Plant Soil (2012) 350:57–69
DOI 10.1007/s11104-011-0870-3

REGULAR ARTICLE

Biochar adsorbed ammonia is bioavailable

Arezoo Taghizadeh-Toosi · Tim J. Clough · Robert R. Sherlock · Leo M. Condron

Received: 30 March 2011 / Accepted: 13 June 2011 / Published online: 6 July 2011
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Abstract Biochar is produced as a by-product of the low temperature pyrolysis of biomass during bioenergy extraction and its incorporation into soil is of global interest as a potential carbon sequestration tool. Biochar influences soil nitrogen transformations and its capacity to take up ammonia is well recognized. Anthropogenic emissions of ammonia need to be mitigated due to negative environmental impacts and economic losses. Here we use an isotope of nitrogen to show that ammonia-N adsorbed by biochar is stable in ambient air, but readily bioavailable when placed in the soil. When biochars, containing adsorbed ^{15}N labelled ammonia, were incorporated into soil the ^{15}N recovery by roots averaged 6.8% but ranged from 26.1% to 10.9% in leaf tissue due to differing biochar properties with plant ^{15}N recovery greater when acidic biochars were used to capture ammonia. Recovery of ^{15}N as total soil nitrogen (organic+inorganic) ranged from 45% to 29% of ^{15}N applied. We provide a proof of concept for a synergistic mitigation option where anthropogenic ammonia emissions could be captured using biochar, and made bioavailable in soils, thus leading to nitrogen capture by crops, while simultaneously sequestering carbon in soils.

Keywords N stable isotope · Ammonia · Biochar · Nitrogen · Ryegrass

Responsible Editor: Johannes Lehmann.

Electronic supplementary material The online version of this article (doi:10.1007/s11104-011-0870-3) contains supplementary material, which is available to authorized users.

A. Taghizadeh-Toosi · T. J. Clough (✉) · R. R. Sherlock · L. M. Condron
Department of Soil and Physical Sciences, Faculty of Agriculture and Life Sciences, Lincoln University, PO Box 84, Lincoln 7647 Canterbury, New Zealand
e-mail: clought@lincoln.ac.nz

L. M. Condron
Bio-Protection Research Centre, Lincoln University, PO Box 84, Lincoln 7647 Canterbury, New Zealand

Introduction

Biochar is produced as a by product of the low temperature pyrolysis of biomass during bioenergy extraction (Lehmann et al. 2006) and its incorporation into soil is of global interest as a potential carbon sequestration tool and soil conditioner (Lehmann and Joseph 2009). It has been estimated that current net emissions of carbon dioxide, methane and nitrous oxide (N_2O) could be reduced by 12% per annum if biochar was used to sequester carbon into soil (Woolf et al. 2010). Biochar can influence soil nitrogen (N) transformations (Clough and Condron 2010) and has been shown to mitigate N_2O emissions in the field (Taghizadeh-Toosi et al. 2011) influence nitrification rates (Ball et al. 2010), alter biological N fixation rates (Rondon et al. 2007) and alter N leaching rates (Singh et al. 2010). It is well recognized that

adsorption of ammonia (NH_3) on to biochar can occur (Asada et al. 2002; Clough and Condron 2010). The observed reduction in the N_2O emissions from ruminant urine affected soil was attributed to adsorption of NH_3 reducing the N pool available for soil microbes (Taghizadeh-Toosi et al. 2011). Under industrial conditions the uptake of NH_3 by biochar has been shown to occur under conditions of ambient temperature and pressure in the presence of carbon dioxide (CO_2) and water (H_2O) (Day et al. 2005; Li et al. 2003) although the bioavailability of this N has not been assessed (Lehmann et al. 2006).

Volatilization of NH_3 from agricultural systems is the major anthropogenic source of atmospheric NH_3 and accounts for 10–30% of fertilizer N and animal excreta N (Bouwman et al. 2002). On average 32 Tg NH_3-N yr^{-1} is emitted from agricultural systems as a result of N fertilizer use (11 Tg NH_3-N yr^{-1}) and animal production (21 Tg NH_3-N yr^{-1}) (Beusen et al. 2008). Ammonia is an atmospheric pollutant that leads to the formation of ammonium containing particulates and aerosols (Forster et al. 2007). This particulate matter can affect human health and alter the transmission of terrestrial and atmospheric radiation (Forster et al. 2007; Miles 2009). Emitted NH_3 is ultimately deposited back on to land or water, contributing to indirect N_2O emissions (Mosier et al. 1998), acidification of water and biodiversity loss (Beusen et al. 2008). The current Intergovernmental Panel on Climate Change default methodology estimates that 1% of NH_3 that is redeposited onto land is re-emitted as N_2O (Mosier et al. 1998). This greenhouse gas has a global warming potential 298 times that of carbon dioxide (Forster et al. 2007) and has the unfortunate distinction of being the dominant ozone-depleting substance in the 21st century (Ravishankara et al. 2009). Mitigation options for reducing N losses by capturing NH_3 emissions and promoting better fertilizer use efficiency are urgently needed.

In agricultural operations, NH_3 forms under ambient temperature conditions where ever urea is hydrolysed, for example, in ruminant urine patches (Clough et al. 2003), animal slurries (Sherlock et al. 2002) and under urea fertiliser granules (Black et al. 1987). Ammonia may also be applied directly as anhydrous ammonia fertilizer. In poultry operations it forms following the microbial degradation of uric acid (Ritz et al. 2004). Thus there are point sources in various agricultural operations where biochar could be placed to uptake NH_3 if there was a demonstrable benefit in doing so. While biochar has the potential to reduce NH_3 emissions, no attention has been paid to the bioavailability of biochar-adsorbed NH_3.

To determine the bioavailability of the adsorbed NH_3 we exposed four biochar materials to NH_3 gas that was isotopically labelled with ^{15}N, and determined the stability of the biochar-NH_3 complex prior to placing ^{15}N-labelled and unlabelled biochar materials into a soil subsequently sown with a pasture grass. Here we demonstrate that biochar adsorbed NH_3-N can be recycled through the soil matrix to the growing plant, resulting in increased N uptake and yield.

