Nitrogen enrichment potential of biochar in relation to pyrolysis temperature and feedstock quality

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ABSTRACT

Nitrogen (N) enrichment of biochar from both inorganic and organic waste N sources has the potential to add economic and environmental value through its use as a slow release N fertilizer. We investigated the sorption of N by, and its release from, biochar made at pyrolysis temperatures of 400, 500 and 600 °C from three feedstocks: poultry litter (PL with a carbon (C) to N ratio (C:N) of 14), softwood chips of spruce-pine-fir (SPF with a C:N of 470), and a 50:50 mixture of PL and SPF (PL/SPF). The prepared biochars were enriched with ammonium nitrate (AN) and urea ammonium nitrate (UAN). PL biochars had the lowest C content (50–56% C), but the highest pH (9.3–9.9), electrical conductivity (EC, 780–960 dS m^{-1}), cation exchange capacity (CEC, 40–46 cmol kg^{-1}), and N content (3.3–4.5%). While N content and hydrogen (H) to C atomic ratio (H:C) decreased with increasing pyrolysis temperature irrespective of the feedstock used, both pH and EC slightly increased with pyrolysis temperature for all feedstocks. The PL and SPF biochars showed similar H:C and also similar N sorption and N release at all pyrolysis temperatures. These biochars sorbed up to 5% N by mass, irrespective of the source of N. However, PL/SPF biochar performed poorly in sorbing N from either AN or UAN. Biochar H:C was found to be unrelated to N sorption rates, suggesting that physical adsorption on active surfaces was the main mechanism of N sorption in these biochars. There were minor differences between N sorbed from NO_3–N and NH_4–N among different biochars. Very small amounts of sorbed N (0.2–0.4 mg N g^{-1} biochar) was released when extracted with 1 M KCl solution, indicating that the retained N was strongly held in complex bonds, more so for NH_4–N because the release of NO_3–N was 3–4 times greater than that of NH_4–N. NH_4–N sorption far exceeded the effective CEC of the biochars, thereby suggesting that most of the sorption may be due to physical entrapment of NH_4^+ in biochar pores. The results of this study suggest that biochar can be used to remove excess N from poultry and dairy manure and be a good mitigation option for reducing N leaching and gaseous losses.

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1. Introduction

Using biochar to improve soil fertility and carbon (C) sequestration has been the subject of increasing research activity among scientists, industry, and governments, with growing interest in policy circles and the general public as well (Sohi et al., 2009). Biochar has generally been found to improve soil fertility resulting in decreased fertilizer requirements and increased crop yields (Lehmann et al., 2006; Biederman and Harpole, 2013), and to reduce soil N_2O and CH_4 emissions under many, but not all, conditions (Van Zwieten et al., 2009; Cayuela et al., 2014). In part this variability is due to the varying physical characteristics of biochar resulting from differing feedstock materials and pyrolysis conditions (Novak and Busscher, 2013). As an engineered material, biochar production can be tailored towards specific characteristics to result in a value-added product, such as a nutrient-enriched biochar that also functions as a slow-release fertilizer. Utilizing waste feedstocks such as poultry litter for biochar production has the

potential to reduce disposal costs, curb odour and decrease emissions of methane (CH_4), nitrous oxide (N_2O) and ammonia (NH_3) during storage, composting and/or disposal in landfills. Hence, the ability to utilize a range of waste biomass sources as feedstocks to produce biochar with predictable physical and chemical characteristics is urgently needed. Blending high and low quality biomass (i.e., high and low C content feedstocks) has shown promise for "tuning" the physicochemical characteristics of biochar from a mix of feedstocks (Sveinson, 2012). There is an urgent need to integrate potential environmental benefits of biochar use for C sequestration (Lehmann, 2007a,b) and pollutant removal (Dias et al., 2007) with the potential economic benefits of increased nutrient use efficiency and crop productivity, and reduced disposal costs of animal waste.

