two sites	Response only at one site (less fertile) with 200% increase (fertilized)	Increase in P and N availability and reduction of exchangeable Al <sup>3+</sup> ; arbuscular mycorrhizal (AM) fungal colonization	Yamato et al (2006)
Secondary forest wood (11t ha <sup>-1</sup> )	Rice and sorghum	Little response with biochar alone, but with a combination of biochar and fertilizer yielded as much as 880% more than plots with fertilizer alone	Not stated	Steiner et al (2007)
Rice husk (10t ha <sup>-1</sup> )	Maize, soybean	10–40% yield increases	Not clearly understood, dependent upon soil, crop and other nutrients	FFTC (2007)
Green waste (0–100t ha <sup>-1</sup> )		No positive effect with biochar up to 100t ha <sup>-1</sup> , but with added N fertilizer, 266% increase in dry matter	Indirect effect of improving physical properties of hard-setting soil	Chan et al (2007c)
Paper mill sludge (10t ha <sup>-1</sup> )	Wheat	Increase in wheat height by 30–40% in acid soil but not in alkaline soil	Mainly liming value	Van Zwieten et al (2007)



(2006), Rondon et al (2007), and Van Zwieten et al (2007) attributed the plant responses to the ability of the biochars applied in increasing or maintaining the pH of the soils. Hoshi (2001) suggested that the 20 per cent increase in height and 40 per cent increase in volume of tea trees were partly due to the ability of the biochar to maintain the pH of the soil. Such ability is related to the liming value of the biochar. In a pot experiment, Van Zwieten et al (2007) reported a nearly 30 to 40 per cent increase in wheat height when biochar produced from paper mill sludge was applied at a rate of 10t ha<sup>-1</sup> to an acidic soil but not to a neutral soil. The lime (as carbonates) in the biochar promoted wheat growth by overcoming toxic effects of exchangeable aluminium (Al) of the acidic soils.

Other reasons offered for the observed positive responses due to biochar application that are not related to plant nutrition included toxin neutralization (Wardle et al, 1998); improved soil physical properties (e.g. increase in water-holding capacity) (Iswaran et al, 1980); or reduced soil strength (Chan et al, 2007c). The latter authors found no positive dry matter response of radish in a pot experiment when green waste biochar was applied alone at rates of up to 100t ha<sup>-1</sup>. However, dry matter increased by up to 266 per cent when N fertilizer was also applied at 100kg N ha<sup>-1</sup> compared to a control that received the same amount of N but no biochar (see Figure 5.1).

As a result, biochar application increased N fertilizer-use efficiency of radish and the authors attributed this to improved soil physical conditions – namely, reduced soil strength and higher field capacity – of the hard-setting soils. In addition, Lehmann et al (2003b) demonstrated the ability of biochar to retain applied fertilizer against leaching with resulting increase in fertilizer-use efficiency. This ability is related to the charge (see Chapter 10) and surface area properties of biochars (see Chapter 2). The above litera-



**Figure 5.1** Dry matter production of radish as a function of biochar application rate, either with (100kg ha<sup>-1</sup>; solid symbol) or without (open symbol) N fertilizer application

Note: LSD = least significant difference.

Source: Chan et al (2007c)

ture review highlights the potential benefits of the indirect nutrient value of biochars when compared to the limited direct nutrient value. In addition to the significant responses in plant productivity that have been reported, soil quality improvements and environmental benefits (e.g. reduced pollution due to reduced fertilizer losses via leaching) are likely to result (Lehmann, 2007).

### Negative yield responses to biochar applications

Kishimoto and Sugiura (1985) reported yield reductions of soybean by 37 and 71 per cent when biochar was applied at 5t ha<sup>-1</sup> and 15t ha<sup>-1</sup>, respectively, and they attributed this to micronutrient deficiency induced by the resulting pH increases. Such pH-induced adverse effect was also reported by Mikan and Abrams (1995), who observed significant retardation of calcifuge plant species in

charcoal hearth areas even after 110 years and attributed this to the elevated pH and calcium (Ca) levels remaining from past charcoal production activities. Therefore, while the alkaline nature and liming value of the biochar might be beneficial for the amelioration of acid soils, with resulting increases in crop production, the same prop-

erties might be deleterious to certain plant species. These observations highlight the specific nature of some of the soil amendment values of biochars, the limitation of the value of some biochars under certain soil conditions, and the importance of a better understanding of the properties of different biochars.

## Factors controlling nutrient properties of biochar

Nutrient composition and availability of biochars depend upon both the nature of the feedstocks and the pyrolysis conditions under which they are produced.

### Nature of feedstock

In addition to plant biomass, an entire range of organic materials, including waste materials such as poultry litter and sewage sludge, can be converted to biochars using pyrolysis. Recently, conversion of these other materials to biochars has been promoted as an alternative way of managing a range of organic wastes (e.g. Bridle and Pritchard, 2004; Shinogi, 2004; Hospido et al, 2005; Lima and Marshall, 2005). Given the vast differences in the properties of the potential feedstocks, biochars can have very different nutrient contents and availability, as discussed earlier.