Materials and methods

Soil and biochar characterisation

A Temuka silt loam soil (Hewitt 1998) of adequate fertility to grow ryegrass was sampled (0–7.5 cm depth) from a grazed pasture site (43° 38′ 58″ S, 172° 27′ 53″ E), air-dried, and sieved to 2 mm. It was characterised for: $pH_{(H2O)}$ using a 1:2, soil to water extraction ratio (Blakemore et al. 1987), while Olsen phosphorous (P) was determined using a 0.5 *M* $NaHCO_3$ extraction followed by molybdenum blue colorimetry (Blakemore et al. 1987). Phosphorus retention was determined using potassium dihydrogen phosphate extraction followed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Blakemore et al. 1987). The total base saturation and cation exchange capacity of the soil were determined following extraction with ammonium acetate and then ICP-OES analysis (Blakemore et al. 1987). Anaerobically mineralizable-N was determined using infrared spectroscopy (Black et al. 1965).

Four biochar materials, subsequently termed BC_1, BC_2, BC_3, and BC_4, were all manufactured from Monterey Pine (*Pinus radiata*) wood chips at pyrolysis temperatures of 300, 300, 350 and 500°C, respectively, and characterised for: cation exchange capacity using a 1 g biochar (sieved<2 mm): 50 ml silver thiourea extraction ratio and analysis by ICP-OES (Blakemore et al. 1987). Anion exchange capacity was determined using the compulsive exchange method with analyses performed using ICP-OES (Sparks 1996). Biochar $pH_{(H2O)}$ was

determined using a 1 g biochar: 10 ml water ratio (Blakemore et al. 1987) while $pH_{(CaCl2)}$ was determined using a 1 g biochar: 10 ml 0.01 *M* $CaCl_2$ ratio (Blakemore et al. 1987). Electrical conductivity of a 1 g biochar: 10 ml deionised water solution was measured using a electrical conductivity meter (Blakemore et al. 1987). The biochar particle density was measured using a conventional pycnometer (density bottle) and displacement with kerosene (Rasul et al. 1999) while bulk density was measured using mercury displacement (Pastor-Villegas et al. 2006). Surface acidity of biochar was determined with Boehm titration (Boehm 1994) and the specific surface area of the biochar was determined using the iodine absorption method (ASTM 2009). The total C and N contents of the biochar materials were determined by combustion using a LECO CNS-2000 Elemental Analyser (LECO, Australia). Biochar volatile organic compounds were determined by automated headspace solid-phase micro-extraction in conjunction with gas chromatography–mass spectrometry (Clough et al. 2010). Total elemental analysis of the biochar materials was performed using microwave digestion (Microwave Solvent Extraction Labstation (Ethos SEL, Italy) and ICP-OES analysis (Kovacs et al. 2000). Water extractable ions in the biochar materials were determined using the compulsive exchange method using ICP-OES (Sparks 1996). The complete list of elements analysed can be seen in supplementary Tables S1 and S2.

^{15}N enrichment of biochar and stability of the biochar adsorbed NH_3

Biochar materials were ^{15}N enriched by exposing them to ^{15}N enriched ammonia (NH_3), which was generated by reacting excess 0.1 *M* sodium hydroxide (NaOH) with a ^{15}N enriched ammonium sulphate solution (0.05 *M* $(NH_4)_2SO_4$) comprising 98.0 atom% $(^{15}NH_4)_2SO_4$ (Isotec, Miamisburg, Ohio) and natural abundance Analar® reagent grade $(NH_4)_2SO_4$, to produce a final ^{15}N enrichment of 5.36 atom%. Petri dishes containing sieved (< 2 mm) oven-dried (105° C) biochar (1.5 g) were placed in Mason jars (0.5 l) above the NaOH solution (55 ml). Gas-tight lids, fitted with septa, were put on to the jars prior to injecting 25 ml of the ^{15}N enriched $(NH_4)_2SO_4$ solution into the NaOH solution contained by the jars. Jars were left sealed for 1 week. No measure of aerobic status was made over this time since generation of NH_3 neither consumes oxygen or produces CO_2, and microbial activity on the biochar was considered negligible. After 1 week excess 0.1 *M* sulphuric acid was injected to neutralize the solution in the jars and to allow any remaining NH_3 gas to be absorbed by the acid solution. The jars were then left for a further 2 h. All the ^{15}N enriched biochar materials were stored in sealed glass vials prior to analysis. Both non-enriched (BC) and enriched (eBC) biochar materials were analysed for total N and ^{15}N enrichment 3 days after ^{15}N labelling using continuous flow isotope ratio mass spectrometry (CFIRMS; 20–20 Sercon Ltd). Biochar inorganic-N concentrations (NH_4^+-N and NO_3^--N) were determined using 2 *M* KCl extraction (biochar: solution ratio of 1 g: 25 ml) and a 1 h shake on an end-over-end shaker. Stability of the biochar adsorbed NH_3 in open air was assessed by placing the eBC_1 material in a fume cabinet, running at a laminar flow rate of 0.65 ms^{-1}, at room temperature, for 12 days. Subsamples of the eBC_1 biochar were taken every other day and analysed, using CFIRMS, for total N content and ^{15}N enrichment.

Plant availability of biochar adsorbed NH_3

Plant availability of the ^{15}N adsorbed onto the four biochar materials was assessed by adding biochar materials to the silt loam soil. To achieve this, ten treatments were replicated four times in a randomized complete block design. These treatments included: soil only, soil + perennial ryegrass (*Lolium perenne L.*), soil + unenriched biochar materials (BC_1 to BC_4) where all biochar treatments also had plants present, and soil + ^{15}N enriched biochar materials (eBC_1 to eBC_4) where again; all biochar treatments had plants present (Table 1). Biochar materials were incorporated with air-dried soil (50 g soil: 1 g biochar), within 4 days of ^{15}N labelling, and the resulting soil-biochar mixture placed into 60 ml pots made from plastic syringe bodies (ME-738/2, BD Drogheda, Ireland). The soil was then brought to field capacity (30% gravimetric water content (θ_g), water-filled pore space = 48%) using deionised water prior to planting five perennial ryegrass seeds into the surface soil of each pot, except for the soil only treatment. Pots were maintained in a growth cabinet for 25 days with a 12 h day length (HPL340, 6 klux