There is a strong potential for enhancing the environmental and economic value of biochar by enriching it with nitrogen (N) from both inorganic and organic sources (Clough et al., 2013). Lehmann et al. (2006) proposed the conversion of organic wastes to biochar by pyrolysis as a new way to mitigate GHG emissions. Research into N enrichment of biochar to date has been limited, with little progress made on its commercial deployment. Sarkhot et al. (2012) found that N content of a low-temperature hardwood activated biochar increased to 8.3% after treatment with filtered liquid dairy manure, and concluded that N-enriched biochar could be used as a slow-release N fertilizer. Taghizadeh-Toosi et al. (2012) enriched small quantities of wood-based biochar in petri dishes with ^{15}N-labelled NH_3 resulting in biochar with a total N content of <1%. Mechanisms for the sorption of NH_3, such as formation of amides or physical entrapment of NH_3 in biochar pores, are discussed in Spokas et al. (2011). Further studies are needed to determine the N sorption capacity and N release for biochars produced at different pyrolysis temperatures and using different feedstock materials. We investigated the performance of a range of biochars made at different pyrolysis temperatures from low-quality biomass (poultry litter, PL, which poses an ongoing waste management issue in British Columbia), high-quality biomass (lumber mill waste as softwood chips of spruce-pine-fir, SPF), and a 50:50 blend of PL and SPF (PL/SPF). Specifically, the objectives of this study were to (i) relate physicochemical characteristics of biochars to feedstock characteristics and pyrolysis temperature, (ii) measure the N-sorption capacity of these biochars, and (iii) evaluate the extent of N release from these N-enriched biochars. We used NH_4NO_3 (AN) and urea ammonium nitrate (UAN) for the N enrichment of the biochar. The latter was included because compounds containing amine groups are known to form organic complexes, with slow release of sorbed N in plant available forms (Seredych and Bandosz, 2007). Using UAN also enables the evaluation of the possibility of enriching biochar with organic N that would be available from existing waste sources such as animal urine and cattle slurry.

2. Material and methods

2.1. Preparation of the biochars

Nine biochars were produced using three feedstocks, each at three different pyrolysis temperatures. The three feedstocks were (i) PL, (ii) SPF chips, and (iii) a 50:50 mixture of PL and SPF. Before use, PL (C, N and H content of 37%, 2.7% and 5.2%, respectively) and SPF (C, N and H content of 47%, 6.1% and 0.1%, respectively) were oven-dried at 100 °C to constant weight to make them completely moisture free. The three pyrolysis temperatures were (a) 400 °C, (b) 500 °C, and (c) 600 °C. The biochars were produced using an electric furnace-based batch-pyrolysis reactor measuring 1.5 m × 1.5 m × 2.5 m (L × W × H) with the reactor chamber holding about 4 L of feedstock. Biomass temperature was monitored continuously to obtain a heating profile and a precise

determination of the highest heating temperature. Batches typically took 1−3 h to come to thermal equilibrium. Each resulting biochar was characterized for basic chemical properties, including pH, electrical conductivity (EC), and elemental C, hydrogen (H), and N following the "Standardized Product Testing Guidelines for Biochar" (International Biochar Initiative, 2012). Briefly, pH and EC were measured in a 1:20 (w:v) biochar:deionized water solution following shaking and equilibration for 1.5 h. Total C and H were estimated using infrared absorption, and total N with thermal conductivity, following dry combustion (Element analyzer model CHN-1000, LECO Corp., St. Joseph, MI). Organic C (C_{org}) was estimated by subtracting from total C the inorganic C content estimated by measuring gas pressure after treating the samples with HCl in a calibrated pressure vessel. Elemental O was obtained as % O = 100 − %(C + H + N + ash). The biochars were also analysed for exchangeable cations, including effective cation exchange capacity (CEC) following 0.1 N barium chloride extraction and analysis using ICP (inductively coupled plasma) mass spectrometry.