### Biochar manufacturing process conditions: Temperature, heating rate and heating time

For the same feedstock, biochar yield is highly dependent upon the conditions under which pyrolysis is carried out – namely, temperature, heating rate, heating time and particle size (Shafizadeh, 1982; Williams and Besler, 1996; Demirbas and Arin, 2002; Uzun et al, 2006; Tsai et al, 2007). While it is well documented that biochar yield decreases with increasing temperature and that the

yield–temperature relationships are different with different feedstocks (Guha et al, 1986; Horne and Williams, 1996; Williams and Besler, 1996; Tsai et al, 2006), much less attention has been paid to the associated changes in biochar properties, particularly total nutrient contents as well as their availability.

Pyrolysis is the degradation of biomass by heat in the absence of oxygen (O), which results in the production of solid (biochar), liquid and gaseous products (Demirbas and Arin, 2002). According to Shafizadeh (1982), pyrolysis of cellulose at <300°C involves reduction in molecular weight (decarboxylation and decarbonylation), evolution of water, carbon dioxide (CO<sub>2</sub>) and carbon monoxide (CO), as well as formation of biochar. On heating to higher temperature (300°C to 500°C), molecules are rapidly depolymerized to anhydroglucose units that further react to provide a tarry pyrolysate. At even higher temperatures (>500°C), the anhydrosugar compounds undergo fission, dehydration, disproportionation and decarboxylation reactions to provide a mixture of low molecular weight gaseous and volatile products, as well as the residual biochar (see Chapter 8).

Depending upon the operating conditions, the complex and varying changes of biomass during pyrolysis affect both the composition and chemical structure of the resulting biochar, with significant implica-



tions for nutrient contents and, especially, nutrient availability to plants. Changes in the composition of biochars during pyrolysis of organic matter using molecular techniques indicate a gradual decrease in the amounts of OH and CH<sub>3</sub> and an increase in C=C with increasing temperature (150°C to 550°C), suggesting a change from aliphatic to aromatic C structure of the biochar (see Chapter 4). By 550°C, most infrared (IR) bands, except those due to the aromatic CH and OH stretches, disappeared, resulting in mainly aromatic biochar. This transformation is confirmed by analyses which indicated that both H/C and O/C ratios of biochars decrease with increasing temperature (see Chapter 4). Furthermore, biochars prepared at higher temperature (500°C to 700°C) are well carbonized, as indicated by low H/C ratios and low O content (<10 per cent) (see Chapter 10), and also have a high surface area (see Chapter 2). In contrast, biochars formed at lower temperatures (300°C to 400°C) are only partially carbonized, with high H/C ratios and O contents, and have a lower surface area. As a consequence, low-temperature biochars are found to have higher amounts of acid–basic surface functional groups. Therefore, increasing temperature during pyrolysis results in changes in the molecular composition, as well as changes in biochar charge properties. Biochars containing large proportions of mineral matter (ash) produced at low temperatures also have a much greater concentration of sub-grain boundaries and defects on the surface than the same biochars produced at high temperatures. Mineral matter in low-temperature biochar is more likely to dissolve since these defects are centres for reactions with liquids and gases (see Chapter 3). These changes should have effects on the total nutrient content as well as their availability. The conversion of aliphatic C to aromatic C during pyrolysis is accompanied by a reduction in C mineralization rates (see Chapter 11). This reduction in mineral-

ization of organic C also suggests a reduction in the availability of nutrients in biochar that are bound in the organic structure, such as N, P and S.

Porosity of biochar significantly increases between 400°C and 600°C (see Chapter 2), and may be attributed to increases in water molecules released by dehydroxylation acting as pore-former and activation agent, thus creating very small (nanometre-size) pores in biochar (Bagreev et al, 2001). These increases in porosity result in significant increases in surface area by orders of magnitudes (see Chapter 2). Therefore, the differences in structural changes as a function of temperature have important consequences in terms of surface area and charge characteristics of the biochar produced under different conditions. These changes, in turn, should have important effects on the indirect nutrient value of biochars – for example, the nutrient retention ability of cations and anions of biochars are dependent upon their cation exchange capacity (CEC) and anion exchange capacity (AEC).

Indeed, CEC proved to be very low at low pyrolysis temperatures and to increase significantly at higher temperature (Lehmann, 2007), which would need to be tested more widely. So far, however, freshly produced biochars have proven minimal CEC compared to soil organic matter (Cheng et al, 2006, 2008; Lehmann, 2007). On the other hand, the AEC of freshly produced biochar is significant at low pH and biochars have a high point of zero net charge (Cheng et al, 2008). Biochars only possess variable charge. Strategies to enhance CEC by manufacturing processes are being explored. Once biochar is exposed to O<sub>2</sub> and water, spontaneous oxidation reactions occur that are most likely enhanced by microbial activity and result in very high CEC (Cheng et al, 2006, 2008; Liang et al, 2006). The changes in charge properties of biochar, once added to soil, are discussed in Chapter 10.

