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Short Communication

Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil

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HIGHLIGHTS

- ▶ Effect of biochar on the leaching of nutrients in soils is not uniform.
- ▶ Sorption of nutrients on biochar varies by biochar and nutrient type.
- ▶ Nutrient sorption characteristics should be studied prior to biochar application.

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ABSTRACT

When applied to soils, it is unclear whether and how biochar can affect soil nutrients. This has implications both to the availability of nutrients to plants or microbes, as well as to the question of whether biochar soil amendment may enhance or reduce the leaching of nutrients. In this work, a range of laboratory experiments were conducted to determine the effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. A total of thirteen biochars were tested in laboratory sorption experiments and most of them showed little/no ability to sorb nitrate or phosphate. However, nine biochars could remove ammonium from aqueous solution. Biochars made from Brazilian pepperwood and peanut hull at 600 °C (PH600 and BP600, respectively) were used in a column leaching experiment to assess their ability to hold nutrients in a sandy soil. The BP600 biochar effectively reduced the total amount of nitrate, ammonium, and phosphate in the leachates by 34.0%, 34.7%, and 20.6%, respectively, relative to the soil alone. The PH600 biochar also reduced the leaching of nitrate and ammonium by 34% and 14%, respectively, but caused additional phosphate release from the soil columns. These results indicate that the effect of biochar on the leaching of agricultural nutrients in soils is not uniform and varies by biochar and nutrient type. Therefore, the nutrient sorption characteristics of a biochar should be studied prior to its use in a particular soil amendment project.

1. Introduction

Excessive application of fertilizer has caused the release of nutrient elements, such as nitrogen and phosphorus, from agricultural fields to aquatic systems. Leaching of nutrients from soils may deplete soil fertility, accelerate soil acidification, increase fertilizer costs for the farmers, reduce crop yields, and most importantly impose a threat to environmental health (Bhargava and Sheldarkar, 1993; Ozacar, 2003; Laird et al., 2010). High nutrient levels in surface and/or groundwater can promote eutrophication, excessive production of photosynthetic aquatic microorganisms in freshwater and marine ecosystems (Karaca et al., 2004). It is therefore very important to develop effective technologies to hold nutrients in soils.

An option to reduce nutrient leaching could be the application of biochar to soils. Biochar, sometimes called agrichar, is a charcoal derived from the thermal decomposition of a wide range of carbon-rich biomass materials, such as grasses, hard and soft woods, and agricultural and forestry residues. The approach of land application of biochar in agriculture is receiving increased attention as a way to create a carbon sink to mitigate global warming, increase soil water holding capacity, and reduce emissions of NO_x and CH_4, as well as to control the mobility of a variety of environmental pollutants, such as heavy metals, pesticides and other organic contaminants (Lehmann et al., 2006; Verheijen et al., 2009; Inyang et al., 2010; Van Zwieten et al., 2010). In addition, it is suggested that application of biochar can increase soil fertility and crop productivity by reducing the leaching of nutrients or even supplying

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nutrients to plants (Glaser et al., 2002; Lehmann et al., 2003; Major et al., 2010).

Only a few studies, however, have investigated the ability of biochars to retain nutrients, particularly for a range of different biochars. For example, Lehmann et al. (2003) reported that amendment of biochar produced from secondary forest residuals significantly reduced the leaching of fertilizer N and increased plant growth and nutrition. Ding et al. (2010) showed that bamboo biochar sorbed ammonium ions by cation exchange and retarded the vertical movement of ammonium into deeper soil layers within the 70-d observation time. Laird et al. (2010) reported the addition of biochar produced from hardwood to typical Midwestern agricultural soil significantly reduced total *N* and *P* leaching by 11% and 69%, respectively.

The overarching objective of this work was to determine the effect of biochar amendment on leaching of nitrate, ammonium, and phosphate in sandy soils. Biochars were produced from a range of commonly used feedstock materials. Laboratory batch sorption experiments were conducted to access the overall aqueous nitrate, ammonium, and phosphate sorption ability of the biochars. In addition, laboratory column experiments were used to examine the leaching dynamics of the three nutrients in a sandy soil amended with two selected biochars.