2.2. Nitrogen enrichment of biochars and its subsequent release

N enrichment of the biochars produced was studied by determining their N sorption capacity using a modified Mizuta et al. (2004) procedure. N sorption was obtained at room temperature (20 ± 2 °C) by treating the biochars with a known concentration of N in 0.01 M $CaCl_2$ (to simulate environmental water, i.e., soil solution). The amount of N sorbed was calculated from the difference between initial and final concentrations of the treatment solution. Before use, the biochar samples were gently crushed and passed through a 100-mesh (0.15 mm) sieve (Chen et al., 2008).

In the first experiment, we added 50 mL of 0.01 M $CaCl_2$ solution in deionized water to three replicates of 2.5-g samples of each biochar in Erlenmeyer flasks, and 0.1 mL of Octan-2-ol to hydrate the biochars. After stirring these mixtures thoroughly, we added to each flask 2.5 mL of 0.01 M $CaCl_2$ solution containing 0.2 g N from AN. This equilibrium N concentration (~4 g N/L) was similar to the N content of fresh urine of sheep, cattle and deer (Hwgendoom et al., 2010). The mixtures were shaken for 4 h on an end-to-end shaker, left overnight to incubate, and filtered using Whatman #1 filter
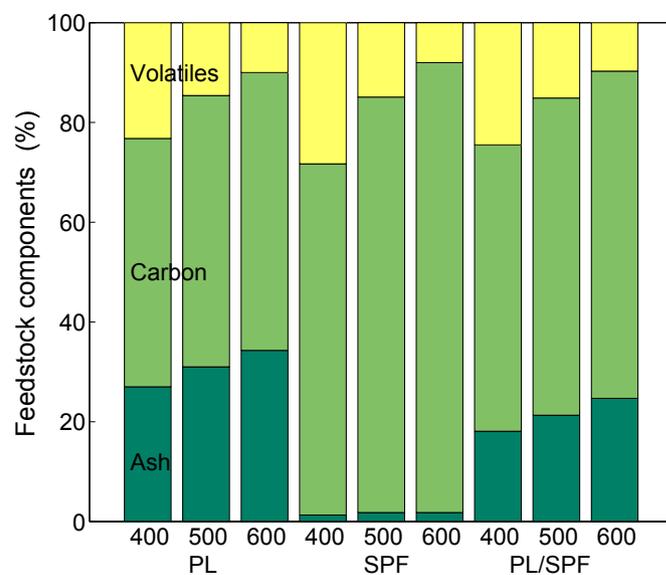

Fig. 1. Physical composition of different feedstocks (poultry litter (PL), spruce-pine-fir wood waste (SPF) and their 50:50 blend (PL/SPF)) after their pyrolysis at 400, 500 and 600 °C.

paper. The supernatant was analysed for NH_4^+ and NO_3^- content. All liquid samples were analysed for NH_4^+ by measuring absorbance spectra using the indophenol blue method on a combined fluorescence/UV–Vis absorbance spectroflorometer (Model Aqualog, Horiba Scientific, Edison NJ, USA), and NO_3^- by ion chromatography (Model AC 861, Metrohm AG, Herisau, Switzerland). The filtrate residue, along with the filter paper, was dried at 50 °C for 24 h to retrieve the N-enriched biochars, from which 1-g subsamples were extracted with 50 mL 1 M KCl solution. These were then shaken for 4 h and filtered, and the supernatant solutions were similarly analysed for NH_4^+ and NO_3^- to determine the release of N from N-enriched biochars.

In the second experiment, a similar procedure was followed as above, except that we used two sources of N, AN and UAN, for enrichment of the biochars with N, and performed total N analysis of all samples of supernatant solution using the high temperature combustion method on a TOC/TN analyzer (Model TOC-V CSH/CSV, Shimadzu Scientific Corporation, Kyoto, Japan).

