Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar–soil mixtures

Atanu Mukherjee [1], Andrew R. Zimmerman *

Department of Geological Sciences, University of Florida, 241 Williamson Hall, P.O. Box 112120, Gainesville, FL 32611, USA

ABSTRACT

Biochar has shown promise as a soil amendment that increases carbon sequestration and fertility, but its effects on dissolved organic carbon (DOC), nitrogen (N) and phosphorus (P) cycling and loss is not well understood. Here, nutrient release from a variety of new and aged biochars, pure and mixed with soils, is examined using batch extraction and column leaching. In successive batch extractions of biochar, cumulative losses were about 0.1–2, 0.5–8 and 5–100% of the total C, N and P initially present, respectively, with greater releases from biochars made at lower temperature and from grass. Ammonium was usually the most abundant N form in leachates but nitrate was also abundant in some biochars, while organic N and P represented as much as 61% and 93% of the total N and P lost, respectively. Release of DOC, N and P into water was correlated with biochar volatile matter content and acid functional group density. However, P release via Mehlich-1 extraction was more strongly related to ash content, suggesting a mineral-associated P fraction. Columns with soil/biochar mixtures showed evidence of both soil nutrient sorption by biochar and biochar nutrient sorption by soil, depending upon biochar and soil type. This study demonstrates that biochars contain a range of nutrient forms with different release rates, explaining biochar's variable effect on soil fertility with soil and crop type and over time.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Biochar is the carbonaceous product obtained by the heat treatment of biomass under limited or no oxygen (pyrolysis). Biochar has recently gained attention for its potential, when used as a soil amendment, to improve the fertility of degraded soils and to store carbon removed from the atmosphere by plants. While there has been much recent work examining biochar's chemical characteristics and effect on plant and microbial growth, the primary mechanism for these effects and the possible environmental consequences that may accompany biochar amendments, such as organic contaminant or nutrient releases, is unclear.

Biochar's positive effects on the soil ecosystem, including both plants and microbes, have been proposed to derive either directly from nutrients within biochar itself, or indirectly from its ability to sorb and retain nutrients (Hammes and Schmidt, 2009; Lehmann et al., 2011). However, nutrient leaching can have negative environmental consequences such as causing eutrophication in surface or ground waters. Recent studies have shown the nutrient content of biochars to range widely and be controlled by both biomass type and combustion conditions (Mukherjee et al., 2011). More relevant to plant and microbial growth, however, is its bioavailable nutrients content. A recent study found that 15–20% of Ca, 10–60% of P and about 2% of N in mallee wood biochar was readily leachable with distilled water, with amounts that varied both with charring temperature and portion of the plant sampled (Wu et al., 2011).

When added to soil, plant available nutrients provided by the biochar will also vary with char and soil type, as both increases and decreases in available nutrients following biochar amendment have been observed. For example, the column leachate of a Norfolk loamy soil amended with a pecan shell biochar made at 700 °C temperature contained greater K and Na, but less P (by about 35%) Ca, Mn and Zn, relative to a control soil with no biochar (Novak et al., 2009). Thus, biochars were hypothesized to exchange multivalent cations for surficially sorbed monovalent cations. Another column leaching experiment using bamboo charcoal pyrolyzed at 600 °C added to a variety of sandy silt soils showed a cumulative reduction in NH_4^+-N loss of 15% over 70 days (Ding et al., 2010). Column experiments with poultry litter and garden waste biochars produced at 550 °C without soil also showed a reduction in NO_3, NH_4^+ and P leaching, but these reduction were not maintained beyond the addition of 20 pore volumes of water (816 mm) suggesting the involvement of either weak surface interactions or water trapping (Downie et al., 2007; Major et al., 2009). In contrast, biochar made from green-waste such as chicken manure may greatly increased extractable (i.e. leachable) nutrient levels in amended soils (Chan and Xu, 2009; Chan et al.,

* Corresponding author. Tel.: +1 352 392 0070; fax: +1 352 392 9294.
 E-mail address: azimmer@ufl.edu (A.R. Zimmerman).
 [1] Now at The Ohio State University, Carbon Management and Sequestration Center, 2021 Coffey Road, 422D Kottman Hall, Columbus, OH 43210, USA.

2008). And a 45-week soil column leaching study using Midwestern agricultural soil (Clarion, fine-loamy) leached with 0.4–0.7 pore volumes of 0.001 M $CaCl_2$ once a week for 500 days showed a slight increase in total N and P leached when amended with 20 g kg^{-1} biochar, but a reduction in N and P leached of 11% and 69%, respectively, when manure was also added, relative to the control with no biochar (Laird et al., 2010). The amount of N immobilization in soil has also been shown to vary greatly with pyrolysis time period (Bruun et al., 2012) and P release varied with pH (Silber et al., 2010).

Whether biochar will ultimately benefit plants by providing nutrient or inhibit plant growth by sequestering them is still an open question. Declines in plant growth in some experiments with biochar have been attributed to a decline in available ammonium (Deenik et al., 2010). Soil column experiment with bagasse biochar made from 400 to 800 °C indicated that higher temperature bagasse biochar can adsorb significant amount of NO_3^- (Kameyama et al., 2012), possibly decreasing the amount of available nutrients in soils and inducing plant N deficiency. However, N exists primarily in soil as organic complexes which are eventually ammonified (NH_4^+) then nitrified (NO_3^-) before plant uptake. There has been no prior study which simultaneously compares the adsorption of these different forms.

The physical properties of some biochars, such as high surface area, porosity and ion exchange capacity, are also likely related to its ability to sorb, and possibly slowly released, OM or nutrients (Liang et al., 2006). But measured biochar cation exchange capacities (CEC) ranging from almost none to about 70 cmol$_c$ kg^{-1}, the latter being found for lower temperature chars (Mukherjee et al., 2011). And, large amounts of anion exchange capacity (AEC) have only been found for aged biochars (Cheng et al., 2008; Mukherjee et al., 2011). Thus, fresh biochars might be expected to retain only NH_4^+ and release any exchangeable NO_3^- and PO_4^{3-}.

The extent to which nutrients may be lost or retained in their organic form is poorly understood. A recent study observed abundant leaching of DOC from fresh grass biochars, but also a large degree of organic compound sorption onto biochars which was controlled by its surface morphology, biomass species, and charring temperature (Kasozi et al., 2010). And in field studies, biochar–amended soils exhibited greatly enhanced concentrations of DOC in leachates from Colombian Savanna Oxisol (Major et al., 2010) and northeast England (Bell and Worrall, 2011). Both ammonium and organic N sorbed onto or released from biochar has been found to be at least partially bioavailable (de la Rosa and Knicker, 2011; Taghizadeh-Toosi et al., 2012). However, there are no studies that examined speciation of DOC, N and P released or retained by biochar or examined a range of biochar types and over time.

Clearly, a better understanding of biochar's nutrient retention or release properties is needed so that the optimum biochar can be selected for application to each particular soil type, both to maximize soil productivity and minimize deleterious environmental effects. An additional need is to be able to predict C losses via leaching so that C sequestration credits may be assigned to those that implement biochar addition projects, if and when such a system is enacted. Here, both batch extraction and column leaching experiments were carried out using a number of types of biochar and soil/biochar mixtures. Specific objectives of this study were to: 1) assess the variation in DOC, N, and P leaching/retention from a range of biochar types including those freshly prepared and aged, 2) explore the interaction between biochar leachate C, N, P and soils, 3) examine the form of N and P lost/gained by biochar and biochar/soil mixtures, and 4) use nutrient loss patterns to predict longer term nutrient loss rates.

2. Materials and methods

2.1. Materials

Biochar was produced from *Quercus lobata* (Laurel oak), *Pinus taeda* (Loblolly pine) and *Tripsacum floridanum* (Gamma grass) by combustion for 3 h at 250 °C in open oven and at 400 and 650 °C in a pyrolyzer continuously flushed with 99% pure gaseous N_2 (designated hereafter as Oak-250, Grass-650, etc.). Detailed information on biochar preparation and characteristics and methods of analysis have been presented elsewhere (Hamdan et al., 2010; Harvey et al., 2012; Kasozi et al., 2010; Mukherjee, 2011; Mukherjee et al., 2011; Podgorski et al., 2012; Zimmerman, 2010) but are summarized in Supplemental Table S1. Only the coarse (Hamdan et al., 2010) (0.25–2 mm) size fraction, separated by sieve and briefly rinsed with double distilled water to remove ash, was used in these experiments. In addition, biochar of each type was aged by placing in containers, fine-mesh screened above and below, so that weathering by air and precipitation, but not sunlight, could occur. Aging took place during the nine month period from Dec. 1, 2009 to Sep. 28, 2010 in Gainesville, Florida, during which time 109 cm of rain fell, almost equal to the 123 cm that is the annual average for this location.

In addition to a quarts sand control, two soils were used in these experiments: a fine sandy Florida Entisol collected from a forest near Gainesville, Florida (BY) and a clay loam Ultisol collected near Jasper, Georgia (GA). Both soil samples integrated 0–10 cm depth horizons and were air dried and sieved (<2 mm) to remove roots and vegetation. Porosity of the sand, BY and GA soils was 30.6%, 35.8% and 50.2%, respectively. Further soil details are provided in Supplemental Tables S1 and S2.