Table 1 Treatment summary and abbreviations

	Treatments	Treatment abbreviation
1	Soil	S
2	Soil+ ryegrass	nBC
3	Soil+ ryegrass+ BC_1	BC_1
4	Soil+ ryegrass+ BC_2	BC_2
5	Soil+ ryegrass+ BC_3	BC_3
6	Soil+ ryegrass+ BC_4	BC_4
7	Soil+ ryegrass+ eBC_1	eBC_1
8	Soil+ ryegrass+ eBC_2	eBC_2
9	Soil+ ryegrass+ eBC_3	eBC_3
10	Soil+ ryegrass+ eBC_4	eBC_4

BC = unenriched treatments; eBC= ^{15}N-enriched treatments

at plant level) and an alternating day/night temperature regime of 20°C/15°C, respectively, with a relative humidity of 70%. Each pot was weighed on a daily basis and any mass loss due to evapotranspiration was replaced with deionised water. After 25 days the ryegrass plants were harvested and separated into leaf and root tissues. Roots were rinsed with distilled water to remove soil particles. Then the leaves and roots were dried at 60°C for 48 h prior to grinding (< 200 μm) and analysed for total-N and ^{15}N enrichment using CFIRMS. Biochar particles were also separated from the soil following plant harvest, and the gravimetric moisture content of the soil and biochar samples determined. Subsamples of soil and biochar were also taken for inorganic-N analyses, again using a 1 h extraction with 2*M* KCl extraction (10 g soil: 50 ml 2*M* KCl; 0.2 g biochar: 5 ml 2*M* KCl). Inorganic-N concentrations were then determined on the filtered extract (Whatman No. 42) using flow injection analysis (Blakemore et al. 1987), while ^{15}N enrichments of the inorganic-N samples were determined using the diffusion method (Stark and Hart 1996). Further biochar subsamples were also taken from the soil and rinsed with deionised water, to remove any visible soil fragments. Then soil and washed biochar samples were dried (105°C) and ground (< 200 μm) prior to determination of total N contents and ^{15}N enrichments using CFIRMS. Recoveries of ^{15}N applied in plant, soil, and biochar fractions were calculated in a routine manner (Cabrera and Kissel 1989).

Statistical procedures

Statistics were performed using Minitab®. One-way analysis of variance was used to determine if treatment means differed, and when differences occurred the comparison between means was made using Tukey's method ($p<0.05$). Linear regression was also performed to determine relationships between variables using Minitab®. The variance of the total ^{15}N recovered was calculated as being equal to the sum of the variances of each N pool plus twice the covariance of all two-way combinations of the N pools (Legg and Meisinger 1982). In the following text all numerals after the ± sign in the text are standard errors of the mean unless otherwise noted.

Results

Soil and biochar properties

Soil properties demonstrate that the soil was of good fertility and not lacking in terms of nutrients required for ryegrass growth (Table 2). The physical and chemical properties of the biochar materials, pertinent to the discussion that follows, showed that the biochar materials varied with respect to cation exchange capacity, pH, and surface acidity with the BC_1 material having the lowest surface acidity, BC_1 and BC_2 having the lowest pH (5.15 to 5.97) and BC_3 having higher cation exchange capacity (Table 3). Volatile organic compounds were also detected (Table 3). For completeness the biochar elemental composition based on

Table 2 Soil properties

Temuka silt loam	
pH(H_2O)	5.5
Olsen phosphorous (mg kg^{-1})	27
Anion storage capacity (%)	36
Potassium ($cmol_c kg^{-1}$)	0.84
Calcium ($cmol_c kg^{-1}$)	3.6
Magnesium ($cmol_c kg^{-1}$)	0.90
Sodium ($cmol_c kg^{-1}$)	0.12
CEC ($cmol_c kg^{-1}$)	14
Total base saturation (%)	39
Anaerobically mineralisable nitrogen (μg g^{-1})	62

Table 3 Biochar manufacturing conditions, physical and chemical properties. (Mean ± SEM, n=2)

Feedstock	BC_1 *Pinus radiata*	BC_2 *Pinus radiata*	BC_3 *Pinus radiata*	BC_4 *Pinus radiata*
Pyrolysis temperature (°C)	300	300	350	500
Pyrolysis vacuum (kPa)	75	75	Unknown	10
Agitation during pyrolysis	Absent	Present	Absent	Absent
CEC ($cmol_c\ kg^{-1}$)	3.09±0.00	2.67±0.05	7.99±0.11	3.86±0.05
AEC ($cmol_c\ kg^{-1}$)	3.32±0.02	5.19±0.01	4.03±0.01	4.96±0.01
pH(H_2O)	5.15±0.01	5.97±0.00	7.77±0.05	6.64±0.06
pH($CaCl_2$)	5.74±0.00	5.56±0.01	7.39±0.01	6.71±0.01
EC ($dS\ m^{-1}$)	0.01±0.00	0.01±0.00	0.53±0.00	0.02±0.00
ρ_p ($g\ cm^{-3}$)	1.55±0.04	1.29±0.02	1.09±0.02	1.60±0.03
ρ_b ($g\ cm^{-3}$)	0.09±0.02	0.13±0.02	0.41±0.02	0.08±0.03
Surface acidity (moles $H^+\ kg^{-1}$)	1.75±0.05	1.30±0.10	1.35±0.05	1.35±0.15
Iodine adsorption[a] ($mg\ g^{-1}$)	21.4±1.7	22.0±1.4	127.4±12.9	56.3±4.3
N content ($mg\ g^{-1}$)	0.40±0.05	1.40±0.02	0.65±0.02	2.20±0.01
C content ($mg\ g^{-1}$)	622±0.1	758±< 0.1	772±< 0.1	826±< 0.1
VOCs detected	-Carboxylic acids -Alcohols	-Carboxylic acid -Alcohols	-Carboxylic acids -Alcohols	-Ethanol
	-Aldehydes	-Aldehydes	-Aldehydes	
	-Esters	-Esters	-Esters	
	-Ethers	-Ethers	-Ethers	
	-Hydrocarbons	-Hydrocarbons	-Hydrocarbons	
	-Ketones	-Ketones	-Ketones	
	-Phenols	-Phenols	-Phenols	

[a] An indirect measurement of specific surface area

acid digestion and water extractable ions are presented in supplementary Tables S1 and S2.

