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Effect of Pine Waste and Pine Biochar on Nitrogen Mobility in Biosolids

Dharini Paramashivam, Timothy J. Clough, Nicholas M. Dickinson, Jacqui Horswell, Obed Lense, Lynne Clucas, and Brett H. Robinson*

Abstract

Humanity produces ~27 kg of dry matter in biosolids per person per year. Land application of biosolids can improve crop production and remediate soils but may result in excessive nitrate N (NO_3^-–N) leaching. Carbonaceous materials can reduce the environmental impact of biosolids application. We aimed to ascertain and compare the potentials for Monterey pine (*Pinus radiata* D. Don)-sawdust-derived biochars and raw sawdust to reduce NO_3^-–N leaching from biosolids. We used batch sorption experiments 1:10 ratio of material to solution (100 mg kg^{-1} of NH_4^+ or NO_3^-) and column leaching experiments with columns containing biosolids (2.7% total N, 130 mg kg^{-1} NH_4^+ and 1350 mg kg^{-1} NO_3^-) mixed with soil, biochar, or sawdust. One type of low-temperature (350°C) biochar sorbed 335 mg kg^{-1} NH_4^+, while the other biochars and sawdust sorbed <200 mg kg^{-1} NH_4^+. None of the materials sorbed NO_3^-. Biochar added at rates of 20 to 50% reduced NH_4^+–N (<1% of total N) leaching from columns by 40 to 80%. Nitrate leaching (<7% of total N) varied little with biochar form or rate but was reduced by sawdust. Incorporating dried sawdust with biosolids showed promise for mitigating NO_3^-–N leaching. This effect likely is due to sorption into the pores of the biochar combined with denitrification and immobilization of N rather than chemical sorption onto surfaces.

Core Ideas

- Dry sawdust reduced nitrate leaching from biosolids; moist sawdust was less effective.
- Biochar was ineffective in reducing nitrate leaching from aged biosolids.
- Biochar chemically sorbed significant amounts of ammonium, whereas sawdust did not.
- Neither biochar nor sawdust chemically sorbed nitrate.
- Sawdust physically sorbed both ammonium and nitrate.

Humanity produces ~27 kg of biosolids (treated sewage sludge) per person per year (Hue, 2014). Applying biosolids to productive land improves plant growth (Ronald et al., 2008) but may result in both high levels of nitrate (NO_3^-) leaching (Correa et al., 2006) and contamination of the soil and food chain. The application of biosolids to prime agricultural land is still unacceptable to many stakeholders, even though many countries have guidelines to manage their environmental impacts. As a consequence, many biosolids are disposed of in landfills, into waterways, or burned. This represents a waste of organic matter and plant nutrients.

Soil degradation is a common problem in most countries. In New Zealand, thousands of hectares of land, formally under Monterey pine (*Pinus radiata* D. Don) plantations (Ministry of Agriculture and Forestry, 2010) have both low soil organic matter levels and soil fertility (Brockerhoff et al., 2005). Similarly, land affected by open-cast mining often fails to develop a vegetative cover and requires remediation. In both cases, biosolids have been used to successfully re-establish soil fertility (Daniels et al., 2003; Novak et al., 2009). However, to achieve a meaningful increase in soil organic matter, high rates (>50 t ha^{-1}) of biosolids are required (Henry et al., 1994). Given that biosolids comprise 2 to 5% N by weight (Daniels et al., 2001), rebuilding degraded soil can result in N rates of up to 2500 kg ha^{-1}, which is well in excess of the maximum rates currently permitted (~200 kg ha^{-1} yr^{-1}) in most jurisdictions (EPA Victoria, 2004; New Zealand Waste Water Association, 2003). Most of the N in biosolids is in an organic form, and as it mineralizes, it provides a source of plant available inorganic N that promotes plant growth with minimal N leaching. However, biosolids can also contain significant amounts of inorganic N as ammonium (NH_4^+–N), which can rapidly nitrify to form NO_3^-–N. In aged biosolids, NO_3^-–N may also be present at significant levels (Smith et al., 1998). In both cases, NO_3^-–N may be leached. Excessive loadings of mineral N are associated with high levels of NO_3^-–N leaching, which can contribute to eutrophication of lakes, rivers, and groundwater (Davis, 2014) and thus, should be prevented.

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Abbreviations: CEC, cation exchange capacity; FIA, flow-injection analysis; IC, inorganic C; TC, total C; TOC, total organic C; VOC, volatile organic compound; WSC, Water-soluble C.

