

Biochar and Emissions of Non-CO₂ Greenhouse Gases from Soil

Lukas Van Zwieten, Bhupinderpal Singh, Stephen Joseph, Stephen Kimber, Annette Cowie and K. Yin Chan

Introduction

Climate change caused by an increase in atmospheric concentrations of greenhouse gases (GHGs) is predicted to cause catastrophic impacts on our planet (IPCC, 2006). This provides the impetus to take action to reduce emissions and increase removal of GHGs from the atmosphere. The soil is both a significant source and sink for the greenhouse gases carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). As the global warming potential of N₂O and CH₄ is 298 and 25 times greater, respectively, than the equivalent mass of CO₂ in the atmosphere (Forster et al, 2007), small reductions in their emissions could potentially provide significant benefits for the environment.

Biochar application to soil has been shown to affect carbon (C) and nitrogen (N) transformation and retention processes in soil (see Chapters 6 and 14). These processes, along with other mechanisms influenced by biochar, can play a significant role in reducing emissions and increasing sink capacity for GHGs. In this chapter we focus

on the role that biochar could play in mitigating soil emissions of two significant non-CO₂ GHGs, N₂O and CH₄.

Factors controlling N₂O and CH₄ emissions from soil

Anthropogenic sources of N₂O contributed 3 giga tonnes (Gt) CO₂e (carbon dioxide equivalents), around 8 per cent of global emissions, in 2004; importantly, agriculture was responsible for 42 per cent of this total (Denman et al, 2007). Nitrogen fertilizers, biological N fixation by associative, free-living and mutualistic bacteria, organic N and the excreta of grazing animals are all sources of N that can lead to N₂O emissions from soil. The factors that significantly influence agricultural and forestry emissions of N₂O are N application rate, crop type, fertilizer type, soil organic C content, soil pH and texture (see review by Dalal et al, 2003).

Methane constituted around 14 per cent of global GHG emissions (CO₂e) in 2004

(Forster et al, 2007, Summary for Policy-Makers, SPM Topic 2.1). Aerobic well-drained soils are usually a sink for CH_4 , due to the high rate of CH_4 diffusion into such soils and subsequent oxidation by methanotrophic microorganisms (Dalal et al, 2008). Globally, soils are a net sink for CH_4 and are estimated to have consumed 30Tg $\text{CH}_4 \text{ yr}^{-1}$ during 2000 to 2004, equivalent to 5 per cent of the annual load of CH_4 to the atmosphere (Denman et al, 2007). The CH_4 uptake capacity of soil varies with land use, management practices (Liebig et al, 2005; Saggart et al, 2007) and soil conditions (Schutz et al, 1990). In contrast, large emissions of CH_4 are common where anaerobic conditions (e.g. wetlands, rice paddies and landfills), coupled with warm temperatures and the presence of soluble C, provide ideal conditions for the generation of CO_2 and incompletely oxidized substrates, thus supporting high activity of methanogenic microorganisms (Dalal et al, 2008).

Potential for greenhouse gas mitigation using biochar as a soil ameliorant

Recent studies have indicated that incorporating biochar within soil reduces N_2O emissions and increases CH_4 uptake from soil, which could contribute to mitigating greenhouse gas emissions (Rondon et al, 2006; Yanai et al, 2007). However, there is currently very limited understanding of the mechanisms through which biochar impacts upon fluxes of CH_4 and N_2O . It is important to understand these mechanisms, both to determine the potential role of biochar in decreasing net GHG emissions and to ensure that there are no negative environmental consequences associated with adding biochar to soils.

In this chapter, we present new data as well as published material demonstrating the potential for biochar to reduce emissions of N_2O and CH_4 from soil. Although the mechanisms for these reductions are not fully understood, it is likely that a combination of biotic and abiotic factors are involved, and these factors will vary according to soil type, land use, climate and the characteristics of the biochar.

Evidence for reduced soil greenhouse gas (GHG) emissions using biochar

Evidence for reduced N_2O emissions

Yanai et al (2007) used biochars (called charcoal) derived from municipal biowaste (pH 9.3 [H_2O] and total C circa 38 per cent) and showed a decrease in emissions of N_2O in laboratory chambers when soil (Typic Hapludand) was re-wetted to 73 per cent water-filled pore space. Reductions from $105 \mu\text{g N}_2\text{O-N m}^{-2}$ in an unamended control to only $11 \mu\text{g N}_2\text{O-N m}^{-2}$ in a biochar-treated

soil over a seven-day incubation were noted. Large amendments of biochar (10 per cent by weight) were used (estimated from the evidence available in the manuscript to be approximately 150 t ha^{-1}). Maximum emission rate of $2620 \mu\text{g N}_2\text{O-N m}^{-2}$ was found in the control soil (see Figure 13.1), while the maximum emission rate in the biochar-amended soil was $383 \mu\text{g N}_2\text{O-N m}^{-2} \text{ hr}^{-1}$. In parallel trials, Yanai et al (2007) compared biochar derived from municipal biowaste and ash derived from the same feedstock (pH

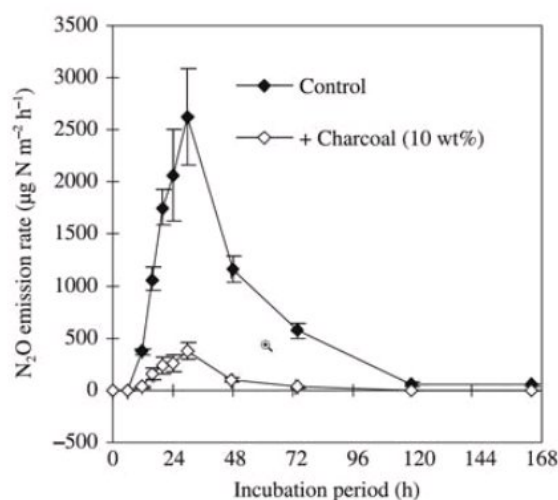


Figure 13.1 *Municipal waste biochar decreased emission of N₂O in an incubation study*

Source: Yanai et al (2007), reproduced with permission by Blackwell Publishing

11.6). Results demonstrated that the reduced N₂O emissions were not linked to the acid-neutralizing capacity of the biochar or ash, as emissions from ash-amended soil were equivalent to the control.

Work conducted by Rondon et al (2006) in unfertile tropical soils has also shown reduced N₂O emissions. Biochar produced from the wood of mango trees was applied to experimental plots (20m²) at a rate of 8t and 20t biochar ha⁻¹. The biochar was ground to <2mm, broadcast on the soil surface and then incorporated by discing to 50mm depth. After four months these plots were sown to maize and a number of other crops and native pasture. Periodically, the grass and the native vegetation (mostly native grasses) was cut to a height of 10cm, simulating grazing, and the biomass produced in each interval was recorded. Gas exchange between the soil and the atmosphere was monitored monthly over a three-year period using a closed chamber method. During the initial year of this experiment, N₂O emissions were reduced, on average, by 15mg N₂O m⁻² for the higher-

rate biochar plots. Rondon et al (2006) noted increases in soil pH, cation exchange capacity (CEC), potassium (K) availability, and possibly higher water retention in the soil.

In laboratory incubation studies conducted by the authors, glass jars (5L) with air-tight lids were filled with 1.5kg dry weight equivalent soil (Ferrosol, 2mm sieved). No fertilizer was added to the soil. Low and high temperature biochars derived from both green waste and poultry litter waste were applied at an equivalent of 10t dry biochar ha⁻¹ (0–0.05m profile), and thoroughly mixed into the soil. Acid-washed sand was added to the control treatment at an equivalent rate to the biochar.

Soil moisture was increased to 70 per cent water-holding capacity and maintained (by mass) for the duration of the incubation. Mesocosms were maintained in the dark at 23°C in a controlled temperature chamber. Results clearly demonstrate that there is potential to reduce N₂O emissions using biochars, although what is clearly evident is that biochars differ in their capacity to reduce emissions (see Figure 13.2). For example, soil amended with poultry litter biochar and high temperature green-waste biochar emitted almost no N₂O during the incubation, while low-temperature green-waste biochar increased N₂O emissions by over 100 per cent that of the control.

The soil analyses following the incubation showed that the initial nitrate concentrations were similar among the biochar-amended and control treatments, and increased up to 3.5-fold over the incubation period in all but one of the treatments (see Table 13.2); N₂O emissions were concomitantly reduced, especially from the poultry biochar-amended soils (see Figure 13.2). However, in soil amended with the low temperature green-waste biochar, the nitrate concentration decreased by 20 per cent over 47 days of incubation concomitant with the increased N₂O produced in this treatment

Table 13.1 Source, pyrolysis conditions and biochar characteristics

Biochar	Feedstock	Pyrolysis conditions	C (%)	N (%)	Colwell P (mg kg ⁻¹)	Acid-neutralizing capacity (% CO ₃ ²⁻)
Litter 1	Poultry litter ¹	Activated ² 550°C	27	0.8	1700	33
Litter 2	Poultry litter	Non-activated 450°C	35	2.2	11,000	14
Green waste 1	Green waste	Activated 550°C	32	0.06	26	<0.5
Green waste 2	Green waste	Non-activated 450°C	36	0.12	14	<0.5

Notes: 1 Poultry litter consists of manure and sawdust bedding.

2 Activation was achieved by cooling the biochars in the presence of steam. Pyrolysis residence time was 45 minutes undertaken by BEST Energies, Australia.

Source: chapter authors

(see Table 13.2 and Figure 13.2). The initial NH₄⁺-N concentration in the biochar-amended treatments was considerably lower than the control. The reason for the decrease in extractable NH₄⁺-N in biochar-amended soils is not clear; but this suggests that biochar application did not add significant amounts of NH₄⁺-N to support high nitrifier activity. The NH₄⁺-N concentration did not significantly increase during incubation in any treatment except for the poultry litter 1 biochar treatment (see Table 13.2).

