

Effect of Biochar Type on Macronutrient Retention and Release from Soilless Substrate

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Abstract. A series of column studies were conducted to determine the influence of three different biochar types on nitrate, phosphate, and potassium retention and leaching in a typical greenhouse soilless substrate. A commercial substrate composed of 85 sphagnum peatmoss : 15 perlite (v:v) was amended with 10% by volume of three different biochar types including: gasified rice hull biochar (GRHB), sawdust biochar (SDB), and a bark and wood biochar (BWB). The non-amended control substrate, along with substrates amended with one of three biochar materials, were each packed into three columns. Columns were drenched with nutrient solution and leached to determine the impact of biochar on nutrient retention and leaching. Nitrate release curves were exponential and peaked lower, at later leaching events, and had higher residual nitrate release over time with each biochar amendment. The impact of biochar amendment on phosphate retention and release was more variable within and across the two experiments. In both experiments, the GRHB was a net source of phosphate, providing more phosphate to the system than the fertilizer application and hence obscuring any retention and release effect it might have. Potassium release varied by amendment type within each experiment, but within each amendment type was relatively consistent across the two experiments. All biochar types were a source of potassium, with GRHB providing more than SDB, but both providing far more potassium than the fertilizer event. The BWB amendment resulted in more leached potassium than the control substrate, but relatively little compared with GRHB and SDB amendments.

Biochar is the charred organic matter that remains after pyrolysis of biomass or manure. The influence of biochar in mineral soil systems has been studied and reviewed extensively (Lehmann et al., 2011; Spokas et al., 2011; Verheijen et al., 2010). In contrast, the influence of biochars on soilless substrates used in greenhouse and nursery containers has not been studied adequately, and only a few citations, summarized previously (Altland and Locke, 2012), are tangentially relevant to current container production systems. Nonetheless, the collection of papers thus far seems to indicate the same potential benefits in soilless substrates including additions of some nutrients (Ruamrungsri et al., 2011), reduction in leaching of nitrates and phosphates (Beck et al., 2011), beneficial shifts in microbial populations (Graber et al., 2010), and improved physical properties (Dumroese

et al., 2011). Recently, we reported that one form of mixed SDB retained and released nitrate and phosphate such that the concentration in the substrate would be moderated against fluctuations in nutrient concentration from intermittent fertilization events (Altland and Locke, 2012). Similarly, Beck et al. (2011) showed that amendment of an unspecified greenroof substrate with 7% biochar increased water retention and decreased total nitrogen (N) and phosphorus (P), nitrate, phosphate, and organic carbon in runoff. Biochars from different feedstocks yield different properties as a result of their differing particle sizes at the time of pyrolysis, inherent ash content of the feedstock (Demirbas, 2004), pyrolysis conditions (Singh et al., 2010), and storage conditions after processing (Spokas et al., 2011). The objective of this research was to determine the influence of three different biochar types on nitrate, phosphate, and P retention and leaching in a typical greenhouse soilless substrate.

Materials and Methods

A standard commercial soilless medium composed of 85 sphagnum peatmoss:15 perlite (v:v) (BM-6, Berger Peat Moss; Saint-Modeste, Quebec, Canada), which contained no incorporated macronutrient fertilizers, was

selected as the base substrate for the study. We used three forms of biochar: GRHB (CharSil, Riceland Food, Inc., Stuttgart, AR), SDB obtained from a local bioenergy pyrolysis unit [Synterra Energy (formerly Red Lion Bio-Energy), Toledo, OH], and a BWB (Royal Oak Charcoal, Roswell, GA). The GRHB is a commercially available product, made by gasification of rice hulls at 815 °C. The SDB uses hardwood sawdust from local lumber mills and is produced at 730 °C. The BWB contains the bark and wood scraps in lumber production and is produced at 815 °C. Each biochar type was characterized for its chemical properties (Table 1) and particle size distribution (Table 2). Percent carbon and N were determined with a PerkinElmer Series II CHNS/O Analyzer (PerkinElmer Instruments, Shelton, CT). Other macronutrients and micronutrients were determined with a Thermo Iris Intrepid inductively coupled plasma optical emission spectrometry (Thermo Electron Corp., Waltham, MA). Particle size distribution was determined by passing ≈30 g oven-dried (72 °C) biochar through soil sieves ranging from 0.106 to 6.30 mm (Table 2). Particles 0.106 mm or less were collected in a pan. Sieves and pan were shaken for 3 min with a RX-29/30 Ro-Tap[®] test sieve shaker (278 oscillations/min, 150 taps/min) (W.S. Tyler, Mentor, OH).

