Greenwaste biochar potentially reduces nitrogen fertiliser losses

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Abstract

This study determined the maximum NH_4^+-N sorption capacity for greenwaste biochar to be 909 mg/kg, equating approximately to a maximum increase in soil NH_4^+-N storage of just under 1kg for each tonne of biochar applied to the soil. Over 90% of the sorbed NH_4^+-N was recovered from the biochar by extraction with 2M KCl indicating that the sorbed NH_4^+-N was exchangeable and plant available. When applied in large quantities (up to hundreds of tonnes) it has potential to reduce losses of mineral nitrogen (N) when in the NH_4^+-N form prior to nitrification. This characteristic of the biochar would account for a significant proportion of the improvements in N fertiliser use efficiency noted in several pot trials. Biochar NO_3^--N retention may have also contributed. Our study has also demonstrated that the impact of the greenwaste biochar is greatest on light sandy soils with naturally low NH_4^+-N retention properties, and that these soils along with weathered tropical soils with low CEC should be targeted for biochar applications, to maximise environmental and economic benefits.

Key Words

Greenwaste, biochar, nitrogen, ammonium, isotherm.

Introduction

Biochars (high carbon materials produced from the slow pyrolysis of biomass) have recently come to prominence because of their potential for sequestering atmospheric carbon to the soil due to the relative stability of biochar organic carbon (Lehmann *et al.* 2006, Lehmann and Joseph 2009). The high fertility of *terra preta* soils in the Amazon has been associated with their high organic carbon content in the form of char originating from the 'slash and char' practice of the pre-Columbian indigenous people of the area (Glaser *et al*. 2001). A series of recent pot trials (Chan *et al.* 2007, Chan *et al.* 2008, van Zwieten *et al.* 2010) have demonstrated higher crop yields with increasing rates of biochar application in the presence of N fertiliser, demonstrating a N fertiliser use efficiency benefit from biochar. This improved N fertiliser use efficiency has been attributed to improved soil physical conditions, liming effect, and increased CEC, but no direct measurements of biochar mineral N retention were done. This study focused on greenwaste biochar with a silty clay loam soil from Camden NSW and a sandy loam soil from Somersby, NSW. A NH_4-N retention isotherm was determined for this greenwaste biochar to determine the biochar's maximum NH_4-N sorption capacity. In addition, soil-biochar mixtures were equilibrated with an NH_4^+-N solution to ascertain the biochar impact on NH_4-N retention in two soil types.

Methods

Soil and greenwaste biochar characteristics

Table 1. Basic chemical properties of the greenwaste biochar and the two soils used in this study.

	Texture	EC	pH_w	N (%)	C (%)	Bicarb. P (mg/kg)	NH_4^+-N (mg/kg)	NO_3-N (mg/kg)	ECEC (cmol/kg)
Char		0.06	5.9	0.15	65	43	13	<0.2	
Soil A	ZCL	0.06	5.6	0.18	2	26	6	59	8.7
Soil B	SL	0.07	6.3	0.17	1.9	150	7	30	6.8

Determining the NH_4-N sorption isotherm for the greenwaste biochar

Standard solutions of NH_4^+-N were made up using ammonium sulphate [$(NH_4)_2SO_4$] and deionised water with 0, 4, 10, 20, 40, 80, and 160 mg NH_4-N / L. A 30 mL aliquot of each of these solutions was added to a 2.0 g o.d.e sample of air dry greenwaste biochar in a 40 mL centrifuge tube and done in duplicate. The tubes of biochar and NH_4^+-N solutions were then shaken end over end for 20 h to ensure equilibration. The samples were then centrifuged in a high speed centrifuge at 10,000 rpm for 15 min, before pouring off the supernatant through a Whatman 42 filter paper for analysis. Filtered supernatant samples were analysed for

NH_4^+-N and NO_3-N using a Lachat Quickchem automated ion analyser (QuickChem method 10-107-064-D for NH_4^+ and 10107-04-1-H for NO_3^-/NO_2^-).

A 40 mg/L NO_3^--N standard solution was also made up with KNO_3 to assess NO_3^--N retention by the soil, and duplicates of 30 mL of this solution and 2.0 g o.d.e biochar samples were run with the above NH_4-N samples and treated identically.