The data presented in Table 13.2 and Figure 13.2 suggest that nitrification would have been either enhanced (in the poultry-litter biochar-amended soils) or remained the

same (in the high-temperature green-waste biochar-amended soils). The reduction in N₂O emissions from the poultry biochar-amended soil suggests that poultry biochar may have contained certain compounds that suppressed the activity of denitrifying enzymes involved in conversion of NO₃⁻-N to N₂O (and this reaction may have also contributed to build up of NO₃⁻-N in these soils), and/or enhanced the activity of denitrifying enzymes involved in conversion of N₂O to N₂, especially in anaerobic micro-sites rich in bioavailable organic C. On the other hand, denitrification activity seems to have been enhanced in the low-temperature green-waste biochar-amended soil.

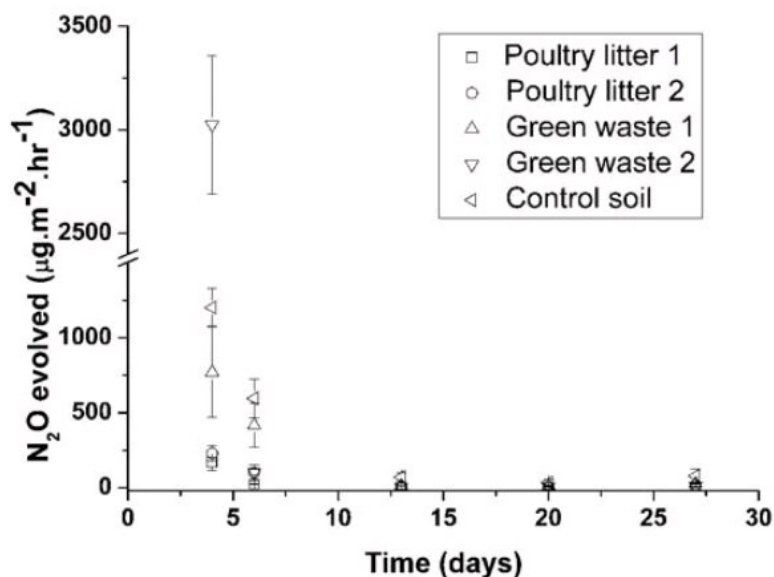


Figure 13.2 N₂O generated from a Ferrosol amended with biochar in laboratory mesocosms

Notes: 1.5kg of soil was amended with 10g kg⁻¹ biochar (described in Table 13.1) (a rate equivalent to 10t ha⁻¹ incorporated to 100mm). Acid-washed sand was added to controls in lieu of biochar. Soils were incubated in triplicate in 5L glass jars, maintained at 70 per cent water-holding capacity. Jars were sealed for 24 hours prior to head-space gas sampling. Mesocosms were maintained at 23°C in the dark.

Source: chapter authors

The effect of these biochars on microbial biomass was also determined by incubating soil for 72 hours and then performing a chloroform fumigation extraction (Vance et al, 1987). The microbial biomass C was decreased by about 40 per cent (from $1.08 \pm 0.12 \text{ mg C g}^{-1}$ dry weight soil to $0.64 \pm 0.32 \text{ mg C g}^{-1}$ dry weight soil) in the low-temperature green-waste biochar. In contrast, poultry litter biochars did not affect the soil microbial biomass C concentrations during this incubation study (data not shown). The data suggest that although there were components in the low-temperature green-waste biochar that suppressed microbial biomass growth, the activity of denitrifying enzymes was enhanced, especially those that are involved in conversion of NO_3^- -N to N_2O .

Thus, it appears that, while biochar application can lead to significant reductions in N_2O emission, this is not universally true for all biochars. It is likely that characteristics of specific biochars affect the activity of microorganisms responsible for N transformations. More research is required to clearly understand the effect of biochar and its associated components (such as contents of mineral oxides, hydroxides and carbonates in ash; the presence of chemicals – e.g. phenolics, inorganic salts, cations, anions, etc.) that could potentially affect the activity of

microbes carrying out N-cycling processes in soil (Gundale and DeLuca, 2006; Yanai et al, 2007), and to distinguish their effects on soil N_2O production as well as reduction, using a range of different biochar types produced from different feedstocks and under different processing conditions.

Evidence of reduced CH_4 emissions

Evidence that biochar increases methane oxidation in soil exists (Rondon et al, 2006); however, only very limited literature is available to support this phenomenon. Rondon et al (2005) found a complete suppression of CH_4 emissions when biochar was applied:

- at 15 g kg^{-1} soil in a grass stand (*Brachiaria humidicola*); and
- at 30 g kg^{-1} soil in soybean.

The biochar feedstock was *Calliandra calothyrsus*. The biochar was ground to $<1 \text{ mm}$ and mixed into the soil prior to sowing. In other work, Rondon et al (2006) demonstrated that applications of 20 t ha^{-1} of wood-derived biochar into a non-fertile tropical soil increased the annual methane sinks in soil by around $200 \text{ mg CH}_4 \text{ m}^{-2}$ relative to controls.

Table 13.2 Nitrate and ammonium concentration in soils following incubation with various biochars for 47 days (mean values of three incubation chambers)

	KCl-extractable Nitrate-N (mg kg^{-1})		KCl-extractable Ammonium-N (mg kg^{-1})	
	Initial	Final	Initial	Final
Control soil	26.3	67.3	3.9	4.0
Poultry litter 1 ¹	27.7	92.7	2.7	4.4
Poultry litter 2	28.3	91.0	2.5	3.5
Green waste 1	21.0	67.3	2.1	2.6
Green waste 2	25.7	20.2	2.6	3.0
Least significant difference		15.3		1.2
Average standard error of the mean		5.4		0.44

Note: 1 Biochars are described in Table 13.1.

Source: chapter authors

Biological mechanisms for reduced GHG emissions following biochar application

Nitrous oxide gas is produced in soil through three biological processes (Wrage et al, 2005):

- 1 *Nitrification*: in the first stage of nitrification, N_2O is produced as a by-product during the oxidation of ammonium to nitrite.
- 2 *Nitrifier denitrification*: in the second stage of nitrification, nitrite is converted to nitrate; however, under low oxygen (O) conditions, specialized nitrifying bacteria (denitrifying nitrifiers) use nitrite as an alternative electron acceptor, in this way producing N_2O .
- 3 *Denitrification*: here, heterotrophic denitrifying aerobic bacteria cause respiratory reduction of nitrate or nitrite to N_2O and N_2 under anoxic conditions.

These processes are thought to occur simultaneously in soil, with process 1 taking place in aerobic micro-sites and the latter two processes confined to sub-oxic and anoxic micro-sites. Many studies have proposed denitrification as the major contributor to soil N_2O emissions, especially when O is limited in soil – for example, when water-filled porosity exceeds 60 to 70 per cent (Dalal et al, 2003). However, under aerobic conditions (e.g. at water-filled porosity of 50 per cent or less), nitrification can be a major source of soil N_2O emissions. Some research has shown that nitrifier denitrification can contribute over 40 per cent of the N_2O released from a silt loam soil at 50 per cent water-filled pore space (Wrage et al, 2005). Further research (Bateman and Baggs, 2005) has indicated that even under the so-called highly aerobic conditions in soil (20 to 50 per cent water-filled porosity), there may be pockets of anaerobic micro-sites that would allow high rates of denitrification, which may

give rise to N_2O release, or that aerobic denitrification (and/or heterotrophic nitrification) can occur at this water-filled porosity.

During denitrification, NO_3^- is sequentially reduced to N_2 via a set of four enzymes: nitrate reductase (*Nar*), nitrite reductase (*Nir*), nitric oxide reductase (*Nor*) and nitrous oxide reductase (*Nos*), which are usually induced under increasingly high anaerobic conditions (Robertson and Groffman, 2007). These enzymes sequentially convert nitrate to nitrite (*Nar*), nitrite to NO (*Nir*), NO to N_2O (*Nor*) and N_2O to N_2 (*Nos*), respectively:



N_2O production through the denitrification process is a balance between N_2O -producing mechanisms, involving *Nar*, *Nir*, *Nor* enzymes and N_2O -reducing mechanisms, involving *Nos* enzyme.

The observed reduction in N_2O emission resulting from application of biochar could therefore be a result of inhibition of either stage of nitrification and/or inhibition of denitrification, or promotion of the reduction of N_2O , and these impacts could occur simultaneously in a soil. The evidence for each of these possibilities is discussed below.

Rather than reducing nitrification, studies using biochar from forest wildfire (DeLuca et al, 2006), commercially produced activated carbon (Berglund et al, 2004) or biochar produced in a laboratory from timber products at 350°C or 800°C (Gundale and DeLuca, 2006) found increases in gross and net nitrification rates in soils from boreal and temperate forests. The forest soils studied by these authors had exceptionally low rates of nitrification, with actual rates of nitrifier activity ranging from negative to 0.02mg kg⁻¹ d⁻¹. The observed

enhancement of nitrification following biochar application could be explained by several indirect processes and effects, such as:

- through removal of nitrifier inhibitory compounds (e.g. phenolics) from soil solution, which are then adsorbed onto activated carbon surfaces on biochar (Berglund et al, 2004; Gundale and DeLuca, 2006);
- by formation of a biofilm of nitrifiers around biochar particles, promoted by adsorption and increased availability of labile organic substrates to microbes on or around biochar surfaces (Berglund et al, 2004);
- by suppressing the activity of substrate (NH₄⁺-N)-competing microorganisms (heterotrophs) (e.g. through low-quality organic matter input), thus increasing the availability of NH₄⁺-N for better proliferation of nitrifiers; and
- by bringing positive changes to soil pH (e.g. through additions of alkalinity through ash and alkaline biochar, which encourages N mineralization and, subsequently, nitrification) (Alexander, 1991).

In contrast to these observations, DeLuca et al (2006) clearly demonstrated that when biochar was added to a soil with high nitrification (three different grassland soils), there was no effect of biochar on nitrification. The results presented in Table 13.2 indicate that nitrifier activity was not limited in this Ferrosol soil, nor that nitrification was reduced in those treatments that showed reduced N₂O emission. Thus, there is no evidence that biochar reduces N₂O release through inhibition of nitrification.