The peatmoss substrate was amended volumetrically with 10% of each biochar type. Resulting substrates, including a non-amended control, were packed into glass columns 4.5 cm i.d. and 38 cm long, with a volume of ≈600 cm³. Columns have a flat, false bottom above a stopcock to prevent compression and to control drainage of added solutions. Each biochar treatment was packed into three columns. Substrate was packed into a column by adding ≈150-cm³ increments of substrate, uniformly packing with a wand, and repeating until the column was full and contained ≈600 cm³ substrate. On 16 Aug. 2011, each column was saturated with 400 mL deionized (DI) water, enough to saturate the entire column of substrate, and let stand for 1 h. The solution was

Table 1. Chemical composition of gasified rice hull biochar (GRHB), sawdust biochar (SDB), and bark and wood biochar (BWB) before amendment in a greenhouse substrate.²

| | Units | GRHB | SDB | BWB |
|------------|---------------------|-------|--------|--------|
| Carbon | (%) | 17.68 | 59.53 | 53.25 |
| Nitrogen | | 0.18 | 0.20 | 0.52 |
| Phosphorus | | 0.30 | 0.07 | 0.03 |
| Potassium | | 0.98 | 0.50 | 0.34 |
| Calcium | | 0.35 | 1.15 | 6.97 |
| Magnesium | | 0.15 | 0.27 | 1.63 |
| Sulfur | | 0.03 | 0.02 | 0.07 |
| Silicon | | 11.72 | 3.01 | 0.49 |
| Boron | mg·kg ⁻¹ | 10.36 | 17.01 | 19.31 |
| Copper | | 8.42 | 10.87 | 6.06 |
| Iron | | 197.3 | 1609.9 | 2091.9 |
| Manganese | | 541.0 | 323.3 | 724.3 |
| Molybdenum | ND ³ | | 4.13 | ND |
| Zinc | | 46.34 | 9.26 | 19.59 |

²All analyses are expressed on a percent or concentration of oven dried biochar (n = 3).

³Not detectable.

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drained through filter paper (Whatman #2 150 mm Qualitative Circular filter papers; Whatman Ltd., Kent, U.K.) into beakers placed in an ice bath. Thereafter, the sample was transferred to a 50-mL vial. After 30 min, most of the solution was collected, stored in plastic vials, and frozen until analyzed. After removing the collected leachates, stopcocks were left open overnight to fully drain. On the second day, the columns were saturated with 200 mL (enough to completely saturate the column) of a 100 mg·L⁻¹ N fertilizer solution (Jack's Professional 20N-4.3P-16.6K Peat-Lite; JR Peters, Inc., Allentown, PA). The fertilizer contained 8% ammoniacal N and 12% nitrate N. The substrates remained saturated for 30 min and then were drained and filtered into vials on ice. Samples were frozen and stopcocks were left open overnight to drain fully. The experiment was conducted in a laboratory at room temperature, ≈23 °C.

The next day, 60 mL of DI water was added to each column leaving the stopcocks open the entire time and retrieving ≈55 mL from each column. The solution was filtered similar to previous collection events and chilled on ice and then frozen. Stopcocks were left open overnight to assure complete drainage. This process was repeated everyday for a total of 12 leaching events. Columns were not leached on weekends. The experiment was conducted on a laboratory bench with three single-column replications per biochar type.

At the time of analysis, samples were thawed and filtered through GF/F binder-free borosilicate glass fiber filter paper (Whatman) to remove particles greater than 0.7 μm. The filtrate was then poured into 5-mL autosampler vials, capped, and analyzed on an ICS 1600 (Ion Chromatography System; Dionex, Bannockburn, IL) for concentrations of nitrate (NO₃⁻), ammonium (NH₄⁺), phosphate (PO₄²⁻), and potassium (K).

The leaching study was repeated 27 Sept. 2011 using the same method with the exceptions that only 11 leaching events were conducted and leachate volumes were recorded, before transferring to the 50-mL vial, to determine the total mass of recovered nitrate, phosphate, and K. Mass of recovered nutrients was compared with the assumed quantity applied through fertilization and biochar amendment.

Data were analyzed with non-linear regression techniques using SAS 9.1 (SAS Systems, Inc., Cary, NC). Nitrate, phosphate, and K release patterns were fit to the following modified exponential equation when possible:

$$y = a + be^{-(x-c)^2/d}$$

where *y* is nitrate or phosphate concentration measured in the leachate on leaching event *x*. The parameter *a* indicates the value of *y*, which the curve approaches asymptotically as *x* increases to infinity. The sum *a* + *b* represents the maximum value of *y* at *x* = *c*. The parameter *c* = the leaching event of peak release and *d* is a scaling factor that reflects the girth of the curve's peak. Fitted curves for each nutrient were compared among biochar

amendments within an experiment using the sums of squares reduction test (Schabenberger and Pierce, 2002) where *P* values were generated to test the hypothesis that the parameters are similar. Likewise, the sums of squares reduction test was used to compare fitted parameters of each nutrient between the two experimental iterations to see if the data from the two experiments could be combined. Mass of nutrients recovered in the initial saturation and fertilization events as well as the sum of all leaching events was subjected to analysis of variance and means separation with Fisher's protected least significant difference test ($\alpha = 0.05$).

Results and Discussion

Ammonium concentrations in all leachates from both experiments were near zero; thus, it was assumed that nitrification in the substrate

occurred rapidly. These column experiments were conducted in a climate-controlled laboratory with air temperature ≈22 °C. Niemiera and Wright (1987a) reported rapid nitrification in containers between 20 and 30 °C, where application of 100 mg·L⁻¹ ammonium resulted in leachates of 2 to 4 mg·L⁻¹ ammonium in just 6 d. Based on nitrate accumulation rates in pine bark substrates, it has been projected that a 40-mg·L⁻¹ ammonium solution could be completely oxidized in 20 h (Niemiera and Wright, 1987b). Concentration of nitrate, phosphate, and K recovered in leachates followed similar trends across the two experiments. However, release of these three nutrients differed significantly ($P < 0.0001$) when compared across the two experiments with the sums of squares reduction test (data not shown) and are thus reported separately with similarities and differences in two experiments discussed.