**Table 5.4** Effect of temperature and holding time on C and N composition and pH (measured in aqueous slurries) of sewage sludge biochar

Temperature (°C)	Holding time (minutes)	C (mg g <sup>-1</sup> )	H (mg g <sup>-1</sup> )	N (mg g <sup>-1</sup> )	pH
400	30	282	20.4	38.3	7.7
600	60	271	11.4	31.9	11.5
800	60	264	4.2	16.1	11.3
950	60	249	3.5	9.4	11.0

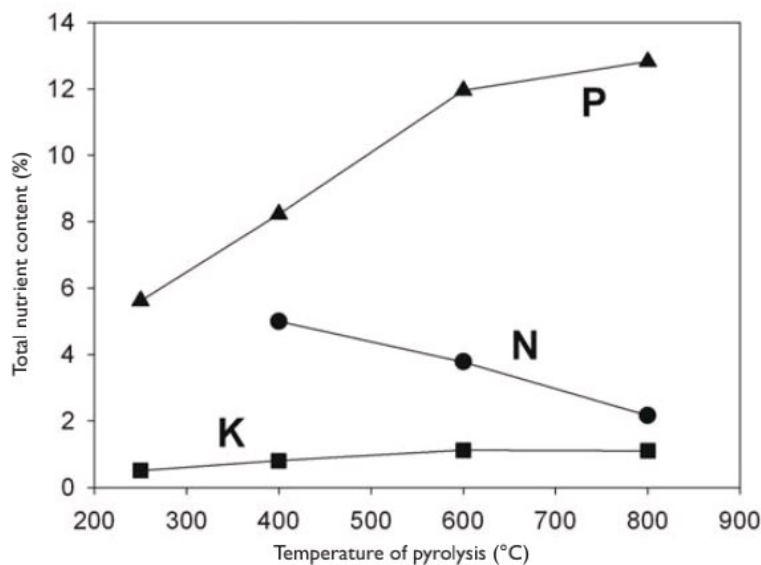
Source: adapted from Bagreev et al (2001)

### Nitrogen

Lang et al (2005) monitored the changes in content of C, H, O, S and N of a range of organic materials – namely, four woody biomass, four herbaceous biomass and two coals under pyrolysis at 275°C to 1100°C. All of the biomass types lost at least half of their N as volatiles by 400°C. During pyrolysis of sewage sludge, total N contents decreased from 3.8 per cent at 400°C to 0.94 per cent at 950°C (see Table 5.4) because of loss of volatile organic matter (Bagreev et al, 2001). Similarly, Shinogi (2004) reported a reduction of total N in biochar from sewage sludge from 5.0 per cent at 400°C to 2.3 per cent at 800°C (see Figure 5.2).

The loss of total N at higher temperatures was also accompanied by a change in

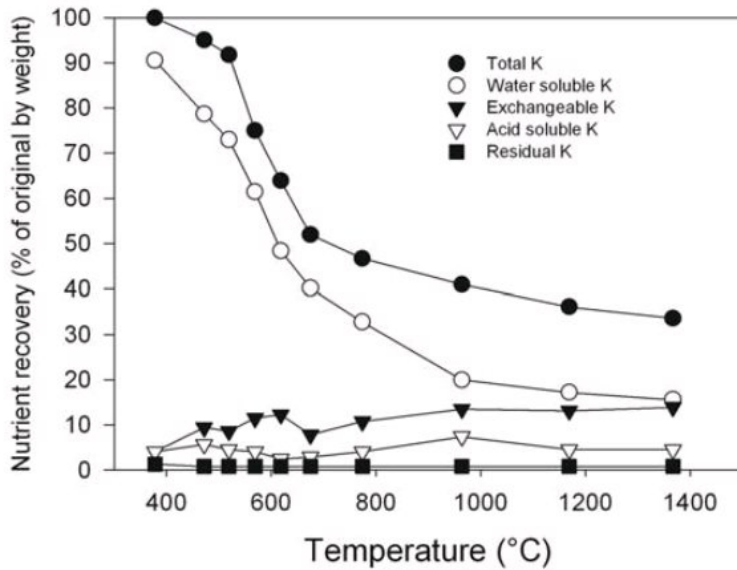
the chemical structure of the remaining N in the biochar. According to Bagreev et al (2001), organic N, probably present as amine functionalities in the material at low temperature, was gradually transformed into pyridine-like compounds with increased basicity of the surface at higher temperatures (>600°C). The change results in reduced availability of N present in the biochar. Significantly, this conversion occurred between 400°C and 600°C, which corresponded to a large increase in pH by 3.8 units as a result of dehydroxylation reactions (see Table 5.4). From the limited data available, N present in biochar products has very low availability. For biochar produced from sewage sludge, despite its relatively high total N content of 6.4 per cent, a laboratory incu-



**Figure 5.2** Changes in total N, P and K concentrations in biochars produced from sewage sludge at different temperatures

Source: adapted from Shinogi (2004)





**Figure 5.3** Changes in K contents of rice straw biochar as a function of temperature during pyrolysis

Source: Yu et al (2005)

bation study with soil at 25°C and field capacity indicated that negligible amounts of mineral N were detectable even after 56 days (Pritchard, 2003). This indicated that N in sewage sludge biochar was in forms that are very resistant to decomposition and mineralization.