A similar methodology to that outlined by Sharpley *et al.* (2008) for calculating P sorption isotherms for soil was followed to determine the isotherm for NH_4-N retention/sorption by the biochar,. The total NH_4-N (mg/kg) sorbed by the char (S) = S1(NH_4-N sorbed by the soil in the 20 h equilibration) +So (Previously sorbed NH_4-N). For the purpose of this calculation, we used 2 M KCl extracted NH_4-N for the char (i.e. 13 mg/kg) as the So value. The Langmuir isotherm for NH_4-N was created by plotting the mean total sorbed NH_4-N mg/kg (S) against solution NH_4-N concentration (mg/L) for the duplicate samples. The equilibrium NH_4-N concentration (ENH_4-NC_0 mg NH_4-N/L), defined as the concentration supported by the biochar sample at which no net sorption or desorption occurs, was calculated as the intercept of the isotherm curve on the x-axis of this graph. The NH_4-N sorption maximum (Smax, mg NH_4-N kg biochar) and the binding energy of NH_4-N to the biochar (k, L mg NH_4 /N) were graphically determined based on the Langmuir sorption equation (1)

$$C/S = 1/[kS_{max}] + C/S_{max} \qquad (1)$$

where S is the total amount of NH_4-N sorbed to the biochar (mg NH_4-N / kg biochar), C is the equilibrium solution concentration after 20 h shaking (mg NH_4-N / kg biochar), Smax is the NH_4-N sorption maximum (mg NH_4-N /kg biochar), and k is a constant relating the binding energy of NH_4-N to biochar (L /mg NH_4-N). The graphical determination of these parameters was based on that outlined by Sharpley *et al.* (2008) that involved plotting C/S vs. C with NH_4-N sorption maximum (Smax) being calculated as the reciprocal of the slope of this plot, and the binding energy (k) being calculated as the slope / intercept of this plot.

Estimating the availability of NH_4-N adsorbed by the biochar to plants
Following decanting of the supernatant NH_4-N solutions from the biochar at the end of the 20 h equilibration period, the biochar samples in the centrifuge tubes were extracted with (i) 20 mL deionised water (wash) shaken end over end for 20 min, (ii) 20 mL 0.01 M $CaCl_2$ shaken for 1 h, (iii) 20 mL 2M KCl shaken for 1 h and (iv) a second extraction with 2 M KCl shaken for 1 h. After each shaking, the samples were centrifuged for 15 min at 10,000 rpm and the supernatant decanted and filtered through a Whatman 42 filter paper for analysis for NH_4-N and NO_3-N. The amount of NH_4-N sorbed by the biochar deemed to be plant available was calculated by adding together the NH_4-N in the supernatant solutions for extractions (ii) and (iii) and then subtracting the original biochar sorbed (KCl extractable) NH_4-N value of 13 mg/kg. The second KCl extraction was thought to represent NH_4-N that would become available to plants with time. The 40 mg/L NO_3-N duplicate char samples were also assessed for NO_3-N retention with the same extraction regime as outlined above for the NH_4-N samples.

Biochar impact on soil NH_4-N adsorption
Samples of the two soil types being studied were chloroform fumigated as done for microbial biomass determination (Vance *et al.* 1987), in order to impede soil microbial activity and associated nitrification of NH_4-N added to the soils. Greenwaste biochar was added to 2.0 g o.d.e of the two fresh fumigated soils (< 2 mm) in a centrifuge tube at rates of 0, 0.28, and 0.56 g o.d.e to create 6 treatments. Assuming a bulk density of 1.2g/cc and an incorporation depth of 10 cm, the six treatments were equivalent to char application rates of 0, 168, and 335 t/ha. The resultant treatments were (i) Soil A only, (ii) Soil A + 168 t/ha biochar, (iii) Soil A +335 t/ha biochar, (iv) Soil B only, (v) Soil B + 168 t/ha biochar, and (vi) Soil B +335t/ha biochar. Each treatment had three replicates. A 30 mL aliquot of the 40 mg NH_4-N /L solution was added to each sample, and the samples were shaken end over end for 10 h to allow equilibration between the NH_4-N solution and the soil-biochar samples. After shaking the samples were centrifuged for 15 min at 2000 rpm before the supernatant was filtered through a Whatman 42 filter paper, and analysed for NH_4-N and NO_3-N using the method previously outlined. The difference between the NH_4-N in the 40 mg NH_4-N / L solution added to the soil-char treatments and the 20 h equilibrated supernatant solution for each sample was calculated as being the NH_4-N sorbed by the soil, and expressed on a mg/kg of dry soil basis. A one way ANOVA was carried out on this data set , and treatment means compared using least significant difference(LSD), with differences considered significant at P=0.05.