Table 2. Particle size distribution of gasified rice hull biochar (GRHB), sawdust biochar (SDB), and bark and wood biochar (BWB) before amendment in a greenhouse substrate (n = 3).

| Sieve size (mm) | GRHB | | SDB | | BWB | |
|-----------------|----------------|-----|----------------|-----|----------------|-----|
| | Percent sample | SD | Percent sample | SD | Percent sample | SD |
| <0.106 | 25.8 | 1.3 | 28.8 | 0.7 | 0.5 | 0.1 |
| 0.106 | 20.2 | 0.9 | 17.0 | 0.5 | 4.1 | 0.3 |
| 0.18 | 13.9 | 0.1 | 11.5 | 0.2 | 30.2 | 1.4 |
| 0.25 | 15.5 | 0.3 | 12.8 | 0.2 | 42.3 | 0.1 |
| 0.35 | 12.1 | 0.5 | 11.1 | 0.4 | 17.9 | 1.2 |
| 0.5 | 9.5 | 1.0 | 9.0 | 0.4 | 4.6 | 0.6 |
| 0.71 | 1.9 | 0.3 | 3.8 | 0.2 | 0.3 | 0.1 |
| 1 | 0.5 | 0.1 | 2.2 | 0.2 | 0.0 | 0.0 |
| 1.4 | 0.5 | 0.1 | 2.0 | 0.1 | 0.0 | 0.0 |
| 2 | 0.1 | 0.1 | 1.2 | 0.1 | 0.0 | 0.0 |
| 2.8 | 0.0 | 0.0 | 0.4 | 0.2 | 0.0 | 0.0 |
| 4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 6.3 | 0.0 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 |

Table 3. Estimated parameters (with SES in parentheses) for macronutrient release curves (Fig. 1) from columns with an 85:15 sphagnum peatmoss:perlite substrate alone or amended with 10% (v/v) gasified rice hull biochar (GRHB), sawdust biochar (SDB), or bark and wood biochar (BWB).^z

| Nutrient | Biochar source | <i>a</i> ^y | <i>b</i> | <i>c</i> | <i>d</i> | <i>r</i> ² |
|-----------|-----------------------------|-----------------------|----------------|------------|-----------------|-----------------------|
| Nitrate | GRHB | -10.70 (10.16) | 160.57 (10.01) | 4.0 (0.15) | 18.77 (3.45) | 0.919 |
| | SDB | -1.09 (7.99) | 176.99 (8.99) | 4.2 (0.11) | 13.03 (1.85) | 0.930 |
| | BWB | -3.71 (5.1) | 182.81 (5.8) | 3.5 (0.09) | 14.93 (1.54) | 0.971 |
| | Control | 5.61 (7.86) | 223.07 (10.45) | 3.1 (0.14) | 11.89 (1.86) | 0.936 |
| | <i>P</i> value ^x | 0.5332 | 0.0001 | 0.0001 | 0.1820 | |
| Phosphate | GRHB | 4.43 (3.64) | 83.88 (4.98) | 1.2 (0.53) | 30.91 (7.79) | 0.962 |
| | SDB | 7.17 (1.35) | 18.85 (1.49) | 3.4 (0.24) | 16.26 (4.3) | 0.848 |
| | BWB | 2.89 (0.5) | 19.44 (0.6) | 3.1 (0.1) | 14.32 (1.56) | 0.971 |
| | Control | 2.46 (0.89) | 35.43 (1.57) | 2.3 (0.13) | 7.20 (1.15) | 0.945 |
| | <i>P</i> value | 0.3634 | 0.0001 | 0.0001 | 0.0001 | |
| Potassium | GRHB | 25.45 (3.83) | 59.85 (3.59) | 2.7 (0.25) | 32.50 (6.74) | 0.959 |
| | SDB | 1.01 (26.7) | 42.98 (27.92) | 0.9 (2.45) | 115.59 (157.95) | 0.827 |
| | BWB ^w | — | — | — | — | — |
| | Control | — | — | — | — | — |
| | <i>P</i> value | 0.0279 | 0.7584 | 0.1617 | 0.1391 | |

^zColumns were fertilized with a 20N-4.3P-16.6K solution, then leached 11 times over 16 d.

^yNitrate, phosphate, and potassium leached from columns were fit to a modified exponential curve in the form of $y = a + be^{-(x-c)^2/d}$, where *y* is the nutrient concentration measured in the leachate on the *x*th leaching event, *a* indicates the value of *y* which the curve approaches asymptotically as *x* increases to infinity, *a* + *b* represents the maximum value of *y* when *x* = *c*, and *d* is a scaling factor.

^xWithin a nutrient, the probability value for the hypothesis test that the variable within the column was similar for each biochar source.

^wPotassium release in BWB and control substrates did not change over time and failed to fit any simple linear or non-linear functions.

