Review

A Review of Biochar and Soil Nitrogen Dynamics

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Abstract: Interest in biochar stems from its potential agronomic benefits and carbon sequestration ability. Biochar application alters soil nitrogen (N) dynamics. This review establishes emerging trends and gaps in biochar-N research. Biochar adsorption of NO_3^-, up to 0.6 mg g^{-1} biochar, occurs at pyrolysis temperatures >600 °C with amounts adsorbed dependent on feedstock and NO_3^- concentration. Biochar NH_4^+ adsorption depends on feedstock, but no pyrolysis temperature trend is apparent. Long-term practical effectiveness of inorganic-N adsorption, as a NO_3^- leaching mitigation option, requires further study. Biochar adsorption of ammonia (NH_3) decreases NH_3 and NO_3^- losses during composting and after manure applications, and offers a mechanism for developing slow release fertilisers. Reductions in NH_3 loss vary with N source and biochar characteristics. Manure derived biochars have a role as N fertilizers. Increasing pyrolysis temperatures, during biochar manufacture from manures and biosolids, results in biochars with decreasing hydrolysable organic N and increasing aromatic and heterocyclic structures. The short- and long-term implications of biochar on N immobilisation and mineralization are specific to individual soil-biochar combinations and further systematic studies are required to predict agronomic and N cycling responses. Most nitrous oxide (N_2O) studies measuring nitrous

oxide (N_2O) were short-term in nature and found emission reductions, but long-term studies are lacking, as is mechanistic understanding of reductions. Stable N isotopes have a role in elucidating biochar-N-soil dynamics. There remains a dearth of information regarding effects of biochar and soil biota on N cycling. Biochar has potential within agroecosystems to be an N input, and a mitigation agent for environmentally detrimental N losses. Future research needs to systematically understand biochar-N interactions over the long term.

1. Introduction

Biochar is defined by Lehmann and Joseph [1] as a carbon (C) rich product derived from the pyrolysis of organic material at relatively low temperatures (<700 °C). Bioenergy production using pyrolysis creates biochar as a bi-product. There is intense interest in using this biochar as a means to sequester C in soils as a tool for offsetting anthropogenic carbon dioxide (CO_2) emissions, and as a soil amendment due to its potential agronomic benefits [1]. An analysis by Woolf *et al.* [2] showed that globally implementing a sustainable biochar program could potentially offset 12% of the current anthropogenic CO_2-C equivalent emissions. Besides potentially sequestering C biochar has been observed to have agronomic benefits [3,4] and to alter the nitrogen (N) dynamics in soils [5]. Since the biochar and N cycling review of Clough and Condron [5] the interest in the potential of biochar has continued to escalate, such that, according to the Web of Science® data base, there have been 442 manuscripts published on various aspects of "biochar" since the beginning of 2011, with 87 of these cross referenced to "nitrogen". The anthropogenically induced global N cascade is resulting in enhanced fluxes of nitrous oxide (N_2O), ammonia (NH_3), and nitrate (NO_3^-) leaching as a consequence of the increasing intensification of agricultural systems [6,7]. In fact, humankind introduces more reactive N into the biosphere via the Haber-Bosch process and legume cultivation than all the natural processes taken together [7]. Thus mitigation options to reduce environmentally harmful N fluxes are keenly sought. Biochar has been shown to have promise in reducing inorganic-N leaching [8], N_2O emissions [9], and ammonia volatilisation [10], while also increasing biological nitrogen fixation [11]. This review focuses on the impacts of biochar on soil N dynamics, in particular the literature since 2010, and recommends future directions for research.

2. Mitigation of Nitrogen Leaching Using Biochar

Several mechanisms have been proposed to explain the apparent retention of N in biochar-amended soils and the reduction of N leaching. These include adsorption of NH_3 or organic-N onto biochar, cation or anion exchange reactions, and enhanced immobilisation of N as a consequence of labile C addition in the biochar. Recent research on these mechanisms is considered below.

2.1. Nitrate Adsorption and Leaching

Recent research has clarified the potential role of biochars with respect to NO_3^- adsorption. Yao *et al.* [12] evaluated 13 biochar materials (sugarcane bagasse, peanut hull, Brazilian pepperwood, and bamboo that had been slowly pyrolysed at 300, 450 or 600 °C, and a hydrochar) to determine their potential to remove NO_3^- from solution. It was found that four high temperature (600 °C) biochars (bagasse, bamboo, peanut hull, and Brazilian pepperwood) were able to remove between 0.12% to 3.7% of NO_3^- (0.02–0.64 mg NO_3^- per g of biochar) from a solution (0.1 g:50 mL of 34.4 mg L^{-1} NO_3^-) with variation in removal due to species of feedstock used. As Yao *et al.* [12] point out, the ability of the higher temperature biochars to remove NO_3^- is consistent with the earlier findings of Mizuta *et al.* [13] who found that bamboo biochar manufactured at 900 °C had a high NO_3^- adsorption capacity. Kameyama *et al.* [14] performed a very informative study using sugarcane bagasse, where they determined NO_3^- adsorption properties of bagasse biochar manufactured at five pyrolysis temperatures (400–800 °C). Significant NO_3^- adsorption occurred at pyrolysis temperatures ≥700 °C. At high pyrolysis temperatures the biochars had high pH (8.7–9.8) and Kameyama *et al.* [14] reasoned that the adsorption of NO_3^- was a result of base functional groups and not a result of physical adsorption since surface area and micropore volumes followed different trends when compared to observed NO_3^- adsorption. Similarly, Dempster *et al.* [15] also showed that a *Eucalyptus* sp. biochar (600 °C) could adsorb NO_3^- when placed in an ammonium nitrate (NH_4NO_3) solution (10 g:100 mL), with up to 80% adsorbed after 24 h when the NO_3^--N concentration was 2.5−5 mg NO_3^--N L^{-1} (0.02–0.04 mg NO_3-N per g biochar), decreasing to 38% at 50 mg NO_3^--N L^{-1} although the adsorbtion rate had increased to 0.19 mg NO_3-N per g biochar.

Based on this increasing body of literature, for a biochar to have any NO_3^- adsorption potential, the pyrolysis process needs to occur at a temperature of at least 600 °C. Clearly there is also a feedstock effect on NO_3^- adsorption potentials and more research is needed to better understand exactly how feedstock characteristics determine NO_3^- adsorption potentials given that high pyrolysis temperatures are deemed a prerequisite.

But what are the practical implications of adding such a NO_3^- retentive biochar to a soil when it comes to reducing NO_3^- leaching? Yao *et al.* [12] tested the significance of this NO_3^- retention mechanism, with respect to NO_3^- leaching, using two biochars with good NO_3^- retention properties (peanut hull and Brazilian pepperwood biochars made at 600 °C). These were incorporated (2% by weight) into a sandy soil, in columns, and a nutrient solution was applied (34.4, 10.0, and 30.8 mg L^{-1} of NO_3^-, NH_4^+, and phosphate (PO_4^{3-}), respectively). After flushing the columns with 4 pore volumes of water over 4 days it was found that the biochar materials reduced NO_3^- leaching by 34% [12]. When the *Eucalyptus* sp. biochar, found by Dempster *et al.* [15] to adsorb NO_3^-, was placed in lysimeter pots (25 t ha^{-1}) holding a sandy soil, fertilised (($NH_4)_2SO_4$; 40 kg N ha^{-1}) and irrigated over 21 days, the cumulative NO_3^- leached was reduced by 25% when compared with a control treatment. Thus NO_3^- adsorbing biochars can reduce NO_3^- leaching. Differences in the magnitude of the reduced NO_3^- leaching between laboratory and column studies may possibly be explained by the fact that column studies contain soil, with rates of biochar and NO_3^- concentrations that differ from the laboratory studies, and they have the potential for other loss pathways such as immobilisation and denitrification of NO_3^- to occur.