2. Materials and methods

2.1. Materials

Biochar samples were produced from commonly used biomass feedstock materials: sugarcane bagasse (BG), peanut hull (PH), Brazilian pepperwood (BP), and bamboo (BB). The raw materials were oven dried (80 °C) and converted into biochar through slow pyrolysis using a furnace (Olympic 1823HE) in a N_2 environment at temperatures of 300, 450 and 600 °C. The resulting twelve biochar samples are henceforth referred to as BG300, BG450, BG600, PH300, PH450, PH600, BP300, BP450, BP600, BB300, BB450, and BB600. Another biochar (hydrochar) was produced through the hydrothermal carbonization of PH submerged in deionized (DI) water in an autoclave at 300 °C for 5 h and is referred to as HTPH. All biochar samples were then crushed and sieved yielding a uniform 0.5–1 mm size fraction. After rinsing with DI water several times to remove impurities, such as ash, the biochar samples were oven dried (80 °C) and sealed in containers for later use. Detailed information about biochar production procedures were reported previously (Yao et al., 2011).

Sandy soil was collected from an agricultural field at the University of Florida in Gainesville, FL. The soil was sieved through a 1 mm mesh (No. 18) and dried (60 °C) in an oven. Basic properties of the soil are listed in Table 1.

Nitrate, ammonium, and phosphate solutions were prepared by dissolving ammonium nitrate (NH_4NO_3) or potassium phosphate dibasic anhydrous (K_2HPO_4) in deionized (DI) water. All the chemicals used in the study were A.C.S certified and obtained from Fisher Scientific.

2.2. Characterization of sorbents

A range of physicochemical properties of the biochar samples produced were determined. The pH of the biochars was measured using a biochar to deionized (DI) water mass ratio of 1:20 followed by shaking and an equilibration time of 5 min before measurement with a pH meter (Fisher Scientific Accumet Basic AB15). Elemental *C*, *N*, and *H* abundances were determined, in duplicate, using a CHN Elemental Analyzer (Carlo-Erba NA-1500) via high-temperature catalyzed combustion followed by infrared detection of the resulting CO_2, H_2 and NO_2 gases, respectively. Major inorganic elements were determined by acid digestion of the samples followed by inductively-coupled plasma atomic emission spectroscopic (ICP-AES) analysis. The surface area of the biochars was determined on Quantachrome Autosorb1 at 77 K using the Brunauer–Emmett–Teller (BET) method in the 0.01–0.3 relative pressure range of the N_2 adsorption isotherm.

Table 1
Basic properties of the sandy soil used in this study.

Texture	Sand (%)	Silt (%)	Clay (%)	Density (g cm^{-3})	Organic matter (%)
Sandy	94.0	3.0	3.0	2.4	1.0

2.3. Sorption of nitrate, ammonium, and phosphate

Batch sorption experiments were conducted in 68 mL digestion vessels (Environmental Express) at room temperature (22 ± 0.5 °C). About 0.1 g of each biochar sample was added into the vessels and mixed with 50 mL 34.4 mg L^{-1} nitrate and 10.0 mg L^{-1} ammonium solution or 30.8 mg L^{-1} phosphate solution. Vessels without either biochar or nutrient elements were included as experimental controls. The mixtures were shaken at 55 rpm in a mechanical shaker for 24 h, and then filtered through 0.22 μm nylon membrane filters (GE cellulose nylon membrane).

In addition to pH, concentrations of nitrate in the supernatants were determined using an ion chromatograph (Dionex Inc. ICS90). Concentrations of ammonium and phosphate in the supernatants were measured using the phenate method (APHA et al., 1992) and the ascorbic acid method (ESS Method 310.1; (USEPA, 1992)), respectively, using a dual beam UV/VIS spectrophotometer (Thermo Scientific, EVO 60). Nutrient elements concentrations on the solid phase were calculated based on the initial and final aqueous concentrations. All the experimental treatments were carried out in duplicate and the average values are reported. The variance between any duplicate measurements in this study was smaller than 5%.