2.2. Batch extraction experiment

Preliminary experiments showed that leaching of nutrients from biochar was not a time limited phenomena but rather varied with extractant volume (i.e. an equilibrium as opposed to a kinetically-driven phenomenon). However, we found that equilibrium was reached after only a few hours in early extractions, and required a few days for later extractions. Because the goal of this research was to estimate the maximum amount of nutrients likely to be release by biochar in the natural environment, we performed successive batch extractions of biochar samples in water, each time with removal and replacement of supernatant, and each time allowing for enough time to reach equilibrium. About 0.5 g of each biochar sample was added to 40 mL of distilled deionized (DI) water in 50 mL plastic centrifuge tubes and placed horizontally on a mechanical platform shaker (150 rpm) in the dark. On days 1, 2, 4, 10 and 20, tubes were weighed and centrifuged (4500 rpm) and the supernatant was carefully removed via pipette. The remaining sample was weighed to determine the amount of entrained solution and 40 mL DI water was added prior to the next round of batch extraction. The pH was not held constant because we wished to simulate nutrient release under natural conditions. However, the pH of leachates of successive water extractions did not change significantly for any particular biochar type.

Upon removal, supernatant solutions were filtered (Whatman 40 filter paper) and stored in a refrigerator for no longer than 1 week prior to chemical analysis. The amount of each component leached was calculated as the product of the solution volume (assuming a density 1 g cm^{-3}) and its concentration, less the amount of the component present at the start of the leach period (the product of the entrained volume and its concentration, that was previously in the supernatant). For comparison, the biochars were also extracted using standard Mehlich-1 (M1) solution over 24 h.

2.3. Column leaching experiment

Column leaching experiments were performed in clear polyvinyl tubes (30.5 cm length × 7.5 cm diameter) screened at the base with a fine mesh polypropylene screen and a fitted rubber stopper at the bottom with a valve inserted into it attached to a tube for control of leachate collection. The columns were packed with 500 g of soil

homogenized with 5 g biochar. This represented an addition of biochar C equivalent to about 20% of the native soil organic carbon and made a soil column 15 cm in height. Experimental control columns consisted of 5 g biochar homogenized with 500 g cleaned combusted (450 °C, 3 h) quartz sand or 500 g soil with no biochar. Distilled water was added gently using a small sprinkler system to disperse the water across the surface of the soil. At the start of each run, soils were saturated by adding water to fill columns to the level of the top of the soil surface and then immediately drained, achieving field water holding capacities of 10%, 35% and 44% for the sand, BY and GA soils respectively. Thereafter, each column was leached three times a day with 100 mL of DI water representing 0.65, 0.56 and 0.45 of the total soil pore volume for the sand, BY and GA soil columns, respectively. A total of 1–1.4 L water was added to the columns over the 3–4 days experimental period. The leachates were refrigerated prior to chemical analyses carried out within 2 weeks.

2.4. Analytical methods

Elemental C and N were analyzed using a Carlo Erba CHNS analyzer. All the batch extraction and column leaching samples were analyzed for DOC on a total organic carbon analyzer (Shimadzu TOC-5000A) after acidification to pH 2–3 with 1 M HCl and sparging for 2 min with carbon-free air to remove inorganic C. Total Kjeldahl nitrogen (TKN: organic $N + NH_4^+$-N), NH_4^+-N, and NO_3^--N were measured using a continuous autoflow analyzer using EPA methods 351.2, 350.1, and 353.2, respectively. Total P and ortho-P were measured using a Spectro Ciros CCD inductively coupled plasma spectroscope using EPA methods 200.7 and 365.1, respectively. All N and P analyses were carried out at the Analytical Research Laboratory, University of Florida. Using these data, organic N was calculated as TKN minus NH_4^+-N while organic P was calculated as total P minus ortho-P. The TKN was measured in all batch and column leachates whereas NH_4^+-N, and NO_3^--N were only measured in initial and final leachate samples. Because little NO_3^--N was found in most of the samples, TKN is referred to here as N or total N unless otherwise specified. Biochar and soil samples were also analyzed for total P and Fe following method AOAC 985.01 (dry ashing 4 h at 500 °C then acid digestion using both HCl and nitric acid) and amorphous Fe and Al extraction from soils using an ammonium oxalate extraction following McKeague and Day (1966). Additional analytical methods used for biochar characterization including ash and volatile matter content and surface acidity are provided in the Supplemental information section.

2.5. Statistical methods and error

All DOC samples were run in triplicate and were determined in duplicate samples and were re-run if coefficient of variation was >5%. For ICP analyses, every 20th sample was run twice. Estimates of uncertainty were ±3.46% for Fe, 6.47% for Al, 2.61% for NH_3, 3.16% for TKN, 3.16% for ortho-P and 3.90 for total P. Regression analyses, which were used to predict long term nutrient release rates and correlation between parameters, were performed using Microsoft Excel (MS, 2003) tool pack.

3. Results

3.1. Batch biochar extraction

During the batch extraction experiment, fresh biochar samples released large amounts of DOC, N and P into water, which generally decreased exponentially with time, or more correctly, with leachate volume (Fig. 1a, b, c). Concentrations of nutrients released by biochar in the first 40 mL of water addition ranged from 355 to 4429 µg DOC g^{-1}, 0 to 302 µg N g^{-1} and 159 to 1536 µg P g^{-1}. By

the third batch extraction, after 120 mL of water addition, nutrient concentrations of all fresh biochars stabilized at ranges of 187–1255 µg DOC g^{-1}, 0–73 µg N g^{-1} and 0–224 µg P g^{-1}. Initial release of P was greater than N, but decreased more rapidly so that N release was greater than that of P in later leachates. On average, lower temperature fresh biochars (250 °C) leached more nutrients (by 66, 67 and 23% for DOC, N and P, respectively) than higher temperature biochars (650 °C) and grass biochars released more nutrients (by 22, 86 and 56% for DOC, N and P, respectively) than oak biochars. Pine biochars generally exhibited behaviors quantitatively intermediate to those of oak and grass of the same charring temperatures. For brevity, pine biochar results are not shown in tables and figures but were used in statistical comparisons of nutrient extraction techniques.

Aged biochar nutrient release trends were similar to that of fresh biochars in regard to greater nutrient release from grass versus oak and from low versus high temperature biochars (Fig. 1d, e, f). Most nutrient concentrations in leachate from aged biochars similarly stabilized by the third water addition (after 120 mL), but there was a greater degree of variability compared to fresh biochars. On a cumulative basis, aged biochars released only 5–37% P than fresh biochars. Unexpectedly, however, both oak and grass high temperature biochars released about a third more DOC than fresh biochar. Also, aged and fresh grass biochars released similar cumulative amounts of TKN, but aged oak biochars released two to six times greater amounts of TKN than freshly made biochars.

Nitrogen and phosphorus speciation in the initial and final batch leachates (i.e. first and fifth 50 ml DI water extraction) collected are shown in Table 1 and percent organic compositions are calculated in Supplemental Table S3. Nitrate concentrations in both the initial and final biochar leachates (0.08 mg L^{-1}, on average, or 0.16 mg g^{-1} biochar) were low. However, while nitrate represented only between 2 and 14% of the total N leached from most of the chars, it represented 36 to 55% of the N lost by those chars which leached very little N (Oak-650 and Oak-250 in later stages of batch leaching). Organic N was absent from oak biochar leachates, but represented about 60% of the N in the initial grass biochar leachates and closer to 80% in the final ones (Supplemental Table S3). Organic P represented between 39 and 83% of the total P in biochar leachates initially, but was absent in the final biochar leachate.

The 24 h Mehlich-1 extraction of biochar yielded similar amounts of DOC, but about twice the amount of N and P of a 24 h single water extraction (Supplemental Table S4). Aged biochars yielded 87% less or 62% less total P then fresh biochar when extracted by Melich1 or water, respectively.

3.2. Column leaching

Column leaching of biochars (in quartz sand) displayed some trends similar to those of batch experiments, but also some distinct features. Similar to the batch extractions, column leaching showed greater nutrient releases from low versus high temperature biochars (sand/biochar columns: Fig. 2a–c). Release of nutrients generally decreased over time, or rather with flush volume, but not exponentially as it did for the batch leachates. In fact, DOC release from Grass-250 biochar was greater in the second flush. Amounts of nutrient release generally did not stabilize until after about 700 mL flush volume.