Mixing carbonaceous substances, such as sawdust or biochar, with biosolids can offset some of the negative environmental effects of biosolids addition (Knowles et al., 2011; Daniels et al., 2001; Schmidt, 2001; Simmler et al., 2013). Composting biosolids with sawdust can reduce NO_3^- leaching (Ammari et al., 2012). The timber industry produces large volumes of wood waste, including sawdust, which is often inappropriately disposed of in wood waste piles (Robinson, 2007; Wendong et al., 2005). Provided the sawdust is not contaminated with timber treatment residues, such as Cu, Cr, and As, this waste material may potentially be used to improve environmental outcomes from biosolids-amended soils. Costs would be greatly reduced if the sawdust could be incorporated with the biosolids on site rather than being composted beforehand. However, it is unclear whether uncomposted mixtures are effective in mitigating NO_3^-–N leaching. Composting of biosolids may improve quality of organic matter, which in turn may beneficial for soil (Bernal et al., 2009). Furthermore, composting can reduce amount of potentially phytotoxic compounds (Borchard et al., 2014). Thus, applying biosolids directly into soil may reduce treatment costs but may risk negative effects on soil health and crop growth that increase costs.

Potentially, NO_3^-–N leaching could also be reduced by pyrolyzing pine waste and using the resulting biochar as a biosolids amendment. The sorptive properties of biochar are profoundly affected by the source material, the pyrolysis temperature (Glaser et al., 2002), the particle size (Kwapinski et al., 2010), and the degree of weathering the biochar has undergone in the soil (Novak et al., 2009). Steam activation of biochar can change the sorptive properties of biochar (Borchard et al., 2012). Ducey et al. (2013) showed that steam activation of biochars increased the microbiological communities in the soil. Fungo et al. (2014) reported that steam activation of biochar derived from *Eucalyptus* spp. wood increased the biochar's capacity to suppress CH_4 and N_2O emissions from soil.

Amending biosolids with biochar has been shown to reduce NO_3^-–N leaching from pasture by over 50% (Knowles et al., 2011) when the biochar was made from Monterey pine pyrolyzed at 350°C. Other authors using the same biochar, have also reported lower concentrations of NO_3^-–N in pasture soils following the application of ruminant urine (Taghizadeh-Toosi et al., 2011).

Reductions in soil NO_3^-–N leaching following biochar amendment to soils have been reported to range from 10 to 96% with results varying widely because of experimental conditions, applied N form, N and biochar rates used, biochar feedstock variations, and pyrolysis temperatures (Guo et al., 2014; Knowles et al., 2011; Sika and Hardie, 2014; Troy et al., 2014). It is unclear why biochar amendment of biosolids reduced NO_3^-–N leaching, although it was speculated that biochar could adsorb NH_4^+–N or NO_3^-–N, thus rendering it less available for leaching and plant uptake or that it inhibited either the mineralization of organic-N or nitrification (Knowles et al., 2011).

We hypothesized that mixing biosolids with either pine sawdust or biochar would reduce the mobility of NO_3^-–N and NH_4^+–N. We aimed to determine the potential of Monterey pine sawdust and various sawdust-derived biochars for N immobilization in biosolids and biosolids-amended soils.

Materials and Methods

Soil (Lismore stony silt loam) was collected (0–30 cm) from the Lincoln University Ashley Dene sheep farm (43°39′05.82″ S, 172°19′41.47″ E), New Zealand. The soil is a low-fertility Lismore soil formed from gravel glacial outwash with a variable depth of silty loess deposited at the surface. The soil is well drained and has moderate to rapid permeability (Waikato Regional Council, 2011). The soil was air-dried to a gravimetric moisture content (θ_g) of 11.85% and sieved to <2 mm. Table 1 and Supplemental Table S1 give the chemical properties of the soil. Biosolids were obtained from the Kaikōura Regional treatment works (42°21′47.78″ S, 173° 41′20.32″ E), New Zealand. Approximately 160 kg of stockpiled and weathered biosolids were collected and homogenized using a concrete mixer and initially passed through a 20-mm sieve. A 2-kg subsample was passed through a 2-mm nylon sieve. Biosolids θ_g equaled 53%. Table 1 and Supplemental Table S1 give the properties of the biosolids.