2.4. Leaching of nutrients from soil columns

Two biochar samples, PH600 and BP600, were selected to study their effect on nutrients retention and transport in a sandy soil. Soil columns were made of acrylic cylinders measuring 16.5 cm in height and 4.0 cm in diameter, and the bottom of the columns were covered with a stainless steel mesh with 60 μm pore size to prevent soil loss. The sandy soil with (2% by weight) or without biochars was wet-packed into the column (200 g total) following procedures reported previously (Tian et al., 2010). These columns were flushed with 10 pore-volumes of DI water before use to precondition the column. A nutrient solution containing 34.4 mg L^{-1} nitrate, 10.0 mg L^{-1} ammonium and 30.8 mg L^{-1} phosphate was then applied to these laboratory soil columns to study biochar effect on nutrients retention and transport. About one pore-volume of DI water was poured into the soil columns on the first day. On days 2 and 3, same amount of nutrient solution was applied to the soil columns. After that, the columns were flushed with one pore-volume DI water each day for another 4 d. All the leachate samples were collected from the outlet at the bottom of the columns and immediately filtered through 0.22 μm filters for further analyses. The nitrate, ammonium and phosphate concentrations in leachate samples were measured using the same method described above.

Table 2
Properties and elemental composition of biochars used in this study.

	Production rate (%,mass based)	BET surface area ($m^2\ g^{-1}$)	pH	Elemental composition (%, mass based)											
				C	H	O[a]	N	P	K	Ca	Mg	Zn	Cu	Fe	Al
BG300	33.4	5.2	7.2	69.5	4.2	24.5	0.9	0.05	0.27	0.46	0.14	0.01	0.00	0.02	0.10
BG450	28.0	15.3	7.9	78.6	3.5	15.5	0.9	0.07	0.25	0.83	0.18	0.01	0.00	0.06	0.11
BG600	26.5	4.2	7.9	76.5	2.9	18.3	0.8	0.08	0.15	0.91	0.21	0.01	0.00	0.05	0.11
PH300	38.4	0.8	7.8	73.9	3.9	19.1	1.6	0.09	0.86	0.32	0.13	0.00	0.00	0.00	0.06
PH450	21.7	21.8	8.2	81.5	2.9	13.0	1.0	0.09	0.94	0.33	0.13	0.00	0.00	0.00	0.06
PH600	30.8	27.1	8.0	86.4	1.4	10.0	0.9	0.10	0.71	0.34	0.12	0.00	0.00	0.00	0.06
HTPH300	44.9	5.6	6.8	56.4	5.6	36.7	0.9	0.08	0.00	0.20	0.02	0.00	0.00	0.07	0.07
BP300	51.5	81.1	6.6	59.3	5.2	34.1	0.3	0.03	0.10	0.73	0.12	0.01	0.00	0.04	0.03
BP450	32.0	0.7	7.3	75.6	3.6	17.2	0.3	0.07	0.25	1.32	0.23	0.00	0.00	0.05	0.03
BP600	28.9	234.7	9.1	77.0	2.2	17.7	0.1	0.09	0.12	1.81	0.29	0.00	0.00	0.08	0.03
BB300	73.2	1.3	6.7	66.2	4.7	27.7	0.4	0.24	0.30	0.22	0.14	0.01	0.00	0.00	0.08
BB450	26.3	18.2	5.2	76.9	3.6	18.1	0.2	0.36	0.35	0.29	0.19	0.01	0.00	0.00	0.04
BB600	24.0	470.4	7.9	80.9	2.4	14.9	0.2	0.50	0.52	0.34	0.23	0.01	0.00	0.00	0.04

[a] Determined by weight difference assuming that the total weight of the samples was made up of the tested elements only.

