



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 NO₃-N and NH₄-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 NH₄-N because the release of NO₃-N was 3–4 times greater than that of NH₄-N. NH₄-N sorption far exceeded the effective CEC of the biochars, thereby suggesting that most of the sorption may be due to physical entrapment of NH₄⁺ 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 N₂O and CH₄ 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

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potential to reduce disposal costs, curb odour and decrease emissions of methane (CH₄), nitrous oxide (N₂O) and ammonia (NH₃) 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 ¹⁵N-labelled NH₃ resulting in biochar with a total N content of <1%. Mechanisms for the sorption of NH₃, such as formation of amides or physical entrapment of NH₃ 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 NH₄NO₃ (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 CaCl₂ (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 CaCl₂ 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 CaCl₂ 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 (Hwengendoom 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

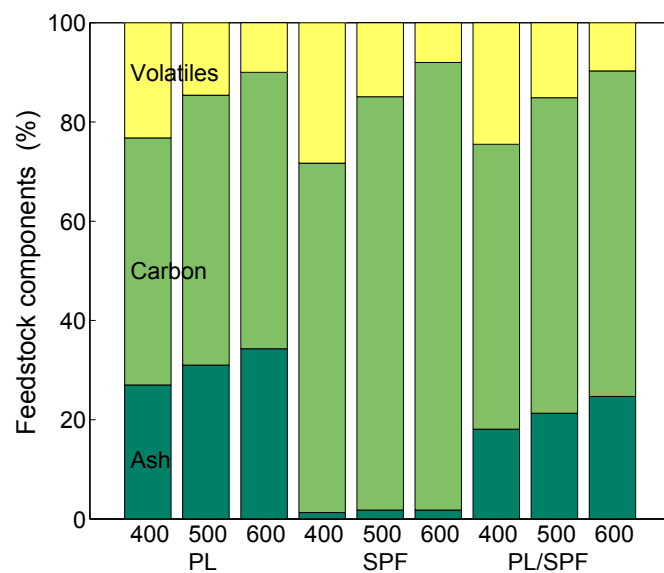


Fig. 1. Physical composition of different feedstocks (poultry litter (PL), spruce-pine-fir wood waste (SPF) and their 50:50 blend (PL/SPF)) after their pyrolysis at 400, 500 and 600 °C.

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