However, other important issues with respect to the potential for biochar to reduce NO_3^- leaching were also raised in the study of Kameyama *et al.* [14]. They questioned if adding biochar could significantly change a soil's physical characteristics with respect to hydraulic conductivity, and if so, could this affect the rate of NO_3^- leaching, negating or amplifying any effect of NO_3^- adsorption? And they also asked how permanent the adsorption of NO_3^- on to biochar was when incorporated in a soil? The answer to the first question will be influenced by the biochars physico-chemical characteristics such as pore size distribution, hydrophobicity and the rate of biochar addition. Kameyama *et al.* [14] found that when a bagasse biochar (800 °C) was applied at a rate ≥5% by weight to a calcaric dark red soil the saturated hydraulic conductivity increased, with the effect likely to also be a function of the meso- and micro-pore fractions in the soil and biochar. Thus, amending soil with biochar could potentially increase hydraulic conductivity, or preferential flow around larger particles, and thus lead to enhanced leaching of NO_3^-. On the other hand, amendment of soil with biochar has been shown to increase water retention capacity [15–17] and this may decrease leaching of NO_3^-. Ideally, the water-holding properties of the soil should be known, and a biochar of suitable pore size distribution should be selected and applied at a rate not likely to enhance leaching. Kameyama *et al.* [14] also examined the permanence of adsorbed NO_3^- by measuring NO_3^- transport in soil columns amended with the same NO_3^- adsorbing bagasse biochar (0%, 5%, or 10% by weight). They found that when a 20 mg N L^{-1} solution of KNO_3 was applied to the soil columns the maximum concentration of NO_3^- in the effluent was ~5% less than in unamended soil, however, cumulative discharge of NO_3^- was similar in all treatments [14]. The authors therefore concluded that NO_3^- was only weakly adsorbed onto biochar, that it could be desorbed by water infiltration, and that the net result may be an increased residence time for NO_3^- in the soil. This in turn may allow a greater opportunity for plant uptake of NO_3^-. Thus, *in situ*, the role of a biochar in reducing NO_3^- leaching will obviously depend on its NO_3^- adsorption capacity (initial pyrolysis temperature and feedstock) and if anion or cation exchange capacities evolve with time in the soil, the biochar rate applied, the resulting rate of NO_3^- adsorption, the N loading of the given ecosystem, the resulting soil hydraulic characteristics, precipitation/irrigation events, soil type, plant and microbial N demand and potential biochar effects on these (e.g., changes in nitrification rates). Further *in situ* studies need to examine NO_3^- leaching and biochar effects, e.g., in large lysimeter experiments over long durations, with both plants and standard fertilizer practices included. Since biochar effects on NO_3^- leaching may only develop over time. For example, Ventura *et al.* [18] observed a 75% reduction in in the second year of a study in an apple orchard in Northern Italy. In addition, some consideration should be given to the potential impacts of biochar particle size on NO_3^- retention and loss from soil, and indeed on the overall effects of biochar amendment on soil N dynamics.

2.2. Immobilisation or NH₃ Volatilisation as Leaching Retardation Mechanisms

Reduced leaching of N has also been observed in the absence of increased ion –retention by biochars. For example, Ippolito *et al.* [19] placed two switchgrass (*Panicum virgatum* L.) biochars, manufactured at either 250 or 500 °C in an Aridosol and determined cumulative NO_3^- leaching 34, 62, 92, and 127 days after the experimental start. Ippolito *et al.* [19] found that less NO_3^- leached when the lowest temperature biochar was present. This was explained by the presence of more easily degradable C compounds at the lowest temperature and greater N immobilisation, thus reducing NO_3^- leaching. A 2 M

KCl extract of the incubated biochar-soil matrix also supported this reasoning with less NO_3^- present in the low temperature biochar-treated soils [19]. However, denitrification was not measured and the lower NO_3^- leaching could just as easily be attributed to denitrification loss of NO_3^- being stimulated by the additional C. Schomberg *et al.* [20], incorporated five biochar materials into soil and after a 127 day incubation reduced N leaching was observed. The rationale supplied for this result was not greater N retention, but rather the promotion of NH_3 losses by the biochar as a consequence of the elevated soil pH resulting from biochar addition [20]. Pollution swapping (e.g., reduced NO_3^- leaching in exchange for greater NH_3 losses) does not solve the problem of N leakage from agricultural systems. It is important to examine the long-term net outcome of biochar in reducing leaching via N immobilisation, changes in nitrification, N sorption onto biochar or promotion of NH_3 volatilisation. Immobilisation of N may only occur for a short term following biochar application, and may lead to a delay in leaching of N. One relatively long-term result to date has shown reduced N leaching in an orchard system [18].

2.3. Ammonium Adsorption and Leaching

Biochar adsorption of NH_4^+ has been examined in several studies. Yao *et al.* [12] found that 9 of the 13 biochars tested in their sorption experiment could remove NH_4^+ from solution (0.1 g biochar in 50 mL of 10 mg NH_4^+ L^{-1}), with removal rates ranging from 1.8%–15.7% (0.05 to 0.79 mg NH_4^+ per g biochar), varying widely with feedstock and pyrolysis temperature, but with no pyrolysis temperature trend. The *Eucalypt* sp. biochar (600 °C) used by Dempster *et al.* [15] adsorbed 75% of the NH_4^+ in solution (10 g biochar in 100 mL) at 2.5 and 5 mg NH_4^+-N L^{-1} (0.02–0.04 mg NH_4^+-N per g biochar) but this was reduced to 54% at 50 mg NH_4^+-N L^{-1}, although the adsorbtion rate had increased to 0.25 mg NH_4^+-N per g biochar.

Placing NH_4^+ retentive biochars into soil has also been shown to affect the leaching of NH_4^+. Ding *et al.* [21] found a bamboo charcoal (pyrolysed at 600 °C and added at 0.5% by weight to 0–10 cm depth) affected soil solution NH_4^+ concentrations at 20 cm depth when added at a rate of 400 kg N ha^{-1} to a sandy silt soil, but no differences were observed at 40 cm depth after 70 days. Dempster *et al.* [15] observed that when a biochar with cation exchange capacity (CEC) of ~10 $cmol_c$ kg^{-1} was added to a sandy soil (CEC of ~2 $cmol_c$ kg^{-1}) NH_4^+ leaching was reduced (15.0 to 12.9 mg pot^{-1}) 21 days following fertilisation ((NH_4)$_2$$SO_4$; 40 kg N ha^{-1}).

The rationale generally given for the adsorption of NH_4^+ onto biochar and the observed reductions in NH_4^+ leaching is the CEC of the biochar. The NH_4^+ retention studies noted above were performed on fresh biochar materials which have relatively low CEC [17,22,23]. *In situ*, cation retention increases with biochar age and depends on climatic conditions, [24,25]. Thus, the practical long-term significance of freshly made biochar in reducing NH_4^+ leaching remains to be tested. However, the short-term practical impact of incorporating a new biochar material into soil on the total (soil + biochar) CEC can be inferred if both the soil's CEC, and the biochar's CEC and application rate are known. For example, Jones *et al.* [26] found no effects of biochar (50 t ha^{-1}) on NH_4^+ adsorption in a three-year field trial where theoretical retention of NH_4^+ by biochar and soil were 3 and 142 kg N ha^{-1}, respectively. In sandy soils this biochar input may be significant in terms of CEC, but may also be insignificant [27], while for many soils that already contain higher levels of organic matter and clay the impact of biochar may be

inconsequential. Further studies need to report on the change in freshly incorporated biochar CEC values over time for biochars that have been placed *in situ.*

Ammonium contained onto biochar surfaces as a result of cation exchange should be readily removable with potassium chloride extraction. However, this was not the case when peanut hull biochar was exposed to NH_4^+ solutions, with $\leq 0.39\%$ of the total sorbed NH_4^+ released [28]. Although the exact mechanism for NH_4^+ retention was not identified it was suggested that physical entrapment of NH_4^+ in biochar pore structures may have been responsible [28]. Given that the NH_4^+ ion has a diameter of 286 pm [29] and there is wide range of pore sizes in biochar materials [30] this is entirely possible. Prost *et al.* [31] also found surface areas of biochars decreased during composting due to compost-derived materials clogging biochar pores with the biochar also absorbing leachate and nutrients. Thus it is also necessary to continue to advance our understanding of mechanisms responsible for the adsorption of N forms onto biochar surfaces and the effect of time on these processes.