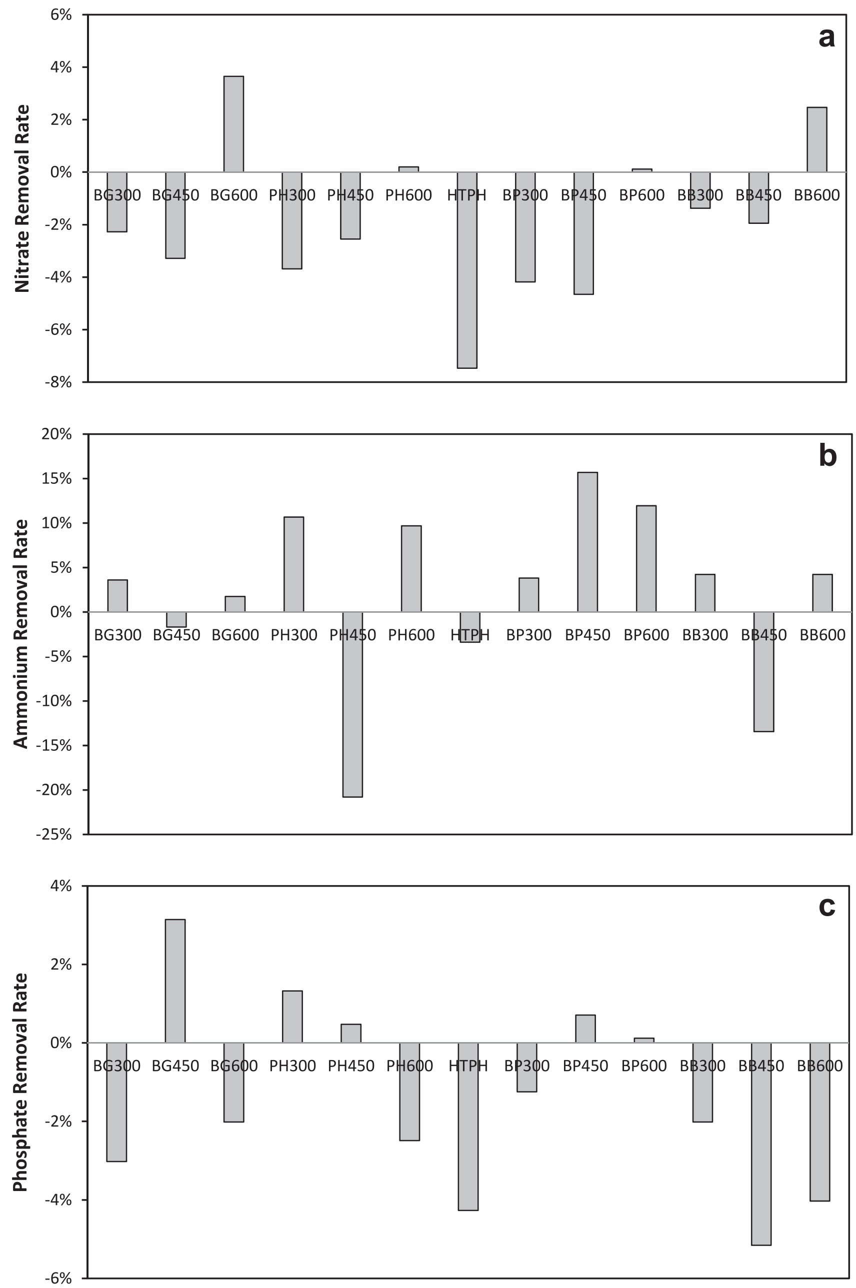

Fig. 1. Removal of nitrate (a), ammonium (b), and phosphate from aqueous solution by different types of biochars (see text for abbreviations).

3. Results and discussion

3.1. Biochar properties

The biochar production rate ranged 21.7–51.5% on a mass basis (Table 2). In general, more biochar was yielded at the lower pyrolysis temperatures due to lower losses of volatile components (Antal and Gronli, 2003; Novak et al., 2009). The pH of the biochars ranged from 5.2 to 9.1 (Table 2). Most of the biochars were alkaline, which is common for thermally produced biochars (Lehmann and Joseph, 2009). While two biochars had considerable N_2 surface area (BP600 and BB600, 234.7 and 470.4 $m^2\ g^{-1}$, respectively), the surface areas of most biochars were relatively very small ranging from 0.70 to 81.1 $m^2\ g^{-1}$ (Table 2). Positive correlation between N_2-measured surface area and pyrolytic temperature was found for all tested biochars, which is consistent with the results of several previous biochar studies (Brown et al., 2006; Li et al., 2011; Mukherjee et al., 2011).

