



## Nutrient release and ammonium sorption by poultry litter and wood biochars in stormwater treatment



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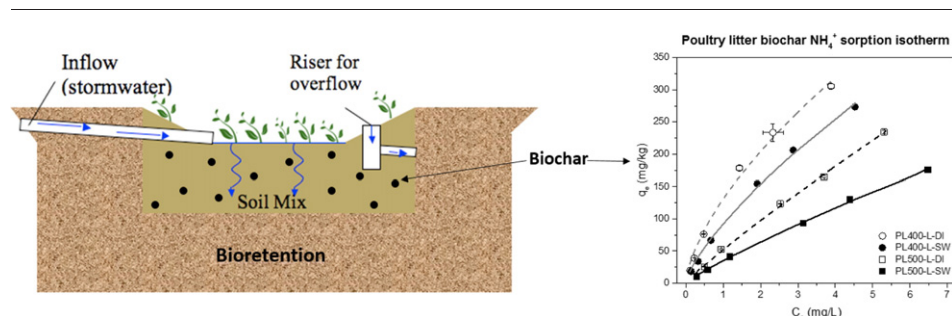
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### HIGHLIGHTS

- Less nutrient leaching and  $\text{NH}_4^+$  sorption for hardwood vs poultry litter biochar.
- Cation exchange capacity (CEC) controlled  $\text{NH}_4^+$  sorption onto biochars.
- $\text{NH}_4^+$  sorption correlated positively with CEC but negatively with BET surface area.
- 10% by mass biochar increased  $\text{NH}_4^+$  removal from stormwater from 1.7% to >90%.
- Hardwood and poultry litter biochars promising for bioretention media.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The feasibility of using biochar as a filter medium in stormwater treatment facilities was evaluated with a focus on ammonium retention. Successive batch extractions and batch ammonium sorption experiments were conducted in both deionized (DI) water and artificial stormwater using poultry litter (PL) and hardwood (HW) biochars pyrolyzed at 400 °C and 500 °C. No measurable nitrogen leached from HW biochars except 0.07  $\mu\text{mol/g}$  of org-N from 400 °C HW biochar. PL biochar pyrolyzed at 400 °C leached 120–127  $\mu\text{mol/g}$  of nitrogen but only 7.1–8.6  $\mu\text{mol/g}$  of nitrogen when pyrolyzed at 500 °C. Ammonium sorption was significant for all biochars. At a typical ammonium concentration of 2 mg/L in stormwater, the maximum sorption was 150 mg/kg for PL biochar pyrolyzed at 400 °C. In stormwater, ion competition (e.g.  $\text{Ca}^{2+}$ ) suppressed ammonium sorption compared to DI water. Surprisingly, ammonium sorption was negatively correlated to the BET surface area of the tested biochars, but increased linearly with cation exchange capacity. Cation exchange capacity was the primary mechanism controlling ammonium sorption and was enhanced by pyrolysis at 400 °C, while BET surface area was enhanced by pyrolysis at 500 °C. The optimal properties (BET surface area, CEC, etc.) of biochar as a sorbent are not fixed but depend on the target pollutant. Stormwater infiltration column experiments in sand with 10% biochar removed over 90% of ammonium with influent ammonium concentration of 2 mg/L, compared to only 1.7% removal in a sand-only column, indicating that kinetic limitations on sorption were minor for the storm conditions studied. Hardwood and poultry litter biochar pyrolyzed at 500 °C and presumably higher temperature may be viable filter media for stormwater treatment facilities, as they showed limited release of organic and inorganic nutrients and acceptable ammonium sorption.

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## 1. Introduction

With increasing urbanization, urban stormwater runoff has received considerable attention due to its impact on water quality. Urban runoff contributes total suspended solids (7.8–5700 mg/L), nitrogen (0.4–20 mg/L), metals (160–914 µg/L), polycyclic aromatic hydrocarbons (677–6477 ng/L), phenols (400–9690 ng/L), pesticides (0.26–247 µg/L) and other contaminants (Lundy et al., 2012, Zgheib et al., 2012, Revitt et al., 2014) to natural water bodies and may require treatment before discharge. Bioretention is one of the most widely used Low Impact Development practices and addresses both hydrologic and water quality issues of urban stormwater runoff. A bioretention system generally consists of a water ponding depression, a surface mulch layer, and a filter media layer, with vegetation growing in the filter media. Bioretention can efficiently remove most stormwater pollutants, such as suspended solids, heavy metals, oil/grease, and pathogenic bacteria (USEPA1999). However, nitrogen removal by bioretention has been reported to be variable and relatively poor (Davis et al., 2009).

Biochar is a thermal decomposition product from biomass heated at relatively low temperature (<700 °C) with limited oxygen (Lehmann and Joseph, 2009). Biochar has been proposed as a soil amendment because it sequesters carbon and retains nutrients (Glaser et al., 2002, Lehmann, 2007, Laird, 2008). Recently other potential benefits of biochar addition to soil have been proposed, including mitigation of greenhouse gas emissions (Singh et al., 2010, Case et al., 2012), removal of environmental pollutants (Cao et al., 2011, Chen et al., 2011), enhanced water retention (Laird et al., 2010a, Dempster et al., 2012), and increased soil microbial activity (Kappler et al., 2014).