Due to their greater nutrient release rates, the two grass biochars (250 and 650 °C) were chosen for column experimentation in combination with soils. In general, soil/Grass-250 exhibited greater nutrients release throughout column leaching experiments compared to each corresponding soil-alone control (Fig. 2d–i). Soil/Grass-650 mixtures, however, exhibited equal or less nutrient release compared to each soil-alone control. For the BY soil, for example, DOC, N and P release was 19, 3 and 69% greater, on average, when combined with Grass-250 biochar and 14, 31, and 77% less, on average, when
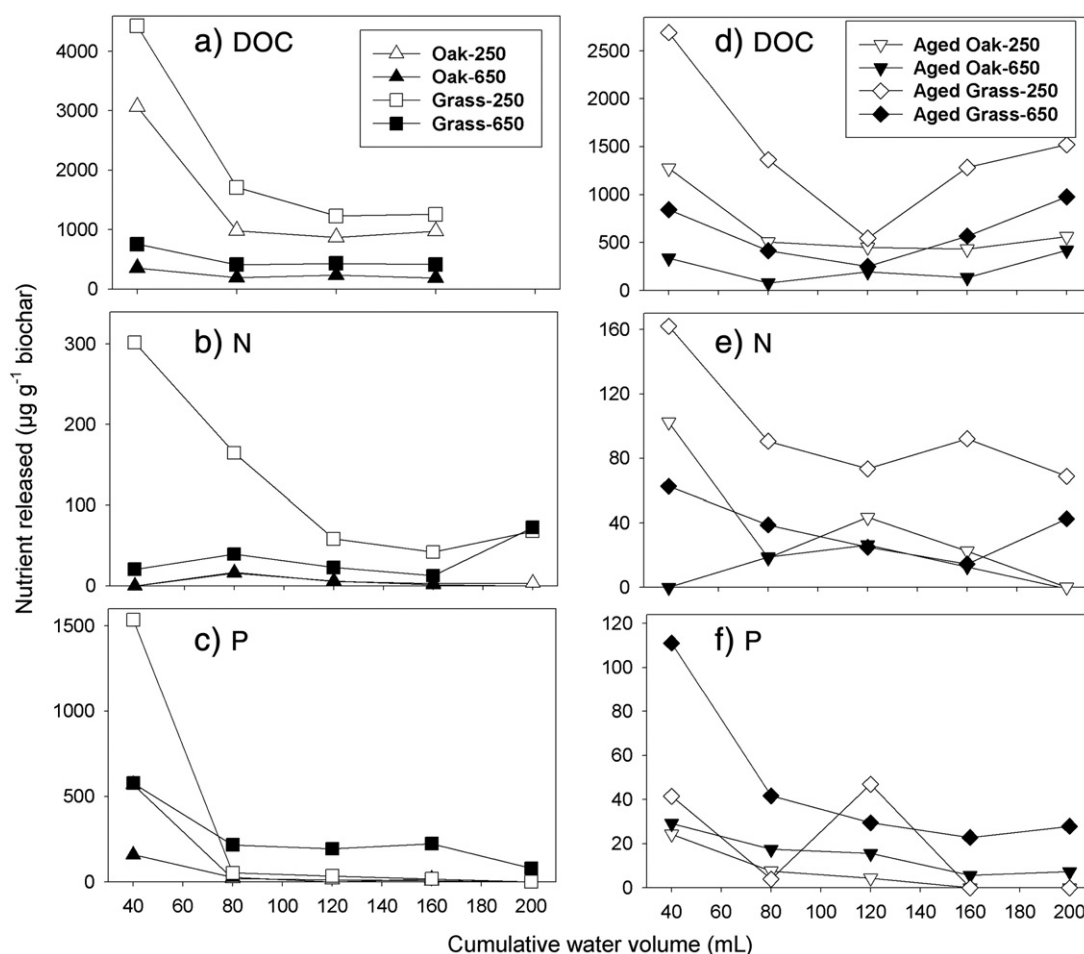
Fig. 1. Dissolved organic carbon (DOC), total Kjeldahl nitrogen (N) and total P concentrations in leachates of successive aqueous batch extractions of fresh biochars (a, b and c, respectively) and aged biochars (d, e and f, respectively), with supernatant replacement. Analytical error of each data point would be smaller than size of symbol.

combined with Grass-650 biochar, respectively. Compared to BY soil, there were smaller differences in nutrient release between columns with GA soil and GA soil/biochar mixtures.

The nutrient species distribution in biochar column leachates varied with biomass type and as leaching of columns progressed (Table 1). Much as in batch leachates, NH_4^+ was usually the largest source of N in most of the biochar/sand leachates. However, nitrate ranged between 2 and 30% of the N in the leachates and organic N was made up the 59% of N in the initial Grass-250 biochar column leachate. Because nitrate usually represented a very small portion of the N leached from the biochars, as found by others (Gaskin et al., 2008; Yao et al., 2010), use of TKN analyses (NH_4^+-N and organic N) as an estimator of total N in other portions of the experiments was justified. Organic P represented a much greater portion of the P in column leachates compared to batch experiments, making up 41 to 93% of the P in the initial leachates and 0 to 67% in the final biochar leachates (Supplemental Table S3).

The initial column leachates from the BY soil (with no biochar) had N forms distributed 3.3, 1.1 and 0.07 mg L^{-1} for organic N, NH_4^+, and NO_3^-, respectively (Table 1). With the addition of Grass-250 biochar, organic N in the initial leachate was 69% greater, NH_4^+ was 43% less and NO_3^- was little changed. This suggests that biochar, at least initially, released organic N and sorbed NH_4^+. In the final leachate, BY soil had only slightly reduced organic N and NH_4^+ concentrations, but there was a large spike in NO_3^-, reaching 19 mg L^{-1}. With the addition of grass biochar, the final leachate was depleted in organic N and even more enriched in NO_3^-, especially for the Grass-250 biochar (74% greater). These N trends were similar for GA soil and GA soil/biochar

combinations except that high concentrations of NO_3^- were not measured (Table 1). Phosphate was consistently the dominant form of P in BY soil and BY/biochar leachates, while in GA soil and GA soil/biochar leachates, while much lower, organic P was the dominant P form.

4. Discussion

One limitations of this study is that there was no replication of experimental treatments (i.e. multiple extractions of the same biochar or soil/biochar column) due to limitations of funds and time.

Due to variation in column packing and thus flow regimes, could lead to slightly different results. However, the replication encompassed in the time series data somewhat reduces this uncertainty and trends in nutrient release were consistent through time and consistently different across various biochar types and nutrient species. Thus, while actual nutrient loss or gain in various biochar–soil-hydrological systems will certainly vary, this research establishes a number of important principles governing biochar nutrient loss which should be universal.

4.1. Nutrient release and control by biochar properties

Cumulative releases of DOC, N and P from fresh biochar in batch extractions as well as column leaching studies were in the range of 464–8622, 23–635, and 46–1664 mg kg^{-1}, respectively (Supplemental Table S5). These were much greater (5 to 100 times) than the measured BY and GA soil nutrient release rates of 85–134, 7–12 and 1–14 mg kg^{-1} for DOC, N and P, respectively, that are typical for soils. In comparison, the only other studies to examine leachates of

Table 1
Concentration of nitrogen and phosphorus forms (all in mg L^{-1}) in first and last leachates of soil and soil/biochar columns.

Batch or column test material	NO$_3$-NO$_2$		NH$_4$-N		TKN[a]		Ortho P		Total P	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Oak-250 (batch[b])	0.07	0.07	0.38	0.07	0.38	0.05	4.23	0.18	7.11	0.08
Oak-650 (batch[b])	0.07	0.09	0.13	0.07	0.13	0.0	0.92	0.26	1.99	0.20
Grass-250 (batch[b])	0.08	0.08	1.25	0.11	3.06	0.89	9.7	0.29	15.87	0.02
Grass-650 (batch[b])	0.08	0.09	0.14	0.18	0.49	0.93	5.31	2.49	30.49	1.28
Sand/Oak-250[c]	0.11	0.05	0.68	0.21	0.48	0.13	0.11	0.79	0.72	1.20
Sand/Oak-650[c]	0.09	0.09	0.22	0.24	0.15	0.05	0.01	0.14	0.11	0.14
Sand/Grass-250[c]	0.07	0.04	1.39	0.30	3.45	0.35	10.54	1.88	17.81	5.78
Sand/Grass-650[c]	0.09	0.05	0.29	0.24	0.17	0.12	0.39	4.11	0.76	4.54
BY soil[c]	0.07	19.46	1.10	1.47	4.40	4.46	2.72	4.46	3.53	4.80
BY/Grass-250[c]	0.09	33.86	0.63	1.54	6.22	3.16	6.40	8.40	8.71	9.44
BY/Grass-650[c]	0.46	21.23	0.93	1.65	3.55	2.64	3.62	4.88	6.48	5.51
GA soil[c]	1.59	0.04	0.83	2.22	3.51	2.91	0.03	0.01	0.21	0.04
GA/Grass-250[c]	0.06	0.04	0.34	2.88	5.19	4.11	0.02	0.02	0.56	0.06
GA/Grass-650[c]	0.04	0.04	0.43	2.04	4.29	2.81	0.04	0.03	0.54	0.09

[a] TKN = total Kjeldahl nitrogen.
[b] Batch extraction experiments, sampled after 40 mL (initial) and 200 mL (final) cumulative leach volume.
[c] Column leaching experiments, sampled after 100 mL (initial) and 1000 mL (final) cumulative leach volume.

pure biochar (1 g biochar in five 20 ml leachings), recorded much lower release rates of 90–1810, 2–9 and 0–1 mg kg^{-1} for DOC, NH$_4$-N and NO$_3$-N, respectively (Gaskin et al., 2008; Gundale and DeLuca, 2006). The little N released from biochars, except in the case of those made from animal waste (Chan et al., 2008), has been noted by others (Gaskin et al., 2010; Joseph et al., 2010; Yao et al., 2010) and has been attributed to the minor amounts of N present in bulk biochar, as well as to the formation of heterocyclic N compounds (so-called 'black N') which cannot be easily solubilized (Knicker, 2010).