^{15}N enrichment of biochar following exposure to ammonia and its stability

After exposure to NH_3 gas the total N content of the enriched biochar material (eBC) increased by an average 6.7 mg g^{-1} (± 0.6) with post exposure concentrations ranging from 7.8 to 10.0 mg g^{-1} eBC. Linear regression showed that the N contents of the eBC materials were strongly related to their initial pH values (r^2=0.92, p<0.05) and their surface acidities (r^2=0.74, p<0.14), which are shown Table 3. Other measured variables showed no relationship with increases in biochar N content. Following exposure to NH_3 the pH of the eBC_1, eBC_2, eBC_3 and eBC_4 materials also increased with values of 8.5, 9.1, 8.8 and 8.4, respectively. The ^{15}N enrichments of the eBC materials ranged from 3.4 to 4.9 atom% ^{15}N with higher enrichment in eBC_1, which was initially the most acidic (pH 5.15) biochar (Fig. 1). The stability of the eBC material, tested by leaving the eBC_1 material under a continuous ambient air-flow of 0.65 ms^{-1} for 12 days, showed that there was no significant change in total N content or its ^{15}N enrichment (Fig. 2), demonstrating that the ^{15}N-biochar matrix was stable under ambient conditions. Extraction of the eBC materials with 2M KCl showed that their ammonium-N (NH_4^+-N) concentrations had increased following exposure to NH_3 (Fig. 3), with BC and eBC materials containing on average 40 (± 1) and 760 (± 153) μg g^{-1} of NH_4^+-N. The initial nitrate-N (NO_3^--N) concentration of the BC materials averaged 200 (± 1) μg g^{-1} of biochar but NO_3^--N was undetectable in the KCl extracts of the eBC materials. Initial biochar pH and surface acidity of the BC materials did not correlate with KCl extractable inorganic-N contents of the ^{15}N enriched biochar materials.

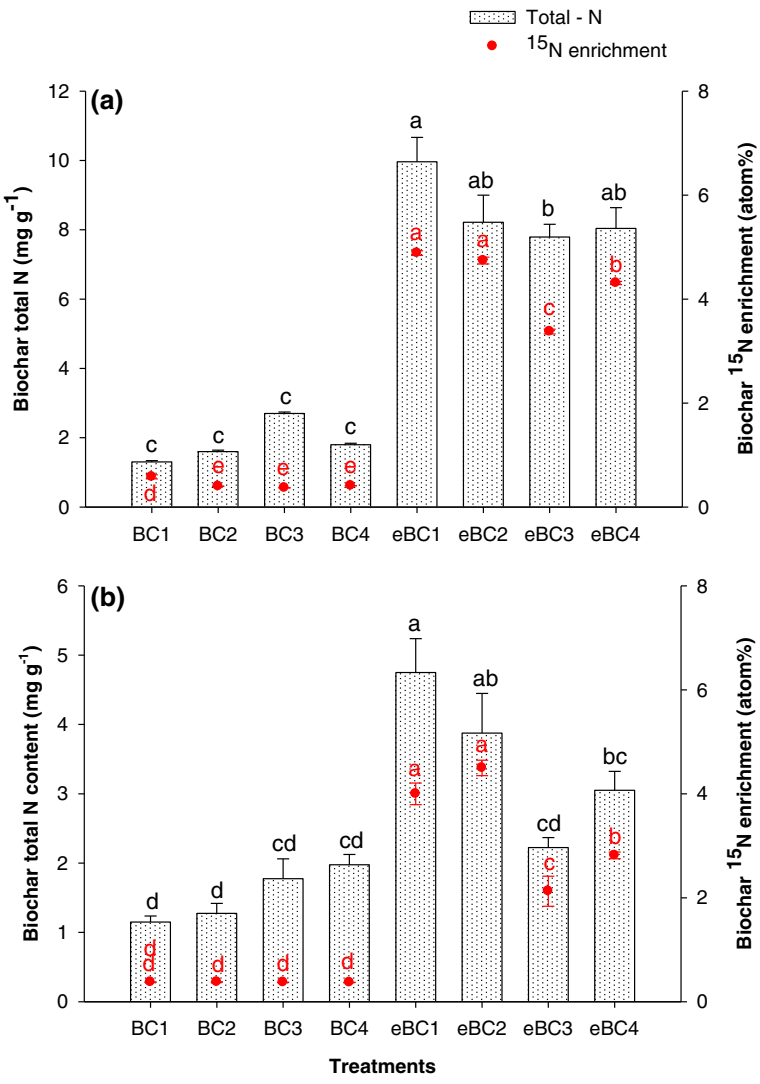

Fig. 1 **a** Total N content and ^{15}N enrichment of four biochar materials pre and post exposure to NH_3-^{15}N. **b** Total N content and ^{15}N enrichment of eBC biochar materials recovered from the soil after 25 days. The eight treatments are: BC1, soil +ryegrass+BC1; BC2, soil +ryegrass+BC2; BC3, soil +ryegrass+BC3; BC4, soil +ryegrass+BC4; eBC1, soil +ryegrass+eBC1; eBC2, soil+ryegrass+eBC2; eBC3, soil+ryegrass+eBC3; eBC4, soil+ryegrass+eBC4; where BC is biochar and eBC is biochar material that was exposed to NH_3. Error bars are plus one s.e.m for Total-N and plus and minus one s.e.m for ^{15}N enrichment. For each variable, lower case letters indicate significant differences between means (Tukey's Test, $p<0.05$). Note the differing scales on the y axes

Plant and soil response to ^{15}N enriched biochar addition

Twenty five days after the addition of the eBC materials to the soil the leaf dry matter yields had increased by 2 to 3-fold, and root dry matter yields by 2-fold, when compared to treatments receiving only the BC materials. No differences in yield occurred due to the addition of the BC materials when compared to the nil-biochar treatment (Fig. 4). The ^{15}N enrichment of the grass root and leaf tissues in the BC treatments averaged 0.369 and 0.371 atom%, respectively, while under the eBC treatments the respective values were 2.529 and 3.110 atom% (Fig. 4). In the case of the eBC_1 and eBC_2 treatments leaf-N contents were higher than in eBC_3 and eBC_4 treatments (Fig. 4). As a consequence of the higher dry matter yields and N contents the uptake of N under the eBC treatments was also higher than under the BC treatments in both root and leaf tissues, with the sole exception the eBC_3 roots which had no elevated N uptake (Fig. 5). The ^{15}N recovery by roots averaged 6.8% (± 1.7) and did not vary with eBC material (Fig. 6). However, ^{15}N recovery in leaf tissues varied with eBC material ranging from 26.1% to 10.9% (Fig. 6) with higher ^{15}N recovery in the eBC_1 and eBC_2 treatments than in the eBC_4 treatment (Fig. 6).