Elemental composition analysis indicated all the biochar samples to be carbon-rich with carbon compositions ranging 56.4–86.4% (Table 2), which is typical of pyrolyzed biomass (Inyang et al., 2011; Zimmerman et al., 2011). The oxygen and hydrogen contents of all the samples ranged 10.0–36.7% and 1.4–5.6%, respectively. As reported in the literature, some of these oxygen and hydrogen contents are likely in organic functional groups on biochar surface (Inyang et al., 2011; Uchimiya et al., 2011). The biochar samples contained relatively small amount of nitrogen (0.1–1.6%) and relatively low levels of phosphorous (0.03–0.5%) and metal elements (Table 2).

3.2. Adsorption of nitrate, ammonium and phosphate by biochars

The four biochars made at a higher temperature (600 °C), BG600, BB600 PH600, and BP600 could remove nitrate from aqueous solution with removal rates of 3.7%, 2.5%, 0.2%, and 0.12%, respectively (Fig. 1a). The rest of the biochars (nine) showed no nitrate removal ability, and even released nitrate into the solution. Thus, increase in pyrolysis temperature may improve the sorption ability of biochars to aqueous nitrate. Mizuta et al. (2004) reported that bamboo biochar made at 900 °C had relatively higher nitrate adsorption capacity even compared to a commercial activated carbon, which is consistent with the findings of this study.

Nine of the thirteen tested biochars showed some ammonium sorption ability, with removal rate ranged 1.8–15.7% (Fig. 1b). The BP biochars had the best overall ammonium sorption performance with removal rates of 3.8%, 15.7% and 11.9% for BP300, BP450 and BP600, respectively. There was no apparent pyrolysis temperature trend in the ammonium sorption data.

Only five biochars had ability to remove phosphate from aqueous solution, with the rest of the biochars releasing phosphate into the solution (Fig. 1c). The BG450 biochar had the highest removal rate of 3.1%. The HTPH, BG300, PH600, and the three bamboo biochars released relatively large amount of phosphate into the solution (>2%). The hydrothermally produced biochar, HTPH, showed no nutrient sorption ability and released the greatest amount of nitrate and phosphate.

It is well-accepted that biochar can be used as a soil amendment to improve soil fertility and crop productivity. Some previous studies attributed this function to the ability of biochar to retain nutrients in soils (Steiner et al., 2008, 2009; Beesley et al., 2011; Lehmann et al., 2011). The sorption experimental results in this work, however, showed that the ability of biochar to adsorb nutrient elements is not universal, but depends on both the nutrient and the biochar type. In fact, most of the biochars tested in this work showed little/no sorption ability to phosphate or nitrate, but performed slightly better in removing ammonium from aqueous solutions. Perhaps it not surprising that biochars are more effective at removing cationic species from solution given that most biochars have been reported to have a net negative surface charge (Beesley et al., 2011; Lehmann et al., 2011).

3.3. Transport in soil columns

Two biochars (PH600 and BP600) with relatively good sorption ability for nutrients were selected for the soil column leaching study. When applied to the sandy soil, the two biochars reduced the leaching of both nitrate and ammonium ions from the column (Fig. 2a and b). Compared to the columns without biochar, after 6 d, the PH600 and BP600 amended soil columns released about 34.3% and 34.0% less of total nitrate and 14.4% and 34.7% less ammonium, respectively. These results are in line with findings of the batch sorption experiment that both biochars could remove nitrate and ammonium from aqueous solutions (Fig. 1).