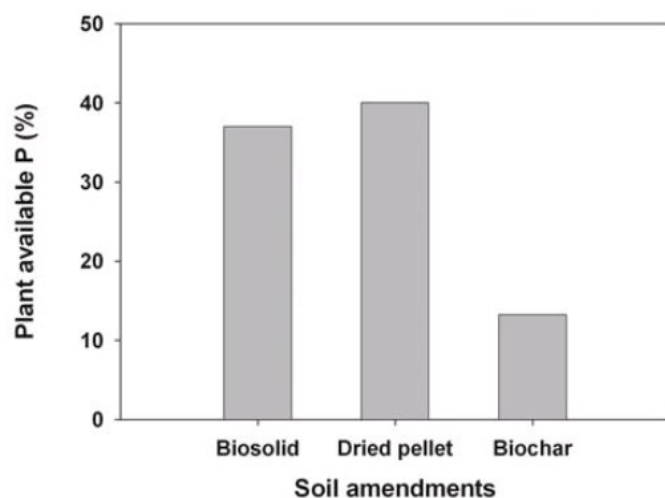
### Base cations

Yu et al (2005) studied the chemical forms and the release of K and Na during pyrolysis of rice straw between 400°C and 1373°C. Between 473°C and 673°C, about half of the total metal content (48 and 55 per cent, respectively, for K and Na) was lost by vaporization, and on further heating to 1373°C, loss was slower and totalled to ~70 per cent. About 90 per cent of total K in rice straw was in water-soluble form and was therefore plant available before pyrolysis: it was this form of K that was lost when heating up to 673°C (see Figure 5.3). With increasing temperature (>600°C), a greater proportion of the remaining K was found in exchangeable and acid extractable form. Wornat et al (1995) found that biochars from pine and switch-grass produced at 625°C contained 15 to 20 per cent O, and using energy dispersive X-ray spectroscopy (EDS), they concluded that

both K and Ca are well dispersed in the biochar matrices and may be bound to the O in biochars as ionic phenoxides (i.e. K phenoxides or as intercalated K). However, further heating to higher temperatures led to further losses by vaporization, as well as incorporation of K into the silicate structure, which is expected to be much less bioavailable. These results were supported by findings by Shinogi (2004), who reported a reduction of available K from 14 to <1 per cent during pyrolysis of sewage sludge, while total K concentrations doubled (0.51 per cent at 250°C to 1.12 per cent at 600°C) (see Figure 5.2).

### Sulphur

Up to 50 per cent of total S from eight biomass types was lost during pyrolysis at 500°C (Lang et al, 2005). Knudsen et al (2004) studied S transformation during pyrolysis of typical Danish wheat straw. Before pyrolysis, S was found to be associated partly as inorganic sulphate (40 to 50 per cent of total S) and partly as proteins (50 to 60 per cent). Results indicated that 35 to 50 per cent of the total S was released to the gas phase during pyrolysis at 400°C as a result of thermal decomposition of organic S.



**Figure 5.4** Available P (bicarbonate extractable) as a percentage of total P of biochar as compared to biosolid and dried biosolid pellet

Source: adapted from Pritchard (2003)

The latter commenced at 178°C to 283°C. At higher temperatures (500°C to 700°C), the residual S contents of biochar did not change significantly. However, the forms of S changed under the highly reducing conditions prevailing during pyrolysis, with a disappearance of inorganic sulphate (to 21.1 per cent at 500°C and to 3.1 per cent at 800°C) due to the conversion to insoluble sulphide (e.g. CaS, K<sub>2</sub>S) in the biochar matrix, or from fixed to reactive biochar surfaces by either addition of S to unsaturated sites or by substitution of O in surface oxides (Knudsen et al, 2004). These forms of S are expected to be water insoluble and biological less available.

### Phosphorus

Less information is available about the transformation of P during pyrolysis. For sewage sludge biochars, total P concentration increased with increasing temperature from 5.6 per cent at 250°C to 12.8 per cent at

800°C (see Figure 5.2). According to Bridle and Pritchard (2004), 100 per cent recovery of P was obtained in a biochar produced from sewage sludge at 450°C, in comparison to 45 per cent of N, which was lost during the same procedure. However, laboratory incubation studies indicated that the availability of P in the biochar is only 13 per cent of total P, much lower than those of the biosolid and dry-pelleted biosolid (30 to 40 per cent) (see Figure 5.4) (Pritchard, 2003). According to Bridle and Pritchard (2004), nearly half of the total P in biochar was in HCl-extractable form (i.e. as Ca-bound inorganic P) and was therefore less plant available, unlike the biosolid samples, which had most of the P in resin and extractable forms. Similarly, results of Shinogi (2004) indicated that available P (measured as citrate-extractable P) in biochar from sewage sludge decreased with increasing temperature, from 0.98 per cent at 250°C to 0.06 per cent at 800°C, despite an increase in total P.