After 25 days, the N contents and ^{15}N enrichments of the BC materials, recovered from the soil, had not

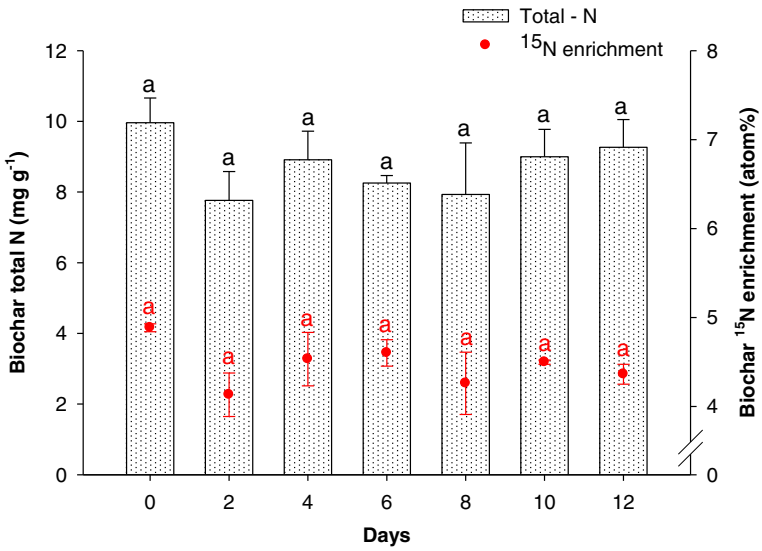

Fig. 2 Total N content and ^{15}N enrichment of the eBC_1 material over 12 days under an ambient air flow of 0.65 ms^{-1}. The error bars indicate the s.e.m. For biochar total-N and biochar ^{15}N enrichment the lower case letters indicate a lack of any significant differences between means (Tukey's Test, $p<0.05$). Note the differing scales on the y axes

changed. However, in the eBC materials the N contents and ^{15}N enrichments had decreased, ranging from 2.2–4.8 mg g^{-1} and 2.127–4.497 atom% ^{15}N, respectively. The N contents of the eBC_3 and eBC_4 materials, after 25 days, were similar to the BC_3 and BC_4 materials (Fig. 1). After 25 days the mean recoveries of ^{15}N applied in the eBC_1, eBC_2, eBC_3 and eBC_4 materials, removed from the soil, equated to 10.6 (± 1.0), 9.7 (± 1.4), 2.5 (± 0.4), and 4.5 (± 0.4)% of the ^{15}N contained in the biochar materials at time zero, respectively (Fig. 1). Total soil-N concentrations (organic-N + inorganic-N (mg g^{-1})) at the end of experiment did not differ due to treatment (average 2.44±0.06). However, ^{15}N enrichment of the total soil-N pool was higher in the eBC treatments (average over all eBC treatments 0.473±0.01) when compared to the BC treatments (average over all BC treatments 0.370±0.0001). This reflected the presence of the ^{15}N enriched inorganic-N pool resulting from eBC addition. Mean recoveries of ^{15}N from the total soil-N pool in the eBC_1, eBC_2, eBC_3 and eBC_4 treatments were 45 (± 1.5), 29 (± 3.7), 47 (± 1.2), and 35 (± 5.6)%, respectively (Fig. 6). Mean total ^{15}N recovery (leaf + root + soil + biochar removed from soil) was higher ($p<0.5$) in the eBC_1 treatment (89.3±1.5) than in the eBC_4 treatment (55.6±5.6), with total recoveries in the eBC_3 and eBC_4 treatments of intermediate values at 70.7 (± 7.6) and 73.4 (± 1.8), respectively

Biochar particles removed from the soil tended to have higher mean concentrations of KCl extractable NH_4^+-N under the eBC treatments than in the BC treatments (1351 (± 702) and 428 (± 350) μg NH_4^+-N g^{-1} biochar, respectively, but these were not statistically significant. The mean NO_3^--N concentrations were 1666 (± 1289) and 89 (± 22) μg NO_3^--N g^{-1} biochar under the eBC treatments and BC treatments, respectively, but again large variation meant no statistical significance occurred. After 25 days the mean soil NH_4^+-N concentrations were less than the detection limit in both the BC and eBC treatments, while the respective mean NO_3^--N concentrations were 1.2±0.2 and 10.9±5.6 μg NO_3^--N g^{-1} soil with no statistical differences.

Discussion

The uptake of ^{15}N labelled NH_3 by the biochar materials was higher than in previously summarised studies (Clough and Condron 2010) where rates of the order of 0.2 to 1.8 mg $g^{-1}$of biochar were noted, and this may be a function of biomass used, biochar pyrolysis conditions and/or the NH_3 concentration the biochars were exposed to. One proposed mechanism for adsorption of NH_3 includes the involvement of acid functional groups (Asada et al. 2002; Kastner et al. 2009). The close relationship observed here between both the biochar pH and surface acidity and the amount of NH_3-N taken up supports this idea, along with the increase in pH following exposure to NH_3 of the eBC materials. Thus the greater uptake of NH_3 by the BC_1 and BC_2 materials was due to their