As suggested above, applying biochar may decrease soil N₂O emissions by affecting the denitrification process (i.e. by encouraging the activity of enzymes involved in reduction of N₂O to N₂) (Yanai et al, 2007). For example, increases in soil pH due to the addition of alkalinity through ash in biochar

could potentially encourage the activity of N₂O-reducing organisms (Yanai et al, 2007). Alternatively, NO₂⁻, NO and N₂O formed in soil through the denitrification process could be chemically adsorbed on biochar surfaces and electrochemically reduced to N₂ (see abiotic mechanisms below).

The influence of biochars on nitrification is complex to interpret from measurement of soil NO₃⁻-N as there are likely to be interacting influences on both nitrifiers and denitrifiers. For example, the increase in NO₃⁻-N in poultry biochar-amended soil may have resulted from increased nitrification; alternatively, nitrification may have been unaffected, and NO₃⁻-N accumulated due to decreased rates of denitrification. The high N₂O emissions from the low-temperature green-waste biochar treatment indicate that the decline in NO₃⁻-N observed in this treatment was probably a result of enhanced activity of denitrifiers causing rapid conversion and loss of NO₃⁻-N in soil through N₂O emissions rather than an inhibition of nitrification.

Note that if nitrification activity increases while the activity of enzymes producing N₂O from NO₃⁻ decreases due to biochar application (such as apparently occurred when biochar from poultry litter was added), there is potential for accumulated nitrate to leach from the soil profile, which may have detrimental off-site impacts.

Besides direct effects of biochar on nitrifying organisms, it is possible that biochar (since it is an organic material with a high C-to-N ratio) could induce strong N immobilization, especially during initial decomposition of N-poor, but labile components of biochar; consequently, biochar application could decrease ammonification and nitrification in the short term (Lehmann et al, 2006; Warnock et al, 2007). However, the increases in nitrate and ammonium during incubation reported in Table 13.2 suggest that there was no inhibition of ammonification or nitrification due to micro-

bial immobilization of organic and inorganic N decreasing supply of N to ammonifiers and nitrifiers in this case.

It is important to understand which component(s) of the N cycles and associated enzymes within N-cycling processes (i.e. mineralization, nitrification, denitrification) are most affected by biochar applications, so that biochar is better managed for mitigation of soil N₂O emissions and reduction of nitrate leaching.

Methane flux measured at the soil-atmosphere interface is the net effect of two processes: methane production by methanogens and methane uptake by methanotrophs (Knowles, 1993). Both methanogens and methanotrophs are ubiquitous in soils, can prevail under unfavourable conditions, and may occur in close proximity to each other (Dalal et al, 2008). A negative CH₄ flux (i.e. uptake or consumption) of CH₄ by soil, occurs when the magnitude of the CH₄ uptake process is larger than its production (Chan and Parkin, 2000). Methane production in soil occurs mainly under anaerobic conditions. Neue et al (1997) suggested that redox potentials below -150mV are generally needed for significant methane production in the presence of easily degradable organic matter and a pH of 6 to 8. Other estimates for critical soil redox values range from -150mV to -215mV (Yu et al, 2001). Substrates for methane production are usually acetate, formate, CO₂ and H₂ produced during anaerobic decomposition of organic matter in soil. Methanotrophs require O₂, which is the main limiting factor for the oxidation of CH₄ in soil (Dalal et al, 2008).

Biochar applications are expected to make soil conditions favourable for methanotrophs and unfavourable for methanogens, thereby increasing the CH₄ sink capacity of soil. Some of the likely mechanisms for biochar action in soil are explained below.

Improved soil physical conditions

Soil is a porous medium; its porosity, pore-size distribution and pore continuity together control important physical and chemical functions in soil ecosystems. Soil moisture retention characteristics, gas and water movement, and aeration (redox potential) are all factors that are controlled by soil structure, which can, in turn, be influenced through application of biochar.

It is well established that soil bulk density (BD) decreases with increases in organic matter content (Adams, 1973) following the relationship:

$$BD = 100 / ((x/K_1) + (100-x/K_2))$$

where:

x = percentage by weight of organic matter;

K₁ = bulk density of organic matter (t m⁻³);

K₂ = bulk density of mineral matter (t m⁻³).

Therefore, adding organic matter to soil can reduce bulk density and increase soil total porosity. Adams (1973) reported that BD decreased from 1.25t m⁻³ to 0.80t m⁻³ as a result of an increase in soil organic matter from 0 to 10 per cent. Applications of compost to soil can significantly reduce BD and increase the number of pores in the ranges of 30µm to 50µm and 50µm to 500µm (Dick and McCoy, 1993). Pores of these sizes (i.e. macroporosity) are usually air-filled under field conditions (drier than field capacity) and are important in maintaining aerobic conditions in the soil (Kay and Angers, 2000).

Given that biochars have a very porous nature and improve soil aggregation (Brodowski et al, 2006, Liang et al, 2006), their application to soils should improve soil aeration. Furthermore, improved water-holding capacity and reduced tensile strength (Chan et al, 2007) have been demonstrated. Improved aeration will be partly due to

increases in macroporosity with resulting higher air-filled porosity and improved supply of oxygen to soil under a wide range of soil water conditions. However, the extent of changes will depend upon the porosity characteristics of different biochars and application rates. Pore-size distribution of biochars depends upon the anatomical structure of parent feedstock and process conditions during pyrolysis, such as charring temperature and activation (see Chapter 2).

The porosity of biochar particles in soil could decrease over time due to the adsorption of 'native' organic molecules onto biochar surfaces, blocking pores (Kwon and Pignatello, 2005). Conversely, biochar, clay and soil organic matter interactions may lead to the formation of micro-aggregates over time (Brodowski et al, 2006; Cheng et al, 2006; Liang et al, 2006), which will improve soil porosity. Overall, biochar addition to soil should increase soil aeration and decrease anaerobic micro-sites per unit volume of soil (Yanai et al, 2007).

By improving the soil physical properties and thereby increasing O₂ diffusion, application of biochar will reduce the incidence of anaerobic conditions required for CH₄ production. Concurrently, these physical changes in soil properties will also favour diffusion of atmospheric CH₄ into the soil atmosphere, which is considered a major limitation to the rate of CH₄ oxidation in soil (Templeton et al, 2006; Tate et al, 2007; Werner et al, 2007) and, thus, may stimulate CH₄ uptake.

Since anoxic or sub-oxic conditions are required for N₂O to be produced through denitrification or nitrifier denitrification, reduction of anoxic or sub-oxic sites in soil is important to mitigate N₂O emissions through these two processes. However, the N₂O-reductase enzyme, which catalyses the reduction of N₂O to N₂ in highly anaerobic conditions in soil, seems to be more sensitive to O₂ than the enzymes involved in the production of N₂O during denitrification

(Tiedje, 1988). This may mean that improved soil aeration caused by biochar application could potentially suppress the reduction of N₂O to N₂ due to inhibition of the *Nos* enzyme. Cavigelli and Robertson (2001) have shown that there is physiological diversity among denitrifiers in terms of O₂ sensitivity of their *Nos* enzyme; thus, changes in denitrifier community composition can also potentially influence the magnitude of *in-situ* soil N₂O fluxes. Biochar applications may bring about changes in functionality and diversity of denitrifiers simply by improving soil aeration.

pH effects on biological mechanisms

It is well documented that biochar applications can significantly alter soil pH (see Chapter 5). Similar to burned plant residues, biochars can contain varying concentrations of ash alkalinity that is directly added into the soil as Ca, Mg, K and Na oxides, hydroxides and carbonates (see Chapter 5). This soluble form of ash alkalinity in biochar can be rapidly released into soil and then leaches down the soil profile to ameliorate soil acidity (Raison, 1979; Brennan et al, 2004).

There is evidence that when pH of a soil is increased (e.g. by liming), denitrification liberates less N₂O and the ratio of N₂O/N₂ is decreased. In other words, alkalinity through biochar addition could potentially encourage the activity of N₂O reductase enzymes of denitrifying microorganisms (Yanai et al, 2007). We could expect similar observations when high-ash biochar (e.g. poultry litter biochar) is applied to soil, compared to low-ash biochar (green-waste biochar). This is reflected in the data presented in Figure 13.2, which show greater decreases in N₂O liberated from soil when poultry litter biochar rather than green-waste biochar was added. In this work, poultry litter biochar 1 increased soil pH from 4.8 (CaCl₂ method) to 6.0, while the low-temperature (lower-ash) poul-

try litter biochar increased soil pH to 5.8. Green-waste biochars did not increase soil pH.

However, oxidation of biochar could lower the pH of soil around the vicinity of biochar particles (Cheng et al, 2006). Thus, one could speculate as to whether the effect of adding alkaline biochar on decreasing N_2O product ratio (N_2O/N_2) during denitrification would be sustained over the longer term.

Both methanogenic and methanotrophic communities can be active under a wide range of soil pH conditions. Studies have shown that soil CH_4 production can increase with an increase in soil pH from 5 to 7.5 (Inubushi et al, 2005), whereas increased soil acidity can reduce CH_4 consumption (Hutsch, 1998) and production (Neue et al, 1997) rates in soil. However, whether biochar application would increase the activity of methanogens or methanotrophs through changes in soil pH will depend upon soil moisture and aeration conditions, as well as the influence of biochars on these conditions.

Biochar application alters quality and availability of substrates

The macro-molecular structure of biochar is dominated by aromatic C, thus making biochar more recalcitrant to microbial decomposition than the parent organic materials (Baldock and Smernik, 2002). Biochar is believed to possess a turnover time of hundreds to thousands of years (see Chapter 11). As a result, biochar will be unlikely to decompose to produce simpler organic molecules (monomers) in significant quantities.

Biochar may, however, contain some proportion of labile organic components (Bird et al, 1999; Hamer et al, 2004), which may serve as energy sources for heterotrophs during the initial stages of decomposition of N-poor biochars and, hence, could potentially induce N immobilization in soil in the short term (Lehmann et al, 2006).