3. Results and discussion

3.1. Physicochemical characteristic of biochars

C content increased with pyrolysis temperature for all feedstocks, with SPF yielding maximum C content (70–90%), followed by PL/SPF (57–66%) and PL (50–56%) (Fig. 1). Ash content also increased with pyrolysis temperature and was minimum for SPF biochar (<2%) and maximum for PL biochar (27–34%). The higher ash content in the PL and PL/SPF biochars is likely related to lower lignin and higher mineral contents in the PL feedstock. The content of volatiles decreased with increasing pyrolysis temperature. Mass loss in volatiles results in higher ash contents. Biochars produced at a higher pyrolysis temperature had higher pH (Table 1), consistent with the increases in ash content (Fig. 1). The increases in biochar pH and ash content with increasing pyrolysis temperature are consistent with the findings of Nguyen and Lehmann (2009).

Biochars produced from PL had the highest pH (9.3–9.9), electrical conductivity (EC, 780–960 dS m^{-1}) and N content (3.3–4.5% N), followed by PL/SPF (9.2–9.5, 560–690 dS m^{-1}, and 2.9–3.4% N, respectively) and SPF (5.4–7.5, 36–49 dS m^{-1}, and 0.3–0.5% N, respectively) (Table 1). The effective CEC was highest (~40 cmol kg^{-1}) for biochar produced from PL, lowest at about 1 cmol kg^{-1} for biochar produced from SPF, and intermediate at about 25 cmol kg^{-1} for PL/SPF biochars, clearly reflecting the CEC of the feedstocks used, and with little effect of pyrolysis temperature. While % N content decreased with pyrolysis temperature, both pH and EC slightly increased with pyrolysis temperature. Inorganic C content of all biochars was low at ≤0.5% (data not shown) and H content varied from 1.5 to 3.6%. The small amount of inorganic C that remains following pyrolysis has been reported to occur

predominantly as $CaCO_3$ and $CaMg(CO_3)_2$, providing liming properties to biochars and also helping to stabilize organic C (Wang et al., 2014). The N incorporated in biochar is generally of low availability due to it being in heterocyclic structures (Knicker and Skjemstad, 2000). However, a small fraction of the embodied N can be bioavailable (Rosa and Knicker, 2011) since a strong correlation between this acid hydrolysable N (amino acids, amino sugars and ammonia) in biochar and soil respiration (i.e., CO_2 emission) following its application to soil has been observed (Wang et al., 2012).

The C and N contents in biochar are expected to increase as the pyrolysis temperature increases as these elements become incorporated into aromatic or heterocyclic rings formed via the preferential loss of H and O from the system (e.g., Almendros et al., 2003). We found that the increase in C content with increase in pyrolysis temperature was prominent for SPF (high quality feedstock) and only slight for PL (low quality feedstock). Increase in pyrolysis temperature increased N content in SPF biochars but decreased it in PL and PL/SPF biochars. It is possible that when pyrolysing ash-rich feedstock, such as PL, the biochar tends to become enriched in the mineral ash component at increasing pyrolysis temperatures, thereby diluting the enrichment of C and N in the pyrolysed material (Wang et al., 2012).

Differential loss of H and O in the form of volatiles during pyrolysis influences atomic H:C and H:O ratios in the resulting biochar, with a higher atomic H:C ratio indicating more functional groups (Novak et al., 2009). Also, atomic H:C represents C stability with lower values of this ratio correlated with greater C stability (e.g., Chen et al., 2008). Significantly, we found that atomic O:C, which represents the relative abundance of hydroxyl and acidic carboxyl functional groups (e.g., Wang et al., 2007), decreased with increasing pyrolysis temperature, with the biochars made from the three feedstocks showing similar characteristics. Removal of

Table 2
Sorption of NO_3^- and NH_4^+ by different biochars when treated with NH_4NO_3 at 1:50 (w:v):: biochar:0.3 M NH_4NO_3-N solution, and release of NO_3^- and NH_4^+ when extracted with 1 M KCl solution at 1:50 (w:v) ratio.