2.4. Dissolved Organic Nitrogen Retention and Leaching

Relatively few studies have examined dissolved organic-N (DON) leaching from soil [32,33], and fewer still have looked at the role of biochar on this. Dempster *et al.* [15] found that biochar had no effect on levels of DON leached from a sandy soil, which initially contained 18.8 mg N kg^{-1} in the 0–10 cm depth (actual values measured in treatments were not reported). However, DON mainly carries a net negative charge. Dempster *et al.* [15] therefore argued that this weakened the case for biochar reducing leaching via adsorption of NO_3^- (despite the fact that the biochar used was capable of NO_3^- adsorption). Thus the authors went on to propose that the observed reductions in NO_3^- leaching were the result of reduced rates of nitrification rather than NO_3^- adsorption, since the biochar was also known to inhibit nitrification [34]. This rationale concurs with the results of Kameyama *et al.* [14], who found no differences in cumulative NO_3^- leaching from a sandy soil over a shorter experimental period when treating a soil with a biochar known to be NO_3^- retentive.

3. Plant Nitrogen Response to Biochar Amendment

Biochar addition to soils does not always result in consistent yield increases (e.g., [35]) and plant responses to biochar addition have been reported to vary considerably. Biochar effects on yield were reviewed by Spokas *et al.* [4] and occur as a result of changes in soil nutrition, water holding capacity and microbial activity, with results varying due to soil type. Positive yield increases were generally associated with hardwood biochars and chars possessing plant nutrients, such as high N content poultry manure biochars [4].

Prendergast-Miller *et al.* [36] also found biochar (charcoal fines from mixed deciduous hardwood, pH 9.3) produced elevated NO_3^- concentrations in the rhizosphere of wheat seedlings, increased wheat root length and decreased root N uptake but with no effect on plant biomass or plant N content. More recently, O'Toole *et al.* [37] reported on a pot experiment growing ryegrass under 4 rates of N fertiliser with 2 rates of a wheat-straw biochar (500–600 °C) and found foliar N concentrations were reduced, possibly due to adsorption or immobilisation of N being stimulated with biochar addition, but with unaffected yields. Kammann *et al.* [16] also observed reductions in foliar N concentrations in a pot trial

with a relatively nutrient-rich peanut hull biochar, but in this case the reduction likely resulted from increased N use efficiency since the authors reported biomass increases of up to 60%.

Longer term *in situ* studies on agronomic effects of biochar, and N cycling in particular, are beginning to appear. Jones *et al.* [26] performed a three-year field trial to examine the agronomic effect of biochar (various tree species at 450 °C; 0, 25 and 50 t/ha) where maize was sown in the first year followed by a forage grass (*Dactylis glomerata*) in years 2 and 3. Maize yield and agronomic performance, along with nutrient content, were unaffected by biochar in the first year. However, subsequent grass crops in the second and third years resulted in greater foliar uptake of N as a result of biochar addition, which was speculated to be due to the biochar interaction with crop rooting depths and soil water. In another 3-year study Unger and Killorn [38] found no differences in maize grain or biomass yields due to biochar addition and no interaction with urea fertiliser. Lentz *et al.* [39] found a hardwood biochar (500 °C) had no effect on maize silage N content or yield after 1 year but decreased silage total-N, yield and cumulative uptake of total-N in year 2, which was reasoned to be due to lower soil mineralization in year 2. Application of a nutrient rich wheat-straw biochar (20 and 40 t ha^{-1}) to a calcareous loamy soil resulted in no changes in soil mineral N concentrations but nevertheless there was a significant maize yield increase, accompanied by increased total soil N content and agronomic N-use efficiency during a 4-month field trial [40]. Uzoma *et al.* [41] conducted a glasshouse experiment where a biochar manufactured from cow manure (500 °C) was applied at increasing rates to a sandy soil, subsequently planted with maize. Both maize yield and N uptake increased with increasing biochar rate, indicating N release from the biochar. Thus, the latter study further supports the conclusion of Spokas *et al.* [4].

Only a few biochar studies have examined, in detail, the actual mechanism for enhanced N uptake by biomass, following biochar addition. One superlative study that does provide a mechanism to explain the contribution of high N content manure biochars to enhanced plant available N showed that low temperature biochar materials made from manures and biosolids contain hydrolysable organic N forms such as amino acids [42]. The hydrolysable N fractions in the biochars decreased as pyrolysis temperatures increased. These results were explained by either N becoming progressively embodied in the increased formation of aromatic and heterocyclic structures [43] or the degradation of labile N forms (e.g., proteins), as clearly shown in the derivative thermogravimetric profiles, as the pyrolysis temperatures increased. Given the fact that plants can assimilate organic N compounds [44], and that mineralization of organic N also provides inorganic-N, it can be inferred to be the cause of increased yields seen under manure derived biochars. Noguera *et al.* [45] examined the effect of a low temperature (350 °C) *Eucalyptus sp.* biochar and earthworms on rice plant growth and associated plant physiological and gene regulation processes in the leaves, finding that biochar increased protein catabolism (proteolytic activity) as well as anabolism via enhanced gene expression of some (but not all) genes associated with the leaf protein turnover, respectively. Given these results and those of Wang *et al.* [42] it would be interesting to identify the available organic-N content of the biochar used by Neurea *et al.* [45] and to see if bioavailable organic-N forms contributed to the enhanced proteolytic activity. A ^{15}N study by de la Rosa and Knicker [46] also examined biochar-^{15}N bioavailability, and confirmed the release of biochar-^{15}N to the soil. After 72 days incubation in an arable soil 10% of the biochar-^{15}N, manufactured from *Lolium perenne* at 350 °C, was found to be taken up by the new grass biomass, clearly showing that biochar N can be decomposed, with subsequent metabolites utilised by

microbes and plants. Similarly, Schouten *et al.* [47] showed ^{15}N labelled biochar-N (pyrolysed digested slurry) was recovered by plants. In the short-term, immobilisation and mineralization may be affected by biochar addition to soil (see below) while effects on soil water availability, root architecture, plant eco-physiology, nutrient supply, microbial form and function may also be affected. Where biochar materials induce a liming effect it may be advisable to also run a lime treatment to assist in differentiating biochar induced soil physical *versus* soil pH effects. However, knowledge of the buffering capacity of both the soil and biochar may also be required. Both short and long-term studies are still needed to further evaluate biochar-N and its effects on agronomic performance. In particular further use of the ^{15}N stable isotope for this purpose is recommended.

4. Mitigation of Nitrous Oxide Emissions Using Biochar

To date, several studies have shown that the addition of biochar to soils can mitigate N_2O emissions *in situ* from soybean and grass ecosystems [48], following ruminant urine deposition [49], in wheat plots [50] and during laboratory or greenhouse incubations under various conditions [8,9,47,51–61] while other studies have found no differences or even increases in cumulative N_2O emissions after biochar addition [61–63].

In many studies where biochar has been shown to reduce N_2O fluxes, a number of mechanisms have been proposed based mainly on prior knowledge of the requirements of nitrifiers and denitrifiers. These include: (i) enhanced soil aeration (reduced soil moisture) inhibiting denitrification due to more oxygen being present; (ii) labile C in the biochar promoting complete denitrification *i.e.*, dinitrogen (N_2) formation; (iii) the elevated pH of the biochar creating an environment where N_2O reductase activity is enhanced thus promoting N_2 formation and higher N_2/N_2O ratios; and (iv) a reduction in the inorganic-N pool available for the nitrifiers and/or denitrifiers that produce N_2O, as a result of NH_4^+ and/or NO_3^- adsorption, greater plant growth, NH_3 volatilisation loss, or immobilisation of N. Increases in N_2O fluxes have been attributed to: (i) the release of biochar embodied-N or priming effects on SOM following biochar addition; (ii) biochar increasing soil water content and improving conditions for denitrification; and (iii) biochar providing inorganic-N and/or carbon substrate for microbes.