The sums of squares reduction test indicated that fitted exponential functions for nitrate, phosphate, and K differed with each biochar amendment ($P < 0.0001$) (Fig. 1). Within each nutrient, P values indicate which parameters were similar and which differed (Table 3). According to the fitted parameters of the exponential curve, nitrate release peaked from the control substrate with $229 \text{ mg}\cdot\text{L}^{-1}$ at 3.1 d of leaching (Table 3). The SDB and BWB-amended substrates peaked at 176 and $179 \text{ mg}\cdot\text{L}^{-1}$ after 4.2 and 3.5 d of leaching, respectively. The GRHB reduced the concentration of peak nitrate release to $150 \text{ mg}\cdot\text{L}^{-1}$ after 4 d of leaching. Similar to previous research (Altland and Locke, 2012), additions of biochar resulted in nitrate release curves that peaked lower and peaked at later leaching events compared with a control substrate. These overall differences in curve shape suggest that nitrate was retained and released more slowly over time in biochar-amended substrates compared with the control substrate.

Results were similar in the second experiment in terms of how biochar type affected nitrate release from the control substrate (Fig. 2; Table 4). Nitrate release peaked from the control substrate at $232 \text{ mg}\cdot\text{L}^{-1}$ after 2.6 d of leaching (Table 4). The BWB-amended substrate reduced peak nitrate slightly and caused the peak to occur later with $174 \text{ mg}\cdot\text{L}^{-1}$ after 2.9 d of leaching. The SDB and GRHB reduced the concentration of peak nitrate further to 119 and $138 \text{ mg}\cdot\text{L}^{-1}$, respectively, and these peaks occurred later in the leaching cycles after 3.5 and 3.1 d of leaching, respectively, compared with the control substrate. Similar to the first experiment, additions of biochar resulted in nitrate release curves that peaked lower, at later leaching events, and had higher residual nitrate release over time compared with the control substrate.

Considering the volume and concentration of fertilizer spiked into each column, a total of 88.5 mg of nitrate should have been recovered in the leachates if all N were leached in the nitrate form. At the time the fertilizer solution was applied, 6% of the applied nitrate was recovered in the leachate from the control substrate. The SDB and BWB-amended substrates yielded less recovered nitrate with $\approx 1.4\%$ and 4% , respectively, of the total amount applied. The GRHB-amended substrate yielded the least nitrate with less than 1% of the total amount applied. Over the course of the leaching events, 43% of the applied nitrate was recovered in the control substrate (Table 4), which was slightly higher than biochar-amended substrates that ranged from 32% to 35% recovery. This differs from previous research (Altland and Locke, 2012) that showed the same substrate amended with 5% or 10% SDB resulted in similar nitrate recovery compared with control substrate, all averaging 47% nitrate recovery. Reduced recovery rates of nitrate are important because this might imply that biochar-amended substrates would absorb or adsorb nitrates for an extended period of time and thus render less nitrate available for plant uptake. Although the release curves

