

# Ammonium, Nitrate, and Phosphate Sorption to and Solute Leaching from Biochars Prepared from Corn Stover (*Zea mays* L.) and Oak Wood (*Quercus* spp.)

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Biochar (BC) was evaluated for nitrogen (N) and phosphorus (P) removal from aqueous solution to quantify its nutrient pollution mitigation potential in agroecosystems. Sorption isotherms were prepared for solutions of ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and phosphate ( $\text{PO}_4\text{-P}$ ) using BC of corn (*Zea mays* L.) and oak (*Quercus* spp.) feedstock, each pyrolyzed at 350 and 550°C highest treatment temperature (HTT). Sorption experiments were performed on original BC as well as on BC that went through a water extraction pretreatment (denoted WX-BC). Ammonium sorption was observed for WX-Oak-BC and WX-Corn-BC, and Freundlich model linearization showed that a 200°C increase in HTT resulted in a 55% decrease in  $K_F$  values for WX-Oak-BC and a 69% decrease in  $K_F$  for WX-Corn-BC. Nitrate sorption was not observed for any BC. Removing metals by water extraction from WX-Oak-350 and WX-Oak-550 resulted in a 25 to 100% decrease in phosphate removal efficiency relative to original Oak-350 and Oak-550, respectively. No  $\text{PO}_4\text{-P}$  sorption was observed using any Corn-BC. Calcium (Ca) leached from BC produced at 550°C was 63 and 104% higher than from BC produced at 350°C for corn and oak, respectively. Leaching of P was two orders of magnitude lower in WX-Oak-BC than in WX-Corn-BC, concurrent with similar difference in magnesium (Mg). Nitrate and  $\text{NH}_4^+$  leaching from consecutive water extractions of all tested BCs was mostly below detection limits.

IN RECENT DECADES, scientists have observed increases in aquatic primary production attributed to N and P overenrichment, resulting in eutrophication (Nixon, 1995; Boesch, 2002). Compounding the problem, algae can produce toxins that have paralytic, diarrhetic, and neurotoxic effects with negative impacts on animals, humans, and aquatic species (Bates et al., 1991; Richardson, 1997). These toxins can reach high concentrations during an algal bloom, impacting reproduction of aquatic species, fishing industries, and coastal economies (Cloern, 2001). The U.S. Environmental Protection Agency (USEPA) has determined that N and P overenrichment is a leading cause of impaired waters (USEPA, 2011). To date, about a quarter of the rivers and streams in the United States (1,500,000 km) have been assessed, of which half are impaired. The primary source of the impairment is nutrient (N and P) discharge from agricultural activities.

Biochar (BC) is a solid residue produced by thermal degradation of organic material during pyrolysis. Biochar is an environmental sorbent and can reduce N and P leaching from soils (Lehmann et al., 2003; Laird et al., 2010). Biochar has been shown to adsorb  $\text{NH}_4^+$  (Ding et al., 2010),  $\text{NO}_3^-$  (Ohe et al., 2003; Mizuta et al., 2004; Mishra and Patel, 2009; Kameyama et al., 2011), and  $\text{PO}_4\text{-P}$  from aqueous solution (Yao et al., 2011). Biomass (feedstock) and highest treatment temperature (HTT) during pyrolysis influence the molecular structure and pore size distribution of BC, which are factors that govern its sorptive behavior in the environment (Keiluweit et al., 2010). The role of feedstock type and HTT on inorganic nutrient sorption has yet to be systematically elucidated. Furthermore, little is known about the effect of BC hydration and chemical weathering on N and P sorption.

The Clean Water Act (Clean Water Act of 1972) calls for research in improved methods of preventing, reducing, and eliminating pollution from agriculture. This paper aims to evaluate BC for mitigating N and P leaching from nonpoint sources. The objectives of this study are to determine (i) how BC feedstock and HTT influence water-extractable nutri-

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**Abbreviations:** AEC, anion exchange capacity; BC, biochar; DI, deionized; HTT, highest treatment temperature; ICP, inductively coupled plasma spectrometer; WX, water extraction.

ents, (ii) the effect of feedstock and HTT on inorganic N and P sorption, and (iii) how chemical weathering caused by BC hydration influences N and P sorption.

## Materials and Methods

### Background

Corn stover (*Zea mays* L.) and oak wood (*Quercus* spp.) feedstocks were slow-pyrolyzed at 350 and 550°C by BEST Energies, Inc. (Daisy Reactor, WI). These feedstocks were chosen to represent leafy and woody biomass, which are pyrolyzed at temperatures that produce distinctly different physical and chemical characteristics. The original BCs are referred to as Corn-350, Corn-550, Oak-350, and Oak-550. A cold water extraction was performed on each BC type, after which the BC was recovered and used in sorption experiments. The water-extracted (WX) BC is denoted WX-Corn-350, WX-Corn-550, WX-Oak-350, and WX-Oak-550. A summary of the physical and chemical differences among the BCs is presented in Table 1 and in the Supplemental Information. Surface area measurements were performed by Rajkovich et al. (2012) on original BC of the same feedstocks pyrolyzed at 400 and 600°C. These values are considered proxies for the BC used in this study, albeit slightly different from the surface areas produced at 350 and 550°C.

### Preparation of the Biochars

All BCs were crushed and sieved to between 500 and 800 μm to obtain a uniform particle size. Glassware was acid washed in a hydrochloric acid bath (1 mol L<sup>-1</sup>) and rinsed with deionized (DI) water before use.