Many studies reporting biochar effects on N_2O emissions have lacked the rigorous experimental design needed to test the hypotheses proposed and interpret the results produced (e.g., N_2O source and fate) when investigating biochar effects on N_2O emissions. For example, Wang *et al.* [59] performed a 60 day aerobic incubation with paddy soils treated with rice husk biochar (350–500 °C) and N fertilizers finding that the cumulative emission of N_2O from N fertilizer was reduced when the biochar was present. However, no detailed examination of the cause was pursued with the rationale for lower N_2O emissions being some of the previously hypothesised theories as outlined above. More recently, Case *et al.* [53] hypothesised that observed reductions in N_2O emissions from a biochar-amended sandy soil (0%–10% biochar by weight) occurred due to enhanced aeration. Case *et al.* [53] maintained the biochar-amended soils at field capacity while measuring N_2O flux and inorganic-N over 168 h. Reduced N_2O fluxes observed at > 2% biochar were hypothesised to occur as a result of greater immobilisation of NO_3^-. However, no supporting measurements of the changes that may have resulted from biochar addition, in the pore size distribution or soil aeration were undertaken, to verify the hypothesis. Aquilar-Chavez *et al.* [51] investigated the effects of charcoal application on N_2O emissions, over 45

days, following the application of wastewater sludge to mesocosms cultivated with wheat. The net result was a decrease in N_2O emissions as charcoal rates increased but the experimental design and measurements provided inconclusive explanations and speculated on the rationales noted above.

However, other studies have included further measurement components in their experiments and have been more successful at describing mechanisms for reduced N_2O fluxes. Saarnio *et al.* [56] demonstrated a plant competition effect for N on N_2O fluxes, showing increased N_2O emissions when plants were absent with less effect from biochar when plants were present due to plant uptake competing with microbes for N. Kammann *et al.* [54] also performed detailed experiments that aimed to examine causes for the variation in N_2O fluxes in response to soil moisture. Kamman *et al.* [54] included wetting-drying cycles (assumed to stimulate microbial N_2O production), while measuring biomass yields and inorganic-N, observing that increased plant growth correlated with reduced N_2O emissions in the biochar treatments. A detailed examination of mechanisms for reduced N_2O emissions from biochar-amended soils was also carried out by Spokas *et al.* [64] who showed the origins and effects of ethylene on N_2O emissions and its role in reducing N_2O emissions. The effect that ethylene has on N_2O production from biochar amended soils needs to be investigated in more detail to further elucidate its role in biochar-N_2O dynamics.

While recent studies have provided an increased perspective on biochar induced decreases in N_2O fluxes further experiments are required to further elucidate the mechanism(s) responsible. The use of ^{15}N stable isotopes can provide insight into the source(s) of the N_2O-N, the reduction of N_2O to N_2, and associated N dynamics of other organic and inorganic-N pools in both the biochar and soil [46,47,49,65,66]. The use of ^{15}N enhances our understanding of biochar N dynamics, N_2O emissions and facilitates modelling [67]. Detailed studies examining the effects of biochar on soil physical conditions and the effect on N_2O emissions where both are measured simultaneously are overdue. We need to know how biochar rates and forms specifically affect gas diffusivities, soil moisture contents and water movement under given conditions. Studies are required that concurrently measure both the soil physical and chemical parameters, inorganic-N species and N_2O and N_2 fluxes following biochar incorporation into soil. Similarly, every opportunity should be taken to assess changes in microbial community form and function to elucidate biochar effects on N_2O emissions. For example, Yoo and Kang [61] attributed an increase in N_2O emissions, after biochar application, in a rice paddy field to abundant pre-existing denitrifiers.

Ultimately the magnitude and duration of any N_2O flux following biochar incorporation into soil is the net result of soil and biochar N availability, soil fertility and moisture, climate, and competition for available N between microbes and plants. While some of the studies measuring N_2O are relatively long-term in nature for incubation experiments (e.g., Kammann *et al.* [54]) they are relatively short when compared to the long term (e.g., 2–3 years) *in situ* experiments now beginning to emerge in the literature. Given that short-term initial effects on N pool dynamics, observed in short term field studies and lab incubations, were not persistent in these longer term trials [26] it might be argued that there will not be persistent changes in N_2O dynamics as a result of initial soil-biochar N dynamics. However, in rice paddies studies in Southern China (summarized by Liu *et al.* [68]) it was shown that N_2O reductions with biochar application rates of 20 and 40 t ha^{-1} persisted beyond the first cropping season. Thus other mechanisms involving plant-microbe interactions, denitrifier gene expression or bacterial-to-fungal ratios may become more important over time in biochar-amended soils. Therefore, the effects of biochar

on soil physical properties, microbial communities and microbial gene expression on N_2O emissions need to be evaluated in the long-term *in situ*. Sampling methods must be of sufficient quality and frequency that rigorous comparisons of seasonal N_2O emissions can be made. There is great scope here for employing automated chamber methodologies. Investigation of old charcoal-rich soils such as Terra preta or charcoal-kiln sites and comparisons with surrounding charcoal-free soils may offer insights into the long-term changes in N cycling, and N_2O emissions associated with biochar application to soils. The long-term measurements need to be made during periods of changing N inputs (e.g., regular fertiliser application) in particular to determine biochar's long-term *in situ* role in mitigating N_2O fluxes.

5. Impacts of Biochar on Nitrogen Mineralization, Immobilisation and Nitrification

Mineralization and immobilisation rates in the soil are a function of the C and N pools available to microorganisms. Typically as C:N ratios increase immobilisation of N occurs. Adding biochar to the soil adds another dimension to both the C and N pools. Addition of biochar to soils has been shown to result in slower mineralisation of the biochar materials than the uncharred biomass [69], decrease net N mineralisation [34,50], cause increased net N mineralisation [50], have no effect on mineralization [20,70], and to have little effect on DON [15]. Furthermore, biochar addition has been shown to have no effect on soil-N immobilisation [71] or promote immobilisation [72].

The N embodied in plant derived biochar has previously been assumed to be of low availability due to it being in heterocyclic structures [73] but a ^{15}N study by de la Rosa and Knicker [46] shows that biochar embodied N can be utilised by biomass. Wang *et al.* [42] showed that acid hydrolysable N (amino acids, amino sugars and ammonia) embodied in manure-derived biochars decreased as pyrolysis temperature increased (250–550 °C) with a strong correlation between this acid hydrolysable N and CO_2 respiration, following biochar addition to soil, indicating that the total acid hydrolysable N represented the available N in the biochar.

Fresh low temperature biochars can contain significant amounts of labile C that can be readily utilised by soil microorganisms [74] which, when delivered to the soil may, in the short term, result in the microbially available soil N becoming immobilised. This was demonstrated by Bruun *et al.* [72] who produced biochar from wheat straw using slow or fast pyrolysis. Fast pyrolysis resulted in a biochar that still contained a labile, un-pyrolysed carbohydrate fraction. When the "slow" and "fast" biochars were placed in the soil the "fast" biochar resulted in immobilisation of mineral N while the "slow" biochar resulted in net N mineralization over a 65 day period. Because addition of biochar to soil involves multiple N pools, tracer studies are needed to elucidate the gross N immobilisation and mineralization rates. Nelissen *et al.* [67] used ^{15}N labelling-tracing to examine and model gross N dynamics following biochar (ensilaged maize pyrolysed at 350 °C or 550 °C, C:N = 43 and 49, respectively) addition (10 g kg^{-1} soil) to a loamy sand (C:N = 9). The authors found that gross N mineralization was stimulated by biochar addition, with most of the N coming from a more recalcitrant fraction, whereas mineralization in the control was mainly from a labile N pool. This was reasoned to be the result of biochar having a priming effect, *i.e.* stimulating microorgansims to mineralize recalcitrant SOM [75,76]. This concurs with the results of Schomberg *et al.* [20] who also found differences in a recalcitrant N fraction when incubating several different biochars over 127 days. Increased turnover of SOM can result from the addition of biochar to soil as a result of priming effects, most likely induced by labile

components of the biochar, and this may increase with increasing soil pH and decreasing pyrolysis temperature [77].

Thus, while biochar may contain bioavailable N forms, its mineralization and release will be dependent on how recalcitrant the biochar and soil N and C pools are, on the soil and biochar C:N ratio, the relative magnitude of the soil and biochar C and N pools, and the studied ecosystems. Further tracer studies with labelled biochar and/or SOM are required to fully understand the effects of various biochar forms on immobilisation and mineralization and to determine if the effects observed are of relatively short duration or more long-term. Long-term modelling of biochar and soil N pools, and processes, over the long-term will be required as previously demonstrated for soil C [78].