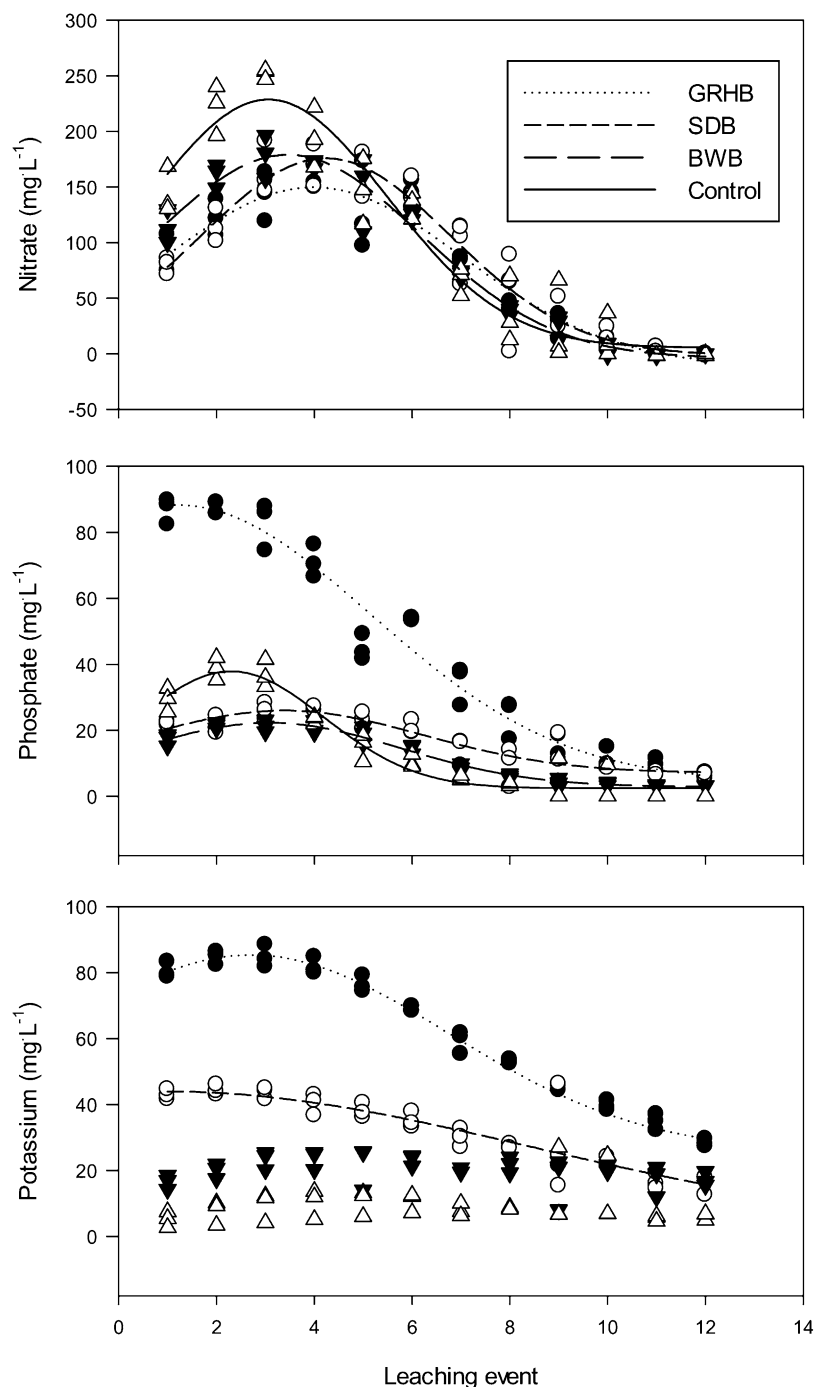


Fig. 1. Nitrate, phosphate, and potassium leaching from 85:15 sphagnum peat:perlite substrates amended with gasified rice hull biochar (GRHB, ●), sawdust (SDB, ○), bark and wood biochar (BWB, ▼), or a non-amended control (△). Columns were initially fertilized with 200 mL of a $100 \text{ mg}\cdot\text{L}^{-1}$ nitrate solution. Columns were then leached 12 times over the course of 16 d by adding 60 mL of water to the top of the column and collecting leachate from the bottom. Parameter estimates of fitted curves are detailed in Table 3.

(Fig. 2) show nitrate levels leaching from each of the substrates had stabilized to a constant level, they were each still releasing 8.6 to $13.4 \text{ mg}\cdot\text{L}^{-1}$ nitrate at the conclusion of the experiment. It is likely, considering the trend of the scatterplots over the last four leaching events, that nitrate would continue to leach from the substrates over time, thus increasing the percent nitrate recovery for all substrates.

Phosphate retention and release was also fit to the same modified exponential equation as nitrate (Fig. 1). Phosphate release from each biochar material differed according to the sums of squares reduction test ($P < 0.0001$). Most striking was the release of phosphate from GRHB. Phosphate release from GRHB peaked at $88 \text{ mg}\cdot\text{L}^{-1}$ after 1.2 leaching events (Table 3). This is in contrast to all other treatments that peaked between 22

Table 4. Estimated parameters (with standard errors in parentheses) for macronutrient release curves (Fig. 2) from columns with an 85:15 sphagnum peatmoss:perlite substrate alone or amended with 10% (v/v) gasified rice hull biochar (GRHB), sawdust biochar (SDB), or bark and wood biochar (BWB).^z

| Nutrient | Biochar source | <i>a</i> ^y | <i>b</i> | <i>c</i> | <i>d</i> | <i>r</i> ² |
|-----------|-----------------------------|-----------------------|----------------|------------|---------------|-----------------------|
| Nitrate | GRHB | 10.86 (5.13) | 127.44 (9.89) | 3.1 (0.11) | 3.78 (0.74) | 0.861 |
| | SDB | 13.37 (5.26) | 106.56 (8.52) | 3.5 (0.13) | 5.38 (1.11) | 0.847 |
| | BWB | 10.17 (4.46) | 164.29 (9.66) | 2.9 (0.07) | 2.79 (0.41) | 0.918 |
| | Control | 8.64 (6.65) | 223.95 (15.14) | 2.6 (0.08) | 2.63 (0.45) | 0.897 |
| | <i>P</i> value ^x | 0.9537 | 0.0001 | 0.0001 | 0.0745 | |
| Phosphate | GRHB | 8.34 (2.52) | 74.14 (3.4) | 2.2 (0.23) | 12.26 (2.47) | 0.949 |
| | SDB | 11.33 (2.3) | 39.38 (3.97) | 3.2 (0.16) | 4.95 (1.3) | 0.780 |
| | BWB | 6.28 (0.9) | 27.68 (1.54) | 3.1 (0.09) | 5.26 (0.78) | 0.921 |
| | Control | 4.64 (1.67) | 40.98 (3.03) | 2.8 (0.13) | 4.94 (1.01) | 0.873 |
| | <i>P</i> value | 0.3735 | 0.0001 | 0.0029 | 0.0403 | |
| Potassium | GRHB | 34.05 (2.27) | 43.94 (3.14) | 3.0 (0.18) | 10.31 (2.36) | 0.884 |
| | SDB | 19.96 (1.7) | 20.68 (1.98) | 1.4 (0.74) | 27.29 (11.49) | 0.911 |
| | BWB ^w | — | — | — | — | — |
| | Control | — | — | — | — | — |
| | <i>P</i> value | 0.0001 | 0.2767 | 0.0421 | 0.1472 | |

^zColumns were fertilized with a 20N–4.3P–16.6K solution, then leached 11 times over 16 d.