Amounts of P extracted from the biochars of this study were similar to that of peanut hull biochars, but 10 times less from poultry litter biochar and 20 times more than pine chip biochar, all made at 400 and 500 °C (Gaskin et al., 2008). Another study, using a corn cob biochar produced by a hydrothermal process at 305 °C, found amounts of extractable P (either by water or Mehlich-3) that were on the order of 100 times less than those of this study, but similar to our aged biochar (Hossain et al., 2011). This indicates, and our data suggests, both that there is much variability in available P among biochar types and that the method of extraction (5 min in the former studies versus 24 h in this study) is a controlling factor.

Tabulation of the total nutrient losses by the biochars relative to their initial concentration (Table 2) shows that C and N losses represented a small, but significant, portion of that initially present in the biochar (0.1–1.7 and 0.8–5.3%, respectively). Losses of P, however, were a substantial portion, ranging from 5 to 151%. The impossible losses of greater than 100% are likely due to the inadequacy of the acid digestion technique used to measure total P in the solid biochar (AOAC 985.01). In other words, not all the P in biochar was extracted by ashing followed by acid digestion, or more likely, much of the organic P was lost during dry ashing. Table 2 also shows that, not only do lower temperature and grass biochars release greater amounts of nutrients, but they also release a much greater proportion of the C, N and P initially present in them. Thus, the nutrients in these chars are likely present in a more solublizable form. Not incidentally, these char types also show the greatest C mineralization rates (Zimmerman, 2010).

The factors that control biochar nutrient loss rates may be related to either the chemical form in which the nutrient occurs or the physical association or location of the nutrient within the biochar. To distinguish between these, linear correlation coefficients (R^2) were calculated for the relationships between various chemical and physical and nutrient release parameters of the biochars (Table 3, using the full set of 18 biochars). Amounts of both DOC and N extracted from biochar were most strongly correlated with the chemical properties of acid functional group density (AFG) and volatile

matter (VM) content. These biochar parameters have been previously found to be inter-correlated and inversely related to micropore surface area (Mukherjee et al., 2011), indicating that the material that fills biochar's pores carries its acidity and also, apparently, contains the portion of biochar C and N most susceptible to leaching. This makes intuitive sense in that it is likely that the material richest in AFG is most hydrophilic. Relatedly, VM was found to be the biochar parameter most strongly correlated to its C mineralization rate (Zimmerman, 2010) and to the stimulation of microbial growth and N immobilization (Deenik et al., 2010). The VM of the aged biochars was not significantly different from the fresh biochars (Mukherjee, 2011), which accounts for the similarity of organic C and N release rates from fresh and aged biochars. However, given that biochar is hypothesized be a very chemically and physically heterogeneous material (Kasozi et al., 2010; Masiello, 2004; Zimmerman, 2010), no single measureable parameter is likely to perfectly represent the nutrient release behavior of a sample. Different leachable components containing different nutrients are likely released at different rates, as evidenced by the increasing time required for desorption equilibrium observed here with increasing extractant volume.

In contrast to DOC and N, extractable P was significantly related to the ash (i.e. mineral) content of biochar. This relationship was stronger for Mehlich extraction versus water whereas water-extractable P was most strongly related to AFG content. This suggests that, a portion of the P (presumably ortho-P, ~50% on average) was only released by enhancing the solubility of mineral-incorporated P such as in iron, aluminum or calcium phosphates with weak acid. Carbonate mineral crystals have been observed on biochar's surface (Inyang et al., 2011) and phosphate sorption from aqueous solution by biochar has been associated with the formation of nano-sized MgO crystals on its surface (Yao et al., 2011). We thus propose that organic P is primarily found, with DOC and N, in the volatile acid-rich portion of biochar, while inorganic P is mineral-bound or incorporated. These results are supported by the work of others that have found biochar P to be mainly found in the ash fraction, with pH-dependent reactions controlling its solubilization (DeLuca et al., 2009). A better understanding of the controlling nutrient release mechanisms could be developed through the measurement of these parameters, along with all species of solubilized DOC, N and P, on a greater number of biochars.

4.2. Soil/biochar interaction with nutrient leachates

Although biochar released DOC, N and P, biochar leachates might be readily sorbed by soil. Conversely, biochar might sorb nutrient forms released from soils, resulting in the sometimes observed net reductions
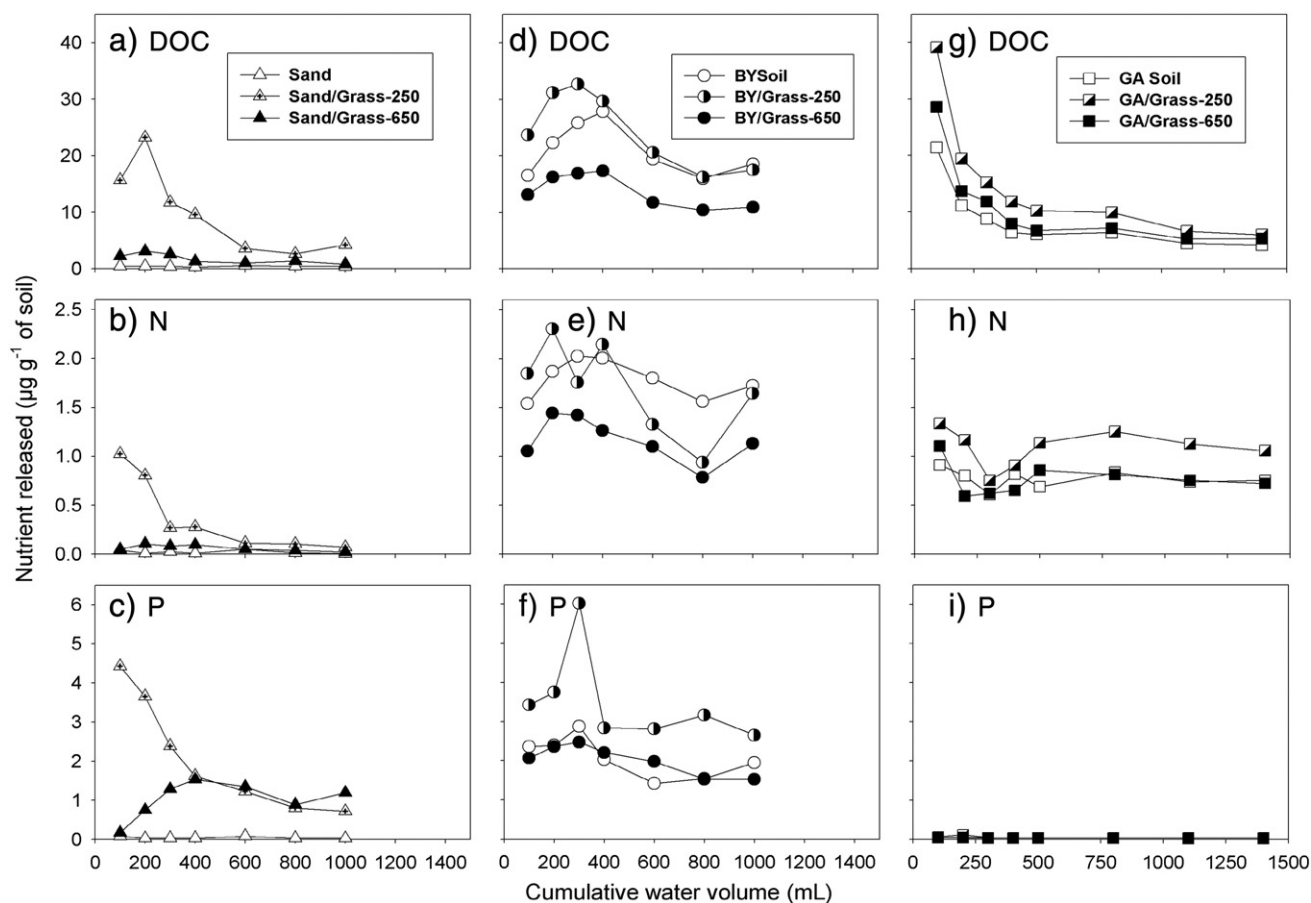
Fig. 2. Dissolved organic carbon (DOC), total Kjeldahl nitrogen (N) and total P concentrations in leachates of successive aqueous column flushes of biochar/sand (a, b, c, respectively) and biochar/BY soil (d, e, f, respectively) biochar/GA soil (g, h, i, respectively) column flushes versus cumulative water volume. Analytical error of each data point would be smaller than size of symbol.

in nutrient leaching following biochar amendment. The cumulative amounts of DOC, N and P leached from soil/biochar columns in this study, 81–172, 5–12, and 0.2–25 mg kg^{-1}, respectively, were generally greater than those from unamended soils (Alva, 2006; Qiang et al., 2004; Yang et al., 2008), as well as the BY and GA soils studied here. So it is likely that biochar leachate nutrients are not completely sorbed by the soils to which they are amended.

To estimate the degree to which released nutrients may have been sorbed, we compare the cumulative mass of nutrients estimated to have been leached from the soil and biochar in each column, separately (i.e. the additive amount assuming no soil–biochar interaction), with that measured to have been leached from columns containing corresponding soil/biochar mixtures (with soil–biochar interaction). Greater than predicted cumulative release of nutrients (Fig. 3, wider open bars) than that actually measured (thinner striped bars), indicate 'lost' leachate nutrients due to soil–biochar interaction. All combinations of soil and biochar showed 'lost' DOC, N and P except in the cases of DOC and N from the GA/biochar columns. The greatest losses of DOC and N were in BY soil columns (20–40%). Losses of P ranged 16–35% in BY soil/biochar columns and were about 97% in GA soil/biochar columns. Mixtures of BY soil with higher temperature biochars lost DOC, N and P to greater degrees than those with lower temperature biochars.