Untreated pine sawdust was obtained from a local sawmill (Shands Road Sawmills Ltd) in New Zealand. After drying at 60°C to a constant weight, the sawdust was sieved to <4 mm. A further portion of the sawdust was kept moist (θ_g = 25%), as collected. The dried sawdust was pyrolyzed at a range of temperatures for varying lengths of time to produce biochars with contrasting properties. A slow pyrolysis method was used to produce

Table 1. Chemical properties of the materials used in the experiments. Values represent the mean (*n* = 3), except pH (median). Values in parentheses are the standard error. Concentrations of other elements can be found in the supplemental data.

	pH (H_2O)	CEC	Bulk density	C	N	C/N ratio	NH_4^+	NO_3^-
		$cmol_c\ kg^{-1}$	$g\ cm^{-3}$	——— % ———			——— $mg\ kg^{-1}$ ———	
Lismore stony silt loam	6.3	13.5 (0.2)	1.1	4.3 (0.1)	0.37 (0.01)	11.6	7.9 (2.9)	181 (10.8)
Biosolids	4.5	16.7 (0.7)	0.7	25.3 (0.4)	2.7 (0.0)	9.4	130 (7.3)	1352 (2.5)
***Pinus radiata* (pyrolysis temperature, time) A = steam activation**								
Sawdust (SD, unpyrolyzed)	5.7	10.6	0.2	51 (0.04)	0.06 (0.00)	850	nd†	nd
Char 350°C, 3 h	5.5	2.2	0.2	71 (0.09)	0.03 (0.00)	2367	nd	nd
Char 350°C, 12 h	5.5	1.3	0.2	72.8 (0.1)	0.03 (0.01)	2427	nd	nd
Bulk biochar 350°C	6.9	9.1	0.2	78.1 (0.08)	0.06 (0.20)	1302	nd	nd
Char 400°C A	6.2	5.9	0.1	75.5 (0.07)	0.04 (0.00)	1888	nd	nd
Char 400°C	5.9	5.2	0.2	75.3 (0.07)	0.04 (0.00)	1883	nd	nd
Char 550°C A	8.1	6.7	0.1	88.4 (0.1)	0.03 (0.00)	2947	nd	nd
Char 550°C	7.9	6.7	0.1	86.5 (0.06)	0.03 (0.00)	2883	nd	nd

† nd, not determined.

low-temperature biochars. A muffle furnace was used to manufacture biochars at 350°C in a low-oxygen environment (Zhang et al., 2015). Sawdust (200 g) was weighed into steel containers covered with aluminum foil. The temperature was monitored using a thermocouple to ensure the temperature of the material was maintained at 350°C. Chars were prepared with pyrolysis times of 3 and 12 h. The target temperature, 350°C, was reached at the rate of 16°C min^{-1}. Higher temperature biochars were produced using a specialized furnace (Hina et al., 2010) equipped with a rotating cylinder of 5-L capacity. Liquefied petroleum gas was used as the heat source to pyrolyze the sawdust at 400 and 550°C. The target temperatures were reached at rates of 38 and 46°C min^{-1}, respectively. Treatments were prepared with and without steam activation. Steam activation (henceforth denoted as "A") was achieved by injecting water into the pyrolysis chamber at a rate of 4 mL min^{-1} with an airflow of 10 mL min^{-1}. A further biochar was also made from pine at 350°C, as previously described by Knowles et al. (2011). This biochar contained particles sizes from <1 to 45 mm and was sieved (<4 mm) and is subsequently referred to as bulk biochar. We included this biochar because Taghizadeh-Toosi et al. (2012) and Knowles et al. (2011) demonstrated that this char affected N fluxes in soil. Table 1 and Supplemental Table S1 show the properties of the sawdust and biochars.

The pH of the materials was determined in water using a sample to water ratio (w/w) of 1:2.5 following the method of Blakemore et al. (1987). Soil carbon (C) and N concentrations were measured using an Elementar Vario MAX CN analyzer (Elementar GmbH). Actual cation exchange capacity (CEC) was measured for all materials using the method described by Blakemore et al. (1987), which uses Ag^+ as the index cation. Extractable NH_4^+ and NO_3^- concentrations in the soil and biosolids were determined using a 2 M KCl extract following the method of Blakemore et al. (1987) and Clough et al. (2001). Water-soluble C (WSC) was determined using cold (20°C) and hot (80°C) water extracts (Ghani et al., 2003). To measure WSC, 3 g of oven-dried material and 30 mL of cold distilled water were placed in polypropylene centrifuge tubes on an end-over-end shaker for 30 min and then centrifuged for 20 min at 2253 *g*. The extracts were then decanted off and filtered through 0.45-μm cellulose nitrate membrane filters. The sample remaining in the centrifuge tube had 30 mL of distilled water added before it was then placed in a hot water bath at 80°C for 16 h then centrifuged and filtered as before. Total carbon (TC), inorganic carbon (IC), and total organic carbon (TOC) concentrations of the WSC samples were measured using a TOC-5000A analyzer (Shimadzu Oceania Pty Ltd.). Total elemental concentrations were measured in acid digests using inductively coupled plasma–optical emission spectrometry (Varian 720-ES) fitted with SPS-3 auto-sampler and ultrasonic nebulizer (Simmler et al., 2013). Digests were prepared with 0.5 g of material mixed with 5 mL of HNO_3 and 1 mL of H_2O_2 (Merck hydrogen peroxide 30%). The mixtures were digested at 175°C for 20 min and diluted up to 25 mL with Milli Q (double deionized water). Wageningen reference soil (ISE 989) and plant (IPE 100) material were analyzed for quality assurance (Van Dijk and Houba, 1998). Recoveries were 95 to 108% for the elements measured.