## **Improving the nutrient value of biochars: Research opportunities and challenges**

### **Optimal pyrolysis conditions and feedstock**

Little research has been undertaken to identify the optimal pyrolysis conditions required for the production of biochars that are suitable as soil amendments. Identification of these conditions is also critical for the production of biochars with consistent quality, an essential requirement for market development. For composts produced from garden organics, a survey of commercially available products revealed high variability of nutrient composition, and this was identified as the major barrier for developing markets for this product in Australia (Chan et al, 2007a). From the discussion above, the most important conditions affecting nutrient composition and availability of biochars is the production temperature. But other factors such as the heating rate and particle size of the feedstocks may also be important. From a resource conservation point of view, it is important to retain as many nutrients of the feedstock as possible in the final biochar products. Typically, large amounts of nutrients such as N, K and S are lost via vaporization at higher temperature during pyrolysis. For instance, based on the literature reviewed earlier, up to 50 per cent of N, K and S are commonly lost when temperatures exceed 500°C. Furthermore, there is evidence suggesting that the remaining nutrient elements tend to become less available with further increases in temperature. For P, while total losses are minimal, available forms of P are also greatly reduced at higher temperature. For the purpose of maintaining high nutrient contents and availability, it is therefore preferable to keep the temperature low – for example, at or below 400°C to 500°C. However, the exact conditions for optimal production of biochars with

improved nutrient properties may be different for different feedstocks, and these require further research and monitoring.

Opportunities also exist to produce biochars with a specific nutrient composition by co-pyrolysis of different feedstocks. For instance, blending of plant biomass with poultry litter as feedstock for pyrolysis may result in biochar with higher available P and liming value than the use of plant biomass alone.

### **Availability of nutrients and toxic metals**

There is clearly a need to better understand the availability of the different nutrients, particularly N in biochars. While biochars are very low in mineral forms of N – namely, nitrate-N and ammonium-N – it is currently not clear if biochars with differing total N content produced from different feedstocks (see Table 5.1) are different in terms of N supply capacity when applied to the soil. Availability, including the rate of mineralization of the organic N present in biochar when applied to soil, will determine its value as a slow-release N fertilizer. This information is also needed for making a decision about the application rates of biochar, as well as in situations when N fertilizer application decisions have to be made. In general, mineralization rates of biochar are expected to be low since the stability of biochars is high (see Chapter 11); therefore, N release and N benefits from decomposition of stable biochar are likely to be minimal over time periods relevant to plant growth. Incubation studies, either in the field or in the laboratory, comparing their potential N mineralization potential (Drinkwater et al, 1996) will help to clarify this.

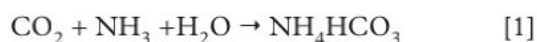
With the current interest in using organic wastes of different origin as feedstock in



pyrolysis (Bridle and Pritchard, 2004; Shinogi, 2004), there is concern regarding the environmental impacts of potentially excessive levels of heavy metals in biochars – particularly, their availability. Some of these organic wastes (e.g. biosolids) can be high in heavy metal contents (such as Cd, Cu and Zn) (Hospido et al, 2005). The authors carried out a life-cycle assessment of different treatments of biosolids, including anaerobic digestion and pyrolysis, and identified heavy metals as having the most negative environmental impact. Of particular concern is the change in availability of the different heavy metals; however, currently, little research has been undertaken. Such research is needed to ensure the safe use of biochar as soil amendments in agriculture.

### Enhancement of biochars

Recently, Day et al (2004, 2005) investigated the production of an N-enriched biochar. The novel system produces biochar and synthetic gas (mainly H<sub>2</sub> and CO<sub>2</sub>) from biomass and NH<sub>4</sub>HCO<sub>3</sub>-biochar is then formed when the ammonia is combined with the biochar, H<sub>2</sub>O and CO<sub>2</sub> at atmospheric pressure and ambient temperature. In the ammonium carbonation process (Li et al, 2003):



the biochar acts as a catalyst and the ammonia required for the process can be produced either from the hydrogen gas (H<sub>2</sub>), a co-product of biochar formation or purchased from outside sources. The product is an N-enriched biochar fertilizer with fibrous deposits of ammonium carbonate permeating inside the fine pore structure of the biochar (Day et al, 2005). The effectiveness of such a