Biochar application may have no effect on gross or net nitrification rates in agricultural soils [50,71], but biochar application has been shown to promote net nitrification in natural ecosystems due to the liming effects of biochar or the removal of inhibiting substances such as polyphenols or tannins [50,79,80]. Volatile organic compounds associated with a biochar or ethylene production can decrease nitrification activity [62,64]. In agricultural ecosystems, the lack of positive effects from adding biochar on net nitrification rates may be because agricultural ecosystems are already characterised by high nitrification rates [80]. The first and apparently only study to date to record biochar stimulation of gross nitrification in an agricultural soil [67] showed that it was due to increased mineralization of NH_4^+ from the recalcitrant soil N pool, where the flux was larger than the simultaneous incorporation of NH_4^+ into the labile soil N pool. Thus, the authors reasoned that the increase in gross nitrification was mainly due to an increase in the NH_4^+ substrate supply. Studies such as that of Nelissen *et al.* [67], using a stable isotope modelling approach, provide detailed information on not just N pool sizes but also the gross N dynamics. These types of studies now need to be applied over longer terms.

6. Biochar and Soil Biota

The known effects of biochar addition to soils on soil biota were extensively covered by Lehmann *et al.* [81] who concluded that there was limited knowledge on the shifts in microbial consortia and that our knowledge of biochar effects in soil on soil biota is limited. This is even more so when confining the discussion to N. Since the review by Lehmann *et al.* [81] the study of Jones *et al.* [26] has measured higher growth rates of bacteria and fungi after incorporating biochar but this effect was not observed after storage of soil in the laboratory leading the authors to speculate that the effect was the result of an indirect rhizosphere effect. While Dempster *et al.* [34] found that the addition of a *Eucalypt* biochar at 25 t ha^{-1} altered the ammonia oxidiser community structure when it was present with inorganic-N, with lower nitrification rates ensuing. The latter was thought to be due to a negative priming effect on the soil organic matter resulting in lower NH_4^+ concentrations, since the potential for NO_3^- adsorption to remove NO_3^- was minimal when biochar was mixed with soil. Anderson *et al.* [75] examined biochar induced soil microbial community changes from soil where biochar had been incorporated during pasture renewal, and found that compared to control soils the abundance of the bacterial families *Bradyrhizobiaceae* and *Hyphomicrobiaceae* increased. During anaerobic phases members of these families can utilise NO_3^-, N_2 and NH_3 and they are capable of N_2 fixation and denitrification. This result may explain the enhanced N_2 fixation previously observed in bean crops with biochar present [11]. Despite a meta-analysis showing root nodulation increases with biochar

addition [82], assumed to be due to soil pH and P availability became more suitable for efficient N fixation, there remains a dearth of information on both the long- and short- term effects of biochar on N_2 fixation. Anderson *et al.* [75] concluded that adding biochar to the soil potentially increased microbial N cycling, especially the abundance of those organisms that may decrease N_2O fluxes and NH_4^+ concentrations. Conversely, Yoo and Kang [61] suggested the higher N_2O fluxes observed in the presence of swine manure-derived biochar in paddy soils was partially a consequence of higher denitrifier abundance.

Noguera *et al.* [83] hypothesised that earthworms and biochar would have a synergistic effect on nutrient availability and plant growth. However, while differences in mineral N were observed with treatments these were soil type dependant and they found few interactions between earthworms and biochar, and no interaction with respect to mineral N, possibly as a result of the short term nature of the mesocosm study. The study by Augustenborg *et al.* [52] found biochar reduced earthworm-induced N_2O fluxes although the mechanisms for this were not clear. Thus, the systematic and rigorous experimentation, called for by Lehmann *et al.* [81], to assess biochar-induced effects on soil biota with regard to soil N cycling is still needed.

7. Biochar as a Carrier for Nitrogen Fertiliser

Besides the release of N intrinsically embodied in the biochar ([42,46,47] there have been attempts to further enhance the delivery of N using biochar by adding nutrients to the biochar prior to soil incorporation. For example, Sarkhot *et al.* [84] mixed biochar with filtered liquid dairy manure, by shaking the mixture for 24 h and then oven drying the biochar, which increased the biochar's N content by 8.3%. When the unamended and N enriched biochars were added to the soil in an 8 week incubation experiment, reductions in net nitrification were 68% and 75%, respectively, while net ammonification rates were reduced by 221% and 229%, respectively. However, enriching biochar with N did not alter the N_2O flux, which averaged a 26% reduction in the biochar treatments [84]. These results were interpreted as being due to adsorption processes rather than enhanced immobilisation, since CO_2 fluxes were also lower under biochar treatments. Sarkhot *et al.* [84] thus concluded that N enriched biochar could be used as a slow release N fertilizer.

Adsorption of NH_3 onto black carbon (defined as thermal-chemical by-products, encompassing graphite's to biochars [85] has been previously recognized [86]. Mechanisms responsible for NH_3 adsorption have been reviewed [87,88] and discussed by Spokas *et al.* [85]. As a result of NH_3 adsorption amides and amines are formed on the black carbon surface [89]. Adsorption of NH_3 by black carbon has been shown to be correlated to the quantity of surface acidic groups on the black carbon (Spokas *et al.* [85] and references therein). The potential for biochar to be used as an N fertilizer, by increasing its N content via NH_3 adsorption, was demonstrated in a study by Taghizadeh-Toosi *et al.* [65] who exposed biochar materials to ^{15}N-labelled NH_3 which became enriched in [15]N. The increase in biochar-N and its ^{15}N enrichment was higher in the more acidic biochars. Twenty five days after the application of these ^{15}N-enriched biochar materials to soil, plant biomass had increased up to 3-fold (non-labeled biochar treatments showed no differences from the controls in terms of biomass yield) and there was transfer of the ^{15}N from the biochar to the soil (2.5%–10.6% [15]N recovery) and subsequent plant N uptake (10.9%–26.1% [15]N recovery). Taghizadeh-Toosi *et al.* [66] then showed that

NH$_3$ generated in the soil from ^{15}N-labelled ruminant urine patches, that are dominated by urea, could also be captured by biochar present in the soil, which effectively acted as a N "sponge" subsequently delivering the ^{15}N to the soil and plant biomass when the biochar was transferred to non-urine treated soil.

The ability for biochar to act as a sink for NH$_3$ was further demonstrated by Doydora *et al.* [90] who acidified pine chip and peanut hull biochars (400 °C) with HCl and then applied the acidified biochars to soil and either surface applied or incorporated poultry litter, hypothesising that NH$_3$ volatilisation would be reduced. After 21 days incubation they found that NH$_3$ volatilisation from poultry litter decreased by 58%–63% and 56%–60% for surface applied and incorporated poultry litters, respectively. Notably the amount of leached inorganic-N was higher due to the retention of non-volatilised N in the soil where acidified biochar had been used. However, plants were not present in this incubation and it can be expected that in a field trial situation poultry litter applications (with acidified biochar) timed to enhance plant N uptake would offset synthetic fertiliser inputs. The role of NH$_3$ uptake, *i.e.*, reduced NH$_3$ volatilization and loss, has also been postulated or observed in composting experiments [10,91,92]. Clearly there is role for biochar in capturing NH$_3$ and for this captured N to be released upon plant demand. However, much remains to be examined. Is all the NH$_3$ adsorbed on the biochar surface released, or plant-available? What is the repeatability of the NH$_3$ adsorption effect? If NH$_3$ adsorbed onto biochar as an amide or amine, for example, is released, can the resulting biochar surface immediately take up further NH$_3$ or is a period of surface restoration required? How will soil moisture conditions affect NH$_3$ uptake? Results from long term field trials are needed to improve our understanding of biochar as a slow-release N fertilizer after N loading or N capture, subsequent N dynamics, and its effect on N$_2$O emissions and N$_2$O-emission-to-yield ratios.