Biochar	N sorbed (mg g^{-1} biochar)			N extracted with 1 M KCL (mg g^{-1} biochar)		
	NO_3-N	NH_4-N	Total	NO_3-N	NH_4-N	Total
PL400	21.0	19.8	40.8	0.17	0.06	0.23
PL500	21.6	19.8	41.4	0.16	0.12	0.28
PL600	20.6	18.1	38.7	0.19	0.06	0.25
SPF400	20.3	28.4	48.7	0.16	0.03	0.19
SPF500	20.4	26.3	46.7	0.15	0.06	0.21
SPF600	19.7	23.8	43.5	0.14	0.03	0.17
PL/SPF400	2.9	0	2.9	0.16	0.16	0.32
PL/SPF500	2.0	1.1	3.1	0.20	0.20	0.40
PL/SPF600	3.0	5.4	8.4	0.34	0.11	0.45

Table 1
Physicochemical characteristics of different biochars.

Biochar[a]	pH	CEC (cmol kg^{-1})	%N	%H	%O	Atomic O:C[b]	Atomic H:C	Atomic (O + N):C
PL400	9.49	48.0	4.48	3.08	15.62	0.24	0.74	0.31
PL500	9.33	36.0	3.99	2.04	8.60	0.12	0.45	0.18
PL600	9.91	47.8	3.27	1.49	5.20	0.07	0.32	0.12
SPF400	5.47	1.0	0.28	3.60	17.70	0.26	0.61	0.26
SPF500	7.13	0.9	0.40	2.99	9.42	0.10	0.43	0.11
SPF600	7.53	1.3	0.54	2.42	4.75	0.04	0.32	0.05
PL/SPF400	9.21	22.8	3.34	3.42	22.44	0.23	0.72	0.28
PL/SPF500	9.31	23.9	3.14	2.54	11.48	0.11	0.48	0.15
PL/SPF600	9.53	31.0	2.87	2.05	5.04	0.05	0.37	0.09

[a] Letters refer to feedstock material as poultry litter (PL), spruce-pine-fir wood waste (SPF) and their 50:50 blend (PL/SPF); numbers refer to pyrolysis temperature in °C.
[b] %C values are shown in Fig. 1.

volatile compounds at higher pyrolysis temperatures caused the resulting biochars to have a higher C content but much lower H and O contents (Novak et al., 2009).

3.2. Nitrogen sorption and its release

Of the biochars tested, SPF biochars sorbed the most N at about 46 mg N g^{-1} biochar, followed by PL (~40 mg N g^{-1} biochar) but the sorption was an order of magnitude lower in PL/SPF biochars (averaging 4 mg N g^{-1}, Table 2). It is interesting to see these appreciable differences in N sorption capacity of these biochars despite the fact that they all had similar atomic H:C values for the three pyrolysis temperatures. There were very little differences between N sorbed from nitrate and ammoniacal N among the different biochars. Sarkhot et al. (2012) found that dairy-manure treatment of mixed-hardwood biochar pyrolysed at 300 °C resulted in sorption of up to 4.2 mg N g^{-1} biochar. The rather low sorption of N by the PL/SPF biochars suggests the possibility of some significant chemical reaction between the two feedstocks during pyrolysis, and requires further investigation. It is surprising to note that the amounts of N released on extraction of the N-enriched biochars with 1 M KCl solution were very small (0.2—0.4 mg N g^{-1} biochar), which suggests that the retained N was strongly held in complex bonds, more so for NH_4—N since the release of NO_3—N was 3—4 times greater than that of NH_4—N. According to Kameyama et al. (2012) and Yao et al. (2012), N not recovered by 2 M KCl extraction may be physically absorbed by the microporous biochar.

Our results further show that the proportion of sorbed N released on extraction with 1 M KCl solution was much higher for the PL/SPF biochars, suggesting that their sorption of N was weaker than the other biochars, although the amounts of N initially sorbed were several-fold lower than for the PL and SPF biochars. Pyrolysis temperature showed almost no effect on both sorption and release of sorbed N regardless of feedstock used. These results differ from those of Asada et al. (2002), who showed that biochar produced at low (500 °C) pyrolysis temperature adsorbed more ammonia than that produced at high temperature (700 °C). However, Clough et al. (2013) reported a lack of influence of pyrolysis temperature on NH_4^+ sorption by biochars but increasing NO_3^- sorption with pyrolysis temperature. We found that total N sorption and release were similar for both AN and UAN forms of applied N (Table 3).