Overall, increases in microbial biomass and growth, and subsequent reduction in available N in soil through microbial immobilization, following biochar application to soil, can potentially occur in three ways:

- 1 Biochar could serve as a source of energy for microorganisms (heterotrophs) (see above).
- 2 Biochar may provide protection from grazing for microorganisms colonizing the pore spaces (Pietikäinen et al, 2000; Samonin and Elikova, 2004).
- 3 By adsorbing labile C substrates and nutrients in soil, biochar could increase metabolic efficiency and growth of microbes proliferating on or around biochar surfaces (Berglund et al, 2004).

Using 11 different biochars, Bhupinderpal-Singh and Cowie (2008) did not find significant interactive effects of biochar type and time (since the start of incubation) on microbial biomass C. When averaged over 196 days (across four different times – i.e. 0, 9, 63 and 196 days after incubation), compared with unamended soil, microbial biomass C (determined according to Vance et al, 1987) was:

- significantly higher at $P < 0.05$ in soil amended with poultry litter biochar (400°C, non-activated), paper sludge biochar (550°C, activated) and leaf litter biochar (400°C, activated);
- significantly higher only at $P < 0.1$ in soil amended with leaf litter biochar (550°C, activated), poultry litter biochar (550°C, activated), cow manure biochar (400°C, non-activated); and
- not significantly different in soil amended with four different wood-waste biochars (400°C/550°C, activated/non-activated) and one cow manure biochar (550°C, non-activated).

Generally, the quantity of microbial biomass C was high for those biochars that decomposed to a greater extent in soil, indicating that microbial growth could be affected by the form of C present in biochar-amended soils (Bhupinderpal-Singh and Cowie, 2008). Moreover, on day 196 of the laboratory incubation, total bacterial and fungal counts determined by the viable plate count method were significantly higher in most of the biochar-amended soils than in the unamended soil (Bhupinderpal-Singh and Cowie, 2008).

As mentioned above, porous biochar particles may provide a safe habitat for microbes colonizing them (Pietikäinen et al, 2000; Samonin and Elikova, 2004; Warnock et al, 2007). Due to differences in body sizes of soil micro-, meso- and macro-organisms, with the sizes of bacteria and fungal hyphae more comparable to the sizes of pores in biochar particles, it is likely that biochar particles will accommodate microorganisms (bacteria and many fungi), but will exclude their larger predators (Warnock et al, 2007). Thus, in the absence of predation, microorganisms in biochar would proliferate, which may induce soil N immobilization and, consequently, reduction of soil N₂O emissions.

Although the ratio of N₂O/N₂ production through denitrification (governed by the activity of the *Nos* enzyme) decreases with the supply of water-soluble, readily decomposable organic matter (Burford and Bremner, 1975; Dalal et al, 2003), high amounts of readily available C tend to result in increased N₂O production in soils, particularly following N fertilizer application (Zebarth et al, 2008). NO₃⁻ was not shown to affect denitrification, but was positively correlated with N₂O production, especially where available C was high (Gillam et al, 2008). As biochar is capable of adsorbing 'native' organic matter in soil (Gundale and DeLuca, 2006), the reduced emissions of N₂O via denitrification from biochar-

amended soils could partially be due to decreased availability of readily decomposable organic matter in whole soil (due to adsorption on biochar surfaces) that is required for supporting the activity of heterotrophic denitrifiers. Alternatively, adsorption of simpler organic molecules on biochar surfaces could enhance their accessibility to microorganisms that flourish on or around biochar (Berglund et al, 2004). Hence, even under optimum soil moisture conditions, biochar particles could create localized anaerobic micro-sites in soil by lowering redox potential in those sites (due to depletion of O₂ around biochar caused by enhanced microbial respiration using adsorbed labile C substrates). This situation will probably support an efficient nitrous oxide reductase activity for conversion of N₂O produced in soil to N₂ (see above).

On the other hand, it is also possible that biochar in soil may serve as a favourable habitat for autotrophic nitrifiers (e.g. by concentrating the supply of labile C substrates in soil on biochar surfaces and by creating high pH micro-sites within its porous structure) (Berglund et al, 2004; Gundale and DeLuca, 2006). Thus, biochar application would enhance nitrification processes and thereby produce greater N₂O during conversion of NH₄⁺-N into NO₃⁻-N and subsequent loss of NO₃⁻-N through denitrification unless a highly reduced (low-O₂) condition is created around biochar particles, as discussed above.

Recent research has shown that biochar applications to soil, particularly when N is limiting, may reduce total microbial activity in soil. Chan et al (2007) observed significant declines in activity, measured by using fluorescein diacetate hydrolysis, in pot trials on a hard-setting Alfisol in the absence of N fertilizer, while slight increases in microbial activity were seen with higher rates of biochar (50t ha⁻¹ and 100t ha⁻¹) when N fertilizer was applied. Gundale and DeLuca (2006) found low quantities of total and soluble

phenols in high-temperature Douglas-fir and ponderosa pine wood and bark biochar (800°C) relative to low-temperature biochar (350°C) from the same materials. High concentration of phenols in low-temperature biochar may be toxic to plant roots, and autotrophic and heterotrophic microorganisms (Fritze et al, 1998; Villar et al, 1998; Berglund et al, 2004; DeLuca et al, 2006; Gundale and DeLuca, 2006).

It is frequently reported that NH_4^+ produced in soil or added through ammoniacal fertilizers competitively inhibits CH_4 oxidation because some methanotrophs are also autotrophic ammonium-oxidizers and can potentially use NH_4^+ as an energy source instead of CH_4 , while using O_2 as an electron acceptor (Bedard and Knowles, 1989; Powlson et al, 1997; Bykova et al, 2007). Biochar application could possibly regulate the supply of NH_4^+ -N in soil for use by methanotrophs – for example:

- through increases in redox potential and CEC, consequently resulting in increased fixation of NH_4^+ -N in 2:1 clay lattices (Schneiders and Scherer, 1998); or
- by inducing microbial N immobilization in soil due to its high C:N ratio (Lehmann et al, 2006).

However, conflicting or no effects of NH_4^+ -N on CH_4 consumption in soil are also reported (e.g. Tate et al, 2006; Jacinthe and Lal, 2006). Differential responses of methanotrophic communities in soil to N fertilization may be responsible for any conflicting effects (e.g. the activity of type I methanotrophs generally increases and type II decreases following application of N fertilizers) (Mohanty et al, 2006). It remains to be seen how biochar will interact with N fertilizer or NH_4^+ availability and the activity of methanotrophic communities in soil to influence CH_4 consumption in soil under different vegetation systems. Concurrently, biochar application may increase the diffu-

sion of atmospheric CH_4 into soil through improved aeration, in this way increasing its availability to soil methanotrophs.

Biochar application alters supply of electron acceptors and redox potential in soil

The order in which electron acceptors are used by microbial populations decreases as follows: $\text{O}_2 > \text{NO}_3^- > \text{SO}_4^{2-} > \text{PO}_4^{3-} > \text{CO}_2$. The mineralization of organic N in soil can be controlled by the availability of inorganic electron acceptors, including NO_3^- and SO_4^{2-} (White and Reddy, 2001). Availability of O_2 , NO_3^- , SO_4^{2-} , PO_4^{3-} and CO_2 (as electron acceptors) and also NH_4^+ and dissolved organic substrates (as electron donors) can be directly or indirectly regulated through the incorporation of biochar. For example, Gundale and DeLuca (2006) have shown that there could be significant differences in the amount of NO_3^- , PO_4^{3-} , NH_4^+ and dissolved organic substrates added through biochar in soil depending upon feedstock type and biochar production temperature. The nitrifiers obtain their energy from oxidation of NH_4^+ , obtain C from soil CO_2 or simpler organic compounds (which may be affected by biochar presence in soil), and use O_2 as the electron acceptor, the supply of which can be enhanced via biochar addition to soil (see above). During the heterotrophic denitrification process, however, denitrifiers use nitrate as the electron acceptor and use C from complex organic compounds and prefer low to zero dissolved O_2 (low redox potential). Thus, biochar application may affect the magnitude of soil N_2O production (occurring via nitrification and denitrification) by directly or indirectly affecting the availability of electron acceptors and donors, with consequent changes in soil redox conditions.

Methane production in soil occurs under anaerobic conditions; but the extent of CH_4 production is further controlled by:

- a supply of intermediate organic substrates (such as acetate) and CO₂ produced during anaerobic decomposition of soil organic matter; and
- the level of redox potential changes brought about by organic matter inputs (Dalal et al, 2008).

For example, after four years of rice-straw incorporation versus burned straw treatments, Bossio et al (1999) found that the redox potential was lower (−275mV versus −225mV) and CH₄ emissions were fivefold higher in soil with rice straw incorporated than in the burned straw treatment over the rice-growing period. Where the C input was from char in burned straw, compared to the uncharred straw input, the reduced CH₄ emissions could have been due to:

- a lower quantity of available, easily decomposable organic matter in soil (Bossio et al, 1999); or
- a lower CH₄/CO₂ ratio of decomposition

products at relatively higher redox potential.

We could expect similar processes (i.e. higher redox potential, reduced rate of C cycling) in soil amended with biochar in comparison to uncharred organic matter.

Biochars can contain significant quantities of available K (see Chapter 5), which is well known to decrease reduction reactions and increase the redox status of flooded soil (Chen et al, 1997). There is evidence that K addition to soil can stimulate methanotrophs and inhibit methanogens (Babu et al, 2006). When soil redox potential increases, CH₄ emissions were found to decrease (Babu et al, 2006). Therefore, by increasing soil redox potential through the supply of K in biochar, as well as via increasing soil aeration and the relative proportion of low-quality (recalcitrant) organic matter in soil following biochar application (see above), one may expect low CH₄ emissions in biochar-amended soil.

Abiotic mechanisms influencing GHG emissions using biochar

Biochar surfaces are heterogeneous, with a complex defect structure and a significant quantity of organic and metallic compounds (see Chapters 3 and 4). The highly porous surfaces of biochars have been shown to adsorb N₂O, CO₂ and CH₄, as well as substrates for N₂O production, including NH₄⁺ and NO₃⁻ (Bagreev et al, 2001; Hitoshi et al, 2002). Once biochar is added in substantial quantities to soil, it is likely that changes to the quantity and composition of the mass and energy flows of gases, absorbed photons from the sun, transfer of heat from water, and movement of electrons and ions will occur at the surface and within biochar. On the soil surface, biochar is likely to absorb more radiant energy than soils and have a higher temperature than the surrounding

environment (Keijzer and Hermann, 1966), possibly increasing reaction rates. It is also possible that metals in biochar, such as TiO₂, can act as catalysts reducing N₂O and oxidizing CH₄ (Oviedo and Sanz, 2005). Abiotic mechanisms are explored below.