Explanations for the generally lower leachate nutrients due to soil–biochar interaction, include 1) soil microbial consumption/transformation of nutrients which may have been stimulated by the presence of biochar, 2) sorption of leached soil nutrients released by biochar, and 3) sorption of leached biochar nutrients by soil. The first mechanism, while possible to some degree, does not likely

predominate because of the short column flushing period, 3–4 days, whereas microbial activity response to biochar addition is typically on the order of weeks to months (Bruun et al., 2008; Zimmerman et al., 2011). It is notable, however, that the spike in NO$_3^-$ in the final BY soil column leachates, which were even greater in BY/biochar columns, might be attributed to nitrification, oxidation of NH$_4^+$ or organic N in biochar leachates. There is evidence, however,

Table 2
Proportion of dissolved organic carbon (DOC), total Kjeldahl nitrogen (TKN) and total phosphorous (P) in bulk biochars cumulatively lost during batch and column leaching experiments and that predicted after 1 year of average annual precipitation (123 cm).

Biochar/experiment	% Nutrient lost		
	DOC	TKN	P
Batch experiment			
Oak-250	0.9	1.5	151
Oak-650	0.1	0.5	22
Grass-250	1.7	5.3	117
Grass-650	0.4	3.0	39
Column experiment			
Sand/Oak-250	0.5	8.2	64
Sand/Oak-650	0.1	1.1	5
Sand/Grass-250	1.4	2.6	119
Sand/Grass-650	0.2	0.8	23
Column (1 year prediction)			
Sand/Oak-250	1.6	12.4	292
Sand/Oak-650	0.3	6.8	35
Sand/Grass-250	3.7	5.4	330
Sand/Grass-650	0.8	2.9	128

Table 3
Linear correlation coefficients (R^2) for relationships between concentrations of various nutrients extracted after 1 day in water (W) or Mehlich-1 (M1) solution and biochar properties (n = 18, includes fresh and aged biochars). Underlined regression coefficients are significant at $p < 0.05$ level while those assigned with a superscripted asterisk are also significant at $p < 0.001$ level and a negative value indicates an indirect linear correlation.

Extraction type[a]	pH	Volatile matter	Ash content	N_2-SA[b]	CO_2-SA[b]	CEC[c]	Total acidity[d]	AFG density[d]
W-DOC	−0.05	0.29	0.13	−0.20	−0.42	0.00	0.25	0.64*
W-TKN	−0.03	0.15	0.19	−0.09	−0.25	0.05	0.07	0.44
W-P	0.03	0.03	0.30	−0.03	−0.14	0.08	0.24	0.56
M1-DOC	−0.07	0.27	0.06	0.10	−0.35	0.06	0.48	0.81*
M1-TKN	−0.02	0.19	0.27	0.10	−0.25	0.03	0.08	0.45
M1-P	0.38	0.03	0.83*	0.00	−0.01	0.00	0.00	0.08

[a] DOC = dissolved organic carbon, TKN = total Kjeldahl nitrogen, P = total phosphorus.
[b] N_2-SA and CO_2-SA = mesopore and micropore surface area determined by N_2 and CO_2 adsorption, respectively.
[c] CEC = cation exchange capacity.
[d] Total acidity = sum of acid functional groups (AFG) measured by Bohem titration, AFG density = AFG content normalized to micropore surface area.

for the occurrence of nutrient sorption, interaction mechanisms #2 and #3. First, the nutrient release curves, at least for BY soil, bear some similarity to typical breakthrough curves, providing evidence for the interaction of leached nutrients with soil. Second, in some cases, more DOC, N or P was 'lost' than was released by biochar, indicating at least some soil nutrient sorption by biochar. In the case of GA/biochar columns, much more P was missing than was released by soil-alone, indicating biochar P sorption by the soil. Third, patterns of nutrient loss indicate both nutrient sorption by both soil and by biochar. For example, soil columns with high temperature biochar usually displayed greatest nutrient sorption, as would be expected given their greater surface area and OM sorption capacity (Kasozi et al., 2010). Also, nearly all P released from GA soil columns was in organic form, suggesting that all PO_4^{3-}-P had been sorbed. This would be expected given that the GA soil had about three times the amorphous iron and alumina content of BY soil and a pH range suitable to 'fix' most of the available organo-P (Supplemental Table S1), driven either by solid-solution equilibrium or ligand exchange. The higher pH and lower in amorphous Fe and Al of the BY soil is likely responsible for its greater loss of biochar-derived P. Notably, the oxyhydroxide and clay minerals of GA soil did not cause enhanced N sorption, as hypothesized by Singh et al. (2010b), perhaps because much of the N was in organic form. As a whole, these data suggests the previously unacknowledged importance of biochar as a source of organic nutrients and the sorption of soil OM by biochar in producing the chemical and biological changed observed in biochar–amended soils. These complexities explain the contradictory results found in past studies of the effect of biochar addition on soil nutrient bioavailability and uptake.

4.3. Long term biochar nutrient leaching trends

Longer term nutrient release rates were calculated using the last four data points collected in the column experiments. This was justified since linear correlation coefficients (R^2) of cumulative leachate nutrient versus cumulative leachate volume were always greater than 0.98. In addition, 1-year field-aged biochars released nutrients at rates not very different from fresh biochars (Supplemental Table S5). Cumulative nutrients predicted to be leached from soil/biochar columns after water additions equivalent to 1 year of average rainfall in Gainesville, Florida (122.8 cm) are given in Supplemental Table S6 and Fig. S1 and as a percentage of bulk biochar composition in Table 2.

On a weight basis, in 1 year, biochar will release 3 to 20 times the N and 6 to 4000 times the amount of P than the soils examined. These losses represent as much as 3.7 and 12.4% of the organic C and total N originally present in the biochar, respectively. But all these nutrients do not become bioavailable as significant portions of these nutrients will be sorbed by the soil (and soil nutrients sorbed by the biochar).
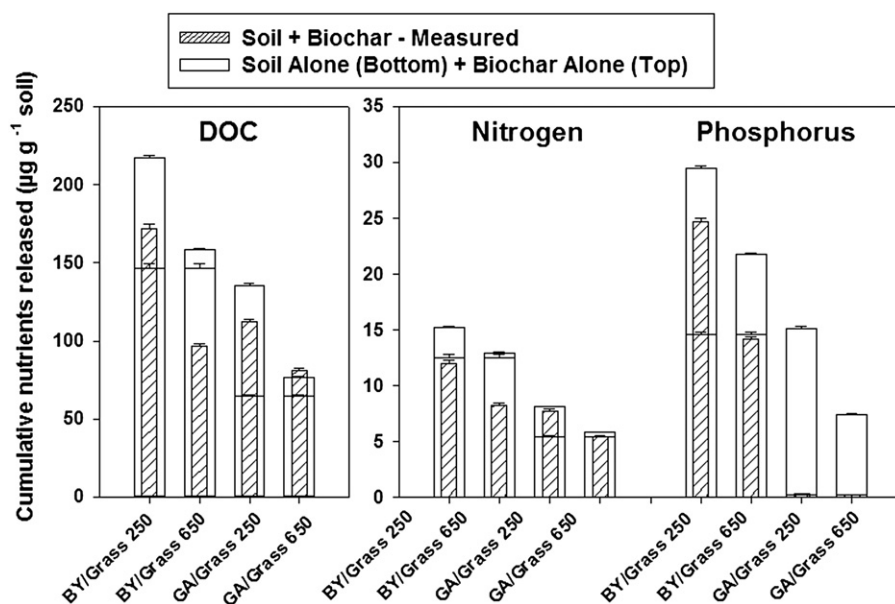

Fig. 3. Cumulative nutrients released after 10 flushes (1000 mL) from BY and GA soil/biochar columns (Note the different y-axis scales). Error bars depict cumulative analytical error from measurement of multiple leachate nutrient concentrations.
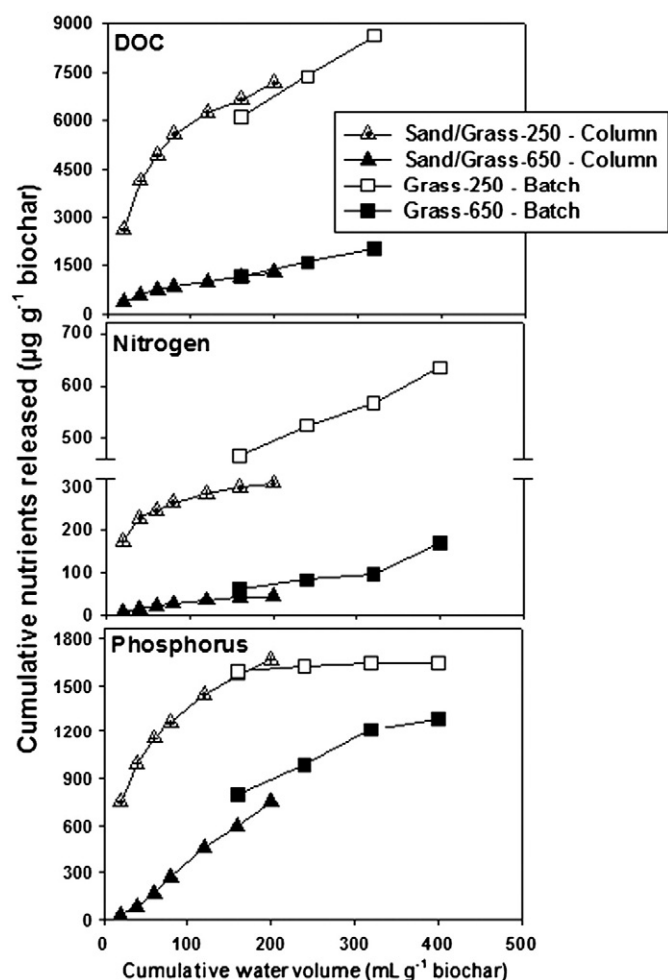
Fig. 4. Cumulative nutrients released from successive grass biochar batch extraction and column leaching experiments versus cumulative water volume added.