product as a slow-release N fertilizer in terms of availability, crop production and reduction in leaching losses has not been tested in the field. However, the value of N-enriched lignin produced using chemical reactions between ammonia and lignocellulosic matrices as a slow-release N fertilizer has been demonstrated (Ramirez et al, 1997). Furthermore, Ramirez et al reported that the soil fertilized with N-functionalized lignin showed lower amounts of nitrate in percolating water than soil fertilized with inorganic fertilizer (ammonium sulphate). In the manufacture of the N-enriched biochar, Day et al (2004) suggested that biochar produced at a lower temperature of 400°C to 500°C is more effective in adsorbing ammonia than that produced at higher temperatures (700°C to 1000°C). Similarly, Asada et al (2002) compared adsorption properties of bamboo biochar prepared at 500°C, 700°C and 1000°C and found that only the biochar prepared at 500°C was effective in adsorbing ammonia. They attributed this to the presence of acidic functional groups, such as carboxyl, formed as a result of thermolysis of cellulose and lignin at temperatures of 400°C to 500°C. Acidic functional groups are effective in chemical adsorption of basic ammonia. Day et al (2004) also proposed using biochar to scrub fossil fuel exhausts from coal-fired power plants in combination with hydrated ammonia. In the process, CO<sub>2</sub>, NO<sub>x</sub> and SO<sub>x</sub> emissions are directly captured at the smokestacks, which reduces air pollution and greenhouse gas emission. The biochar is converted in the process to valuable N and S fertilizers with C sequestration value. However, as pointed out by Asada et al (2002), the effectiveness of gas capture by biochar depends upon the pyrolysis temperature, which is different for varying nutrient elements.



## Conclusions

Based on the information available, biochars are extremely variable in nutrient composition and availability depending upon feedstocks used and the pyrolysis conditions under which they were produced. Much of the positive crop responses from biochar application reported cannot be directly attributed to the nutrient content of the biochars, but instead to the indirect effect of increasing fertilizer-use efficiency. However, freshly produced biochars possess very little ability to retain cations. More research is needed to identify and quantify the indirect nutrient attributes of biochars made from different feedstocks and under different pyrolysis conditions, and how the ability of cation retention can be increased. Review of

the pyrolysis conditions of biochar production highlights the importance of temperature in controlling the losses of essential plant nutrients such as N and K, as well as the conversion of nutrients to biologically unavailable forms. To promote the use of biochars, more consistent products with higher nutrient values and improved nutrient retention are desirable. Research is needed to identify these conditions for different feedstocks and blends of feedstocks. Research opportunities also exist to enhance the nutrient value of biochar by further reaction with nutrients and blending of different feedstocks to develop different products to suit different crops and soils.

## References

- Asada, T., Ishihar, S., Yamane, T., Toba, A., Yamada, A. and Oikawa, K. (2002) 'Science of bamboo charcoal: Study on carbonising temperature of bamboo charcoal and removal capability of harmful gases', *Journal of Health Science*, vol 48, pp473–479
- Bagreev, A., Bandosz, T. J. and Locke, D. C. (2001) 'Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage-derived fertiliser', *Carbon*, vol 39, pp1971–1979
- Blackwell, P. S., Shea, S., Storer, P., Solaiman, Z., Kerkmans, M. and Stanley, I. (2007) 'Improving wheat production with deep banded oil mallee charcoal in Western Australia', in *Proceedings of the Conference of the International Agrichar Initiative*, 30 April–2 May 2007, Terrigal, NSW, Australia
- Bridle, T. R. and Pritchard, D. (2004) 'Energy and nutrient recovery from sewage sludge via pyrolysis', *Water Science and Technology*, vol 50, pp169–175
- Burgess, J. (1993) *Organic Fertiliser: An Introduction*, Agfact AC.20, NSW Agriculture, NSW, Australia
- Chan, K. Y., Dorahy C. and Tyler S. (2007a) 'Determining the agronomic value of composts produced from garden organics from metropolitan areas of New South Wales, Australia', *Australian Journal of Experimental Agriculture*, vol 47, pp1377–1382
- Chan, K. Y., Van Zwieten, L., Meszaros, I., Downie, A. and Joseph, S. (2007b) 'Assessing the agronomic values of contrasting char materials on Australian hardsetting soil', in *Proceedings of the Conference of the International Agrichar Initiative*, 30 April–2 May 2007, Terrigal, NSW, Australia
- Chan, K. Y., Van Zwieten, L., Meszaros, I., Downie, A. and Joseph, S. (2007c) 'Agronomic values of green waste biochar as a soil amendment', *Australian Journal of Soil Research*, vol 45, pp629–634
- Cheng, C. H., Lehmann, J., Thies, J. E., Burton, S. D. and Engelhard, M. H. (2006) 'Oxidation of black carbon through biotic and abiotic processes', *Organic Geochemistry*, vol 37, pp1477–1488
- Cheng, C. H., Lehmann, J. and Engelhard, M. (2008) 'Natural oxidation of black carbon in