8. Conclusions

The increasing body of biochar literature provides further evidence that biochar affects N cycling in soils and that it offers potential options for tightening the N cycle in agricultural ecosystems. Much of the biochar-soil research to date, with respect to N cycling, is fragmented with results as diverse as the types of biochar used and the biochar-soil combinations tested. However, trends do emerge. It is apparent biochar can take up N via ion exchange, remove NH$_3$ via adsorption, and stimulate immobilisation with flow on consequences for NO$_3^-$ leaching. Biochar can also stimulate mineralization, supply N embodied in the biochar to biomass, and reduce N$_2$O emissions. Future research efforts need to continue the assessment of biochars role in soil N cycling, but in a systematic way, making use of N isotopes where possible, so that mechanisms responsible for variations in N cycling and the potential mitigation tools are more fully understood and identified. In particular, there is a dearth of soil microbial studies and *in situ* studies examining the role of biochar and N cycling over the longer term. Furthermore, biochar N studies should also aim to elucidate the effects and potential risks, if any, that biochar may have in the future by investigating long-term analogs such as charcoal-rich soils, or aged *versus* fresh biochars. As an environmentally beneficial agricultural management tool, the most promising prospects for biochar, to date, are: (i) the reduction of NH$_3$ volatilisation via adsorption processes (urine patches, animal housing filters, composting); (ii) the development of slow release N fertilisers; and (iii) the reduction of N$_2$O emissions using fresh biochar additions to soils. However, even

these areas require further research since the use of biochar as a mitigation tool demands a deeper mechanistic understanding and at the same time an increase in our ability to predict net effects over time.

References

1. Lehmann, J.; Joseph, S. Biochar for environmental management: An introduction. In *Biochar for Environmental Management, Science and Technology*; Lehmann, J., Joseph, S., Eds.; Earthscan: London, UK, 2009; pp. 1–12.

2. Woolf, D.; Amonette, J.E.; Stree-Perrott, F.A.; Lehmann, J.; Joseph, S. Sustainable biochar to mitigate global climate change. *Nat. Commun.* **2010**, *1*, 56.

3. Sohi, S.P.; Krull, E.; Lopez-Capel, E.; Bol, R. A review of biochar and its use and function in soil. *Adv. Agron.* **2010**, *105*, 47–82.

4. Spokas, K.A.; Cantrell, K.B.; Novak, J.M.; Archer, D.A.; Ippolito, J.A.; Collins, H.P.; Boateng, A.A.; Lima, I.M.; Lamb, M.C.; McAloon, A.J.; *et al*. Biochar: A synthesis of its agronomic impact beyond carbon sequestration. *J. Environ. Qual.* **2012**, *41*, 973–989.

5. Clough, T.J.; Condron, L.M. Biochar and the nitrogen cycle. *J. Environ. Qual.* **2010**, *39*, 1218–1223.

6. Galloway, J.N.; Townsend, A.R.; Erisman, J.W.; Bekunda, M.; Cai, Z.; Freney, J.R.; Martinelli, L.A.; Seitzinger, S.P.; Sutton, M.A. Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. *Science* **2008**, *320*, 889–892.

7. Galloway, J.; Aber, J.D.; Erisman, J.W.; Seitzinger, S.P.; Howarth, R.W.; Cowling, E.B.; Cosby, J. The nitrogen cascade. *Biosci. Biotechnol. Biochem.* **2003**, *53*, 341–356.

8. Singh, B.P.; Hatton, B.J.; Singh, B.; Cowie, A.L.; Kathuria, A. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *J. Environ. Qual.* **2010**, *39*, 1224–1235.

9. Spokas, K.; Reicosky, D.C. Impacts of sixteen different biochars on soil greenhouse gas production. *Ann. Environ. Sci.* **2009**, *3*, 179–193.

10. Steiner, C.; Das, K.C.; Melear, N.; Lakly, D. Reducing nitrogen losses during poultry litter composting using biochar. *J. Environ. Qual.* **2010**, *39*, 1236–1242.

11. Rondon, M.A.; Lehmann, J.; Ramírez, J.; Hurtado, M. Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with bio-char additions. *Biol. Fertil. Soils* **2007**, *43*, 699–708.

12. Yao, Y.; Gao, B.; Zhang, M.; Inyang, M.; Zimmerman, A.R. Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere* **2012**, *89*, 1467–1471.

13. Mizuta, K.; Matsumoto, T.; Hatate, Y.; Nishihara, K.; Nakanishi, T. Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal. *Bioresour. Technol.* **2004**, *95*, 255–257.

14. Kameyama, K.; Miyamoto, T.; Shiono, T.; Shinogi, Y. Influence of sugarcane bagasse-derived biochar application on nitrate leaching in calcaric dark red soil. *J. Environ. Qual.* **2012**, *41*, 1131–1137.

15. Dempster, D.N.; Jones, D.L.; Murphy, D.M. Clay and biochar amendments decreased inorganic but not dissolved organic nitrogen leaching in soil. *Soil Res.* **2012**, *50*, 216–221.

16. Kammann, C.; Linsel, S.; Gößling, J.; H-W, K. Influence of biochar on drought tolerance of *Chenopodium quinoa* willd and on soil-plant relations. *Plant Soil* **2011**, *345*, 195–210.

17. Lehmann, J.; da Silva, J.P.; Steiner, C.; Nehls, T.; Zech, W.; Glaser, B. Nutrient availability and leaching in an archaeological anthrosol and a ferralsol of the central amazon basin: Fertilizer, manure and charcoal amendments. *Plant Soil* **2003**, *249*, 343–357.

18. Ventura, M.; Sorrentib, G.; Panzacchib, P.; Georgea, E.; Tonona, G. Biochar reduces short-term nitrate leaching from a horizon in an apple orchard. *J. Environ. Qual.* **2013**, *42*, 76–82.

19. Ippolito, J.A.; Novak, J.M.; Busscher, W.J.; Ahmedna, M.; Rehrah, D.; Watts, D.W. Switchgrass biochar affects two aridisols. *J. Environ. Qual.* **2012**, *41*, 1123–1130.

20. Schomberg, H.H.; Gaskin, J.W.; Harris, K.; Das, K.C.; Noval, J.M.; Busscher, W.J.; Watts, D.W.; Woodroof, R.H.; Lima, I.M.; Ahmedna, M.; *et al.* Influence of biochar on nitrogen fractions in a coastal plain soil. *J. Environ. Qual.* **2012**, *41*, 1087–1095.

21. Ding, Y.; Liu, Y.X.; Wu, W.X.; Shi, D.Z.; Yang, M.; Zhong, Z.K. Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. *Water Air Soil Pollut.* **2010**, *213*, 47–55.

22. Lehmann, J. Bio-energy in the black. *Front. Ecol. Environ.* **2007**, *5*, 381–387.

23. Liang, B.; Lehmann, J.; Solomon, D.; Kinyangi, J.; Grossman, J.; O'Neill, B.; Skjemstad, J.O.; Thies, J.; Luizão, F.J.; Petersen, J.; *et al.* Black carbon increases cation exchange capacity in soils. *Soil Sci. Soc. Am. J.* **2006**, *70*, 1719–1730.

24. Cheng, C.H.; Lehmann, J.; Thies, J.E.; Burton, A.J.; Engelhard, M. Oxidation of black carbon by biotic and abiotic processes. *Org. Geochem.* **2006**, *37*, 1477–1488.

25. Cheng, C.H.; Lehmann, J.; Thies, J.E.; Burton, S.D. Stability of black carbon in soils across a climatic gradient. *J. Geophys. Res.* **2008**, doi:10.1029/2007JG000642.

26. Jones, D.L.; Rousk, J.; Edwards-Jones, G.; DeLuca, T.H.; Murphy, D.V. Biochar-mediated changes in soil quality and plant growth in a three year field trial. *Soil Biol. Biochem.* **2012**, *45*, 113–124.

27. Schulz, H.; Glaser, B. Effects of biochar compared to organic and inorganic fertilizers on soil quality and plant growth in a greenhouse experiment. *J. Plant Nutr. Soil Sci.* **2012**, *175*, 410–422.

28. Saleh, M.E.; Mahmoud, A.H.; Rashad, M. Peanut biochar as a stable adsorbent for removing NH_4-N from wastewater: A preliminary study. *Adv. Environ. Biol.* **2012**, *6*, 2170–2176.

29. Späth, A.; König, B. Molecular recognition of organic ammonium ions in solution using synthetic receptors. *Beilstein J. Org. Chem.* **2010**, *6*, 1–111.