The trends in one-year predicted nutrient release from soil/biochar columns (Supplemental Fig. S1) were similar to those measured during the experimental period. These results do not account, however, for possible changes in microbial activity or oxidation on biochar's surface (Liang et al., 2006; Singh et al., 2010a) which may occur with aging.

4.4. Comparison of nutrient release measurement methods

The amount of each nutrient predicted to be lost from biochar in 1 year was compared to the amount extracted by other techniques (Supplemental Table S7). In the case of DOC, significant inter-correlations between all of the extraction techniques and long-term predicted C loss indicate that even the simplest technique, such as a single water extraction, would suffice to compare one biochar against another. None of the techniques, however, performed well at predicting long-term N or P losses from biochar.

The greater P released by Mehlich-1 extractant compared to water (Supplemental Table S4) may indicate that a portion of the available P in biochar is present in a Ca-phosphate mineral (de Alcantara et al., 2008), which agrees with the finding of a strong relationship between extractable P and ash content. The lack of increased DOC or N extracted by Mehlich-1 solution indicates that these nutrients are not present in biochar as surface exchangeable species.

Cumulative nutrients released from grass biochar in batch and column experiments are compared in Fig. 4 and from oak biochar in Supplemental Fig. S2, after normalization to both water volume and

biochar weight. The near coherence of the batch and column curves shows that the amount of nutrient released from each biochar was little affected by contact time or energy of mixing, varying instead with the solvent/solute ratio. This indicates no kinetic inhibition of nutrient release and implicates solid-solution equilibrium-driven dissolution as the main biochar nutrient release mechanism. Some studies have found no difference between soil batch extraction and column leaching (for organic compounds, Comans, 2001; Kalbe et al., 2008) while others have for metals (Dalgren et al., 2011). In any case, column leaching is a lengthy procedure compared to batch extraction and successive batch extraction experiments apparently provides similar information to predict biochar nutrient leaching trends.

4.5. Environmental implications

This study shows that each biochar alters soil nutrient and OM dynamics differently and varyingly over time. Appropriate biochar should be chosen carefully for each given amendment project. As sandy soils are less able to retain nutrients, a higher temperature or aged biochars is recommended as they have a lower tendency to release sudden pulses of nutrients. This is of less concern in acidic or oxide-rich soils which have considerable nutrient retention capacity, particularly for the organic nutrient forms released by biochar. Processes relating to nutrient dynamics in biochar–amended soils not addressed in this study include alteration to fungal or microbial community composition or activity that may occur with biochar addition (Zimmerman, 2010; Zimmerman et al., 2011). It is also known that biochar increases water retention and aeration of soils (Chan et al., 2007). These were not accounted for in these experiments which were carried out under water-saturated conditions. Further experiments should focus on measuring long-term rates of nutrient leaching from biochar–amended soils, taking care to test a spectrum of biochar and soil types and all species of nutrients including organic and inorganic forms.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.geoderma.2012.10.002.

References

Alva, A.K., 2006. Sustainable nutrient management in sandy soils — fate and transport of nutrients from animal manure versus inorganic sources. Journal of Sustainable Agriculture 28, 139–155.

Bell, M.J., Worrall, F., 2011. Charcoal addition to soils in NE England: a carbon sink with environmental co-benefits? Science of the Total Environment 409, 1704–1714.

Bruun, S., Jensen, E.S., Jensen, L.S., 2008. Microbial mineralization and assimilation of black carbon: dependency on degree of thermal alteration. Organic Geochemistry 39, 839–845.

Bruun, E.W., Ambus, P., Egsgaard, H., Hauggaard-Nielsen, H., 2012. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. Soil Biology and Biochemistry 46, 73–79.

Chan, Y.K., Xu, Z., 2009. Biochar: nutrient properties and their enhancement. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, pp. 67–84.

Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A., Joseph, S., 2007. Agronomic values of greenwaste biochar as a soil amendment. Australian Journal of Soil Research 45, 629–634.

Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A., Joseph, S., 2008. Using poultry litter biochars as soil amendments. Australian Journal of Soil Research 46, 437–444.
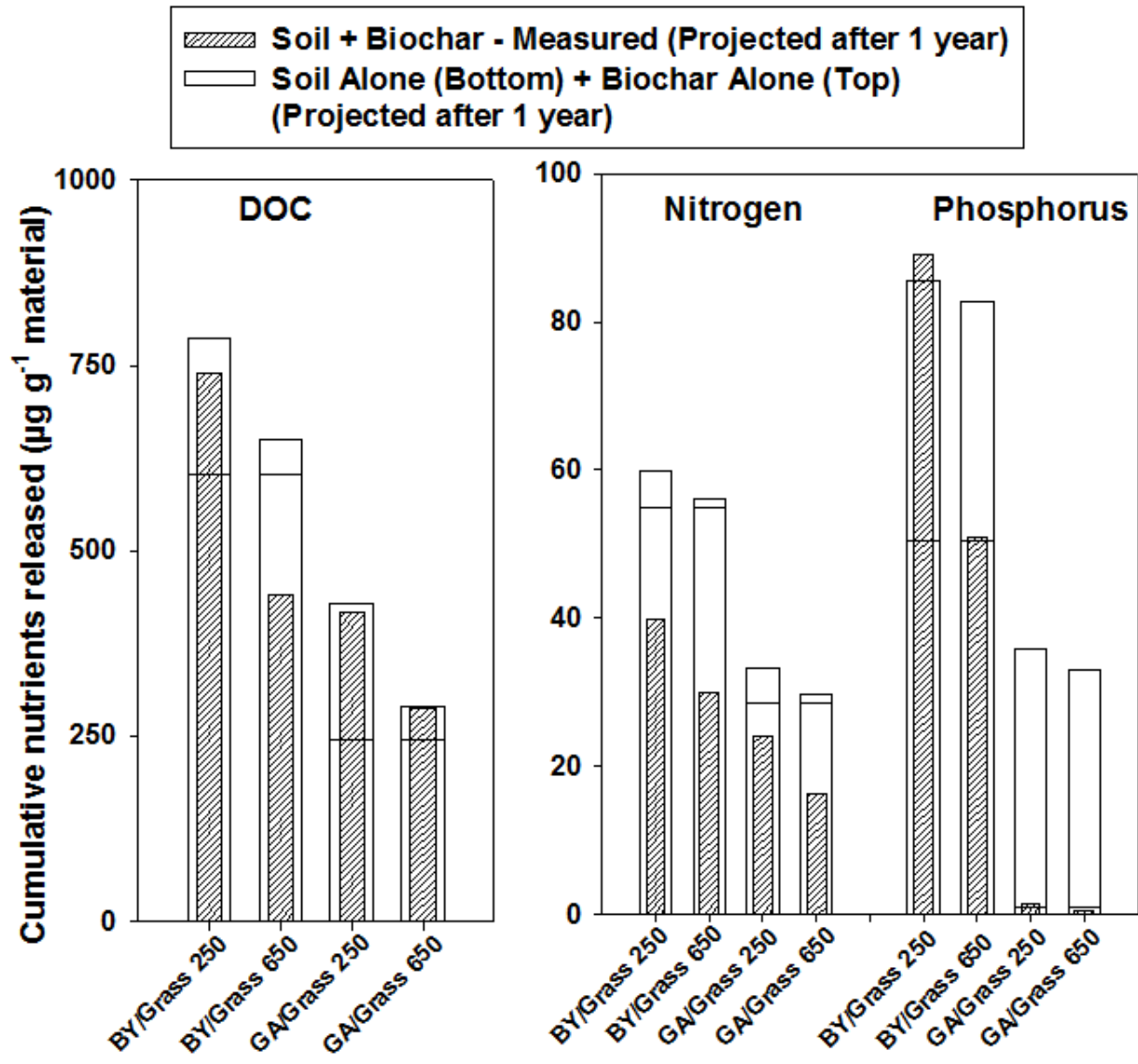
Cheng, C.H., Lehmann, J., Engelhard, M.H., 2008. Natural oxidation of black carbon in soils: changes in molecular form and surface charge along a climosequence. Geochimica et Cosmochimica Acta 72, 1598–1610.

Comans, R.N.J., 2001. Development of standard leaching tests for organic pollutants in soil, sediments and granular waste materials. ECN-C-01-121 ECN Clean Fossil Fuels, Emission Characterization and Reduction.