### Cold Water Extraction and Nutrient Analysis

Each BC type went through multiple cold water extractions, was filtered, and the filtrate was analyzed for P, NH<sub>4</sub>-N, NO<sub>3</sub>-N, Ca, and Mg. The BC samples were continuously stirred for 16 h in an Erlenmeyer flask with DI water and a magnetic stir bar. The approximate solid-to-liquid (w/w) ratio of BC to DI water was 1:45 for Corn-350 and Corn-550, 1:20 for Oak-350, and 1:40 for Oak-550 (a limited supply of Oak-350 was available for water extraction). Each extraction slurry was passed through a 0.45-μm vacuum filter apparatus, and the BC that remained on the filter was rinsed back into the Erlenmeyer flask and refilled with DI water. This procedure was repeated until the pH of the filtrate stabilized between two consecutive extractions (± pH 0.02).

The pH of the filtrate was measured immediately after filtering, and approximately 300 mL of filtrate from each extraction was

stored in an airtight container at 4°C until analyzed for elemental and nutrient concentrations (4–16 wk after filtering). Extraction solution equilibrium concentrations of Ca, Mg, and P ( $C_c^{Ca}$ ,  $C_c^{Mg}$ , and  $C_c^P$ , respectively) were determined using an inductively coupled plasma spectrometer (ICP; Thermo Jarrell Ash ICAP 61E Trace Analyzer). Ammonium concentration was determined using the phenate colorimetric method (AWWA, 1999) with a Hewlett-Packard diode array ultraviolet–visible spectrophotometer. Nitrate was measured with a Dionex ion chromatograph installed with an IONPAC AS14A analytical column. Phosphate samples were acidified and measured with an O-I Analytical FS 3000 phosphorus analyzer (P-flow analyzer). Quality control on the P analysis methods confirmed that P measured by the ICP correlated strongly to P measured by the P-flow analyzer.

The concentration of Ca, Mg, and P in BC ( $C_{BC}^{Ca}$ ,  $C_{BC}^{Mg}$ , and  $C_{BC}^P$ , respectively) over the course of the extraction series was determined by mass balance (Eq. [1] and [2]). Results from the extraction series were compared between each BC at the point where the mass of extraction water used was about 200 times the mass of BC (WX-Corn-350 Extraction 4; WX-Corn-550 Extraction 4; WX-Oak-350 Extraction 9; WX-Oak-550 Extraction 5).

$$M_{\text{final}}^i = M_o^i - \sum M_{\text{leached}}^i \quad [1]$$

where  $i$  = element being measured;  $M_{\text{final}}$  = total mass of element in BC at the end of a given extraction (μmol);  $M_o$  = initial mass of element in BC (μmol);  $M_{\text{leached}}$  = mass of element measured in solution at the end of each extraction (μmol).

The concentration of Ca, Mg, and P in the BC was calculated by dividing the calculated mass of each element by the dry weight of the BC:

$$C_{BC}^i = M_{\text{final}}^i / M_{BC} \quad [2]$$

where  $C_{BC}^i$  = element ( $i$ ) concentration in BC at the end of a given extraction (μmol g<sup>-1</sup>);  $M_{\text{final}}$  = total mass of element ( $i$ ) in BC at the end of a given extraction (μmol); and  $M_{BC}$  = dry mass of BC used (g).

### Sorption Experiments

Preliminary sorption experiments were performed to evaluate BC-to-liquid ratios and to obtain preliminary sorption results for NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>-</sup>P. All sorption experiments were performed in triplicate at 24°C ± 2°C with a Burrell wrist action

**Table 1. Physical and chemical properties of corn and oak biochars. Surface area and pore volume were measured with nitrogen (N<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) sorbates. Mean elemental concentrations are expressed with standard deviation (± SD),  $n = 3$ . Data are compiled from a previous study (Rajkovich et al., 2012).**

Biochar type	Surface area measurements				Elemental concentration		
	N <sub>2</sub> sorbate surface area	N <sub>2</sub> sorbate pore volume	CO <sub>2</sub> sorbate surface area	CO <sub>2</sub> sorbate pore volume	Ca	Mg	P
	m <sup>2</sup> g <sup>-1</sup>	mL g <sup>-1</sup>	m <sup>2</sup> g <sup>-1</sup>	mL g <sup>-1</sup>	μmol g <sup>-1</sup>		
Corn-350	6.7†	0.010†	281.9†	0.050†	61.00 (2.33)	153.11 (4.24)	259.48 (0.92)
Corn-550	4.8†	0.006†	527.1†	0.100†	67.58 (7.19)	244.62 (7.93)	365.80 (4.16)
Oak-350	3.5†	0.001†	449.8†	0.090†	0.36 (0.36)	27.36 (1.53)	1.69 (0.23)
Oak-550	0.9†	0.007†	547.8†	0.095†	0.94 (0.53)	40.14 (2.34)	1.71 (0.17)

† Data for the exact highest treatment temperature (HTT) of a given feedstock are unavailable and respective data for the next closest HTT (400 or 600°C) are reported instead.

shaker at 400 rpm, where 0.50 g of BC was added to Corning 50-mL centrifuge tubes along with 50 mL of liquid (DI water or nutrient solution depending on experiment). The tubes were shaken for 24 h and then left quiescent for 24 h before the supernatant was passed through a 0.45- $\mu\text{m}$  vacuum filter apparatus.

Ammonium solutions were prepared using anhydrous ammonia chloride for concentrations of 1, 10, 100, 1000, and 10,000 mg  $\text{NH}_4\text{-N L}^{-1}$ . A set of BC mixed with DI water was also included to measure  $\text{NH}_4^+$  leached from 24 h of continuous shaking. Only WX-Corn-BC and WX-Oak-BC were used for these sorption experiments as  $\text{NH}_4^+$  sorption to BC has been widely studied (Nguyen and Lehmann, 2009; Cheng et al., 2006). Data were analyzed using the Freundlich adsorption model:

$$q^* = K_F C_e^{1/n} \quad [3]$$

where  $q^*$  = mass of  $\text{NH}_4^+$  adsorbed per mass of BC at equilibrium;  $K_F$  = experimentally derived constant;  $C_e$  = equilibrium concentration of  $\text{NH}_4^+$  in solution; and  $1/n$  = experimentally derived constant.