^yNitrate, phosphate, and potassium leached from columns were fit to a modified exponential curve in the form of $y = a + be^{-(x-c)/d}$, where *y* is the nutrient concentration measured in the leachate on the *x*th leaching event, *a* indicates the value of *y* which the curve approaches asymptotically as *x* increases to infinity, *a* + *b* represents the maximum value of *y* when *x* = *c*, and *d* is a scaling factor.

^xWithin a nutrient, the probability value for the hypothesis test that the variable within a column was similar for each biochar source.

^wPotassium release in BWB substrates with a simpler exponential function of $y = 22.43[1 - e(-0.76x)]$ ($r^2 = 0.727$). Release in control substrate was better fit with a linear function, where $y = 1.68 + 0.63x$ ($r^2 = 0.796$).

and 38 mg·L⁻¹ after 2.3 to 3.4 leaching events. The girth of the peak portion of the exponential curve was 30.9 for GRHB, nearly twice the value of the next highest *d*-value in SDB. Thus, the phosphate release curve for GRHB had a higher and wider peak than those for other substrates. The wood-based biochar materials, SDB and BWB, had lower peaks that peaked later and wider than the control substrate. This is similar to previous research (Altland and Locke, 2012) showing that SDB retained and released fertilizer phosphates from a liquid fertilization event.

In the second experiment, phosphate release curves from GRHB-amended substrate peaked higher, sooner, and wider than all other substrates (Fig. 2; Table 4), just as it did in the first experiment. However, there were only minor differences among the other three substrates. Phosphate from the BWB substrate peaked lower than the control substrate (34 vs. 46 mg·L⁻¹), slightly later (3.2 vs. 2.8 d), and with a slightly wider girth (5.3 vs. 3.9 d). In contrast to the previous experiment, the SDB-amended substrate peaked higher and with a similar girth to the control substrate. Taking results from these two experiments together, it appears that GRHB provided phosphates beyond that provided by the fertilizer event, whereas SDB and BWB biochars had only a slight and variable effect on phosphate retention and release.

During the saturation event, the columns released between 0.5 and 10.5 mg phosphate. Because this occurred before the fertilization event, there should have been no recovered phosphate from any of the columns. Evans et al. (2011) reported 1.3 to 2.5 mg·L⁻¹ P extracted with water from a sphagnum peatmoss

substrate periodically over 56 d. If we assume a mean value of 1.9 mg·L⁻¹ P leached from sphagnum peatmoss, we would have expected 1.14 mg phosphate to be leached from the sphagnum peat portion of our columns considering the mean volume of leachate collected from the saturation event (232 mL). This would explain the levels of phosphate in the SDB, BWB, and control substrates; however, it does not account for the level of phosphates observed in the GRHB-amended substrates. The total P determined for GRHB was higher than all other biochar materials (Table 1). Assuming all of the total P was available as reactive phosphate, there would be a potential of 106.8 mg phosphate in the GRHB-amended substrates. Assuming 1.14 mg phosphate originated from the sphagnum peat, like in the control substrate, 9.1 mg phosphate recovered in the GRHB-amended substrates that would have originated from the GRHB. A total of 13.5 mg of phosphate was added to the columns from the fertilization event. The control substrate leached 2.4 mg phosphate. Assuming again that 1.9 mg·L⁻¹ P is leached from the sphagnum peatmoss fraction of the substrate, we calculate that the sphagnum peatmoss would contribute 1.1 mg phosphate to that recovered; thus, 1.3 mg phosphate would have been contributed by the fertilizer solution. Assuming a similar quantity of phosphate would have leached from the GRHB-amended substrates, 10.2 of the 12.6 mg phosphate recovered from these columns can be attributed directly to the biochar. After the saturation and fertilization events, the GRHB had already contributed 9.1 and 10.2 mg phosphate, which was ≈18% of the total P available in this form of biochar.

Summing over the 12 leaching events, the control substrate yielded 10.6 mg phosphate, of which 3.7 mg could be attributed to the sphagnum peatmoss. Thus, 6.9 mg phosphate recovered in the leaching events could be attributed to the fertilizer solution along with 1.3 mg phosphate in the fertilization event for a total of 8.2 mg phosphate of the total 13.5 mg phosphate (61%) applied in the fertilization event. The GRHB-amended substrate yielded 20.9 mg phosphate, which could be corrected to 17.2 mg phosphate if we assumed 3.7 mg was attributable to the sphagnum peatmoss. An additional 16.1% of the total P in GRHB was released over the 12 leaching events, which in combination with the 18% released in the saturation and fertilization events means that ≈35% of the total P in GRHB was released as phosphate over the course of the experiment.

Potassium release from GRHB and SDB-amended substrates were fit to the same exponential functions used for nitrate and phosphate release (Fig. 1; Table 3). Potassium leached from GRHB and SDB peaked at 85 and 44 mg·L⁻¹, respectively. Potassium release from BWB and control substrates could not be fit to linear or non-linear functions, suggesting K release rates from these two substrates were constant over time.