It has been shown that during pyrolysis at 400—500 °C, acidic functional groups such as carboxyl are formed (Nishimaya et al., 1998), which can preferentially adsorb basic compounds like ammonia making it the primary process for N sorption by biochar particles. Mukerjee et al. (2011) showed that recently produced

Table 3
Sorption of N by different biochars when treated with NH_4NO_3 (AN) and urea ammonium nitrate (UAN) at 1:50 (w:v):: biochar:0.3 MN solution, and release of N when extracted with 1 M KCl solution at a 1:50 (w:v) ratio.

Biochar	N sorbed (mg g^{-1} biochar)		N extracted with 1 M KCL (mg g^{-1} biochar)	
	AN	UAN	AN	UAN
PL400	35.8	35.8	0.54 (1.5)[a]	0.46 (1.3)[a]
PL500	39.4	36.2	0.38 (1.0)	0.27 (0.8)
PL600	38.4	38.6	0.31 (0.8)	0.32 (0.8)
SPF400	34.8	36.6	0.18 (0.5)	0.32 (0.8)
SPF500	34.8	36.6	0.13 (0.4)	0.28 (0.8)
SPF600	34.1	35.6	0.14 (0.4)	0.18 (0.5)
PL/SPF400	7.7	3.0	0.31 (4.0)	0.28 (9.3)
PL/SPF500	7.9	3.8	0.79 (10.0)	0.43 (11.3)
PL/SPF600	8.4	4.0	0.92 (10.9)	0.48 (12.0)

[a] Numbers in parentheses indicate % of sorbed N.

biochar surfaces were mainly characterized by negative surface functional groups thereby sorbing more cations than anions. Biochars with higher atomic H:C, O:C and (O + N):C are expected to be more interactive with polar compounds such as ammonia (Wang et al., 2007). We found these ratios to be significantly higher for biochars obtained at lower pyrolysis temperature (e.g., 400 °C) (Table 1), but there was little relationship between these ratios and N sorption (Table 2).

Biochars with higher H:C (as well as O:C) have more functional groups thereby providing more chemical bonding with polar compounds (Wang et al., 2007). Our results showed that atomic H:C decreased with increasing pyrolysis temperature irrespective of the feedstock used, but this had no effect on N sorption, thereby suggesting that physical adsorption on active surfaces was the main mechanism of N retention in these biochars. However, such sorption would be expected to be reversible resulting in faster release of retained N. Kameyama et al. (2012) reasoned that as sorption of NO_3^- was due to base functional groups and not due to physical sorption, it was only weakly adsorbed onto biochar. Nitrate sorption on the biochar surface may be mainly due to electrostatic interactions (outer-sphere complexation mechanism) and to a lesser extent to ionic exchange mechanisms (Mukerjee et al., 2011). Also, the surface of biochar may develop negative charge at high pH values, resulting in OH$^-$ ions competing with NO_3^- thereby limiting the sorption of NO_3^- (Chintala et al., 2013).

Regarding sorption of NH_4^+, it is considered to be mainly due to the CEC of the biochar (e.g., Lehmann, 2007b). However, as calculations show that a CEC of 1 cmol kg^{-1} is equivalent to a maximum sorption of 0.14 mg NH_4^+ — N kg^{-1} biochar, and we found that NH_4^+ — N sorption far exceeded the CEC of the biochars, our results suggest that most of the sorption must be due to physical entrapment of NH_4^+ in biochar pores (Spokas et al., 2011). It is also likely that the NH_4^+ ions directly adsorbed on the biochar surfaces were retained, whereas those further from the surface in the diffuse double layer, as suggested by Beaton et al. (1960), were released during desorption. Furthermore, were CEC the main source of NH_4^+ sorption, it should have been readily extractable with KCl, but we did not observe significant release. Saleh et al. (2012) also found that only 0.4% of the total sorbed NH_4^+ was released when peanut hull biochar was exposed to 2 M KCl, indicating strong sorption. These authors suggested that physical entrapment of NH_4^+ in biochar pore structures may have been responsible. Also, NH_4^+ cations are able to bind via electrostatic exchange with other cationic species on the biochar surface (Hale et al., 2013; Mukerjee et al., 2011).