Nitrate sorption experiments were performed on both water-extracted and original Corn-350, Corn-550, and Oak-350 (a limited supply of Oak-550 prevented it from being used in the nitrate sorption experiments). A solution of 10 mg  $\text{NO}_3\text{-N L}^{-1}$  was prepared from anhydrous potassium nitrate. These BCs were also mixed with DI water to quantify nitrate leached from 24 h of continuous shaking. Two-tailed  $t$  tests are used to compare equilibrium concentration ( $C_e$ ) to initial concentration ( $C_0$ ) to determine whether to accept the null hypothesis that  $C_e$  and  $C_0$  are not different.

Phosphate sorption experiments were performed on all WX-BC using pH-adjusted solutions. Two sets of solutions were made from dibasic anhydrous potassium phosphate ( $\text{KH}_2\text{PO}_4$ ) with concentrations of 0.1, 1, and 10 mg P  $\text{L}^{-1}$ . One set of concentrations was adjusted to pH 4 ( $\pm 0.02$ ) using HCl and sodium hydroxide as needed. The other set was buffered with sodium bicarbonate ( $\text{NaHCO}_3$ ) and adjusted to pH 7 ( $\pm 0.02$ ) with HCl and NaOH as needed. Water adjusted to pH 4 and pH 7 was also mixed with WX-BC to measure P leaching. For original BC, sorption experiments were performed using 10 mg  $\text{PO}_4\text{-P L}^{-1}$  solutions buffered to pH 7.

## Results

### Water-leachable Nutrients

Oak-350-BC showed the largest change in pH between the initial (pH 4.32) and final (pH 5.88) values, whereas Corn-350-BC showed the least change in pH between initial (pH 7.95) and final (pH 7.75) extractions (Table 2). The color of the filtrate from WX-Corn-350 was distinctly yellow but became more transparent with consecutive extractions. The same was observed for WX-Corn-550 and WX-Oak-350, but the color was less intense.

The N leached during the extraction series was minimal. Ammonium leaching was often below detection limits, yet each BC leached a small amount with Corn-BC leaching slightly more than Oak-BC. For nitrate leaching, none of the extraction solutions exceeded 0.2 mg  $\text{NO}_3\text{-N L}^{-1}$ , which was the detection limit of the ion chromatograph.

Low-HTT BC released a larger percentage of its initial P than the high-HTT BC (Table 2). The WX-Corn-350 and WX-Corn-550 leached 37 and 16  $\mu\text{mol P g}^{-1}$ , respectively. The WX-Oak-350 and WX-Oak-550 leached 0.18 and 0.24  $\mu\text{mol P g}^{-1}$ , respectively (Table 2).

The WX-Corn-350 released a large percentage of P in the first extraction, resulting in a high  $C_e^P$  relative to WX-Corn-550. For subsequent extractions,  $C_e^P$  was similar between the WX-Corn-BCs (Fig. 1A). A trend of decreasing  $C_{BC}^P$  with decreasing  $C_e^P$  was observed for WX-Corn-BC ( $P < 0.05$ ; Table 3) but not for WX-Oak-BC ( $P > 0.05$ ; Table 3).

The low-HTT BC showed a larger decrease in  $C_{BC}^{Mg}$  than the high-HTT BC (Table 2). The WX-Corn-BC and WX-Oak-350 demonstrated a trend of decreasing  $C_{BC}^{Mg}$  with decreasing  $C_e^{Mg}$  ( $P < 0.05$ ; Table 3), whereas WX-Oak-550 did not ( $P > 0.05$ ; Table 3). The WX-Corn-350 and WX-Corn-550 leached 72 and 59  $\mu\text{mol Mg g}^{-1}$ , respectively. The WX-Oak-350 and WX-Oak-550 leached 0.18 and 0.1  $\mu\text{mol Mg g}^{-1}$ , respectively (Table 2).

High-HTT BC achieved a higher  $C_e^{Ca}$  than low-HTT BC (Fig. 1E). The WX-Corn-350 and WX-Corn-550 leached 9 and 15  $\mu\text{mol Ca g}^{-1}$ , respectively. Similarly, Ca leaching from WX-Oak-350 and WX-Oak-550 was 8 and 17  $\mu\text{mol Ca g}^{-1}$ , respectively (Table 2).

### Ammonium Sorption Results

Low-HTT BC showed a higher sorptive capacity for  $\text{NH}_4\text{-N}$  relative to high-HTT BC of the same feedstock (Fig. 2 and Table 4). At low  $C_e^{NH_4}$  WX-Corn-BC adsorbed more  $\text{NH}_4\text{-N}$  than WX-Oak-BC of the same HTT, yet as  $C_e^{NH_4}$  increased WX-Oak-BC adsorption exceeded WX-Corn-BC. The WX-Oak-BC also fit the isotherm model better than the WX-Corn-BC (Table 4). A preliminary study using original BC (comparable to Oak-350) yielded a  $K_F$  value of 0.129 (Supplemental Information), which is several orders of magnitude higher than the WX-Oak-BC and indicates that water extraction decreased the sorptive capacity of BC for ammonium.

### Nitrate Sorption Results

The mean  $C_e$  values from the  $\text{NO}_3^-$  sorption experiments showed no difference compared to the mean  $C_0$ , indicating that no  $\text{NO}_3^-$  sorption took place (test statistic  $< t$ -critical value; Table 5). There was also no nitrate detected ( $\geq 0.2$  mg  $\text{L}^{-1}$ ) in any of the DI solutions that were shaken with each of the BC types listed above.