Dalgren, K.E., Duker, A., Arwidsson, Z., von Kronhelm, T., van Hees, P.A.W., 2011. Re-cycling of remediated soil — evaluation of leaching tests as tools for characterization. Waste Management 31, 215–224.

de Alcantara, F.A., Neto, A.E.F., Curi, N., Resende, A.V., 2008. Extraction methods for phosphorus and their relationship with soils phosphorus-buffer capacity estimated by the remaining-phosphorus methodology — a pot study with maize. Communications in Soil Science and Plant Analysis 39, 603–615.

de la Rosa, J.M., Knicker, H., 2011. Bioavailability of N released from N-rich pyrogenic organic matter: an incubation study. Soil Biology and Biochemistry 43, 2368–2373.

Deenik, J.L., McClellan, T., Uehara, G., Antal, M.J., Campbell, S., 2010. Charcoal volatile matter content influences plant growth and soil nitrogen transformations. Soil Science Society of America Journal 74, 1259–1270.

DeLuca, T.H., MacKenzie, D., Gundale, M., 2009. Biochar effects on soil nutrient transformations. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, London, pp. 251–270.

Ding, Y., Liu, Y.X., Wu, W.X., Shi, D.Z., Yang, M., Zhong, Z.K., 2010. Evaluation of biochar effects on nitrogen retention and leaching in multi-layered soil columns. Water, Air, and Soil Pollution 213, 47–55.

Downie, A., Van Zwieten, L., Chan, K.Y., Dougherty, W., Joseph, S., 2007. Nutrient retention characteristics of agrichar and the agronomic implications. Poster presented at the International Agrichar Initiative Conference, April, 2007, Terrigal, NSW, Australia.

Gaskin, J.W., Steiner, C., Harris, K., Das, K.C., Bibens, B., 2008. Effect of low-temperature pyrolysis conditions on biochar for agricultural use. Transactions of the ASABE 51, 2061–2069.

Gaskin, J.W., Speir, R.A., Harris, K., Das, K.C., Lee, R.D., Morris, L.A., Fisher, D.S., 2010. Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and yield. Agronomy Journal 102, 623–633.

Gundale, M.J., DeLuca, T.H., 2006. Temperature and source material influence ecological attributes of Ponderosa pine and Douglas-fir charcoal. Forest Ecology and Management 231, 86–93.

Hamdan, R., Zimmerman, A.R., Cooper, W.T., 2010. Effect of biomass type and pyrolysis conditions on the speciation of carbon and phosphorus in biochars as determined by solid-state C-13- and liquid-state P-31-NMR spectroscopy. Geochimica et Cosmochimica Acta 74, A373–A.

Hammes, K., Schmidt, M., 2009. Changes in biochar in soil. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management. Earthscan, pp. 169–182.

Harvey, O.R., Kuo, L.J., Zimmerman, A.R., Louchouarn, P., Amonette, J.E., Herbert, B.E., 2012. An index-based approach to assessing recalcitrance and soil carbon sequestration potential of engineered black carbons (biochars). Environmental Science & Technology 46, 1415–1421.

Hossain, M.K., Strezov, V., Chan, K.Y., Ziolkowski, A., Nelson, P.F., 2011. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. Journal of Environmental Management 92, 223–228.

Inyang, M.D., Gao, B., Ding, W.C., Pullammanappallil, P., Zimmerman, A.R., Cao, X.D., 2011. Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse. Separation Science and Technology 46, 1950–1956.

Joseph, S.D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C.H., Hook, J., van Zwieten, L., Kimber, S., Cowie, A., Singh, B.P., Lehmann, J., Foidl, N., Smernik, R.J., Amonette, J.E., 2010. An investigation into the reactions of biochar in soil. Australian Journal of Soil Research 48, 501–515.

Kalbe, U., Berger, W., Eckardt, J., Simon, F.G., 2008. Evaluation of leaching and extraction procedures for soil and waste. Waste Management 28, 1027–1038.

Kameyama, K., Miyamoto, T., Shiono, T., Shinogi, Y., 2012. Influence of sugarcane bagasse-derived biochar application on nitrate leaching in calcaric dark red soil. Journal of Environmental Quality 41 (4), 1131–1137.

Kasozi, G.N., Zimmerman, A.R., Nkedi-Kizza, P., Gao, B., 2010. Catechol and humic acid sorption onto a range of laboratory-produced black carbons (biochars). Environmental Science & Technology 44, 6189–6195.

Knicker, H., 2010. "Black nitrogen" — an important fraction in determining the recalcitrance of charcoal. Organic Geochemistry 41, 947–950.

Laird, D., Fleming, P., Wang, B.Q., Horton, R., Karlen, D., 2010. Biochar impact on nutrient leaching from a Midwestern agricultural soil. Geoderma 158, 436–442.

Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D., 2011. Biochar effects on soil biota: a review. Soil Biology and Biochemistry 43, 1812–1836.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizao, F.J., Petersen, J., Neves, E.G., 2006. Black carbon increases cation exchange capacity in soils. Soil Science Society of America Journal 70, 1719–1730.

Major, J., Steiner, C., Downie, A., Lehmann, J., 2009. Biochar effects on nutrient leaching. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, pp. 271–288.

Major, J., Lehmann, J., Rondon, M., Goodale, C., 2010. Fate of soil-applied black carbon: downward migration, leaching and soil respiration. Global Change Biology 16, 1366–1379.

Masiello, C.A., 2004. New directions in black carbon organic geochemistry. Marine Chemistry 92, 201–213.

McKeague, J.A., Day, D.H., 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Canadian Journal of Soil Science 46, 13–22.

MS, 2003. Microsoft Excel. Microsoft Office XP Professional.

Mukherjee, A., 2011. Physical and chemical properties of a range of laboratory-produced biochars. PhD Dissertation, University of Florida.

Mukherjee, A., Zimmerman, A.R., Harris, W.G., 2011. Surface chemistry variations among a series of laboratory-produced biochars. Geoderma 163, 247–255.

Novak, J.M., Busscher, W.J., Laird, D.L., Ahmedna, M., Watts, D.W., Niandou, M.A.S., 2009. Impact of biochar amendment on fertility of a southeastern coastal plain soil. Soil Science 174, 105–112.

Podgorski, D.C., Hamdan, R., McKenna, A.M., Nyadong, L., Rodgers, R.P., Marshall, A.G., Cooper, W.T., 2012. Characterization of pyrogenic black carbon by desorption atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry. Analytical Chemistry 84, 1281–1287.

Qiang, Z., Speir, T.W., van Schaik, A.P., 2004. Leaching of nutrients from soil cores treated with a single large dose of digested sewage sludge. Biology and Fertility of Soils 40, 284–289.

Silber, A., Levkovitch, I., Graber, E.R., 2010. pH-dependent mineral release and surface properties of cornstraw biochar: agronomic implications. Environmental Science & Technology 44, 9318–9323.

Singh, B., Singh, B.P., Cowie, A., 2010a. Characterisation and evaluation of biochars for their application as a soil amendment. Australian Journal of Soil Research 48, 516–525.

Singh, B.P., Hatton, B.J., Singh, B., 2010b. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. Journal of Environmental Quality 39, 1224–1235.

Taghizadeh-Toosi, A., Clough, T.J., Sherlock, R.R., Condron, L.M., 2012. Biochar adsorbed ammonia is bioavailable. Plant and Soil http://dx.doi.org/10.1007/s11104-011-0870-3.

Wu, H.W., Yip, K., Kong, Z.Y., Li, C.Z., Liu, D.W., Yu, Y., Gao, X.P., 2011. Removal and recycling of inherent inorganic nutrient species in mallee biomass and derived biochars by water leaching. Industrial and Engineering Chemistry Research 50, 12143–12151.

Yang, Y.G., He, Z.L., Stoffella, P.J., Yang, X.E., Graetz, D.A., Morris, D., 2008. Leaching behavior of phosphorus in sandy soils amended with organic material. Soil Science 173, 257–266.

Yao, F.X., Camps, A.M., Virgel, S., Blanco, F., Arostegui, J., Maciá-Agulló, J.A., Macías, F., 2010. Simulated geochemical weathering of a mineral ash-rich biochar in a modified Soxhlet reactor. Chemosphere 80, 724–732.

Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X.D., Pullammanappallil, P., Yang, L.Y., 2011. Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. Journal of Hazardous Materials 190, 501–507.

Zimmerman, A.R., 2010. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). Environmental Science & Technology 44, 1295–1301.