To conclude, biochars made from low (i.e., PL) and high (i.e., SPF) quality biomass differed in pH, electrical conductivity, CEC, C and N content; however, they showed similar atomic H:C and also similar N sorption and release, irrespective of pyrolysis temperature. Biochars produced using a 50:50 mixture of PL and SPF performed poorly in retaining N from either of AN or UAN, despite similar atomic H:C values. Both PL and SPF biochars sorbed up to 5% N, irrespective of the form of the applied N. Very small amounts of sorbed N (0.2—0.4 mg N g^{-1} biochar or ~0.5% of the sorbed N) was released when extracted with 1 M KCl solution, indicating that the retained N was strongly held in complex bonds, thereby suggesting that biochars pre-enriched with N may be useful as slow N release carriers. Furthermore, NH_4—N sorption far exceeded the CEC of the biochars suggesting that most of the sorption must be due to physical entrapment of NH_4^+ in biochar pores. With biochar application to soil at about 5 Mg ha^{-1}, the biochars enriched with 5% N would be considered suitable for field applications; however, the release of this N under field conditions remains to be determined. Other implications of this research are (1) biochars made using low-quality biomass are equally effective in N sorption as those

using high-quality biomass, and (2) biochars can potentially be used to remove excess N from poultry and dairy manure slurries, which would help in reducing N leaching and gaseous losses.

References

Almendros, G., Knicker, H., González-Vila, F.J., 2003. 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. 34, 1559—1568.

Asada, T., Ishihara, S., Yamane, S., Toba, T., Yamada, A., Oikawa, K., 2002. Science of bamboo charcoal: study on carbonizing temperature of bamboo charcoal and removal capability of harmful gases. J. Health Sci. 48, 473—479.

Beaton, J.D., Peterson, H.B., Bauer, N., 1960. Some aspects of phosphate adsorption by charcoal. Soil Sci. Soc. Am. Proc. 24, 340—345.

Biederman, L.A., Harpole, W.S., 2013. Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. GCB Bioenergy 5, 202—214.

Cayuela, M.L., van Zwieten, L., Singh, B.P., Jeffery, S., Roig, A., Sánchez-Monedero, M.A., 2014. Biochar's role in mitigating soil nitrous oxide emissions: a review and meta-analysis. Agric. Ecosyst. Environ. 191, 5—16.

Chen, B., Zhou, D., Zhu, L., 2008. Transitional adsorption and partition of contaminants by biochars of pine needles with different pyrolytic temperatures. Environ. Sci. Technol. 42, 5137—5143.

Chintala, R., Mollinedo, J., Schumacher, T.E., Papiernik, S.K., Malo, D.D., Clay, D.E., Kumar, S., Gulbrandson, S.K., 2013. Nitrate sorption and desorption in biochars from fast pyrolysis. Micropor. Mesopor. Mater. 179, 250—257.

Clough, T.M., Condron, L.M., Kammann, C., Muller, C., 2013. A review of biochar and soil nitrogen dynamics. Agronomy 3, 275—293.

Dias, J.M., Alvim-Ferraz, M., Almedia, M., Rivera-Utrilla, J., Sanchez-Polo, M., 2007. Waste materials for activated carbon preparation and its use in aqueous-phase-treatment: a review. J. Environ. Manag. 85, 833—846.

Hale, S.E., Alling, V., Martinsen, V., Mulder, J., Breedveld, G.D., Cornelissen, G., 2013. The sorption and desorption of phosphate-P, ammonium-N and nitrate-N in cacao shell and corn cob biochars. Chemosphere 91, 1612—1619.