Structural interactions between biochar surfaces

Biochar has a very complex chemical and physical structure. It consists of regions of microcrystalline graphene sheets that are surrounded by an amorphous carbon phase. As the temperature of pyrolysis increases above 450°C, microcrystalline graphene sheet formation occurs. Kercher et al (2003) has hypothesized that as the temperature increases

the disordered C decomposes and becomes incorporated within the graphene sheets of the turbostratic C. The rigid covalent structure of the disordered C cannot rearrange during decomposition to allow the non-uniform growth of turbostratic crystallites. Instead, some graphene sheets grow extensively, and other sheets become terminated and pinned by structural defects (these are a source of micropores). Based on these observations, it is possible that a reduction of N_2O could take place at active defect sites at the end of the graphene sheets, especially in the presence of metal ions (Kapteijn et al, 1996).

It is also well documented that many biochars have surfaces that can adsorb a range of gases (LeLeuch and Bandosz, 2007), and these gases can then interact with the water or cations in the water and on the surface of the biochar. In addition, a wide range of highly oxygenated volatile compounds (e.g. levoglucosan, hydroxyacetaldehyde, furfurals, methoxyphenols and carboxylic compounds) are retained on the surface of the pores of biochar pyrolysed at temperatures below $500^\circ C$. Some of these compounds have the potential to react with N_2O (Milne et al, 1998).

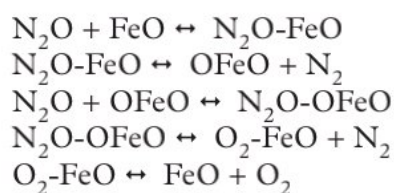
Biochar surfaces are complex (see Chapter 3) and there will be areas where there are concentrations of dangling bonds, dislocations and vacancies in the lattice structure, which will be preferential sites for adsorption and reduction of N_2O . Mineral phases in biochar may also have surfaces with a range of broken edges, steps and related defects that would minimize the energy required to reduce N_2O . Many fresh biochars have both acidic and basic sites on their surfaces (Cheng et al, 2008). Oxidized biochars and high mineral-ash biochars that have a highly variable composition of cations and anions on their surfaces (see Chapter 5) will, when placed in soil, probably interact with clay and water. N_2O is more likely to be electro-catalytically reduced on metallic

surfaces where the $pH > 7$ (Wang and Li, 1998).

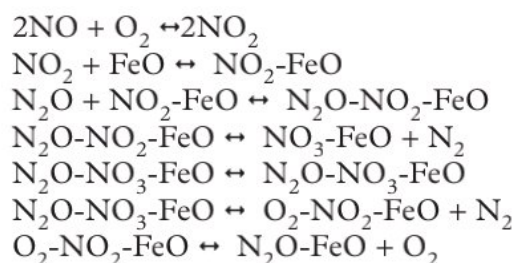
Metallic and metal oxide catalytic reactions on biochar surfaces

Considerable research has shown that some mineral elements, such as TiO_2 , will reduce N oxides in the presence of ultraviolet light (Oviedo and Sanz, 2005, 2007). Thus, it is possible that N_2O will react with biochars that have high concentrations of this mineral at the soil surface. Plane-wave pseudo-potential density-functional theory calculations undertaken by Oviedo and Sanz (2007) indicate that the following is a probable mechanism for N_2O reduction on TiO_2 surfaces. The O atom of the N_2O molecule is adsorbed onto the surface site that has an O vacancy in the TiO_2 lattice. The molecule bends and feels the force of an adjacent Ti atom. A bridge molecule is then formed and the NO bond breaks, leading to an N_2 molecule and an O atom. It is yet to be determined whether TiO_2 with or without light will catalyse the reduction of N_2O on biochar surfaces and whether there is sufficient residence time for the gas in the pores for the reactions to go to completion.

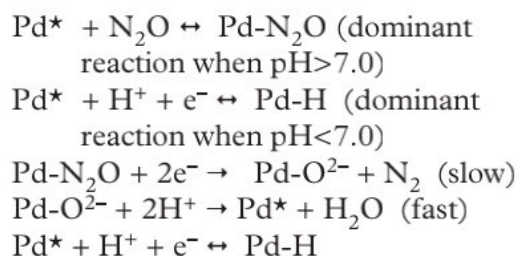
Sang et al (2005) have noted that the oxidation–reduction properties of Fe cations exchanged into zeolites have been known for some time, and zeolites that contain ion-exchanged Fe are now known to be catalytically active for the decomposition of N_2O . The active Fe is believed to exist as isolated ion-exchanged ferric cations that have no other Fe species in close proximity. High mineral-ash biochars appear to have similar properties to zeolites; thus, a similar reaction scheme could be partly responsible for the reduction of N_2O . Sang et al (2005) proposed the following reaction mechanism as being the most likely to fit their experimental data for the reduction of N_2O :



Sang et al (2005) also note that in the presence of nitrate and NO species around the biochar particle, it is possible that a further mechanism could be involved in the reactions on the biochar surface. The authors proposed the following nitrite-nitrate redox cycle as replacing the oxide-oxo cycle in the presence of NO:



N₂O is commonly employed in radiation chemistry in aqueous media as a scavenger for hydrated electrons. Wang and Li (1998) have noted that N₂O can be reduced electrocatalytically on C electrodes that have a deposit of palladium (Pd) catalyst in alkali conditions. The mechanism proposed by Wang and Li (1998) for the electrolytic reduction of N₂O is given below:



Biochar produced from the pyrolysis of coal has been used to reduce N₂O and NO in power station applications (Bueno-López et al, 2006). Experimental work has been carried out at temperatures ranging from 100°C to 600°C using a range of catalysts at

relatively high rates of NO and N₂O concentrations in the gas stream (higher than is measured from soil). Bueno-López et al (2006) found that pyrolysed coal (containing approximately 13 per cent ash) impregnated with 15 per cent by weight of K reduced NO and N₂O by approximately 60 per cent at temperatures of 400°C in a gas stream containing 5 per cent O and 0.2 per cent NO_x. Higher results were achieved using biochar doped with copper (Cu) and rubidium (Rb). Soriano-Mora et al (2007) reported that pellets manufactured with K-doped coke could operate at even lower temperatures. Kim et al (2006) reported that activated carbon impregnated with K could adsorb NO and O at 150°C. The NO reacted with the O to form NO₂, which is then further oxidized to produce N₂. Given the differences in concentration of N₂O in the aqueous soil environment and the much higher concentrations in gaseous combustion, it is not possible to determine whether these mechanisms are significant.

Hayhurst and Lawrence (1992) demonstrated that heterogeneous reactions between N₂O with CaO and biochar surfaces are a significant process for N₂O destruction during coal combustion. This is particularly relevant for biochars with high concentrations of Ca²⁺, such as those derived from poultry litter or paper mill wastes. These authors have characterized the decomposition of N₂O by the following consecutive reactions:

- the adsorption of N₂O on biochar surfaces;
- decomposition of the adsorbed molecule with N₂ formation to leave surface O; and
- desorption of O₂ by combination with another surface O atom or by direct reaction with another N₂O molecule.

In these circumstances, the dissociative adsorption of N₂O on vacant lattice sites leads to a progressive development of an O

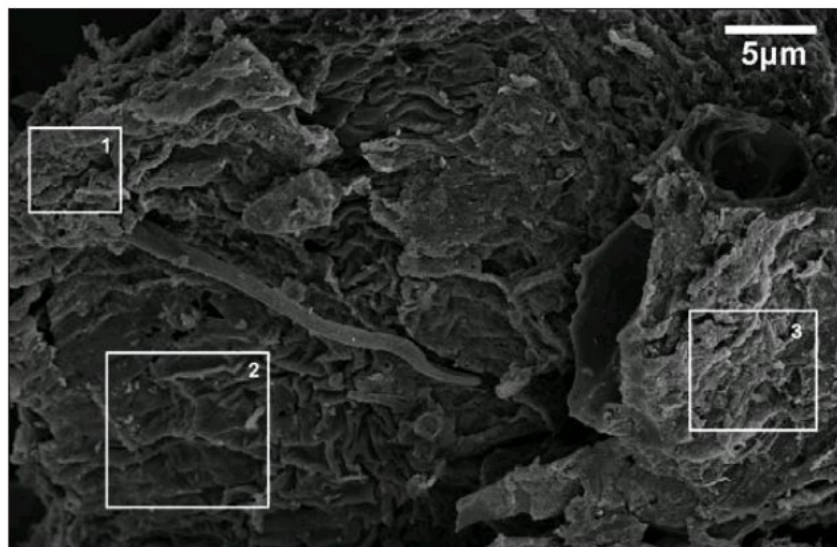


Figure 13.3 Scanning electron microscopy (SEM) of aged (six months in a Ferrosol) poultry litter biochar with regions of energy dispersive spectroscopy (EDS) analysis (UNSW Electron Microscope Unit)

Note: Clay platelets are bonded to the biochar. Regions 1 and 3 are described in the text. Biochar manufactured by BESTEnergies Pty.

Source: chapter authors

layer that inhibits the adsorption and consequent reaction of more N_2O . In the presence of H_2 (and H radicals), CO, carboxylic acid and CH_4 , the reductant regenerates the reduced active sites by removing the adsorbed O atoms. The reactions take place preferentially at sites that have K^+ and Ca^{2+} atoms or oxides of Fe, Mg and Ti (Parmon et al, 2005).