Batch Sorption Experiments

Batch sorption experiments were performed with all individual materials (not mixtures) using an ambient solution of 0.01 M $CaCl_2$ solution containing 100 mg L^{-1} NH_4^+ [pH 5.1 as $(NH_4)_2SO_4$] or NO_3^- (pH 7.0 as KNO_3) following the method of Wang et al. (2010). Samples (20 g of dry matter) were weighed into 250-mL centrifuge tubes and replicated thrice. Controls were also performed and had no sample addition. Then 200 mL of either the $(NH_4)_2SO_4$ or KNO_3 solution was added and the samples were then placed on an end-over-end shaker for 6 h. Previous experiments had indicated that this was the minimum time required for the biochar samples to equilibrate with the NH_4^+ solution (data not shown). Harmayani and Anwar (2012) showed that equilibrium times for biochars in batch experiments varied from 1 to 96 h.

The effect of pH on sorption was determined for the bulk biochar. Batch sorption experiments used 10 g of bulk biochar and 100 mL of a 100 mg L^{-1} NH_4^+ [as $(NH_4)_2SO_4$ in a 0.01 M $CaCl_2$ matrix]. The pH of the initial mixtures (pH = 5.1) were adjusted downward by adding 400 and 200 μL of 0.6 M HCl to give pH values of 3.4 and 4.2, respectively. The pH was adjusted upward by adding 450 μL of 0.03 M KOH or 750 μL of 0.3 M KOH to give pH values of 6.1 and 7.1, respectively. After shaking (2 h), samples were centrifuged at 2253 *g* for 10 min, filtered (Whatmann 52), then analyzed for residual NH_4^+ and NO_3^- concentrations using flow-injection analysis (FIA; Alpkem FS 3000 twin channel analyzer).

The biosolids were not sterile. Thus, a test of the potential microbial activity on sorption experiment results was performed over a 48-h sorption experiment where the Lismore soil and bulk biochars were mixed with the $(NH_4)_2SO_4$ solution at a ratio of 1:10. Unsterilized and sterilized (using 1 mL of 5% v/v phenol) treatments were included. Samples were again shaken on an end-over-end shaker with subsamples collected at 10-min and 6-, 24-, and 48-h intervals, with all samples analyzed for both NH_4^+ and NO_3^- concentrations.

Column Leaching Experiments

Leaching columns (4-cm height by 4-cm diam.) with an internal volume of 50.3 cm^3 were filled with mixtures of biosolids (sieved to <2 mm), pyrolyzed or unpyrolyzed (sawdust) pine wood (sieved to <4 mm), and quartz sand (<1 mm). Supplemental Table S2 lists, in detail, the treatments with the masses of each material. There were three replicates of each treatment. The total dry matter in each column was 15 g. Column bulk densities ranged between 0.5 and 1.5 g cm^{-3}. The volume of water in the columns at field capacity varied between 9.4 (sand) and 28.9 cm^3 (sawdust plus biosolids). Each column was irrigated daily with 5 mL of deionized water. The eluent was collected weekly and analyzed for both NO_3^-–N and NH_4^+–N concentrations using FIA. Columns were leached under laboratory conditions (20°C) for at least 3 mo or until the NH_4^+–N and NO_3^-–N concentrations in the eluent had stabilized at levels equal to <5% of the concentrations recorded in the initial flush.

Data were analyzed using Minitab 16 (Minitab, 2010). Data sets were analyzed using ANOVA with Fisher's LSD post hoc test to compare means. The level of significance was 0.05.

Results and Discussion

Inorganic Nitrogen Sorption

All of the materials tested, with the exception of sawdust, sorbed significant amounts of NH_4^+ ranging from 14 to 335 mg NH_4^+ kg^{-1} material (Fig. 1). However, only the biochar produced at 350°C for 12 h and the bulk biochar sorbed more NH_4^+ than the soil (Fig. 1; $p < 0.05$). The amounts of NH_4^+ sorbed by the biochars in the current study were relatively small compared with previous reports. For example, Sarkhot et al. (2013) reported biochar produced from hardwood shavings pyrolyzed at 300°C sorbed up to 5300 mg NH_4^+ kg^{-1}. Differences in biochar sorptive capacity for NH_4^+ have been shown to result from feedstock type, for example, *Thalia* spp. and *Schinus* spp. have been shown to sorb NH_4^+ up to 785 and 3700 mg kg^{-1} by Yao et al. (2012) and Zeng et al. (2013), respectively.