Hwgendoom, C.J., Betteridge, K., Costall, D.A., Ledgard, S.F., 2010. Nitrogen concentration in the urine of cattle, sheep and deer grazing a common ryegrass/cocksfoot/white clover pasture. N. Z. J. Agric. Res. 53, 235—243.

International Biochar Initiative (IBI), 2012. Standardized Product Definition and Testing Guidelines for Biochar that is Used in Soil. IBI, p. 47.

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

Knicker, H., Skjemstad, J.O., 2000. Nature of organic carbon and nitrogen in physically protected organic matter of some Australian soils as revealed by solid-state ^{13}C and ^{15}N nmr spectroscopy. Aust. J. Agric. Res. 23, 329—341.

Lehmann, J., 2007a. A handful of carbon. Nature 447, 143—144.

Lehmann, J., 2007b. Bio-energy in the black. Front. Ecol. Environ. 5, 381—387.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems — a review. Mitig. Adapt. Strateg. Glob. Change 11, 395—419.

Mizuta, K., Matsumoto, T., Hatate, Y., Nishihara, K., Nakanishi, T., 2004. Removal of nitrate-N from water using charcoal. Biores. Technol. 95, 255—257.

Mukerjee, A., Zimmerman, A.R., Harris, W., 2011. Surface chemistry variations among a series of laboratory-produced biochars. Geoderma 163, 247—255.

Nguyen, B.T., Lehmann, J., 2009. Black carbon decomposition under varying water regimes. Org. Geochem. 40, 846—853.

Nishimaya, K., Hata, T., Imamura, Y., Ishihara, S., 1998. Analysis of chemical structure of wood charcoal by X-ray photoelectron spectroscopy. J. Wood Sci. 44, 56—61.

Novak, J.M., Lima, I., Xing, B., Gaskin, J., Steiner, C., Das, K., Ahmedna, M., Rehrah, D., Watts, D., Busscher, W., Schomberg, H., 2009. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Ann. Environ. Sci. 3, 195—206.

Novak, J.M., Busscher, W.J., 2013. Selection and use of designer biochars to improve characteristics of degraded soils. Ch 7. In: Lee, J.W. (Ed.), Advanced Biofuels and Bioproducts. Springer, New York.

Rosa, D.L., Knicker, J.M., 2011. Bioavailability of n released from N-rich pyrogenic organic matter: an incubation study. Soil Biol. Biochem. 43, 2368—2373.

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

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

Sohi, S.P., Lopez-Cape, E., Krull, E., Bol, B., 2009. Biochar's Roles in Soil and Climate Change: a Review of Research Needs. CSIRO Land & Water Sci, p. 64. Report 05/09.

Sveinson, K., 2012. Making Biochars with Specified Properties: Modelling for Designer Biochar. Presentation at US Biochar Initiative Conference, Sonoma State University, July 19—August 1.

Spokas, K., Novak, J.M., Ventera, R.T., 2011. Biochar's role as an alternative N-fertilizer: ammonia capture. Plant Soil 350, 57—69.

Taghizadeh-Toosi, A., Clough, T., Sherlock, R., Condron, L., 2012. Biochar adsorbed ammonia is bioavailable. Plant & Soil 350, 57—69.

Van Zwieten, L., Singh, B., Joseph, S., Kimber, S., Cowie, A., Chan, K.Y., 2009. Biochar and emissions of non-CO_2 greenhouse gases from soil. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management. Earthscan Publications Ltd., pp. 227—249. ISBN.

Wang, T., Arbestain, C., Hedley, M., Bishop, P., 2012. Chemical and bioassay characterisation of nitrogen availability in biochar produced from dairy manure and biosolids. Organ. Geochem. 51, 45—54.

Wang, T., Arbestain, C., Hedley, M., Singh, B., Calvelo-Pereira, R., Wang, C., 2014. Determination of carbonate-C in biochars. Soil Res. 52, 495—504.

Wang, X.R., Cook, S., Tao, S., Xing, B., 2007. Sorption of organic contaminants by biopolymers. Chemosphere 66, 1476—1484.

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