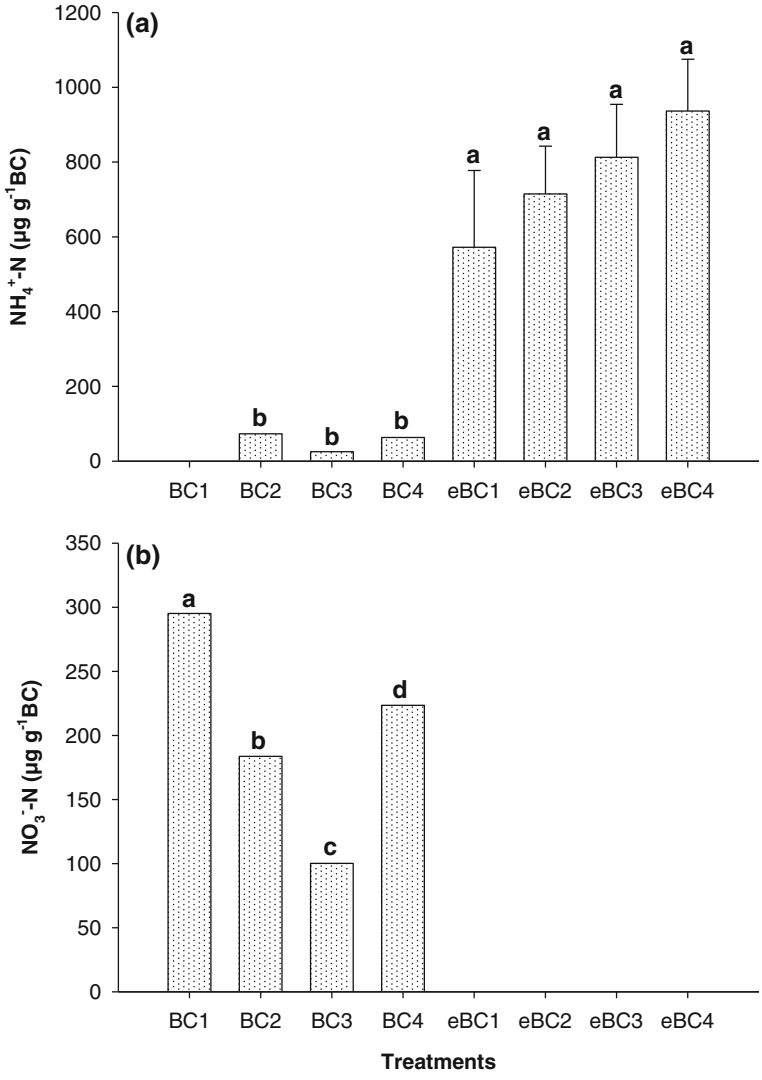

Fig. 3 Mean inorganic-N concentrations of the biochar materials following exposure to NH_3. a, NH_4^+-N b, NO_3^--N. The four unexposed biochar materials are BC_1 to BC_4 while the biochar materials exposed to NH_3 are eBC_1 to eBC_4. The error bars indicate plus one s.e.m. Lower case letters indicate significant differences between means (Tukey's Test, $p<0.05$). Note the differing scales on the y axes. No NO_3^--N was detected on the eBC materials following exposure to NH_3

relatively acidic nature. While a detailed explanation of the mechanism for biochar adsorption of NH_3 is beyond the scope of this study other literature provides some insight. Li et al. (2003) demonstrated that flue-gas CO_2 could be removed via formation of ammonium carbonate (NH_4HCO_3) when NH_3 was present. Day et al. (2005) used scanning electron microscopy (SEM) to observe the formation of a white powder (NH_4HCO_3) on a biochar material produced at 400°C. We used similar SEM magnification (2000 x) as Day et al. (2005) on the BC and eBC materials, but we failed to see any visible difference in the biochar materials (Supplementary Fig. S1). This doesn't rule out the possibility of NH_4HCO_3 formation, since experimental conditions and substrate rates used here will have differed. However, it raises the possibility of other mechanisms sequestering the NH_3. The close relationship between biochar pH and surface acidity, and the stability of the eBC_1 material over time suggests that NH_3 was sequestered into the biochar in an NH_4^+ form. A fact supported by the increase in KCl extractable NH_4^+. However, a comparison of the increase in the total N content and the elevation in NH_4^+ following exposure to NH_3 shows that NH_4^+ only accounts for a fraction of the increase in total N following exposure to NH_3. The stability of the eBC material tested in terms of its N content and ^{15}N enrichment showed that the N compound formed on the biochar was not subject to sublimation. The disappearance of KCl extractable