There are significant interactions between clays and biochars that influence their aging and reactivity in soil. Figure 13.3 demonstrates clay/mineral coatings over chicken manure biochar using scanning electron microscopy (SEM). Energy dispersive spectroscopy (EDS) analysis of region 1 had high C and Ca contents, typical of the analysis of poultry biochars (see Chapter 5), while region 3 had significant contents of minerals, especially Si, Al, Fe, K and Ti. These interactions between the clay and biochar may

influence not only abiotic mechanisms for N_2O reduction, but possibly also the CEC of the biochar (see Chapter 5).

Interactions with organic molecules in biochar

Most biochars produced below $550^\circ C$ initially contain a range of non-aromatic organic compounds on their internal and external surfaces. These organic compounds are not particularly stable (Bridgwater et al, 1999). Biochars can also adsorb a range of soil organic compounds (see Chapter 18). Avdeev et al (2005) report that a range of aromatic and aliphatic compounds have been oxidized by N_2O . Calculations indicate that an O atom is transferred through the 1,3-dipolar cyclo-addition of N_2O to the $C=C$ bond (see Figure 13.4). Next, the resulting intermediate decomposes, yielding a ketone

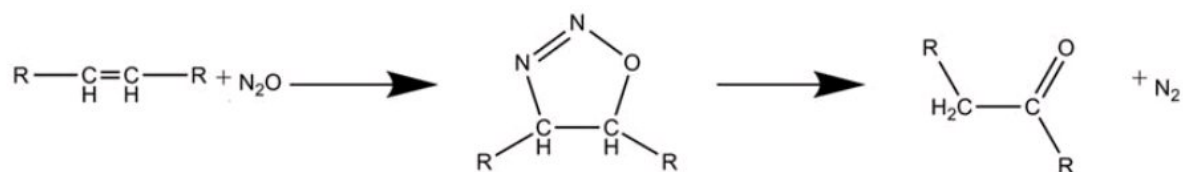


Figure 13.4 Proposed oxidation of aromatic C by N_2O

Source: adapted from Avdeev et al (2005)

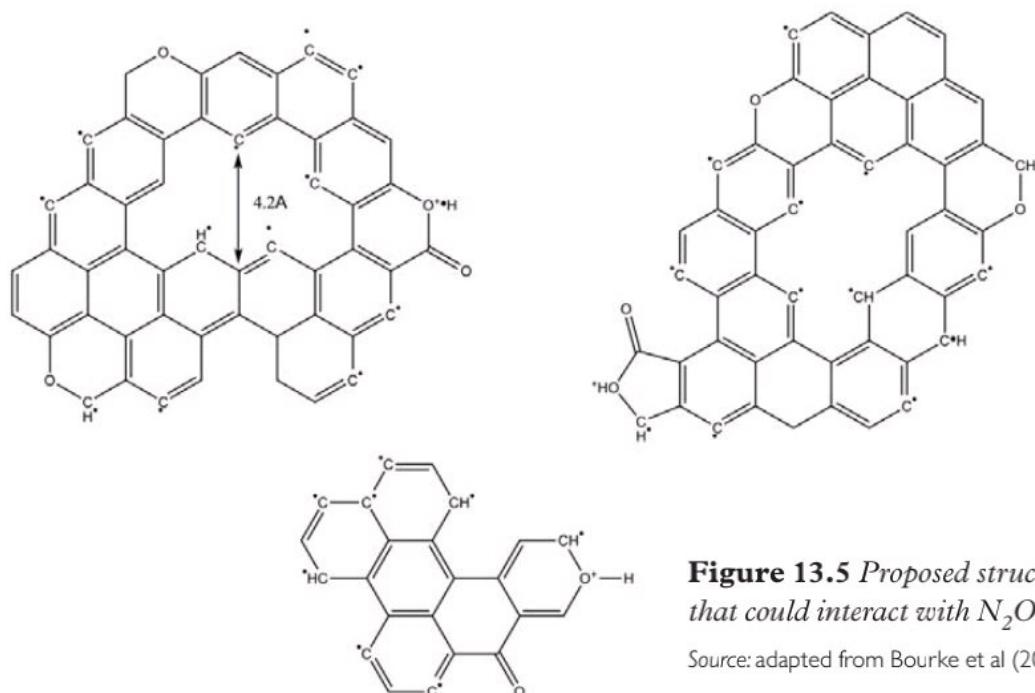


Figure 13.5 Proposed structure of biochar that could interact with N₂O

Source: adapted from Bourke et al (2007)

and releasing N₂ to the gas phase. Therefore, given that biochar surfaces adsorb aromatic and aliphatic compounds as mentioned above, it would seem possible that these compounds may be partly responsible for the reduction in N₂O emissions observed in biochar-amended soils.

Using electron spin resonance (ESR), Bourke et al (2007) measured a high concentration of free radicals associated with C aromatic rings. The concentration of these radicals decreases as the temperature of pyrolysis increases. Bourke et al (2007) also

found that there are micropores of 0.3 nm to 1 nm, which he attributed to voids within the hexagonal C planes. These voids will have concentrations of radicals and dangling bonds that could contribute to the chemisorption properties of biochars (see Figure 13.5). It is probable that there is a significant concentration of O singlets that could react with CH₄ to produce CO₂. Bourke et al (2007) attributed the propensity of fresh biochars to combust at temperatures below 100°C to the high concentration of free radicals.

Conclusions

In this chapter, we have shown that biochar can, under certain conditions, reduce soil N₂O and CH₄ emissions. A range of both biotic and abiotic mechanisms for this reduction were discussed. The development of biochar as a tool to reduce GHG emissions from soil will require detailed understanding of the interactions between biochar and site-

specific soil and climate conditions, and management practices that alter the greenhouse source sink capacity of soils. We need to explore how the key non-CO₂ GHG emission control mechanisms (e.g. soil aeration, moisture, pH, microbial processes, soil structure, nutrient levels and easily mineralizable C pools) interact with biochar to influence

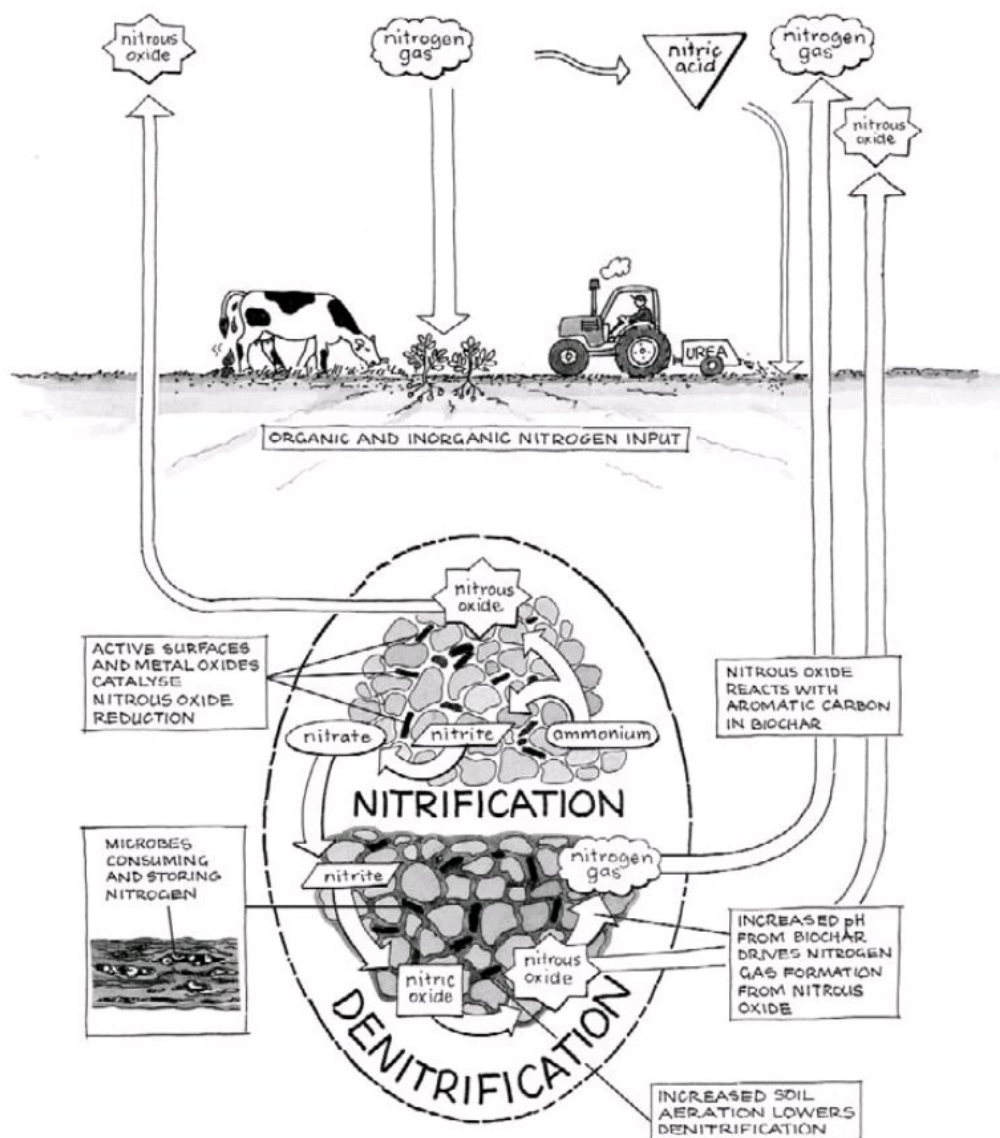


Figure 13.6 Summary schematic for reduced emissions of N_2O from soil

Source: chapter authors

soil GHG emissions. Figure 13.6 summarizes some of the key mechanisms for both the production of N_2O in soil, as well as its reduction through the application of biochar.

Variations in these controlling factors can play a significant role in altering soil micro-site conditions, which will probably alter diurnal dynamics of soil non- CO_2 GHG emission and uptake. Seasonal and inter-annual variations in rainfall patterns, temperature, land-use change, and plant

growth behaviour can also alter dynamics of soil N_2O emissions and CH_4 uptake; but the processes through which biochar interacts with these long-term controls to influence soil GHG fluxes are still unclear. An improved understanding of the role of biochar in reducing non- CO_2 GHG emissions will promote its incorporation within climate change mitigation strategies and, ultimately, its commercial availability and application.