### Phosphate Sorption Results

Water-extracted and original Corn-BC did not show additional  $\text{PO}_4\text{-P}$  sorption (Fig. 3A) and regression line slopes for the WX-Corn-BC isotherms are all near zero (Table 6). Oak-350 demonstrated  $\text{PO}_4\text{-P}$  sorption of 1.5  $\mu\text{mol P g}^{-1}$  and Oak-550 showed  $\text{PO}_4\text{-P}$  sorption of 2.5  $\mu\text{mol P g}^{-1}$  (Fig. 3B). Very little  $\text{PO}_4\text{-P}$  sorption occurred on WX-Oak-550 at higher  $C_e^P$ , as evidenced by a weak positive slope of the regression line ( $P < 0.05$ ; Table 6). Phosphate sorption to WX-BC is not greatly affected if the  $\text{PO}_4\text{-P}$  solution is adjusted to pH 4 or pH 7.

**Table 2.** Data gathered from the water extraction of each biochar (BC). The initial mean elemental concentration for each BC is compiled from a previous study (Rajkovich et al., 2012) with standard deviation ( $\pm$  SD),  $n = 3$ . Elemental concentrations and ratios throughout the extraction series were based on the initial mean concentrations of each element, for each BC.

BC sample	Extraction no.	pH of extraction solution	Cumulative volume of water used to extract	Mass of water used per mass BC	Mass $\text{NH}_4\text{-N}$ leached per mass BC	Mass $\text{NO}_3\text{-N}$ leached per mass BC	Elemental content of biochar at end of extraction			Cumulative percentage of element leached		
							P	Ca	Mg	P	Ca	Mg
			L	$\text{g g}^{-1}$	$\mu\text{mol g}^{-1}$			%				
Corn-350	–	–	–	–	–	–	61.00 (2.33)	153.11 (4.24)	259.48 (0.92)	–	–	–
WX-Corn-350	1	7.95	1.54	42	0.89	<1.60	36.69	149.21	213.03	40	3	18
WX-Corn-350	2	7.93	3.29	90	<0.65	<1.60	29.18	146.47	198.39	52	4	24
WX-Corn-350	3	7.62	4.86	132	<0.65	<1.60	25.99	145.47	193.86	57	5	25
WX-Corn-350	4	7.77	6.40	174	<0.65	<1.60	23.62	144.05	187.53	61	6	28
WX-Corn-350	5	7.75	8.19	223	<0.65	<1.60	22.12	142.91	182.91	64	7	30
Corn-550	–	–	–	–	–	–	67.58 (7.19)	244.62 (7.93)	365.80 (4.16)	–	–	–
WX-Corn-550	1	9.76	1.70	47	0.69	<1.60	59.88	239.46	331.63	11	2	9
WX-Corn-550	2	9.52	3.47	96	0.88	<1.60	54.92	236.48	318.36	19	3	13
WX-Corn-550	3	9.5	5.27	146	<0.65	<1.60	52.65	233.15	311.17	22	5	15
WX-Corn-550	4	9.11	7.01	193	<0.65	<1.60	51.23	229.87	306.88	24	6	16
WX-Corn-550	5	9.06	8.68	240	1.49	<1.60	49.40	224.69	300.46	27	8	18
WX-Corn-550	6	9.06	10.52	290	<0.65	<1.60	48.15	219.26	295.90	29	10	19
Oak-350	–	–	–	–	–	–	0.36 (0.43)	27.36 (1.53)	1.69 (0.23)	–	–	–
WX-Oak-350	1	4.32	0.91	22	0.36	<0.75	0.36	23.98	1.62	0	12	4
WX-Oak-350	2	4.5	1.78	43	<0.30	<0.75	0.32	22.64	1.57	11	17	7
WX-Oak-350	3	5.01	2.68	64	<0.30	<0.75	0.30	21.85	1.56	16	20	8
WX-Oak-350	4	5.25	3.56	85	<0.30	<0.75	0.29	21.23	1.55	21	22	8
WX-Oak-350	5	5.7	4.47	107	<0.30	<0.75	0.27	21.01	1.55	26	23	9
WX-Oak-350	6	5.25	5.36	128	0.32	<0.75	0.26	20.63	1.54	29	25	9
WX-Oak-350	7	5.59	6.25	149	<0.30	<0.75	0.22	20.05	1.53	38	27	9
WX-Oak-350	8	5.88	7.09	170	<0.30	<0.75	0.20	19.53	1.52	44	29	10
WX-Oak-350	9	5.88	8.02	192	<0.30	<0.75	0.18	19.08	1.51	49	30	10
Oak-550	–	–	–	–	–	–	0.94 (0.53)	40.14 (2.34)	1.71 (0.17)	–	–	–
WX-Oak-550	1	6.81	1.01	45	0.68	<1.50	0.91	37.68	1.69	4	6	1
WX-Oak-550	2	7.29	1.92	86	0.62	<1.50	0.87	31.67	1.67	8	21	2
WX-Oak-550	3	7.46	2.85	128	<0.50	<1.50	0.80	27.26	1.65	15	32	3
WX-Oak-550	4	7.14	3.81	171	<0.50	<1.50	0.77	23.97	1.65	18	40	3
WX-Oak-550	5	6.74	4.47	201	<0.50	<1.50	0.70	23.23	1.61	26	42	6
WX-Oak-550	6	6.89	5.31	238	<0.50	<1.50	0.67	22.10	1.61	29	45	6
WX-Oak-550	7	6.91	6.19	278	<0.50	<1.50	0.62	21.48	1.61	34	46	6

## Discussion and Conclusions

### Leachability of Nutrients

The extraction solution pH of WX-Corn-BC was higher than that of WX-Oak-BC (Table 2), which is consistent with another study that used the same BC materials (Nguyen and Lehmann, 2009). The ash percentage of Corn-BC is greater than that of Oak-BC (Supplemental Information) and is a likely cause of higher pH in extraction solutions of WX-Corn-BC relative to WX-Oak-BC and for the increase of pH with higher HTT. The relationship between high ash content and high pH occurs widely in BC made from plant biomass (Glaser et al., 2002; Singh et al., 2010). There is loss of acidic carboxyl functional groups with increased HTT (Nguyen and Lehmann, 2009). A loss of carboxyl groups and decrease in surface acidity was observed between wood of *Eucalyptus saligna* Smith pyrolyzed at 400 and 550°C (Singh et al., 2010).