30. Downie, A.; Crosky, A.; Munroe, P. Physical properties of biochar. In *Biochar for Environmental Management. Science and Technology*; Lehmann, J., Joseph, S., Eds.; Earthscan: London, UK, 2009; pp. 13–32.

31. Prost, K.; Borchard, N.; Siemens, J.; KAutz, T.; Séquaris, J.-M.; Möller, A.; Amelung, W. Biochar affected by composting with farmyard manure. *J. Environ. Qual.* **2013**, *42*, 164–172.

32. Murphy, D.V.; Macdonald, A.J.; Stockdale, E.A.; Goulding, K.W.T.; Fortune, S.; Gaunt, J.L.; Poulton, P.R.; Wakefield, J.A.; Webster, C.P.; Wilmer, W.S. Soluble organic nitrogen in agricultural soils. *Biol. Fertil. Soils* **2000**, *30*, 374–387.

33. Van Kessel, C.; Clough, T.J.; Van Groenigen, J.W. Dissolved organic nitrogen: An overlooked pathway of nitrogen loss from agricultural systems? *J. Environ. Qual.* **2009**, *38*, 393–401.

34. Dempster, D.N.; Gleeson, D.B.; Solaiman, Z.M.; Jones, D.L.; Murphy, D.V. Decreased soil microbial biomass and nitrogen mineralisation with eucalyptus biochar addition to a coarse textured soil. *Plant Soil.* **2012**, *354*, 311–324.

35. Van Zwieten, L.; Kimber, S.; Morris, S.; Chan, K.Y.; Downie, A.; Rust, J.; Joseph, S.; Cowie, A. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant Soil.* **2010**, *327*, 235–246.

36. Prendergast-Miller, M.T.; Duvall, M.; Sohi, S.P. Localisation of nitrate in the rhizosphere of biochar-amended soils. *Soil Biol. Biochem.* **2011**, *43*, 2243–2246.

37. O'Toole, A.; Knoth de Zarruk, K.; Steffens, M.; Rasse, D.P. Characterization, stability, and plant effects of kiln-produced wheat straw biochar. *J. Environ. Qual.* **2012**, doi:10.2134/jeq2012.0163.

38. Unger, R.; Killorn, R. Effect of the application of biochar on selected soil chemical properties, corn grain, and biomass yields in Iowa. *Commun. Soil Sci. Plant Anal.* **2012**, *42*, 2441–2451.

39. Lentz, R.D.; Ippolito, J.A. Biochar and manure affect calcareous soil and corn silage nutrient concentrations and uptake. *J. Environ. Qual.* **2012**, *41*, 1033–1043.

40. Zhang, A.; Liu, Y.; Pan, G.; Hussain, Q.; Li, L.; Zheng, J.; Zhang, X. Effect of biochar amendment on maize yield and greenhouse gas emissions from a soil organic carbon poor calcareous loamy soil from central china plain. *Plant Soil* **2012**, *351*, 263–275.

41. Uzoma, K.C.; Inoue, M.; Andry, H.; Fujimaki, H.; Zahoor, A.; Nishihara, E. Effect of cow manure biochar on maize productivity under sandy soil condition. *Soil Use Manag.* **2011**, *27*, 205–212.

42. Wang, T.; Camps Arbestain, M.; Hedley, M.; Bishop, P. Chemical and bioassay characterisation of nitrogen availability in biochar produced from dairy manure and biosolids. *Org. Geochem.* **2012**, *51*, 45–54.

43. Almendrosa, G.; Knicker, H.; González-Vilac, F.J. Rearrangement of carbon and nitrogen forms in peat after progressive thermal oxidation as determined by solid-state ^{13}C- and ^{15}N-NMR spectroscopy. *Org. Geochem.* **2003**, *34*, 1559–1568.

44. Schimel, J.P.; Bennett, J. Nitrogen mineralization: Challenges of a changing paradigm. *Ecology* **2004**, *85*, 591–602.

45. Noguera, D.; Barot, S.; Laossi, K.-R.; Cardosso, J.; Lavelle, P.; de Carvalho, M.H.C. Biochar but not earthworms enhances rice growth through increased protein turnover. *Soil Biol. Biochem.* **2012**, *52*, 13–20.

46. De la Rosa, J.M.; Knicker, H. Bioavailability of n released from N-rich pyrogenic organic matter: An incubation study. *Soil Biol. Biochem.* **2011**, *43*, 2368–2373.

47. Schouten, S.; Van Groenigen, J.W.; Oenema, O.; Cayuela, M.L. Bioenergy from cattle manure? Implications of anaerobic digestion and subsequent pyrolysis for carbon and nitrogen dynamics in soil. *Glob. Change Biol. Bioenergy* **2012**, *4*, 751–760.

48. Rondon, M.; Ramirez, J.A.; Lehmann, J. Charcoal Additions Reduce Net Emissions of Greenhouse Gases to the Atmosphere. In Proceedings of the 3rd Symposium on Greenhouse Gases and Carbon Sequestration, Baltimore, MD, USA, 21–24 March 2005; p. 208.

49. Taghizadeh-Toosi, A.; Clough, T.J.; Condron, L.M.; Sherlock, R.R.; Anderson, C.R.; Craigie, R.A. Biochar incorporation into pasture soil suppresses *in situ* N$_2$O emissions from ruminant urine patches. *J. Environ. Qual.* **2011**, *40*, 468–476.

50. Castaldi, S.; Riondino, M.; Baronti, S.; Esposito, F.R.; Marzaioli, R.; Rutigliano, F.A. Impact of biochar application to a mediterranean wheat crop on soil microbial activity and greenhouse gas fluxes. *Chemosphere* **2012**, *85*, 1464–1471.

51. Aguilar-Chavez, A.; Diaz-Rojas, M.; Cardenas-Aquino, M.R.; Dendooven, L.; Luna-Guido, M. Greenhouse gas emissions from a wastewater sludge-amended soil cultivated with wheat (*Triticum* spp. L.) as affected by different application rates of charcoal. *Soil Biol. Biochem.* **2012**, *52*, 90–95.

52. Augustenborg, C.A.; Hepp, S.; Kamman, C.; Hagan, D.; Schmidt, O.; Muller, C. Biochar and earthworm effects on soil nitrous oxide and carbon dioxide emissions. *J. Environ. Qual.* **2012**, *41*, 1203–1209.

53. Case, S.D.C.; McNamara, N.P.; Reay, D.S.; Whitaker, J. The effect of biochar addition on N_2O and CO_2 emissions from a sandy loam soil—The role of soil aeration. *Soil Biol. Biochem.* **2012**, *51*, 125–134.

54. Kammann, C.; Ratering, S.; Eckhard, C.; Muller, C. Biochar and hydrochar effects on greenhouse gas (carbon dioxide, nitrous oxide, and methane) fluxes from soils. *J. Environ. Qual.* **2012**, *41*, 1052–1066.

55. Lho, C.F.B.V.; Cardoso, A.D.; Alves, B.J.R.; Novotny, E.H. Biochar and soil nitrous oxide emissions. *Pesquisa Agropecuaria Brasileira* **2012**, *47*, 722–725.

56. Saarnio, S.; Heimonen, K.; Kettunen, R. Biochar addition indirectly affects N_2O emissions via soil moisture and plant n uptake. *Soil Biol. Biochem.* **2012**, *58*, 99–106.

57. Spokas, K.A.; Koskinen, W.C.; Baker, J.M.; Reicosky, D.C. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a minnesota soil. *Chemosphere* **2009**, *77*, 574–581.

58. Van Zwieten, L.; Kimber, S.; Morris, S.; Downie, A.; Berger, E.; Rust, J.; Scheer, C. Influence of biochars on flux of N_2O and CO_2 from ferrosol. *Aust. J. Soil Res.* **2010**, *48*, 555–568.

59. Wang, J.; Zhang, M.; xiong, Z.Q.; Liu, P.R.; Pan, G. Effects of biochar addition on N_2O and CO_2 emissions from two paddy soils. *Biol. Fertil. Soils* **2011**, *47*, 887–896.

60. Yanai, Y.; Toyota, K.; Okazaki, M. Effects of charcoal addition on N_2O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. *Soil Sci. Plant Nutr.* **2007**, *53*, 181–188.