Biochar retention of NH_4^+ is a function of the materials' CEC, which besides being a function of feedstock type, is also the result of the biochar production method (Libra et al., 2011). Specifically, the CEC of a biochar is a function of both the pH and porosity (Mukherjee et al., 2011), which varies with pyrolysis temperature. This was demonstrated by Lehmann (2007), using *Robinia pseudoacacia* L. as a feedstock, who showed a strong correlation between increasing biochar pH and increasing CEC as the pyrolysis temperature was increased, with an optimal CEC of 20 cmol$_c$ kg^{-1} at a temperature of 450°C and pH ~ 9. Similar results were observed by Zhang et al. (2015) for *Quercus* spp. Xiao and Pignatello (2015) demonstrated that maple (*Acer* spp.) wood biochars pyrolyzed at 300 to 700°C all had negative zeta potentials above pH 3 with a large increase in negative charge between pH 3 and pH 5.5. In the current study, increasing the pH during the batch sorption experiments also increased the sorption of NH_4^+ (Fig. 2), and this is consistent with the surface charge varying with pH and directly influencing the biochar's CEC (Lehmann, 2007).

Other studies specifically measuring CEC following the pyrolysis of *Pinus* spp. at 400 and 600°C have shown CEC to range from 10 to 38 cmol$_c$ kg^{-1} at near neutral biochar pH (Mukherjee et al., 2011). The lower CEC values in this range are consistent with the lower CEC values for the materials in the current study (Table 1). For non-*Pinus* spp., CEC is reported to range from 0.2 to 25 cmol$_c$ kg^{-1} and varies with different feedstock and pyrolysis conditions (Cheng et al., 2006; Gundale and DeLuca, 2007; Lehmann, 2007; Nguyen and Lehmann, 2009; Sarkhot et al., 2013). In the current study, there was no significant correlation ($r = 0.19$, $p > 0.05$) between the CEC of the materials tested and their ability to sorb NH_4^+. Sterilizing the solutions using phenol addition during the batch sorption experiments showed no significant differences occurred in terms of NH_4^+ sorption. This observation, and the lack of any increase in the NO_3^- concentration (results not shown), indicates that microbial activity did not affect the results of our batch-sorption experiments.

The lack of any significant sorption of NH_4^+ by the sawdust may be due to several reasons. Sawdust cell walls are active ion exchange sites resulting from the presence of cellulose, lignin, and hydroxyl groups (Shukla et al., 2002). However, cation adsorption onto sawdust is pH dependent, in the case of heavy metals, and thus in the current study, lack of NH_4^+ sorption may be due to nonoptimum pH conditions for maximum CEC expression. Another factor that prevents cation exchange on sawdust includes competition for cation sorption sites. In the current study, the Ca^{2+} ions in the assay matrix may have competed with NH_4^+ and been selectively adsorbed on the sawdust (Shukla et al., 2002). The molar ratio of Ca^{2+} to NH_4^+ in our study was 18:1. Furthermore, Harmayani and Anwar (2012) found the initial cation concentrations and extraction time also affected sorption onto pine sawdust. Thus these factors may not have been optimal in the current study for sorption of NH_4^+ by sawdust. Based on these results, the chemical sorption of NH_4^+ is not a mechanism that will reduce the potential leaching of NO_3^- when mixing biosolids with biochars or sawdust and soil.

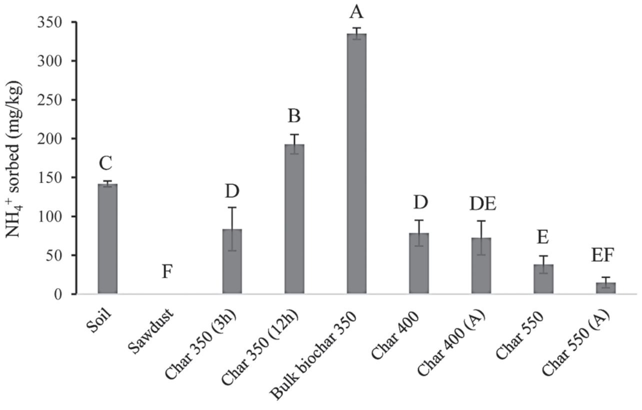

Fig. 1. Ammonium (NH_4^+) sorbed (mg kg^{-1} dry wt.) by soil, sawdust, and biochar from a 100 mg L^{-1} NH_4^+ solution after 6 h of agitation. Material/solution ratio = 1:10. Bars represent the standard error of the mean ($n = 3$). Bars with the same letter are not significantly different.