References

- Adams, W. A. (1973) 'The effect of organic matter on the bulk and true densities of some uncultivated podsollic soils', *Journal of Soil Science*, vol 24, pp11–17
- Alexander, M. (1991) *Introduction to Soil Microbiology*, Krieger Publishing Co, FL, US
- Avdeev, V. I., Ruzankin, S. F. and Zhidomirov, G. M. (2005) 'Molecular mechanism of direct alkene oxidation with nitrous oxide: DFT Analysis', *Kinetics and Catalysis*, vol 46, pp177–188
- Babu, J. Y., Nayak, D. R. and Adhya, T. K. (2006) 'Potassium application reduces methane emission from a flooded field planted to rice', *Biology and Fertility of Soils*, vol 42, pp532–541
- Bagreev, A., Bandosz, T. J. and Locke, D. C. (2001) 'Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer', *Carbon*, vol 39, pp1971–1977
- Baldock, J. A. and Smernik, R. J. (2002) 'Chemical composition and bioavailability of thermally altered *Pinus resinosa* (red pine) wood', *Organic Geochemistry*, vol 34 pp1093–1109
- Bateman, E. J. and Baggs, E. M. (2005) 'Contributions of nitrification and denitrification to N₂O emissions from soils at different water-filled pore space', *Biology and Fertility of Soils*, vol 41, pp379–388
- Bedard, C. and Knowles, R. (1989) 'Physiology, biochemistry, and specific inhibitors of CH₄, NH₄⁺, and CO oxidation by methanotrophs and nitrifiers', *Microbiology Reviews*, vol 53, pp68–84
- Berglund, L. M., DeLuca, T. H. and Zackrisson, O. (2004) 'Activated carbon amendments to soil alters nitrification rates in Scots pine forests', *Soil Biology and Biochemistry*, vol 36, pp2067–2073
- Bhupinderpal-Singh and Cowie, A. L. (2008) 'A novel approach, using ¹³C natural abundance, for measuring decomposition of biochars in soil', in L. D. Currie and J. A. Hanly (eds) *Carbon and Nutrient Management in Agriculture: Proceedings of a Fertilizer and Lime Research Centre Workshop*, Massey University, Palmerston North, New Zealand, Occasional Report no 21, p4
- Bird, M. I., Moyo, C., Veenendaal, E. M., Lloyd, J. and Frost, P. (1999) 'Stability of elemental carbon in savanna soil', *Global Biogeochemical Cycles*, vol 13, pp923–932
- Bossio, D. A., Horwath, W. R., Mutters, R. G. and Van Kessel, C. (1999) 'Methane pool and flux dynamics in a rice field following straw incorporation', *Soil Biology and Biochemistry*, vol 31, pp1313–1322
- Bourke, J., Manley-Harris, M., Fushimi, C., Dowaki, K., Nunoura, T. and Antal, M. J. Jr. (2007) 'Do all carbonized charcoals have the same chemical structure? 2. A model of the chemical structure of carbonized charcoal', *Industrial and Engineering Chemistry Research*, vol 46, pp5954–5967
- Brennan, R. F., Bolland, M. D. A. and Bowden, J. W. (2004) 'Potassium deficiency, and molybdenum deficiency and aluminium toxicity due to soil acidification, have become problems for cropping sandy soils in south-western Australia', *Australian Journal Experimental Agriculture*, vol 44, pp1031–1039
- Bridgwater, A. V., Meier, D. and Radlein, D. (1999) 'An overview of fast pyrolysis of biomass', *Organic Geochemistry*, vol 30 pp1479–1493
- Brodowski, S., John, B., Flessa, H. and Amelung, W. (2006) 'Aggregate-occluded black carbon in soil', *European Journal of Soil Science*, vol 57, pp539–546
- Bueno-López, A., Soriano-Mora, J. M. and García-García, A. (2006) 'Study of the temperature window for the selective reduction of NO_x in O₂-rich gas mixtures by metal-loaded carbon', *Catalysis Communications*, vol 7, pp678–684
- Burford, J. R. and Bremner, J. M. (1975) 'Relationships between denitrification capacities of soils and total, water-soluble and readily decomposable soil organic matter', *Soil Biology and Biochemistry*, vol 7, pp389–394
- Bykova, S., Boeckx, P., Kravchenko, I., Galchenko, V. and Van Cleemput, O. (2007) 'Response of CH₄ oxidation and methanotrophic diversity to NH₄⁺ and CH₄ mixing ratios', *Biology and*

- Fertility of Soils*, vol 43, pp341–348
- Cavigelli, M. A. and Robertson, G. P. (2001) 'Role of denitrifier diversity in rates of nitrous oxide consumption in a terrestrial ecosystem', *Soil Biology and Biochemistry*, vol 33, pp297–310
- Chan, A. S. K. and Parkin, T. B. (2000) 'Evaluation of potential inhibitors of methanogenesis and methane oxidation in a landfill cover soil', *Soil Biological and Biochemistry*, vol 32, pp1581–1590
- Chan, K. Y., Van Zwieten, L., Meszaros, I., Downie, A. and Joseph, S. (2007) 'Agronomic values of greenwaste biochar as a soil amendment', *Australian Journal of Soil Research*, vol 45, pp629–634
- Chen, J., Xuan, J., Du, C. and Xie, J. (1997) 'Effect of potassium nutrition of rice on rhizosphere redox status', *Plant and Soil*, vol 188, pp131–137
- Cheng, C. H., Lehmann, J., Thies, J. E., Burton, S. D. and Engelhard, M. H. (2006) 'Oxidation of black carbon by biotic and abiotic processes', *Organic Geochemistry*, vol 37, pp1477–1488
- Cheng, C. H., Lehmann, J. and Engelhard, M. H. (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
- Dalal, R. C., Wang, W. J., Robertson, G. P. and Parton, W. J. (2003) 'Nitrous oxide emission from Australian agricultural lands and mitigation options: A review', *Australian Journal of Soil Research*, vol 41, pp165–195
- Dalal, R. C., Allen, D. E., Livesley, S. J. and Richards, G. (2008) 'Magnitude and biophysical regulators of methane emission and consumption in the Australian agricultural, forest, and submerged landscapes: A review', *Plant and Soil*, vol 309, pp43–76
- DeLuca, T. H., MacKenzie, M. D., Gundale, M. J. and Holben, W. E. (2006) 'Wildfire-produced charcoal directly influences nitrogen cycling in ponderosa pine forests', *Soil Science Society of America Journal*, vol 70, pp448–453
- Denman, K. L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P. M., Dickinson, R. E., Hauglustaine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., da Silva Dias, P. L., Wofsy, S. C. and Zhang, X. (2007) 'Coupling between changes in the climate system and biogeochemistry', in S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor and H. L. Miller (eds) *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, UK, pp499–587
- Dick, W. A. and McCoy, E. L. (1993) 'Enhancing soil fertility by addition of compost', in H. A. J. Hoitink and H. M. Keener (eds) *Science and Engineering of Composting*, Renaissance Publication, OH, US, pp 622–643
- Forster, P., Ramaswamy, V., Artaxo, P., Bernsten, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M. and Van Dorland, R. (2007) 'Changes in atmospheric constituents and radiative forcing', in S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor and H. L. Miller (eds) *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, UK, pp129–234
- Fritze, H., Pennanen, T. and Kitunen, V. (1998) 'Characterization of dissolved organic carbon from burned humus and its effects on microbial activity and community structure', *Soil Biology and Biochemistry*, vol 30, pp687–693
- Gillam, K. M., Zebbarth, B. J. and Burton, D. L. (2008) 'Nitrous oxide emissions from denitrification and the partitioning of gaseous losses as affected by nitrate and carbon addition and soil aeration', *Canadian Journal of Soil Science*, vol 88, pp133–143
- Gundale, M. J. and DeLuca, T. H. (2006) 'Temperature and source material influence ecological attributes of ponderosa pine and Douglas fir charcoal', *Forest Ecological and Management*, vol 231, pp86–93
- Hamer, U., Marschner, B., Brodowski, S. and Amelung, W. (2004) 'Interactive priming of black carbon and glucose mineralisation', *Organic Geochemistry*, vol 35 pp823–830
- Hayhurst, A. N. and Lawrence, A. D. (1992) 'Emissions of nitrous oxide from combustion sources', *Progress in Energy and Combustion*