61. Yoo, G.; Kang, H.J. Effects of biochar addition on greenhouse gas emissions and microbial responses in a short-term laboratory experiment. *J. Environ. Qual.* **2012**, *41*, 1193–1202.

62. Clough, T.J.; Bertram, J.E.; Ray, J.L.; Condron, L.M.; O'Callaghan, M.; Sherlock, R.R.; Wells, S. Unweathered wood biochar impact on nitrous oxide emissions from a bovine-urine-amended pasture soil. *Soil Sci. Soc. Am. J.* **2010**, *74*, 852–860.

63. Scheer, C.; Grace, P.R.; Rowlings, D.W.; Kimber, S.; Van Zwieten, L. Effect of biochar amendment on the soil-atmosphere exchange of greenhouse gases from an intensive subtropical pasture in northern new south wales, australia. *Plant Soil* **2011**, *345*, 47–58.

64. Spokas, K.A.; Baker, J.M.; Reicosky, D.C. Ethylene: Potential key for biochar amendment impacts. *Plant Soil.* **2010**, *333*, 443–452.

65. Taghizadeh-Toosi, A.; Clough, T.J.; Sherlock, R.R.; Condron, L.M. Biochar adsorbed ammonia is bioavailable. *Plant Soil* **2012**, *350*, 57–69.

66. Taghizadeh-Toosi, A.; Clough, T.J.; Sherlock, R.R.; Condron, L.M. A wood based low-temperature biochar captures NH₃-N generated from ruminant urine-N, retaining its bioavailability. *Plant Soil.* **2012**, doi:10.1007/s11104-11011-11010-11109.

67. Nelissen, V.; Rütting, T.; Huygen, D.; Staelens, J.; Ruysschaerta, G.; Boeckx, P. Maize biochars accelerate short-term soil nitrogen dynamics in a loamy sand soil. *Soil Biol. Biochem.* **2012**, *55*, 20–27.

68. Liu, X.Y.; Qu, J.J.; Li, L.Q.; Zhang, A.F.; Zheng, J.F.; Zheng, J.W.; Pan, G.X. Can biochar amendment be an ecological engineering technology to depress N₂O emission in rice paddies?—A cross site field experiment from south china. *Ecol. Eng.* **2012**, *42*, 167–173.

69. Knoblauch, C.; Maarifat, A.A.; Pfeiffer, E.M.; Haefele, S.M. Degradability of black carbon and its impact on trace gas fluxes and carbon turnover in paddy soils. *Soil Biol. Biochem.* **2012**, *43*, 1768–1778.

70. Streubel, J.D.; Collins, H.P.; Garcia-Perez, M.; Tarara, J.; Granatstein, D.; Kruger, C.E. Influence of contrasting biochar types on five soils at increasing rates of application. **2011**, *75*, 1402–1413.

71. Cheng, Y.; Cai, Z.C.; Chang, S.X.; Wang, J.; Zhang, J.B. Wheat straw and its biochar have contrasting effects on inorganic N retention and N₂O production in a cultivated black chernozem. *Biol. Fertil. Soils* **2012**, *48*, 941–946.

72. Bruun, E.S.; Ambus, P.; Egsgaard, H.; Huggaard-Nielsen, H. Effects of slow and fast pyrolysis biochar on soil c and n dynamics. *Soil Biol. Biochem.* **2012**, *46*, 73–79.

73. Knicker, H.; Skjemstad, J.O. Nature of organic carbon and nitrogen in physically protected organic matter of some australian soils as revealed by solid-state ¹³C and ¹⁵N nmr spectroscopy. *Aust. J. Agric. Res.* **2000**, *23*, 329–341.

74. Smith, J.L.; Collins, H.P.; Bailey, V.L. The effect of young biochar on soil respiration. *Soil Biol. Biochem.* **2010**, *42*, 2345–2347.

75. Anderson, C.R.; Condron, L.M.; Clough, T.J.; Fiers, M.; Stewart, A.; Hill, R.A.; Sherlock, R.R. Biochar induced soil microbial community change: Implications for biogeochemical cycling of carbon, nitrogen and phosphorus. *Pedobiologia* **2011**, *54*, 309–320.

76. Zimmerman, A.R.; Gao, B.; Ahn, M. Poistive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biol. Biochem.* **2011**, *43*, 1169–1179.

77. Luo, Y.; Durenkamp, M.; De Nobili, M.; Lin, Q.; Brookes, P.C. Short term soil priming effects and the mineralisation of biochar following its incorporation to soils at different ph. *Soil Biol. Biochem.* **2011**, *43*, 2304–2314.

78. Woolf, D.; Lehmann, J. Modelling the long-term response to positive and negative priming of soil organic carbon by black carbon. *Biogeochemistry* **2012**, *111*, 83–95.

79. Ball, P.N.; MacKenzie, M.D.; DeLuca, T.H.; Holben, W.E. Wildfire and charcoal enhance nitrification and ammonium-oxidizing bacterial abundance in dry montane forest soils. *J. Environ. Qual.* **2010**, *39*, 1243–1253.

80. DeLuca, T.H.; MacKenzie, M.D.; Gundale, M.J.; Holben, W.E. Wildfire-produced charcoal directly influences nitrogen cycling in ponderosa pine forests. *Soil Sci. Soc. Am. J.* **2006**, *70*, 448–453.

81. Lehmann, J.; Rillig, M.C.; Thies, J.; Masiello, C.A.; Hockaday, W.C.; Crowley, D. Biochar effects on soil biota—A review. *Soil Biol. Biochem.* **2011**, *43*, 1812–1836.

82. Biederman, L.A.; Harpole, W.S. Biochar and its effects on plant productivity and nutrient cycling: A meta-analysis. *Glob. Change Biol. Bioenergy* **2013**, *5*, 202–214.

83. Noguera, D.; Rondon, M.; Laossi, K.-R.; Hoyos, V.; Lavelle, P.; de Carvalho, M.H.C.; Barot, S. Contrasted effect of biochar and earthworms on rice growth and resource allocation in different soils. *Soil Biol. Biochem.* **2010**, *42*, 1017–1027.

84. Sarkhot, D.V.; Berhe, A.A.; Ghezzehei, T.A. Impact of biochar enriched with dairy manure effluent on carbon and nitrogen dynamics. *J. Environ. Qual.* **2012**, *41*, 1107–1114.

85. Spokas, K.A.; Novak, J.M.; Venterea, R.T. Biochar's role as an alternative N-fertilizer: Ammonia capture. *Plant Soil* **2012**, *350*, 35–42.

86. Holmes, J.M.; Beebe, R.A. An example of desorption hysteresis at low relative pressures on a non-porous adsorbent: Ammonia on graphitized carbon black. *J. Phys. Chem.* **1957**, *61*, 1684–1686.

87. Jansen, R.J.J.; van Bekkum, H. Amination and ammoxidation of activated carbons. *Carbon* **1994**, *38*, 1507–1516.

88. Seredych, M.; Bandosz, T.J. Mechanism of ammonia retention on graphite oxides: Role of surface chemistry and structure. *J. Phys. Chem. C* **2007**, *111*, 15596–15604.

89. Petit, C.; Kante, K.; Bandosz, T.J. The role of sulfur-containing groups in ammonia retention on activated carbons. *Carbon* **2010**, *48*, 654–667.

90. Doydora, S.A.; Cabrera, M.L.; Das, K.C.; Gaskin, J.W.; Sonon, L.S.; Miller, W.P. Release of nitrogen and phosphorus from poultry litter amended with acidified biochar. *Int. J. Environ. Res. Public Health* **2011**, *8*, 1491–1502.

91. Hua, L.; Wu, W.; Liu, Y.; Mcbride, M.; Chen, Y. Reduction of nitrogen loss and Cu and Zn mobility during sludge composting with bamboo charcoal amendment. *Environ. Sci. Pollut. Res.* **2009**, *16*, 1–9.

92. Chen, Y.X.; Huang, X.D.; Z.Y., H.; Huang, X.; Hu, B.; Shi, D.Z.; Wu, W.X. Effects of bamboo charcoal and bamboo vinegar on nitrogen conservation and heavy metals immobility during pig manure composting. *Chemosphere* **2010**, *78*, 1177–1181.