Similar to the first experiment, potassium release from GRHB and SDB-amended substrates were fit to an exponential function (Fig. 2; Table 4) with peaks at 78.0 and 40.6 mg·L⁻¹, respectively, and leveling off to 34.1 and 20.0 mg·L⁻¹, respectively. Potassium release from BWB was fit to an exponential growth function where it plateaued at a maximum of 22.4 mg·L⁻¹. Similar to the other biochar-amended substrates, it was not certain how long K release at this concentration would be maintained. Potassium release from the control substrate was fit to a simple linear function (Fig. 2; Table 4) and resulted in a gradual increase from 1.6 to 9 mg·L⁻¹ throughout the experiment. Potassium release from the control substrate was similar to leachable K levels in sphagnum peat reported by others (Evans et al., 2011; Gachukia and Evans, 2008).

Similar to phosphate, GRHB-amended substrates released more K than other substrates, particularly through the first six leaching events. The GRHB was comprised of 0.98% K (Table 1) and thus the amended substrate had a potential of 110.3 mg K from the GRHB in addition to the 16.6 mg from the fertilizer for a total of 79.8 mg K. There was 21.0 mg of K released from the water saturation event alone (Table 5), which accounted for 19% of the potentially available K from the GRHB. By the conclusion of the 12 leaching events, a total of 65.8 mg K had been recovered from the saturation, fertilization, and leaching events to account for 52% of the potentially available K. The control substrate leached 4.9 mg K, most of which was presumably from the fertilizer. The SDB contained approximately half the amount of K found in GRHB but released its K proportionally at about the same rate with 20% at

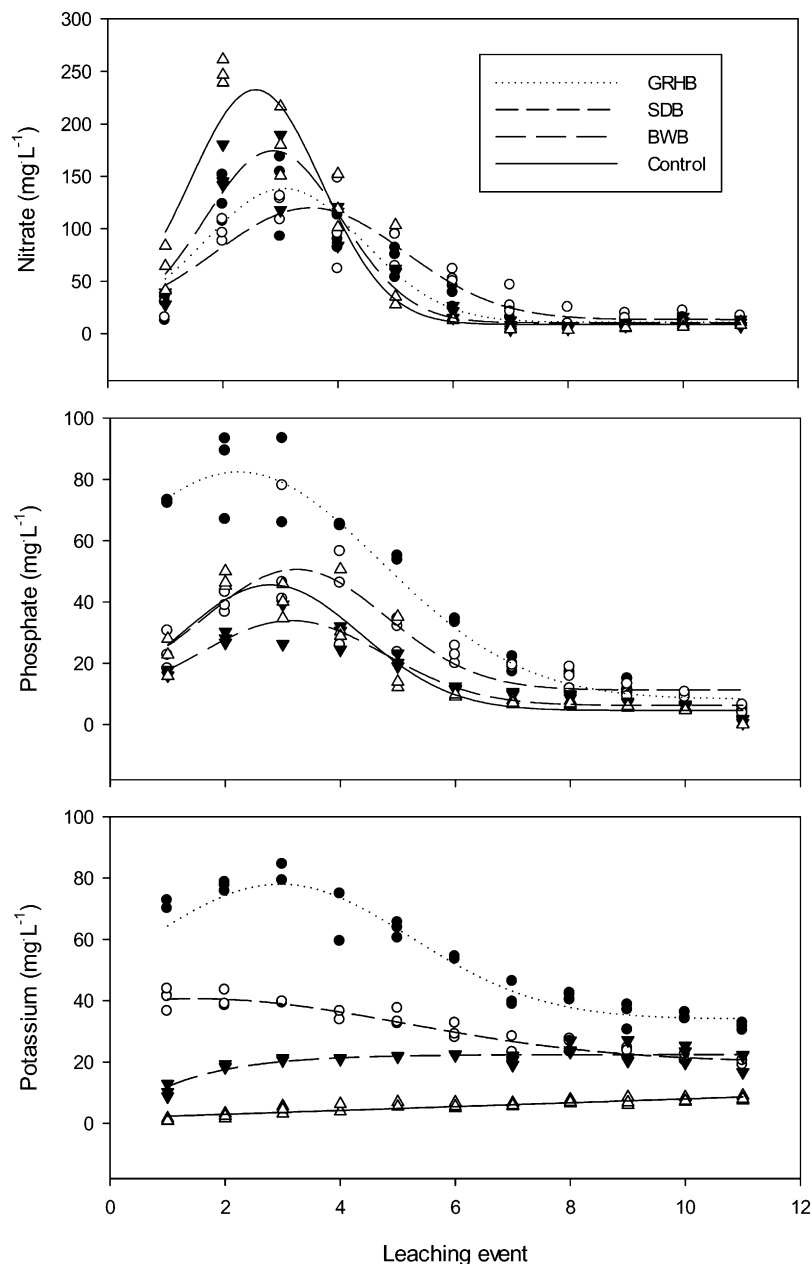


Fig. 2. Nitrate, phosphate, and potassium leaching from 85:15 sphagnum peat:perlite substrates amended with gasified rice hull biochar (GRHB, ●), sawdust (SDB, ○), bark and wood biochar (BWB, ▼), or a non-amended control (△). Columns were initially fertilized with 200 mL of a 100 mg·L⁻¹ nitrate solution. Columns were then leached 11 times over the course of 16 d by adding 60 mL of water to the top of the column and collecting leachate from the bottom. Parameter estimates of fitted curves are detailed in Table 4.

saturation (compared with 19% for GRHB) and 53% summed overall leaching events (compared with 52% for GRHB). The BWB-amended substrates leached just 9% at the saturation event and 33% of K from the biochar and fertilizer over the course of the experiment.