Ammonium leaching was minimal from WX-Corn-BC and WX-Oak-BC and  $\text{NO}_3^-$  leaching was not detected from any BC. Although N comprises about 1% of Corn-BC and 0.1% of the Oak-BC (Supplemental Information), the N is bound in a sparsely water soluble form (Bridle and Pritchard, 2004). Biochar derived from plant biomass is not considered a significant source of  $\text{NH}_4^+$  or  $\text{NO}_3^-$  (Glaser et al., 2002; Bridle and Pritchard, 2004; Graber et al., 2010; Singh et al., 2010). Another study performed a water extraction of citrus wood BC (having 0.6% N), which leached  $0.2 \mu\text{g NH}_4\text{-N g}^{-1}$  BC and  $0.6 \mu\text{g NO}_3\text{-N g}^{-1}$  BC (Graber et al., 2010). They found that N (in the form of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) was the least water extractable element by several orders of magnitude compared to other elements leached (Ca, K, Mg, Mn, P, S, Na).

The WX-Corn-350 and WX-Corn-550 released large quantities of P and Mg during the first extraction, unlike WX-Oak-BC. These elements may have been present on the surface of Corn-BC in highly soluble mineral salts that accumulated on the surface during pyrolysis (Glaser et al., 2002).



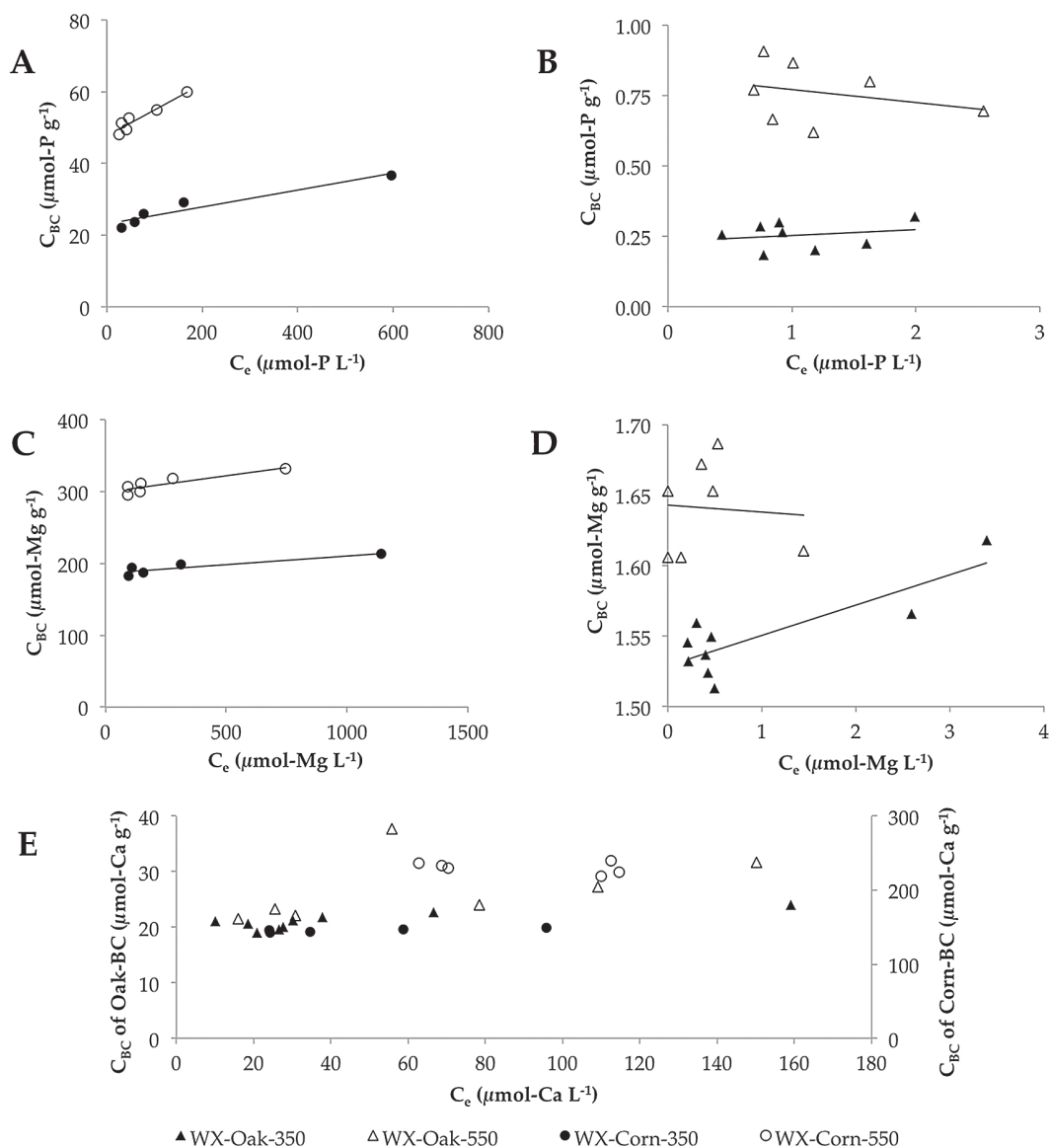


Fig. 1. Desorption isotherms showing the molar (A–B) phosphorus (P), (C–D) magnesium (Mg), and (E) calcium (Ca) contents of water-extracted corn biochar (WX-Corn-BC) and water-extracted oak biochar (WX-Oak-BC) vs. the equilibrium concentrations of P, Mg, and Ca in extraction solutions. In part E, WX-Oak-BC Ca content is on the primary y-axis and WX-Corn-BC Ca content is on the secondary y-axis.