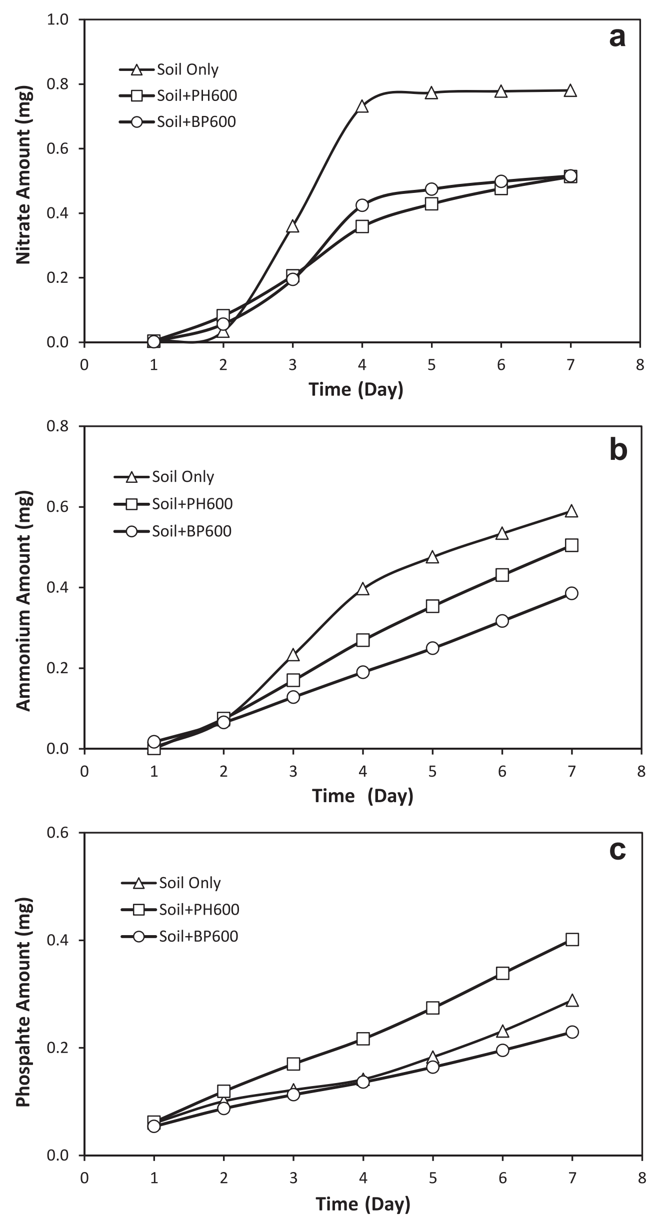

Fig. 2. Cumulative amounts of nitrate (a), ammonium (b), and phosphate (c) in the leachates from biochar-amended and unamended soil columns (see text for abbreviations).

The two biochar's effect on the leaching of phosphate from the soils columns was different (Fig. 2c). BP600 reduced the total amount of phosphate in the leachates by about 20.6%, whereas PH600 increased the amount of phosphate leached from the soil columns by about 39.1%. These results are also consistent with the results of the batch sorption experiment (Fig. 1). Although multiple mechanisms could be responsible to the enhanced or reduced retention of nutrients in the biochar amended soil (Sposito, 1989), several recent studies have suggested that, when applied to soils, biochar may not only affect soil ion exchange capacity but also provide refugia for soil microbes to influence the binding of nutritive cations and anions (Liang et al., 2006; Atkinson et al., 2010). Further investigations are still needed to unveil the governing mechanisms of nutrient retention and leaching in biochar amended soils.

4. Conclusions

Biochar land application is commonly assumed to be an effective way to sequester carbon and improve soil fertility by reducing nutrient leaching. The finding from this work, however, suggests that the effect of biochar on the retention and release of nutrient ions (i.e., nitrate, ammonium, and phosphate) varies with nutrient and biochar type. Of the thirteen biochars tested in this study, most of them showed little or no nitrate or phosphate sorption ability. However, nine biochars removed aqueous ammonium. When two selected biochars with relatively good sorption ability were used in soil columns, they could effectively reduce the leaching of nitrate and ammonium. Only one biochar, however, could reduce the leaching of phosphate from the soil columns. The results obtained from the leaching column study were consistent with finding from the sorption experiments, suggesting the effect of biochar on nutrients in soils could be determined through laboratory batch sorption studies. It is also recommended that sorption ability of biochars to nutrients should be determined before their applications to soils as amendment.

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