Results

The Langmuir sorption isotherm for NH_4-N and greenwaste biochar and associated parameters determined by this study are presented in Figure 1. The NH_4-N sorption maximum for biochar was determined to be 909 mg/kg (Figure 1b). This equates to a maximum increase in soil NH_4-N storage capacity of just under 1 kg for each tonne of greenwaste biochar applied to the soil. The 0.01 M $CaCl_2$ extraction and the first 2 M KCl extraction recovered between 71% and 89% of NH_4-N adsorbed by the biochar (Table 2) suggesting that the majority of the NH_4-N adsorbed by the biochar is exchangeable and plant available. Except for the highest concentration NH_4-N solution treatment, >90% of the NH_4-N adsorbed by the char was recovered after the 2nd 2 M KCl extraction (Table 2), suggesting that only a very small proportion of the NH_4-N adsorbed by the biochar is likely to be unavailable to plants in the medium term. A curious result was that the biochar was found to adsorb 129 mg/kg of NO_3-N from the 40 mg/L NO_3-N solution indicating the possible presence of some anionic exchange capacity in the biochar. This was less than half the amount of NH_4-N that was adsorbed by the biochar from NH_4-N solution of the same concentration.

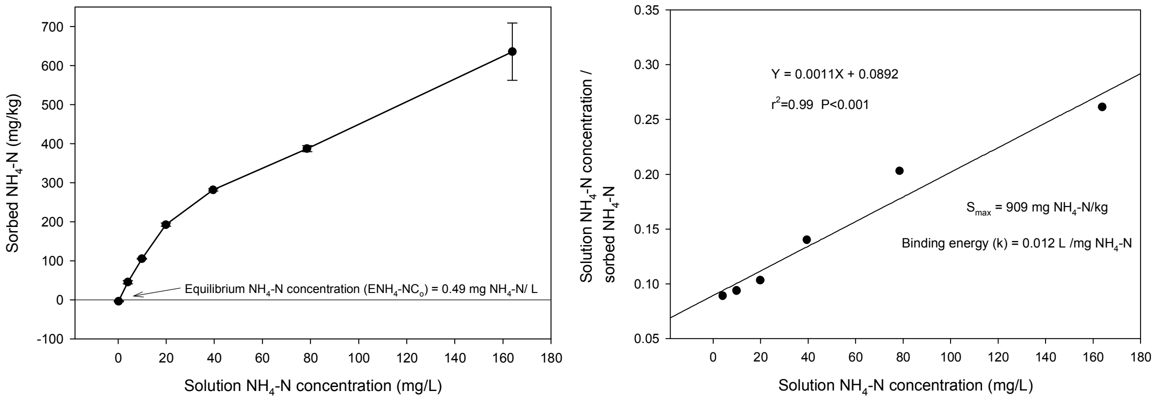

Figure 1. The Langmuir NH_4-N sorption isotherm for greenwaste biochar-mean values with SE bars (a), and a plot of C/S vs. C with derived values of maximum NH_4-N sorption (S_{max}) and bonding energy (k) for the greenwaste biochar (b).

Table 2. Recovery of adsorbed NH_4-N and NO_3-N from biochar in 0.01 M $CaCl_2$ and 2 M KCl extractions.

Solution NH_4-N (mg/L)	NH_4-N adsorbed T=20 h (mg/kg char) [mean ± SE]	NH_4-N recovered in Extracts 1 and 2^A (mg/kg char) [mean ± SE]	Adsorbed NH_4-N recovered in extracts 1 and 2 (%)	NH_4-N recovered in extract 3^A (mg/kg char) [mean ± SE]	Aadsorbed NH_4-N recovered in extracts 1, 2 and 3 (%)
0	-16 ± 1.0				
4	33 ± 4.1	29 ± 0.0	89	10 ± 0.4	100
10	92 ± 1.1	73 ± 1.3	80	18 ± 1.6	100
20	179 ± 4.1	132 ± 0.5	73	31 ± 1.1	90
40	269 ± 2.7	203 ± 2.6	75	42 ± 0.8	91
80	374 ± 8.0	289 ± 4.2	77	59 ± 4.1	93
160	622 ± 73.4	440 ± 39.1	71	80 ± 8.3	84