The release of P and Mg from WX-Oak-BC during the first few extractions was several orders of magnitude less than from WX-Corn-BC, which might be attributed not only to lower initial concentrations of each element but also because fewer mineral salts accumulate on BC made from wood feedstock vs. BC made from leaves (Singh et al., 2010).

Table 3. Regression line data for phosphorus and magnesium desorption isotherms for the water-extracted (WX-) corn and oak biochar (BC) extraction series.

BC type	Element <i>i</i>	$C_{BC}^i = m \times C_e^i + b$	$R^2$	<i>P</i> level
WX-Corn-350	P	$C_{BC}^P = 0.02 \times C_e^P + 23.16$	0.92	0.01
WX-Corn-550	P	$C_{BC}^P = 0.07 \times C_e^P + 47.69$	0.92	<0.01
WX-Oak-350	P	$C_{BC}^P = 0.02 \times C_e^P + 0.23$	0.05	0.60
WX-Oak-550	P	$C_{BC}^P = -0.05 \times C_e^P + 0.81$	0.03	0.53
WX-Corn-350	Mg	$C_{BC}^{Mg} = 0.02 \times C_e^{Mg} + 186.40$	0.84	0.03
WX-Corn-550	Mg	$C_{BC}^{Mg} = 0.05 \times C_e^{Mg} + 299.27$	0.80	0.02
WX-Oak-350	Mg	$C_{BC}^{Mg} = 0.02 \times C_e^{Mg} + 1.53$	0.68	0.01
WX-Oak-550	Mg	$C_{BC}^{Mg} = -0.01 \times C_e^{Mg} + 1.64$	0.01	0.88

Increased Ca leaching from high-HTT BC could be caused by thermally induced changes in Ca compounds during pyrolysis that result in increased Ca solubility. Pyrolysis temperature has been shown to alter Ca compounds in activated and nonactivated BC made from *E. saligna* (Singh et al., 2010). X-ray diffraction analysis revealed the major crystalline phase of *E. saligna* BC produced at 400°C was whewellite [calcium oxalate monohydrate,  $Ca(C_2O_4) \cdot H_2O$ ], yet the structure was carbon rich and poorly crystalline. When the feedstock was pyrolyzed at 550°C, the whewellite structure was lost and calcite ( $CaCO_3$ ) was formed in all of the samples. An increase

Table 4. Freundlich model terms for ammonium adsorption to water-extracted (WX-) biochar (BC).

BC type	$K_f$	<i>n</i>	$R^2$	<i>P</i> level
WX-Corn-350	4.9e-4	2.52	0.86	<0.01
WX-Corn-550	1.5e-4	2.26	0.69	<0.01
WX-Oak-350	6.5e-5	1.32	0.93	0
WX-Oak-550	2.9e-5	1.18	0.96	0

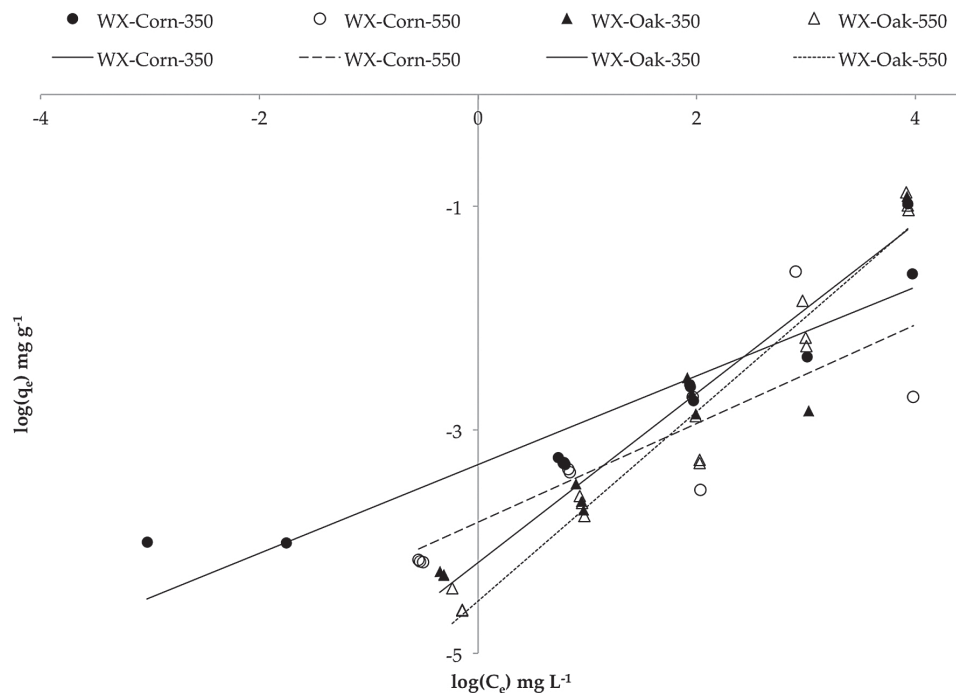


Fig. 2. A linearized Freundlich isotherm for ammonium adsorption to water-extracted corn biochar (WX-Corn) and water-extracted oak (WX-Oak) biochar.

in exchangeable Ca was also observed in the higher-temperature *E. saligna* BCs (Singh et al., 2010). Calcite was observed using X-ray diffraction in cornstraw BC pyrolyzed at 500°C (Silber et al., 2010). The same study measured the kinetic release of minerals and found that Ca detached quickly, followed by a zero-order release reaction after 24 h. The solubility of calcite,  $\log K_{sp} = -7.92$  (Knoel, 2008), is higher than that of calcium oxalate monohydrate,  $\log K_{sp} = -8.64$  (Knoel, 2008) and could explain the increased leaching of Ca from BC prepared at 550°C compared to BC prepared at 350°C.