- soils: Changes in molecular form and surface charge along a climosequence', *Geochimica et Cosmochimica Acta*, vol 72, pp1598–1610
- Cogger, S. G., Forge, T. A. and Neilsen, G. H. (2006) 'Biosolids recycling: Nitrogen management and soil ecology', *Canadian Journal of Soil Science*, vol 86, pp613–620
- Colwell, J. D. (1963) 'The estimation of the phosphorus fertiliser requirements of wheat in southern New South Wales by soil analysis', *Australian Journal of Experimental Agriculture and Animal Husbandry*, vol 3, pp190–198
- Day, D., Evans, R. J., Lee, J. W. and Reicosky, D. (2004) 'Valuable and stable co-product from fossil fuel exhaust scrubbing', *Prepr. Paper – American Chemical Society Div. Fuel Chemistry*, vol 49, pp352–355
- Day, D., Evans, R. J., Lee, J. W. and Reicosky, D. (2005) 'Economical CO<sub>2</sub>, SO<sub>x</sub> and NO<sub>x</sub> capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration', *Energy*, vol 30, pp2558–2579
- Demirbas, A. and Arin, G. (2002) 'An overview of biomass pyrolysis', *Energy Sources*, vol 24, pp471–482
- Drinkwater, L. E., Cambardella, C. A., Reder, J. D. and Rice, C. W. (1996) 'Potentially mineralisable nitrogen as an indicator of biological active soil nitrogen', in J. W. Doran and A. J. Jones (eds) *Methods for Assessing Soil Quality*, SSSA Special Publication 49, Soil Science Society of America, Madison, US, pp217–229
- FFTC (Food and Fertilizer Technology Center) (2007) 'Application of rice husk charcoal', [www.agnet.org/library/pt/2001004/](http://www.agnet.org/library/pt/2001004/), accessed 24 January 2008
- Glaser, B., Haumaier, L., Guggenberger, G. and Zech, W. (2001) "'The Terra Preta" phenomenon: A model for sustainable agriculture in the humid tropics', *Naturwissenschaften*, vol 88, pp37–41
- Glaser, B., Lehmann, J., Steiner, C., Nehls, T., Yousaf, M. and Zech, W. (2002) 'Potential of pyrolysed organic matter in soil amelioration', in *Proceedings of the 12th International Soil Conservation (ISCO) Conference*, Beijing, China
- Guha, R., Grover, P. D. and Guha, B. (1986) 'Low temperature pyrolysis of pine needles', *Research and Industry*, vol 31, pp60–63
- Horne, P. A. and Williams, P. T. (1996) 'Influence of temperature on the products from the flash pyrolysis of biomass', *Fuel*, vol 75, pp1051–1059
- Hoshi, T. (2001) 'Growth promotion of tea trees by putting bamboo charcoal in soil', in *Proceedings of 2001 International Conference on O-cha (Tea) Culture and Science*, Tokyo, Japan, pp147–150
- Hospido, A., Moreira, M. T., Martin, M., Rigola, M. and Feijoo, G. (2005) 'Environmental evaluation of different treatment processes for sludge from urban wastewater treatments: Anaerobic digestion versus thermal processes', *International Journal of Life Cycle Analysis*, vol 5, pp336–345
- Iswaran, V., Jauhri, K. S. and Sen, A. (1980) 'Effect of charcoal, coal and peat on the yield of moog, soybean and pea', *Soil Biology and Biochemistry*, vol 12, pp191–192
- Keeney, D. R. (1982) 'Nitrogen – availability indices', in A. L. Page (ed) *Methods of Soil Analysis Part 2: Chemical and Microbiological Properties*, American Society of Agronomy, Madison, WI, US, pp711–733
- Kishimoto, S. and Sugiura, G. (1985) 'Charcoal as a soil conditioner', in *Symposium on Forest Products Research, International Achievements for the Future*, vol 5, pp12–23
- Knudsen, J. N., Jensen, P. A., Lin, W., Frandsen, F. J. and Dam-Johnson, K. (2004) 'Sulfur transformations during thermal conversion of herbaceous biomass', *Energy and Fuels*, vol 18, pp810–819
- Lang, T., Jensen, A. D. and Jensen, P. A. (2005) 'Retention of organic elements during solid fuel pyrolysis with emphasis on the peculiar behaviour of nitrogen', *Energy and Fuels*, vol 19, pp1631–1643
- Leeper, G. W. and Uren, N. C. (1993) 'The nitrogen cycle', in *Soil Science: An Introduction*, Melbourne University Press, Melbourne, Australia, pp166–183
- Lehmann, J. (2007) 'Bio-energy in the black', *Frontiers in Ecology and the Environment*, vol 5, pp381–387
- Lehmann, J., Kern, D., German, L., McCann, J., Martins, G. and Moreira, A. (2003a) 'Soil fertility and production potential', in J. Lehmann, D. C. Kern, B. Glaser and W. I. Woods (eds.) *Amazonian Dark Earths: Origin,*