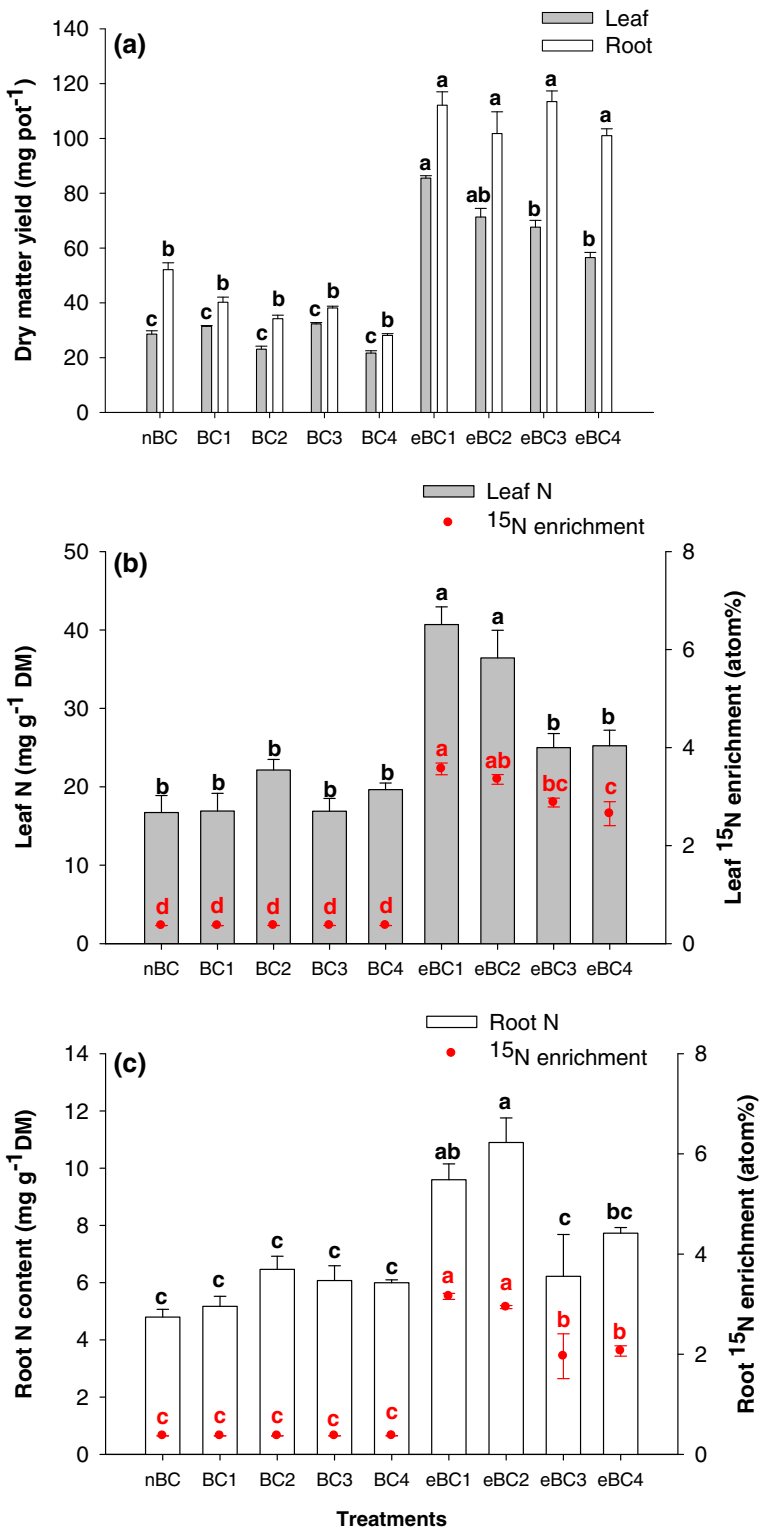

Fig. 4 Dynamics between dry matter yields, leaf and root tissue N contents and ^{15}N enrichments following the 25 day growth cabinet study. **a** Dry matter yields of the leaf and root tissues. **b** Root N content and ^{15}N enrichment of the root tissues. **c** Leaf N content and ^{15}N enrichment of the leaf tissues. The nine treatments are: nBC, soil+ryegrass; BC1, soil+ryegrass+BC1; BC2, soil+ryegrass+BC2; BC3, soil+ryegrass+BC3; BC4, soil+ryegrass+BC4; eBC1, soil+ryegrass+eBC1; eBC2, soil+ryegrass+eBC2; eBC3, soil+ryegrass+eBC3; eBC4, soil+ryegrass+eBC4; where BC is biochar and eBC is biochar material that was exposed to NH_3. Error bars are plus one s.e.m for bars and plus and minus one s.e.m for symbols. For each variable, lower case letters indicate significant differences between means (Tukey's Test, $p<0.05$). Note the differing scales on the y axes

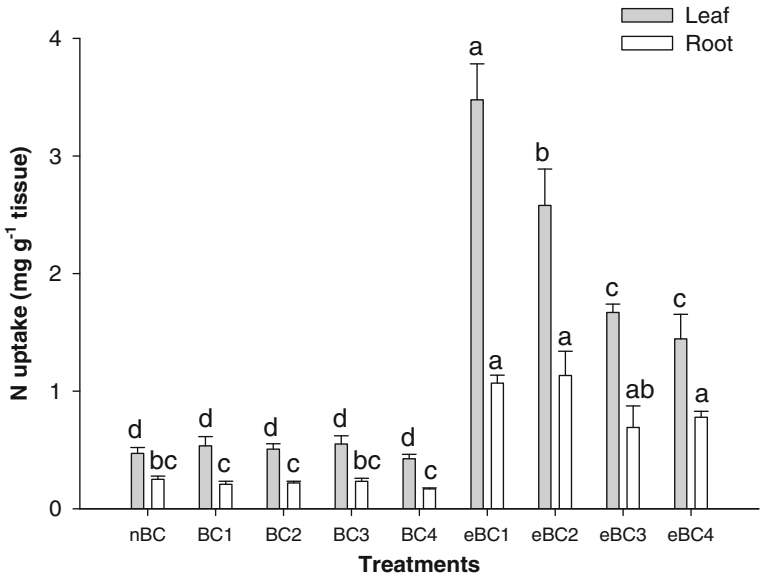

Fig. 5 Nitrogen uptake by leaf and root tissues after 25 days. The nine treatments are: nBC, soil+ryegrass; BC_1, soil +ryegrass+BC_1; BC_2, soil+ryegrass+BC_2; BC_3, soil+ryegrass +BC_3; BC_4, soil+ryegrass+BC_4; eBC_1, soil+ryegrass+eBC_1; eBC_2, soil+ryegrass+eBC_2; eBC_3, soil+ryegrass+eBC_3; eBC_4, soil+ryegrass+eBC_4; where BC is biochar and eBC is biochar material that was exposed to NH_3. The error bars are plus one s.e.m. For leaf and root variables, lower case letters indicate significant differences between means within the variable measured (Tukey's Test, $p<0.05$)

NO_3^- from the biochar materials following exposure to NH_3 is not readily explainable and further work is required to determine the mechanism of its loss.

The use of ^{15}N stable isotope unequivocally demonstrates that NH_3 adsorbed onto biochar can provide a source of N for plants when the biochar-NH_3 complex is placed in the soil-plant matrix. Increases in dry matter yield were a consequence of the increased soil N availability under the eBC treatments, as demonstrated by the recovery of ^{15}N