## Sorption

All WX-BC adsorbed  $\text{NH}_4^+$  but low-HTT BC sorbed more than high-HTT BC for each feedstock. The decrease in cation exchange capacity with increasing HTT (Nguyen and Lehmann, 2009) can be attributed to the loss of carboxyl functional groups during pyrolysis (Cheng et al., 2006; Lianget al., 2006). The relative proportion of carboxyl groups in the corn and oak BC decreases by half between the HTT range of 300 to 600°C (Nguyen and Lehmann, 2009). The two feedstocks have very similar carboxyl

group proportions at these temperatures, yet they do not adsorb ammonium the same way. The cation exchange capacity increases with increasing solution pH (Silber et al., 2010), which might allow greater adsorption by Corn-BC at low  $\text{NH}_4^+$  solution concentrations when compared to Oak-BC of the same HTT.

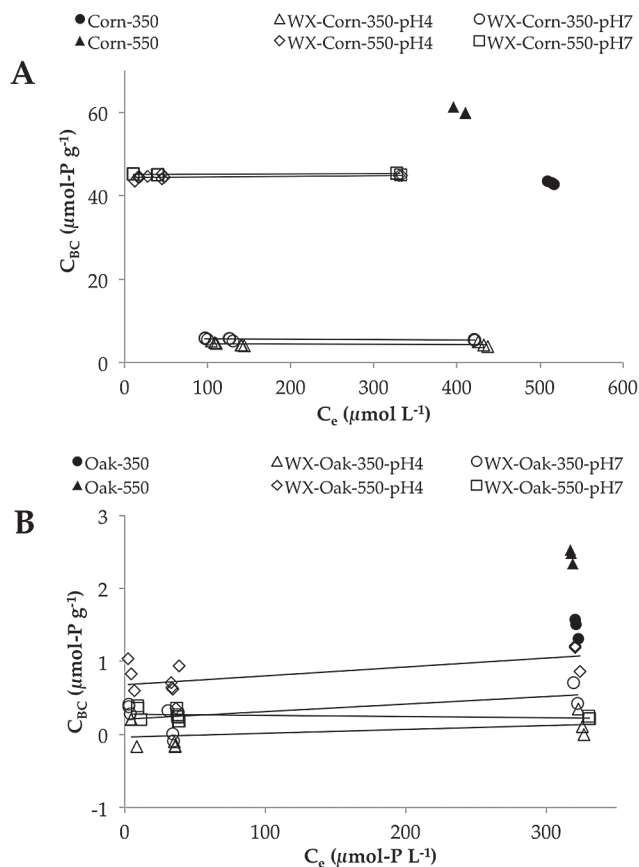
Oak-BC shows a better fit to the Freundlich adsorption model compared to Corn-BC (Table 4), which might be a result of the increased fractal dimensions of Oak-BC due to higher micropore surface area (Mikhailovsky et al., 2005). The  $1/n$  term of the Freundlich equation (Eq. [3]) has been shown to be directly proportional to the fractal dimension of the adsorbent (Tatlier and Sebatakar, 1999). The Freundlich adsorption isotherm for Corn-BC does not linearize well because  $\text{NH}_4^+$  sorption is variable over the concentration range. This could be due to a lower fractal dimension as expressed by the smaller  $1/n$  terms and smaller micropore surface area. Ammonium sorption for Oak-BC remains linear with a larger  $1/n$  term, which coincides with a larger micropore surface area. The constant ( $K^*_F$ ) for Oak-BC is lower than Corn-BC (Table 4), which might result from lower solution pH induced by the Oak-BC.

Table 5. Results of two-tailed *t*-tests comparing equilibrium concentration ( $C_e$ ) to initial concentration ( $C_0$ ) for nitrate sorption experiments using water-extracted (WX-) and original biochars, calculated at the 5% level. Sample size for each variable is 3, each test having 4 degrees of freedom.

$C_e$ of BC type	Comparison to $C_0$		
	Test statistic	<i>t</i> -critical value (5%)	<i>P</i> level
WX-Corn-350	0.55	2.78	0.61
Corn-350	1.63	2.78	0.18
WX-Corn-550	0.85	2.78	0.44
Corn-550	2.14	2.78	0.10
WX-Oak-350	1.22	2.78	0.29
Oak-350	2.03	2.78	0.11

Table 6. Linear regression results for phosphate sorption isotherms.

BC type	Initial pH of $\text{PO}_4$ solution	$C_{BC}^p = m \times C_e^p + b$	$R^2$	<i>P</i> level
WX-Corn-350	4	$C_{BC}^p = -0.001 \times C_e^p + 4.56$	0.04	0.59
	7	$C_{BC}^p = -0.001 \times C_e^p + 5.77$	0.34	0.10
WX-Corn-550	4	$C_{BC}^p = 0.002 \times C_e^p + 44.37$	0.17	0.06
	7	$C_{BC}^p = 0.001 \times C_e^p + 45.10$	0.26	0.16
WX-Oak-350	4	$C_{BC}^p = 0.001 \times C_e^p + 0.04$	0.18	0.26
	7	$C_{BC}^p = 0.001 \times C_e^p + 0.21$	0.34	0.09
WX-Oak-550	4	$C_{BC}^p = 0.001 \times C_e^p + 0.68$	0.41	0.03
	7	$C_{BC}^p = -0.0002 \times C_e^p + 0.28$	0.10	0.32



**Fig. 3. Phosphate sorption isotherms for (A) water-extracted (WX-Corn) and original corn and (B) water-extracted oak (WX-Oak) biochar.**

Yet, the fact that  $q^*$  values for Oak-BC exceed that of Corn-BC at high  $\text{NH}_4^+$  concentrations might indicate better access to micropores by virtue of a smaller hydrated radius (1.04–3.31 Å) or weak hydration (Tansel et al., 2006). This could allow access to more sorption sites as Oak-BC has more total surface area than Corn-BC at the same HTT (Table 1).