- Science*, vol 18, pp529–552
- Hitoshi, T., Ai, F. and Haruo, H. (2002) 'Development of advanced utilization technologies for organic waste: (Part 1) Greenhouse gas and nutrient salt adsorption properties of wood-based charcoal', *Denryoku Chuo Kenkyujo Abiko Kenkyujo Hokoku*, Research Report of Abiko Research Laboratory, no U02010
- Hutsch, B. W. (1998) 'Methane oxidation in arable soil as inhibited by ammonium, nitrite, and organic manure with respect to soil pH', *Biology and Fertility of Soils*, vol 28, pp27–35
- Inubushi, K., Otake, S., Furukawa, Y., Shibasaki, N., Ali, M., Itang, A. M. and Tsuruta, H. (2005) 'Factors influencing methane emission from peat soils, comparison of tropical and temperate wetlands', *Nutrient Cycling in Agroecosystems*, vol 71, pp93–99
- IPCC (Intergovernmental Panel on Climate Change) (2006) *2006 IPCC Guidelines for National Greenhouse Gas Inventories*, National Greenhouse Gas Inventories Programme, Hayama, Japan, www.ipcc-nggip.iges.or.jp/public/2006gl/index.html
- Jacinthe, P. A. and Lal, R. (2006) 'Methane oxidation potential of reclaimed grassland soils as affected by management', *Soil Science*, vol 171, pp772–783
- Kapteijn, F., Rodriguez-Mirasol, J. and Moulijn, J. (1996) 'Heterogeneous catalytic decomposition of nitrous oxide', *Applied Catalysis B: Environmental*, vol 9, pp25–64
- Kay, B. D. and Angers, D. A. (2000) 'Soil structure', in M. E. Sumner (ed) *Handbook of Soil Science*, CRC Press, Boca Raton, FL, ppA229–A276
- Keijzer, S. D. and Hermann, R. K. (1966) 'Effect of charcoal on germination of Douglas fir seed', *Northwest Science*, vol 40, pp155–163
- Kercher, K., Dennis, C. and Nagle, D. (2003) 'Microstructural evolution during charcoal carbonization by X-ray diffraction analysis', *Carbon*, vol 41, pp15–27
- Kim, B., Kim, J. and Park, J. (2006) 'Characteristics in NO reduction by a powder type impregnated activated carbon on the filter support system', *Fourth International Conference on Combustion, Incineration/Pyrolysis and Emission Control*, Kyoto, Japan
- Knowles, R. (1993) 'Methane: Process of production and consumption', in G. A. Peterson, P. S. Baenzinger and R. J. Luxmoore, (eds) *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change: Proceedings of a Symposium*, American Society of Agronomy, Madison, WI, pp145–178
- Kwon, S. and Pignatello, J. J. (2005) 'Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): Pseudo pore blockage by model lipid components and its implications for N₂-probed surface properties of natural sorbents', *Environmental Science and Technology*, vol 39, pp7932–7939
- Lehmann, J., Gaunt, J. and Rondon, M. (2006) 'Bio-char sequestration in terrestrial ecosystems – a review', *Mitigation and Adaptation Strategies for Global Change*, vol 11, pp403–427
- LeLeuch, L. M. and Bandosz, T. J. (2007) 'The reactive adsorption of ammonia on modified activated carbons', *Carbon*, vol 45, pp568–578
- 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
- Liebig, M. A., Morgan, J. A., Reeder, S. J., Ellert, B. H., Gollany, H. and Schuman, G. E. (2005) 'Greenhouse gas contributions and mitigation potential of agricultural practices in northwestern USA and western Canada', *Soil and Tillage Research*, vol 83, pp25–52
- Milne, T. A., Evans, R. J. and Abatzoglou, N. (1998) *Biomass Gasifier 'Tars': Their Nature, Formation, and Conversion*, Report no NREL/TP-570-25357, National Renewable Energy Laboratory, Colorado, www.nrel.gov/docs/fy99osti/25357.pdf, accessed July 2008
- Mohanty, S. R., Bodelier, P. L. E., Floris, V. and Conrad, R. (2006) 'Differential effects of nitrogenous fertilizers on methane-consuming microbes in rice field and forest soils', *Applied and Environmental Microbiology*, vol 72, pp1346–1354
- Neue, H. U., Wassmann, R., Kludze, H. K., Wang, B. and Lantin, R. S. (1997) 'Factors and processes controlling methane emissions from rice fields', *Nutrient Cycling in Agroecosystems*, vol 49, pp111–117

- Oviedo, J. and Sanz, J. F. (2005) 'TiO₂ (110) from dynamic first principles calculations', *Journal of Physical Chemistry B*, vol 109, pp16,223–16,226
- Oviedo, J. and Sanz, J. F. (2007) 'Influence of temperature on the interaction between Pd clusters and the TiO₂ (110)', *Physical Review Letters*, vol 99, article number 066102
- Parmon, V. N., Panov, G. I., Uriarte, A. and Noskov, A. S. (2005) 'Nitrous oxide in oxidation chemistry and catalysis: Application and production', *Catalyst Today*, vol 100, pp115–131
- Pietikäinen, J., Kiikkilä, O. and Fritze, H. (2000) 'Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus', *Oikos*, vol 89, pp231–242
- Powlson, D. S., Goulding, K. W. T., Willison, T. W., Webster, C. P. and Hütsch, B. W. (1997) 'The effect of agriculture on methane oxidation in soil', *Nutrient Cycling in Agroecosystems*, vol 49, pp59–70
- Raison, R. J. (1979) 'Modification of the soil environment by vegetation fires, with particular reference to nitrogen transformations: A review', *Plant and Soil*, vol 51, pp73–108
- Robertson, G. P. and Groffman, P. M. (2007) 'Nitrogen transformations', in E. A. Paul (ed) *Soil Microbiology and Biochemistry*, Elsevier Academic Press, Oxford, UK, pp341–362
- Rondon, M., Ramirez, J. A. and Lehmann, J. (2005) 'Greenhouse gas emissions decrease with charcoal additions to tropical soils', in *Proceedings of the Third USDA Symposium on Greenhouse Gases and Carbon Sequestration*, Soil Carbon Center, Kansas State University, United States Department of Agriculture, Baltimore, p208, <http://soilcarboncenter.k-state.edu/conference/USDA%20Abstracts%20html/Abstract%20Rondon.htm>, accessed June 2008
- Rondon, M. A., Molina, D., Hurtado, M., Ramirez, J., Lehmann, J., Major, J. and Amezquita, E. (2006) 'Enhancing the productivity of crops and grasses while reducing greenhouse gas emissions through bio-char amendments to unfertile tropical soils', in *18th World Congress of Soil Science*, 9–15 July, Philadelphia, PA, <http://crops.confex.com/crops/wc2006/techprogram/P16849.HTM>, accessed June 2008
- Saggar, S., Tate, K. R., Giltrap, D. L. and Singh, J. (2007) 'Soil-atmosphere exchange of nitrous oxide and methane in New Zealand terrestrial ecosystems and their mitigation options: A review', *Plant and Soil*, vol 309, pp25–42
- Samonin, V. V. and Elikova, E. E. (2004) 'A study of the adsorption of bacterial cells on porous materials', *Microbiology*, vol 73, pp810–816
- Sang, C., Kim, B. H. and Lund, R. F. H. (2005) 'Effect of NO upon N₂O decomposition over Fe/ZSM-5 with low iron loading', *Journal of Physical Chemistry B*, vol 109, pp2295–2301
- Schneiders, M. and Scherer, H. W. (1998) 'Fixation and release of ammonium in flooded rice soils as affected by redox potential', *European Journal of Agronomy*, vol 8, pp181–189
- Schutz, H., Seiler, W. and Rennenberg, H. (1990) 'Soil and land use related sources and sinks of methane (CH₄) in the context of the global methane budget', in A. F. Bouwman (ed) *Soils and the Greenhouse Effect*, Wiley, Chichester, NY, US, pp269–285
- Soriano-Mora, J. M., Bueno-López, A., García-García, A., Perry, R. E. and Snape, C. E. (2007) 'NO_x removal by low-cost char pellets: Factors influencing the activity and selectivity towards NO_x reduction', *Fuel*, vol 86, pp949–956
- Tate, K. R., Ross, D. J., Scott, N. A., Rodda, N. J., Townsend, J. A. and Arnold, G. C. (2006) 'Post-harvest patterns of carbon dioxide production, methane uptake and nitrous oxide production in a *Pinus radiata* D. Don plantation', *Forest Ecology and Management*, vol 228, pp40–50
- Tate, K. R., Ross, D. J., Saggar, S., Hedley, C. B., Dando, J., Singh, B. K. and Lamb, S. J. (2007) 'Methane uptake in soils from *Pinus radiata* plantations, a reverting shrubland and adjacent pastures: Effects of land-use change, and soil texture, water and mineral nitrogen', *Soil Biology and Biochemistry*, vol 39, pp1437–1449
- Templeton, A. S., Chu, K. H., Alvarez-Cohen, L. and Conrad, M. E. (2006) 'Variable carbon isotope fractionation expressed by aerobic CH₄-oxidizing bacteria', *Geochimica et Cosmochimica Acta*, vol 70, pp1739–1752
- Tiedje, J. M. (1988) 'Ecology of denitrification and dissimilatory nitrate reduction to ammonium', in A. J. B. Zehnder (ed) *Biology of Anaerobic Microorganisms*, Wiley, Chichester, UK, pp179–244

- Vance, E. D., Brookes, P. C. and Jenkinson, D. S. (1987) 'An extraction method for measuring soil microbial biomass C', *Soil Biology and Biochemistry*, vol 19, pp703–707
- Villar, M. C., González-Prieto, S. J. and Carballas, T. (1998) 'Evaluation of three organic wastes for reclaiming burnt soils: Improvement in the recovery of vegetation cover and soil fertility in pot experiments', *Biology and Fertility of Soils*, vol 26, pp122–129
- Wang, B. and Li, X.-Y. (1998) 'Electrocatalytic properties of nitrous oxide and its voltametric detection at palladium electrodeposited on a glassy carbon electrode', *Analytical Chemistry*, vol 70, pp2181–2187
- Warnock, D. D., Lehmann, J., Kuyper, T. W. and Rillig, M. C. (2007) 'Mycorrhizal responses to biochar in soil – concepts and mechanisms', *Plant and Soil*, vol 300, pp9–20
- Werner, C., Kiese, R. and Butterbach-Bahl, K. (2007) 'Soil-atmosphere exchange of N₂O, CH₄ and CO₂ and controlling environmental factors for tropical rain forest sites in western Kenya', *Journal of Geophysical Research*, vol 112, pp1–15
- White, J. R. and Reddy, K. R. (2001) 'Influence of selected inorganic electron acceptors on organic nitrogen mineralization in Everglades soil', *Soil Science Society of America Journal*, vol 65, pp941–948
- Wrage, N., van Groeningen, J. W., Oenema, O. and Baggs, E. M. (2005) 'Distinguishing between soil sources of N₂O using a new ¹⁵N- and ¹⁸O-enrichment method', *Rapid Communications in Mass Spectrometry*, vol 19, pp3298–3306
- Yanai, Y., Toyota, K. and Okazaki, M. (2007) 'Effects of charcoal addition on N₂O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments', *Soil Science and Plant Nutrition*, vol 53, pp181–188
- Yu, K., Wang, Z., Vermoesen, A., Patrick, Jr. W. and Van Cleemput, O. (2001) 'Nitrous oxide and methane emissions from different soil suspensions: Effect of soil redox status', *Biology and Fertility of Soils*, vol 34, pp25–30
- Zebarth, B. J., Rochette, O. and Burton, D. L. (2008) 'N₂O emissions from spring barley production as influenced by fertilizer nitrogen rate', *Canadian Journal of Soil Science*, vol 88, pp197–205