It is hypothesized that incorporating biochar into bioretention filter media could enhance nitrogen removal by enhancing anaerobic conditions for denitrification through increased water retention, or nutrient sorption. Currently, bioretention filter media mainly consist of sandy loam or loamy sand, amended with organic matter such as peat moss or compost. In Delaware, for example, bioretention filter media contain 60% concrete sand, 20% triple-shredded hardwood mulch, and 20% aged compost by volume (DNREC, 2013). North Carolina requires a homogeneous soil mix of 85–88% by weight sand, 8–12% fines (silt and clay), and 3–5% organic matter (such as peat moss) as filter media (NCDWQ, 2007). Prince George's County, Maryland stipulates that filter media consist of 50–60% sand, 20–30% leaf compost, and 20–30% topsoil by volume (PGDER, 2007). The organic matter in these filter media provide nutrients for plants and microbes, but may degrade quickly and leach nutrients. Biochar might replace some organic matter in these media since it 1) retains nutrients, especially cations (e.g.  $\text{NH}_4^+$ ), due to its high cation exchange capacity (Cheng et al., 2008), high surface area, negative surface charge, and high charge density (Liang et al., 2006); 2) provides a source of plant-available ammonium, if ammonium is sorbed from stormwater (Taghizadeh-Toosi et al., 2012); and 3) is more recalcitrant than typical organic matter found in filter media (Lehmann, 2007).

The ability of biochar to enhance ammonium retention within soil has been noted in several studies (Clough and Condon, 2010, Spokas et al., 2011). A bamboo biochar pyrolyzed at 600 °C and added to the surface soil layer at 0.5% mass fraction retarded ammonium movement to deeper layers and reduced leaching of  $\text{NH}_4\text{-N}$  at 20 cm by 15.2% (Ding et al., 2010). Yao et al. (2012) showed that a Brazilian pepperwood biochar pyrolyzed at 600 °C and added to a sandy soil column at 2% mass reduced  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  leaching by 34.7%, 34.0%, and 20.6%, respectively, compared to the soil alone. Dempster et al. (2012) reported that Jarrah wood biochar applied to soil at 0.5% mass fraction reduced cumulative ammonium leaching by 14% over 21 days. While Yao et al. (2012) tested four types of biochar pyrolyzed at 300 °C, 450 °C, and 600 °C, only Brazilian pepperwood biochar removed  $\text{NH}_4^+$  from aqueous solution at all three pyrolysis temperatures; other biochars showed  $\text{NH}_4^+$  removal for 300 °C and 600 °C biochar, but  $\text{NH}_4^+$  release for 450 °C biochar. Thus, the effect of biochar on ammonium sorption is

mixed and appears dependent on biochar properties, which are a function of feedstock, pyrolysis conditions, and perhaps aging after biochar is mixed with soil.

Based on biochar's ability to retain nutrients and improve soil water retention for some soils (Brockhoff et al., 2010, Dempster et al., 2012, Herath et al., 2013, Barnes et al., 2014, Mukherjee et al., 2014), biochar has been evaluated as an amendment in urban stormwater treatment systems. Beck et al. (2011) found that a biochar produced from a mixture of agricultural waste and passenger car tires when incorporated at 7% (w/w) into a prototype greenroof soil increased water retention and decreased total nitrogen (TN), total phosphorus (TP),  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and organic carbon discharge. In a series of column experiments Reddy et al. (2014) used 100% 520 °C wood biochar to treat pollutants in artificial stormwater: total suspended solids (TSS),  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  in the stormwater effluent were reduced by 86%, 86% and 47%, respectively, and heavy metals decreased by 18–75%. While demonstrating positive results, these studies are limited in that the mechanisms for pollutant removal while postulated were not quantified, making it difficult to predict the degree of pollutant removal with addition of different amounts of biochar to stormwater infiltration media.

The purpose of this study was to evaluate the feasibility of using poultry litter biochar and hardwood biochar as filter media amendments to enhance ammonium sorption in stormwater treatment facilities. Nitrogen leaching from these biochars into stormwater was also evaluated. Over 44 million tons of poultry litter are generated annually by the US poultry industry (Bolan et al., 2010), and large-scale accumulation of wastes may lead to disposal and pollution problems without sustainable management technologies. Poultry litter was examined as a feedstock to utilize this waste material. For comparison, a wood-based biochar was selected because of its low nutrient concentrations (Mukome et al., 2013), high specific surface area (Keiluweit et al., 2010, Kizito et al., 2015), and the benefits of using this waste product from wood gasifiers. Wood biochars are also commercially available in sufficient quantities to be used in stormwater bioretention facilities (Wallin, 2015).

## 2. Materials and methods

### 2.1. Biochar preparation

Poultry litter (PL) biochar was prepared by pyrolyzing granular poultry litter, which was made from raw poultry litter (consisting of a combination of manure and bedding material resulting from the poultry industry) via pasteurizing, milling, and pelletizing at Perdue AgriRecycle, LLC (Seaford, DE). Hardwood (HW) biochar was made from Pennington Nature's Heat hardwood pellets manufactured for household heating. PL and HW pellets were pyrolyzed using an electrical muffle furnace connected to a condenser and a water washer (Song and Guo, 2012). Ground PL or HW pellets were packed into a cylindrical aluminum canister 11 cm inner diameter × 13 cm height. The canister was covered with an aluminum lid with a 5 mm diameter hole for volatiles emission before placement in the muffle furnace for heating. Depending on the experiment, the temperature in the muffle furnace was set at 400 °C or 500 °C, with temperatures rising from ambient conditions at an average rate of 20 °C/min until the desired pyrolysis temperature was reached. The pyrolysis temperature was maintained until no visible smoke entered the condenser, which indicated pyrolysis was complete. The 400 °C and 500 °C PL biochars (PL400 and PL500) required approximately 8 and 6 h for complete pyrolysis, whereas the 400 °C and 500 °C HW biochars (HW400 and HW500) required 4 and 2 h, respectively. After the process was finished, the canister was taken out of the furnace and the ventilation hole in the lid was sealed immediately with a metal plug. After the canister cooled to room temperature, all biochars were removed and sieved to 0.8–1.0 mm particle size and stored in sealed plastic bags for one month until use.

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