- Properties, Management*, Kluwer Academic Publishers, The Netherlands, pp105–124
- Lehmann, J., da Silva, J. P., Steiner, C., Nehls, T., Zech, W. and Glaser, B. (2003b) 'Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: Fertiliser, manure and charcoal amendments', *Plant and Soils*, vol 249, pp343–357
- Li, X., Hagaman, E., Tsouris, C. and Lee, J. W. (2003) 'Removal of carbon dioxide from flue gas by ammonia carbonation in the gas phase', *Energy and Fuel*, vol 17, pp69–74
- Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J. O., Thies, J., Luizão, F. J., Petersen, J. and Neves, E. G. (2006) 'Black carbon increases cation exchange capacity in soils', *Soil Science Society of America Journal*, vol 70, pp1719–1730
- Lima, I. M. and Marshall, W. E. (2005) 'Granular activated carbons from broiler manure: Physical, chemical and adsorptive properties', *Bioresource Technology*, vol 96, pp699–706
- Mikan, C. J. and Abrams, M. D. (1995) 'Altered forest composition and soil properties of historic charcoal hearths in southeastern Pennsylvania', *Canadian Journal of Forest Research*, vol 25, pp687–696
- Muralidhara, H. S. (1982) 'Conversion of tannery waste to useful products', *Resources and Conservation*, vol 8, pp43–59
- Pritchard, D. (2003) *Nutrient Properties of Char*, Report prepared for ESI by Curtin University of Technology, Perth, Western Australia
- Ramirez, F., Gonzalez, V., Crespo, M., Faix, O. and Zuniga, V. (1997) 'Amoxidized kraft lignin as a slow-release fertilizer tested on *Sorghum vulgare*', *Bioresource Technology*, vol 61, pp43–46
- Rondon, M. A., Lehmann, J., Ramirez, J. and Hurtado, M. (2007) 'Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with bio-char additions', *Biology and Fertility of Soils*, vol 43, pp699–708
- Shafizadeh, F. (1982) 'Introduction to pyrolysis of biomass', *Journal of Analytical and Applied Pyrolysis*, vol 3, pp283–305
- Shinogi, Y. (2004) 'Nutrient leaching from carbon products of sludge', ASAE/CSAE Annual International Meeting, Paper number 044063, Ottawa, Ontario, Canada
- Steiner, G., Teixeira, W. G., Lehmann, J., Nehls, T., de Macedo, J., Blum, W. E. H. and Zech, W. (2007) 'Long term effect of manure, charcoal and mineral fertilisation on crop production and fertility on a highly weathered Central Amazonian upland soil', *Plant and Soil*, vol 291, pp275–290
- Sullivan, D. M. and Miller, R. O. (2001) *Compost Quality Attributes, Measurements and Variability*, CRC Press, Boca Raton, FL
- Topoliantz, S., Pong, J. and Ballof, S. (2005) 'Manioc peel and charcoal: A potential organic amendment for sustainable soil fertility in the tropics', *Biology and Fertility of Soils*, vol 41, pp15–21
- Tsai, W. T., Lee, M. K. and Chang, Y. M. (2006) 'Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor', *Journal of Analytical and Applied Pyrolysis*, vol 76, pp230–237
- Tsai, W. T., Lee, M. K. and Chang, Y. M. (2007) 'Fast pyrolysis of rice husk: Product yields and composition', *Bioresource Technology*, vol 98, pp22–28
- Uzun, B. B., Putun, A. E. and Putun, E. (2006) 'Fast pyrolysis of soybean cake: Product yields and compositions', *Bioresource Technology*, vol 97, pp569–576
- Van Zwieten, L., Kimber, S., Downie, A., Chan, K. Y., Cowie, A., Wainberg, R. and Morris, S. (2007) 'Papermill char: Benefits to soil health and plant production', in *Proceedings of the Conference of the International Agrichar Initiative*, 30 April–2 May 2007, Terrigal, NSW, Australia
- Wardle, D. A., Zackrisson, O. and Nilsson, M. C. (1998) 'The charcoal effect in Boreal forests: Mechanisms and ecological consequences', *Oecologia*, vol 115, pp419–426
- Williams, P. T. and Besler, S. (1996) 'The influence of temperature and heating rate on the slow pyrolysis of biomass', *Renewable Energy*, vol 7, pp233–250
- Wornat, M. J., Hurt, R. H., Yang, N. C. and Headley, T. (1995) 'Structural and compositional transformations of biomass chars during combustion', *Combustion and Flame*, vol 100, pp131–143
- Yamato, M., Okimori, Y., Wibowo, I. F., Anshori, S. and Ogawa, M. (2006) 'Effects of the application of charred bark of *Acacia mangium* on the

yield of maize, cowpea and peanut and soil chemical properties in south Sumatra, Indonesia', *Soil Science and Plant Nutrition*, vol 52, pp489–495

Yu, C., Tang, Y., Fang, M., Luo, Z. and Cen, K. (2005) 'Experimental study on alkali emission during rice straw pyrolysis', *Journal of Zhejiang University (Engineering Science)*, vol 39, pp1435–1444