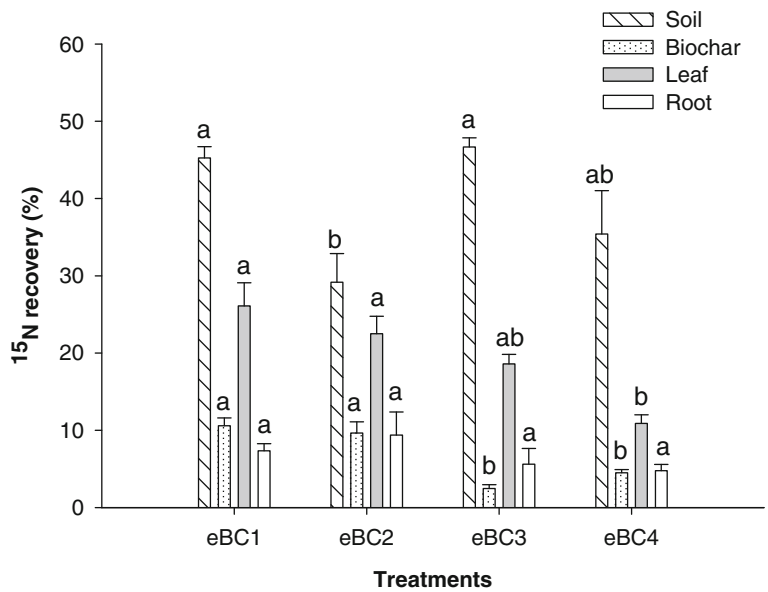

Fig. 6 Recovery of ^{15}N applied in leaves and root tissues as a percentage of the ^{15}N applied in the biochar materials following the 25 day growth cabinet study. The four treatments are: eBC1, soil+ryegrass +eBC1; eBC2, soil +ryegrass+eBC2; eBC3, soil+ryegrass+eBC3; eBC4, soil+ryegrass+eBC4; where eBC is biochar material that was exposed to NH_3. Error bars are plus one s.e.m. For leaf and root variables, lower case letters indicate significant differences between means (Tukey's Test, $p<0.05$). Note the differing scales on the y axes

isotope in the grass tissues and in the soil itself. Again the eBC_1 and eBC_2 treatments were most successful at delivering N to the plants. While this study was not designed to compare the efficacy of biochar adsorbed NH_3 against other N fertiliser forms, it can be noted that the leaf ^{15}N recovery and leaf N content of the eBC treatments in the current study are of a similar magnitude to other studies that have examined the plant uptake of ruminant urine-N or fertiliser-N deposition to pasture (Clough et al. 1998; Recous et al. 1988). It is assumed that any ^{15}N unaccounted for was lost via leaching or gaseous emissions.

Another point to note is the fact that the BC materials were not toxic to the plants when added to the soil, since leaf and root yields did not differ between nBC and BC_1 to BC_4 treatments, despite these being unweathered fresh biochars. Previous work has shown that volatile organic compounds associated with biochar can be deleterious to plant growth (Deenik et al. 2010). Similarly the exposure of the BC materials to NH_3 did not create any observable toxic effects on the plant-soil matrix, but rather the reverse with leaf and root dry matter yields increasing by 2–3 and 3 fold, respectively, under eBC treatments. After 25 days in the soil the biochar materials still contained ^{15}N and long-term in-situ trials are now required to further examine the delivery mechanism(s) and efficacy of the biochar-N, resulting from NH_3 adsorption, and factors affecting these.

The eBC material which had the least effect on leaf dry matter yields was in fact the eBC_3 material which had the highest pH. In order to maximise the potential uptake of NH_3, biomass pyrolysis conditions need to be tuned to enhance the acidity of the biochar material produced. Further testing must now be performed to ascertain in-situ biochar uptake rates of NH_3 under conditions where anthropogenic NH_3 emissions occur. For example, air quality surveys of NH_3 concentrations in livestock buildings have recorded mean NH_3 concentrations equalling 37, 21, and 16 $\mu L\ L^{-1}$ in calf houses, broiler poultry houses, and swine facilities, respectively (Seedorf and Hartung 1999). This is sufficient for NH_3 adsorption onto biochar (Kastner et al. 2009). Our study shows the BC_1 material captured the equivalent of 8.7 kg of NH_3-N $tonne^{-1}$ of biochar. A typical broiler production facility (Ritz et al. 2004) may produce 1135 kg NH_3 $year^{-1}$ which would require 130 tonnes of biochar to fully mitigate. At 30 tonnes of biochar ha^{-1}, a rate shown to have no detrimental effects on pasture growth (Taghizadeh-Toosi et al. 2011), this would require about 4.3 ha of land. However, annual crop demands will certainly be considerably less, possibly in the order of 200 kg N ha^{-1} $year^{-1}$, so potentially 24 ha of land could be fertilised if all NH_3-N recovered using biochar adsorption was plant available. Ammonia volatilisation losses have also been shown to be reduced during the composting of animal waste with biochar (Steiner et al. 2010) and it may be possible to recycle N from animal housing facilities if biochar adsorbed NH_3 proves to be bioavailable following composting. Thus further research is required to identify the best location for the biochar to achieve optimum NH_3 in an animal housing facility. Should it be used to scrub ambient air or capture NH_3 at 'source' on the floor of the housing facility? The latter approach may be thwarted if the acidic pH of the biochar is neutralized by manure

The potential for biochar to uptake NH_3, and its subsequent bioavailability also needs to be explored where biochar has been previously incorporated into the soil and where NH_3 forms in situ e.g. in grazed pastures under ruminant urine patches, under urea fertiliser applications, and during anhydrous-NH_3 use. Under urine patch conditions NH_3 fluxes would be expected to be equally high if not higher than those found in animal housing facilities and concentrations of 41 $\mu L\ L^{-1}$ have been recorded in the headspace above synthetic urine patches after 5 min (Clough et al. 2003). Soil atmosphere concentrations are likely to be larger. Likewise the direct injection of anhydrous ammonia results in a significant concentration of free NH_3 in the soil which is susceptible to volatilization. Assuming that NH_3 adsorption occurs in-situ, and there are no reasons to suggest otherwise, then biochar previously incorporated into the soil may act as a slow release N pool for plants once NH_3 has been produced and adsorption occurs.

Our study demonstrates a proof of concept for dramatically reducing the leakage of N from agricultural systems and its recycling by using biochar to capture NH_3 emissions. This work highlights another beneficial use of biochar and demonstrates further benefit and use for the material. This information should now be used when considering the logistics of biochar manufacture and distribution. It would make sense to have some biochar production facilities sited at economically feasible distances from point sources of NH_3 to allow its capture, and also near potential

land-users that require a source of N fertilizer and who can sequester soil C as biochar.

Acknowledgements Authors wish to thank Carbonscape™ for supplying three of the biochar materials used.

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