None of the materials tested sorbed NO_3^- (data not shown). Using sugarcane (*Saccharum officinarum* L.) bagasse as a biochar feedstock, Kameyama et al. (2012) reasoned that the increased sorption of NO_3^- with increasing temperature was the result of N-containing basic functional groups on the biochar surface increasing in number with increasing pyrolysis temperature. Wang et al. (2015) also found NO_3^- sorption increased with increasing biochar manufacturing temperature. Clough et al. (2013) reviewed the studies examining NO_3^- sorption on biochar and concluded that sorption of NO_3^- onto a biochar surface was unlikely to occur unless the pyrolysis temperature during biochar manufacture was >600°C, with the degree of

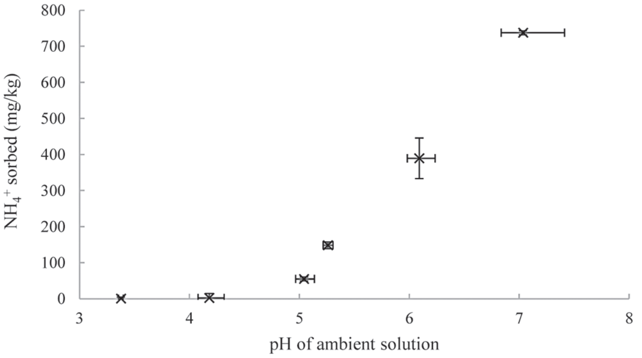

Fig. 2. Ammonium (NH_4^+) sorbed (mg kg^{-1} dry wt.) by the bulk biochar from a 100 mg L^{-1} NH_4^+ solution after 2 h of agitation at various solution pH values. Material/solution ratio = 1:10. Bars represent the standard error of the mean ($n = 3$).

NO_3^- sorption also dependent on feedstock type. Other more recent studies, also showing low sorption of NO_3^- by biochar, have generally examined biochar manufactured at pyrolysis temperatures <600°C (Gai et al., 2014; Hale et al., 2013; Zhang et al., 2015). Chintala et al. (2013) showed that NO_3^- sorption of a biochar produced at 650°C was only significant in acidic conditions. Thus, ignoring feedstock type as an issue, the lack of NO_3^- sorption in the current experiment is most likely because the low pyrolysis temperatures in our study were insufficient for the formation of N-containing basic functional groups (Kameyama et al., 2012). Shafeeyan et al. (2010) reported that significant numbers of N-containing basic functional groups only form at temperatures >700°C. Sawdust materials can retain cations, but they are not able to bind anions unless they are chemical modified (Ebrahimi and Roberts, 2013; Keränen et al., 2015; Mishra and Patel, 2009; Sousa et al., 2010; Su et al., 2012). For example, Keränen et al. (2015) modified sawdust to sorb NO_3^- using epichlorohydrin, ethylenediamine, and trimethylamine in the presence of N,N-dimethylformamide. It is therefore unlikely that chemical sorption of NO_3^- by the sawdust or biochars will reduce NO_3^- leaching.

Inorganic Nitrogen Leaching

Ammonium N in the leachate accounted for <1% of N applied (Fig. 3). The assumption is made that given the N content of the biochar (Table 1), the source of the NH_4^+–N in the leachate is the biosolids. When biochar materials were mixed with biosolids in the leaching columns, the biochars reduced the amount of NH_4^+–N leached when expressed as a percentage of the total N initially present in the biosolids (Fig. 3). The effect of increasing biochar rate observed with the bulk biochar treatment was to further reduce NH_4^+ leaching. This is most likely a consequence of the increasing CEC, since the amount of NO_3^-–N leached did not vary with the bulk biochar rate applied (Fig. 4). This also indicates that increasing the rate of biochar addition did not significantly accelerate nitrification via potential liming effects, which could in turn have enhanced subsequent NO_3^-–N leaching (Clough et al., 2013). Incorporating biochar into acidic agricultural soils accelerates nitrification and thus, weakens the liming effects of biochar (Zhao et al., 2014).

The low-temperature biochars (350°C) reduced NH_4^+–N leaching more than the high-temperature chars (400 and 550°C), while steam activation did not have a consistent effect on NH_4^+–N leaching (Fig. 3). Park et al. (2003) and Shafeeyan et al. (2010) reported that although steam activation increased the surface area and micropore volume of biochar, it depleted the surface functional groups, possibly offsetting any increase in sorption capacity.