All three biochar types evaluated in these two experiments affected macronutrient retention and release, but each macronutrient responded differently, and each biochar type had a different impact. All biochar amendments affected nitrate release curves with lower and wider peaks that occurred later in the series of leaching events. It had been

hypothesized previously (Altland and Locke, 2012) that exponential release curves such as those described in this article with lower and wider peaks could result in more moderated nitrate levels in a substrate. With lower and wider peaks of nitrate in substrate solution, there would be less drastic and fewer spikes between high and low nitrate availability. The impact on biochar amendment on phosphate retention and release was more variable within and across the two experiments. The BWB and SDB amendments reduced phosphate release curve peaks, shifted the peaks later in the series of leaching cycles, and caused wider peaks than those of control

substrates. This was similar to previous research (Altland and Locke, 2012) and would presumably have the same moderating effect on fluctuating phosphate levels in a container substrate. However, these two materials had similar phosphate release curves to the control substrate in the second experiment as well as yielding similar quantities of phosphate summed overall the leaching events, demonstrating that this phenomena of temporary phosphate retention and release requires more study to determine what other factors might influence it. In both experiments, the GRHB was a net source of phosphate, providing more phosphate to the system than the fertilizer application and hence obscuring any retention and release effect it might have. Potassium release varied by amendment type within each experiment but within each amendment type was relatively consistent across the two experiments. All biochar types were a source of K with GRHB providing more than SDB but both providing far more K than the fertilizer event. The BWB amendment resulted in more leached K than the control substrate but relatively little compared with GRHB and SDB amendments.

It has been speculated that biochar amendments might retain and release nitrates, phosphates, and other agrichemicals (Altland and Locke, 2012; Beck et al., 2011). Although this has not been ruled out, the subtlety of the effect we were able to measure regarding the three biochar materials in these experiments on macronutrient leaching suggests that it would be difficult to manifest measurable differences in macronutrient leaching in actual plant culture. What is more interesting from these results is the use of some biochar materials, GRHB in particular, as a source of macronutrients. Each column used in this study was packed with 600 cm³ substrate, which is about the same volume used to fill a 10-cm diameter round pot. The fertilizer event in this experiment provided 13.2 mg phosphate and assuming all of that was leached from the column, an additional 30.7 mg phosphate was provided by the GRHB-amended substrate. Likewise, the GRHB-amended substrate provided 49.2 mg K. Other research by the authors in 10-cm pots (unpublished) showed that sunflower (*Helianthus annuus* 'Pacino Gold'), tomato (*Lycopersicon lycopersicum* 'Mega Bite'), zinnia (*Zinnia elegans* 'Oklahoma White'), geranium (*Pelargonium xhortorum* 'Maverick Red'), and pansy (*Viola xwittrockiana* 'Mammoth Blue Deep Dazzle') require ≈35.8, 17.1, 33.4, 59.4, and 24.5 mg phosphate (11.7, 5.6, 10.9, 19.4, and 8.0 mg P) for the shoot portion of the plant, respectively. Thus, phosphate provided by GRHB would nearly satisfy the needs of all these crops with the exception of geranium. Likewise for K, this research showed that the same plants would require 79, 57, 54, 142, and 43 mg K, respectively, for their shoots. Thus, the GRHB would have sufficient K to supply all but the sunflower and geranium. Further research will evaluate the possibility of GRHB to replace P and K in commercial fertilizer formulations for greenhouse-grown crops.

Table 5. Mass of fertilizer nutrients collected in leachates from columns with an 85:15 sphagnum peat:moss:perlite substrate alone or amended with 10% (v/v) gasified rice hull biochar (GRHB), sawdust biochar (SDB), or bark and wood biochar (BWB) and fertilized with a 20N-4.3P-16.6K solution.^z

| Nutrient | Event | GRHB | SDB | BWB | Control | LSD ^y |
|-----------|-----------------------|--------------|------|------|---------|------------------|
| | | -----mg----- | | | | |
| Nitrate | Water saturation | 0.0 | 0.0 | 0.2 | 0.0 | 0.2 |
| | Fertilizer saturation | 0.5 | 1.3 | 3.8 | 5.1 | 1.5 |
| | Summed leach events | 28.7 | 30.2 | 31.3 | 37.7 | 6.2 |
| Phosphate | Water saturation | 10.5 | 2.3 | 0.5 | 1.0 | 1.0 |
| | Fertilizer saturation | 12.6 | 3.0 | 1.7 | 2.4 | 2.4 |
| | Summed leach events | 20.9 | 14.5 | 9.4 | 10.6 | 3.4 |
| Potassium | Water saturation | 21.0 | 11.4 | 3.5 | 0.2 | 0.7 |
| | Fertilizer saturation | 15.5 | 8.5 | 2.6 | 0.2 | 2.6 |
| | Summed leach events | 29.4 | 18.9 | 11.9 | 4.5 | 4.5 |

^zLeachates were collected after an initial water saturation, a fertilizer saturation, and then leached 12 times over 16 d.

^yFisher's protected least significant difference value ($\alpha = 0.05$) for comparing means within a row.

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