Solution NO_3-N (mg/L)	NO_3-N adsorbed T=20 h (mg/kg char) [mean ± SE]	NO_3-N Recovered in Extracts 1 and 2^A (mg/kg char) [mean ± SE]	Adsorbed NO_3-N recovered in extracts 1 and 2 (%)	NO_3-N Recovered in extract 3^A (mg/kg char) [mean ± SE]	Adsorbed NO_3-N recovered in extracts 1, 2 and 3 (%)
40	129 ± 12.8	92 ± 0.8	71	11± 0.7	80

^{A}Extraction 1- 20 mL 0.01M $CaCl_2$, Extraction 2 and 3- 20 mL 2M KCl.

The results of the biochar-soil equilibration study at 40 mg NH_4-N /L (Figure 2) reveal that both biochar application rates (168t/ha and 335 t/ha) significantly ($p<0.05$) increased the NH_4-N sorption in both soil types. But the relative proportional increase in NH_4-N adsorption compared to the soil only treatment was much greater in the sandy loam soil with a low ECEC than in the silty clay loam soil with a moderate ECEC. The 168 t/ha and 335 t/ha biochar applications increased the NH_4-N adsorption in soil B (sandy loam) by 63 mg/kg (90% increase) and 104 mg/kg (149% increase). In contrast, the same biochar applications to soil A (silty clay loam) led to increases in NH_4-N adsorption of 30 mg/kg (20%) and 60 mg/kg (40%).

Conclusion

This study has shown that greenwaste biochar increased the NH_4-N retention capacity of soils by up to around 1kg NH_4-N / t of biochar, and that when applied in large quantities (up to hundreds of tonnes) it has potential to reduce losses of mineral N when in the NH_4-N form prior to nitrification. This characteristic of the biochar may account for a significant proportion of the improvements in N fertiliser use efficiency noted in several studies. Our study has also demonstrated that the impact of biochar is greatest on light sandy soils with naturally low NH_4-N retention properties, and that these soils should be targeted for biochar applications, in order to maximise the environmental and economic benefits from the biochar. Similarly weathered tropical soils with characteristically low CEC are likely to benefit greatly. The characterisation of biochar products should include NH_4-N and NO_3-N retention.

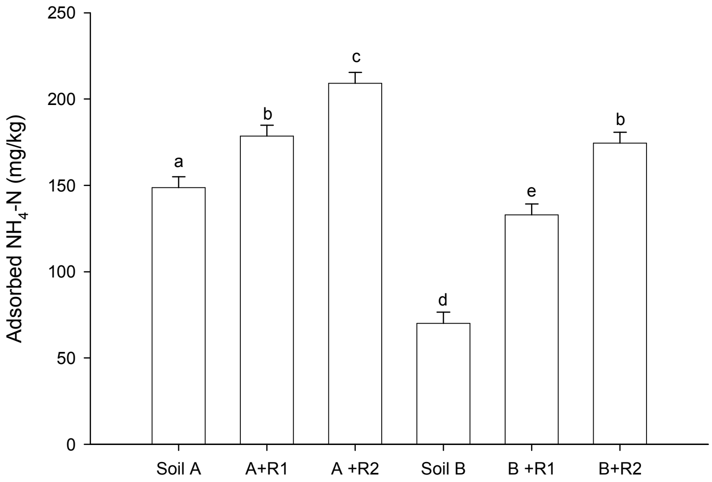

Figure 2. Mean NH_4-N adsorbed by two fumigated soils mixed with greenwaste biochar following a 10h equilibration with a 40 mg/L NH_4-N solution. Error bars are LSD at p=0.05. Different letters represent a significant difference between the treatments at p<0.05. [Soil A=Soil A (Silty clay loam) only; A+R1= Soil A + 168 t/ha biochar; A+R2=Soil A + 335 t/ha biochar; Soil B= Soil B (sandy loam) only; B+R1= Soil B + 168 t/ha; B+R2= Soil B + 335 t/ha biochar].

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