The inability of BC to adsorb  $\text{NO}_3^-$  has been observed in sorption experiments using sugarcane (*Saccharum officinarum* L.) bagasse-BC (particle sizes 250–500  $\mu\text{m}$ ) of the HTT range of 400 to 600°C (Kameyama et al., 2011), yet the same study observed  $\text{NO}_3^-$  sorption to bagasse-BC above 700°C HTT. Approximately 7.14  $\mu\text{mol NO}_3^- \text{N g}^{-1}$  adsorbed to the 800°C HTT bagasse-BC when mixed with a solution of 20 mg  $\text{NO}_3^- \text{N L}^{-1}$ . One study concluded the optimal equilibrium pH for  $\text{NO}_3^-$  sorption to bamboo-BC (300–500  $\mu\text{m}$ ) occurred at pH 2.4 and used the Langmuir adsorption model to predict a maximum sorption capacity of 31.5  $\mu\text{mol NO}_3^- \text{N g}^{-1}$  (Ohe et al., 2003). Another study utilized the Langmuir model to predict a sorption capacity of 89.29  $\mu\text{mol NO}_3^- \text{N g}^{-1}$  for 900°C HTT bamboo-BC powder (~80  $\mu\text{m}$ ) (Mizuta et al., 2004). Two scenarios to account for  $\text{NO}_3^-$  sorption to BC might include: (i) the development of basic functional groups with increasing HTT that provide anion exchange sites (Kameyama et al., 2011), and (ii) an increase of the surface positive charge with decreasing pH (pH 3–7) for new BC (Cheng et al., 2008; Cheng and Lehmann, 2009). However, anion exchange capacity (AEC) is known to be low and transient in Corn-BC and Oak-BC in the HTT range of 350 to 600°C and they do not have strong AEC after repetitive rinsing (Cheng et al.,

2008). It can be concluded that the water-extracted and original BC used in this study do not have sufficient AEC to adsorb  $\text{NO}_3^-$ .

Additional  $\text{PO}_4\text{-P}$  sorption did not occur on any of the WX or original Corn-BC (Fig. 3A), yet some additional  $\text{PO}_4\text{-P}$  sorption occurred on original Oak-BC where Oak-550 sorbed more  $\text{PO}_4\text{-P}$  than Oak-350 (Fig. 3B). The WX-BC does not appear to have AEC since sorption was not affected by phosphate ionic charge ( $\text{H}_2\text{PO}_4^-$  or  $\text{HPO}_4^{2-}$ ) induced by solution pH. Some additional  $\text{PO}_4\text{-P}$  was sorbed on the WX-Oak-BC at the highest equilibrium concentration tested, but this is likely not caused by AEC because no  $\text{NO}_3^-$  sorbed to any of the WX-BC. The original Oak-BC shows more sorption than the WX-Oak-BC at the same P concentration (Fig. 3B), which implies that  $\text{PO}_4\text{-P}$  sorption capacity is lost after cold water extraction. Mineral salts present on Oak-BC surfaces might provide  $\text{PO}_4\text{-P}$  sorption sites, but are easily leached on hydration. Yao et al. (2011) found that biochar made from anaerobically digested sugar beet (*Beta vulgaris* L.) tailings pyrolyzed at 600°C had the ability to adsorb  $\text{PO}_4\text{-P}$  and attributed this to precipitation by nanosized periclase ( $\text{MgO}$ ) on the BC surface. Easily weathered compounds on Oak-BC surfaces appear to provide it a transient  $\text{PO}_4\text{-P}$  sorption capacity.

Since the BC used in this study does not have strong AEC,  $\text{PO}_4\text{-P}$  cannot be adsorbed by electrostatic forces. Another possibility is precipitation of calcium phosphate compounds such as hydroxyapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ], which requires available  $\text{Ca}^{2+}$ ,  $\text{PO}_4\text{-P}$ , and  $\text{OH}^-$  without chemical species or conditions that would enable substitutions to form thermodynamically favorable and relatively soluble complexes of amorphous Ca phosphate [ $\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ ], octacalcium phosphate [ $\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$ ], dicalcium phosphate dihydrate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) or whitlockite [ $\text{Ca}_3(\text{MgFe})(\text{PO}_4)_6\text{PO}_3\text{OH}$ ] (Ferguson and McCarty, 1971; van der Houwen et al., 2003; Cao et al., 2007; Cao and Harris, 2008). Hydroxyapatite crystallization is inhibited by  $\text{Mg}^{2+}$  through  $\text{Ca}^{2+}$  substitution and the presence of organic acids (oxalic acid or larger acids) can reduce hydroxyapatite precipitation rate up to 94% (Cao et al., 2007). The yellow coloration of the extraction solutions from WX-Corn-BC and WX-Oak-350 could be evidence of organic acid leaching, which would decrease  $\text{PO}_4\text{-P}$  removal through precipitation. Additionally, Mg increases the solubility of P and increases P leaching from Ca-rich soils (Josan et al., 2005; Cao and Harris, 2008) and BC additions to soil have resulted in significant releases of Mg and P (Rondon et al., 2007). It is unlikely that  $\text{PO}_4\text{-P}$  precipitation will occur on BC prepared at low HTT or from leafy biomass due to the high Mg leachability from these BCs (Singh et al., 2010). Low-HTT BCs also have more carboxyl groups (Nguyen and Lehmann, 2009), which can inhibit hydroxyapatite formation (Cao et al., 2007).

The results of this study show that BC made from corn and oak feedstocks can mitigate nonpoint  $\text{NH}_4^+$  pollution through adsorption, but this sorptive capacity diminishes with chemical weathering. Biochar prepared from oak at 550°C has a transient sorptive capacity for  $\text{PO}_4\text{-P}$  but this capacity is lost after multiple hydration events. Neither Corn-BC nor Oak-BC prepared at or below 550°C has the ability to mitigate nonpoint  $\text{NO}_3^-$  pollution through adsorption.

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