Another possible mechanism for reducing NH_4^+–N leaching declining with increasing biochar rate is microbial immobilization of NH_4^+. The C to N ratios of most of our biochar–biosolids and sawdust–biosolids mixtures (calculated from Table 1) were above 25, the value required to trigger immobilization (McLaren and Cameron, 1996). We did not measure any microbiological parameters; however, if there were significant microbial immobilization, then there would be a negative correlation between WSC (Supplemental Table S3) and the mass of NH_4^+–N leached (Fig. 3, 5). However, the hot and cold WSC concentrations did not correlate with the reduction in NH_4^+–N leaching observed ($r = -0.35$, $P > 0.05$ NS).

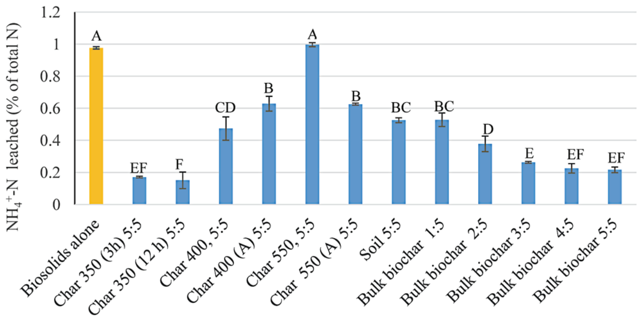

Fig. 3. Ammonium-N leached (as a percentage of total N in the columns) from columns with soil or biochars mixed with biosolids. Number ratios indicate the ration of mass of material (g) to mass of biosolids (g). Bars represent the standard error of the mean (*n* = 3).

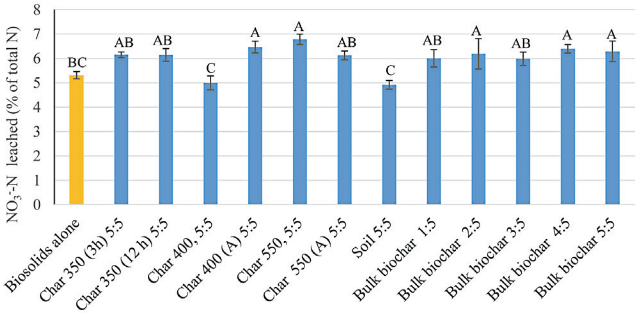

Fig. 4. Ammonia-N (as a percentage of total N in the columns) from columns with soil or biochars mixed with biosolids. Number ratios indicate the ratio of mass of material (g) to mass of biosolids (g). Bars represent the standard error of the mean (*n* = 3).

While NH_3 adsorption onto biochar can occur (Taghizadeh-Toosi et al., 2011) the likelihood of NH_3 adsorption occurring in the biochar material, as a mechanism for reducing NH_4^+ in solution, is unlikely a result of the pH being too low (<7.0). The pH values of the solutions in our batch sorption experiments ranged from 4.2 to 5.8.

Nitrate leaching from the column experiment accounted for <7% of the N applied (Fig. 4) and showed few differences as a consequences of biochar–biosolids treatment. Most of the N

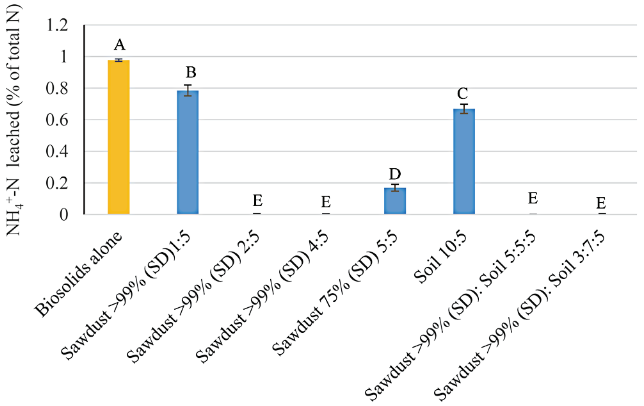

Fig. 5. Ammonium-N leached (as a percentage of total N in the columns) from columns with soil or sawdust mixed with biosolids. Number ratios indicate the ratio of mass of material (g) to mass of biosolids (g). Bars represent the standard error of the mean (*n* = 3).

in the biosolids remained as organic N. None of the biochar treatments caused a significant decrease in NO_3^-–N leaching (Fig. 4), in fact, the high temperature biochars and the high rates of the bulk biochar caused an increase ($p < 0.05$) in NO_3^-–N leaching. Reasons for the greater NO_3^-–N leaching could include greater aeration of the biosolids material, resulting in higher rates of mineralization and subsequent nitrification causing more NO_3^-–N leaching. Our result deviates from the findings of Knowles et al. (2011), who reported that the bulk biochar significantly reduced NO_3^-–N leaching from biosolids-amended soil. However, the experimental conditions described in Knowles et al. (2011) were significantly different. Their experiment was performed in the field with large lysimeters containing intact soil cores with pasture present (*Lolium perenne* L.) and thus, plant N uptake occurred.

Volatile organic compounds (VOCs) may be present in biochars and sawdust (Spokas et al., 2011) and can potentially reduce nitrification (Clough et al., 2010) and mineralization. Borchard et al. (2014) demonstrated that VOCs from biochar influence N cycle and can reduce greenhouse gas emissions from soil. The fact that the NO_3^-–N leached as a percentage of N applied was higher ($p < 0.05$) under the biochar treatments than in the biosolids alone (Fig. 4) indicates that if biochar-borne VOCs were inhibiting nitrification, then the effect was small.

Sawdust caused a significant reduction ($p < 0.05$) in both NH_4^+–N and NO_3^-–N leaching from both biosolids and biosolids-amended soil treatments (Fig. 5, 6). Rates of more than two parts of sawdust to five parts of biosolids eliminated NH_4^+–N leaching and reduced NO_3^-–N leaching by >40% (Fig. 6). These results cannot be explained by chemical sorption mechanisms because the batch experiments revealed that the sawdust sorbed neither NH_4^+–N nor NO_3^-–N. Adding sawdust increased the C to N ratio (Table 1) of the mixtures, which may have resulted in microbial immobilization of biosolids derived N. The sawdust's C to N ratio of 850 is well in excess of the value required to trigger immobilization (C/N of >25:1 McLaren and Cameron (1996). The WSC extracts (Supplemental Table S3) also indicate that in the unmixed materials, C was readily available for microbial immobilization to occur. Consistent with this theory are the results of Daniels et al. (2001), who showed that adding sawdust to biosolids at a rate of 3:2 reduced NO_3^-–N in soil pore water by >50%. In contrast, Schmidt (2001) showed that a 1:1 biosolids to sawdust mixture was ineffective in reducing NO_3^-–N leaching in the first growing season. The high WSC availability also raises the possibility of other heterotrophic activity, such as denitrification, also consuming NO_3^-–N and contributing to the decrease in NO_3^-–N leaching observed. Schipper and Vojvodic-Vukovic (1998) showed that soil amended with sawdust will remove NO_3^-–N from the groundwater via denitrification. Sawdust with a moisture content of 25% had a significantly smaller effect on NH_4^+–N and NO_3^-–N leaching than dry sawdust (Fig. 5, 6). This indicates that the sawdust may have irreversibly sorbed some of the N-rich pore water from the fresh biosolids and that physical sorption may be an important mechanism for the retention of N in these experiments. Our experiments did not provide any information on the mechanisms of such physical sorption. Biochar containing some partially pyrolyzed or unpyrolyzed material may therefore also mitigate N leaching. In this case, partial pyrolysis may be a low-cost means of drying the material. As the material weathers in the soil, the CEC of the biochar may increase (Glaser et al., 2002; Liang et al., 2006), further retaining NH_4^+–N in the root-zone where plant uptake can occur.

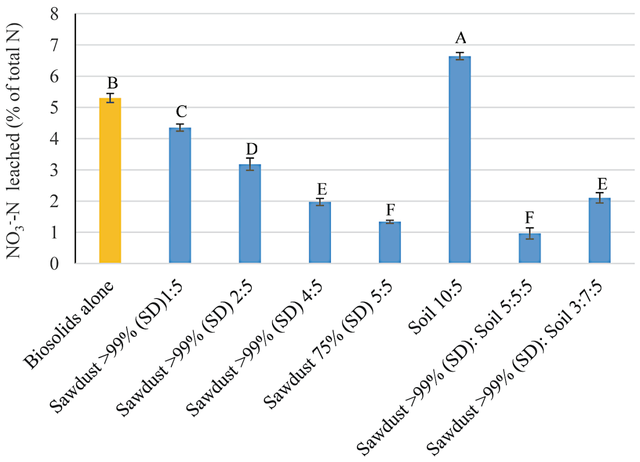

Fig. 6. Ammonia-N leached (as a percentage of total N in the columns) from columns with soil or sawdust mixed with biosolids. Number ratios indicate the ratio of mass of material (g) to mass of biosolids (g). Bars represent the standard error of the mean (*n* = 3).

Conclusions

The potential for unweathered biochars derived from sawdust feedstock to mitigate NO_3^-–N leaching from biosolids-amended soils is low and the biochars may even accelerate NO_3^-–N leaching. However, pine waste and pine biochars significantly reduced NH_4^+–N mobility. Conversely, including raw, dried sawdust when amending soils with biosolids shows significant promise to limit N mobility in biosolids and potentially reduce NO_3^-–N leaching. Future work should look to better understand the reasons for this while optimizing rates and methods to achieve NO_3^-–N leaching mitigation.

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