Zimmerman, A.R., Gao, B., Ahn, M.Y., 2011. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. Soil Biology and Biochemistry 43, 1169–1179.
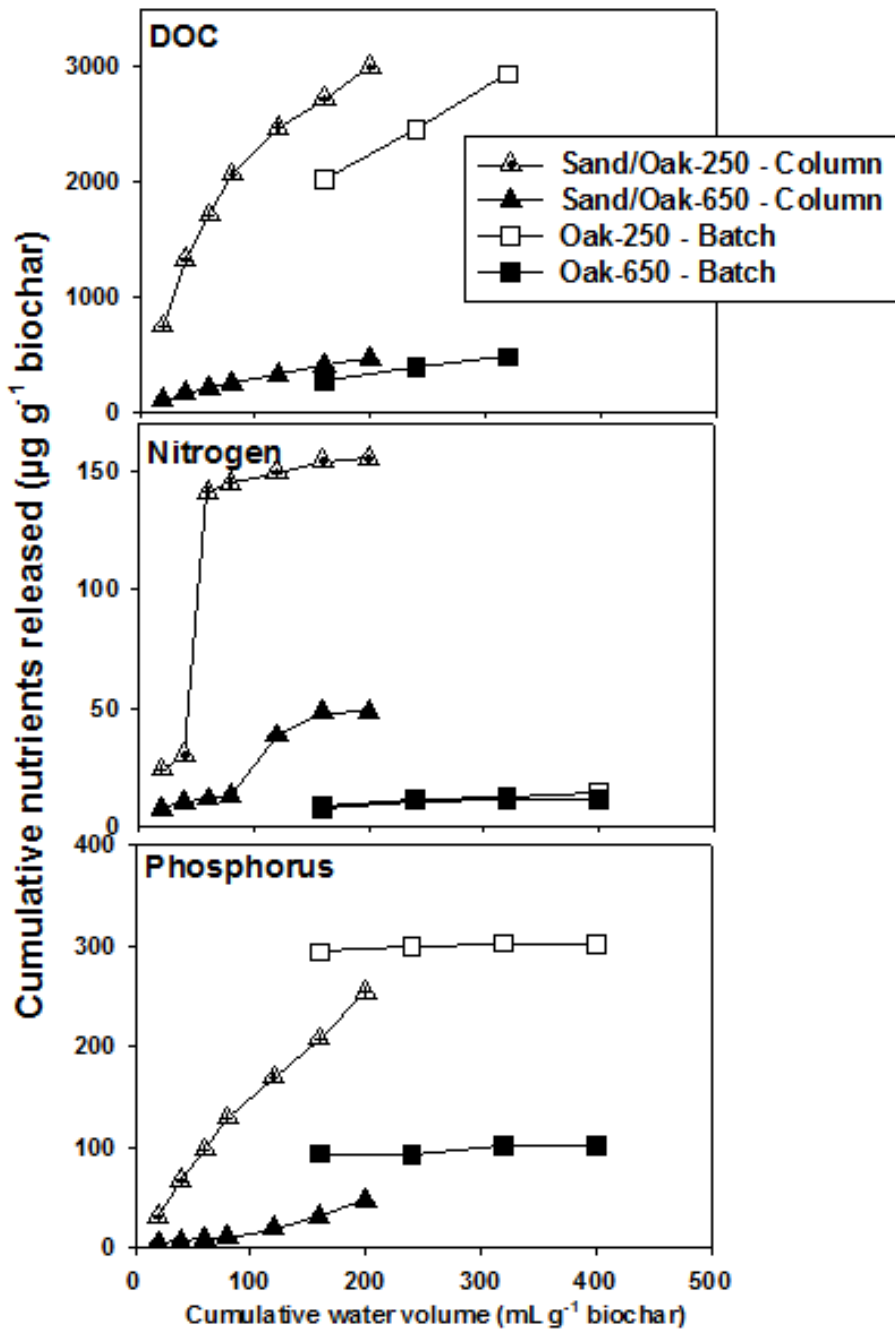
Mukherjee and Zimmerman, Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar-soil mixtures

Additional biochar characterization method information

Volatile matter, ash content, acid functional groups (AFG), and AFG density were determined following the similar procedure as described by Mukherjee et al. {, 2011 #445}. In short, Volatile matter (VM%) and ash content were determined using standard ASTM method for wood charcoal: D-1762-84 {ASTM, 1990 #436}. The VM% was determined as quick weight loss after combustion in a ceramic crucible with a loose ceramic cap at 850–900 °C in an oven for 6 min and ash content was determined as weight loss after combustion at 750 °C for 6 h with no ceramic cap. The AFG were determined using Boehm titration method {Boehm, 1964 #362;Goertzen, 2010 #427}. About 0.50 g of biochar sample was added to 50 mL of 0.05 M $NaHCO_3$, Na_2CO_3, and NaOH. The mixtures, along with a control solution without any biochar, were shaken for 24 h and then filtered to remove particles. Then, one mL of aliquot from each filtrate was mixed with 10 mL of excess 0.05 M acid (to ensure complete neutralization of bases) and back-titrated with 0.05 M NaOH solution. The endpoint was determined using phenolphthalein indicator. The total surface acidity was calculated as moles neutralized by NaOH, the carboxylic acid fraction as the moles neutralized by $NaHCO_3$, and the lactonic group fraction as those neutralized by Na_2CO_3. The difference between molar NaOH and Na_2CO_3 was assumed to be the phenolic functional group content following Rutherford et al. {, 2008 #360}. The AFG density was calculated as total acidity divided by surface area obtained from CO_2 sorptometry.

Supplemental Figure S1. Projected cumulative nutrients released after one year of average North Florida rainfall (122.8 cm) based on column leaching rate data (Note the different y-axis scales)

Supplemental Figure S2. Cumulative nutrients released from successive oak biochar batch extraction and column leaching experiments versus cumulative water volume added

Supplemental Table S1. Selected characteristics of biochars and soils used in the study

Biochar or soil	Bulk composition (mg g^{-1})					pH	SA (m^{2}g^{-1})		VM	AC
	C[c]	N[c]	P[d]	Fe[d]	Al		N$_2$	CO$_2$	(%)	
Fresh Oak-250	626 ± 32	1.9 ± 0.3	0.4	0.2	na	3.5	331 ± 66	1.0 ± 1.0	66.0 ± 4.4	1.4 ± 0.1
Fresh Oak-650	754 ± 14	4.6 ± 0.4	0.9	0.0	na	9.1	528 ± 57	225 ± 9.0	36.4 ± 1.1	3.7 ± 0.2
Fresh Grass-250	494 ± 31	12 ± 2	1.4	0.1	na	4.5	221 ± 106	3.0 ± 2.0	62.5 ± 2.9	6.8 ± 0.2
Fresh Grass-650	557 ± 5	5.7 ± 0.4	3.3	0.2	na	10.0	427 ± 115	77 ± 27	33.0 ± 1.2	15.9 ± 0.5
Aged Oak-250	594 ± 22	2.5 ± 0.3	0.1	0.0	na	4.0	208 ± 17	0.6 ± 0.0	66.1 ± 0.9	2.0 ± 0.3
Aged Oak-650	813 ± 2	2.8 ± 1.2	0.8	0.0	na	6.7	556 ± 10	35 ± 19	29.4 ± 4.3	2.9 ± 0.8
Aged Grass-250	575 ± 20	9.8 ± 1.2	0.2	0.2	na	4.2	238 ± 17	4.6 ± 2.2	65.2 ± 1.4	7.7 ± 0.1
Aged Grass-650	704 ± 24	15 ± 1.8	1.9	0.5	na	7.0	517 ± 9	39 ± 8	41.5 ± 3.1	10.0 ± 0.3
BY soil[a]	28 ± 2	2.0 ± 0.1	1.1	0.6[e]	0.8[e]	5.8	0.5 ± 0	9 ± 1	0.5 ± 0	9 ± 1
GA soil[b]	29 ± 2	1.1 ± 0.0	0.2	1.6[e]	2.2[e]	4.2	18 ± 0	32 ± 3	18 ± 0	32 ± 3

Notes:

Abbreviations: C = total carbon, N = total nitrogen, P = total phosphorus, SA = surface area, VM = volatile matter, AC = ash content

a: BY soil = Gainesville, Florida, U.S.A., Entisol

b: GA soil = Big Canoe, Georgia, U.S.A., Ultisol (red clayey soil)

c: Obtained via CNH Elemental analyzer

d: Digested acid extraction procedure (AOAC 985.01)

e: Amorphous iron (Fe) and aluminium (Al) via oxalate extraction

na: Not analyzed

Supplemental Table S2. Soil sample background information

Soil	latitude	longitude	Soil Series	%sand	%silt	%clay
BY soil[a]	34.4836	-84.3227	Edneyville loam	63	27	10
GA soil[b]	29.6015	-82.3624	Blichton sand	97	3	0

Supplemental Table S3. Proportion of organic nitrogen (N) and organic phosphorous (P) in initial and final leachates of soil and soil/biochar columns

Batch or column test material	% Organic N		% Organic P	
	Initial	Final	Initial	Final
Oak-250-(Batch[a])	0	0	41	0
Oak-650-(Batch[a])	2	0	54	0
Grass-250-(Batch[a])	58	81	39	0
Grass-650-(Batch[a])	61	74	83	0
Sand/Oak-250[b]	0	0	85	34
Sand/Oak-650[b]	0	0	93	0
Sand/Grass-250[b]	59	13	41	67
Sand/Grass-650[b]	0	0	49	10
BY soil[b]	74	13	23	7
BY/Grass-250[b]	89	4	27	11
BY/Grass-650[b]	65	4	44	11
GA soil[b]	53	23	85	83
GA/Grass-250[b]	92	30	96	73
GA/Grass-650[b]	89	27	93	64

Notes:

a: Batch extraction experiments, sampled after 40 mL (initial) and 200 mL (final) cumulative leach volume

b: Column leaching experiments, sampled after 100 mL (initial) and 1000 mL (final) cumulative leach volume

Supplemental Table S4. One-day water and Mehlich 1 extractable dissolved organic carbon (DOC), total Kjeldahl Nitrogen (TKN) and total phosphorous (P) from fresh and aged biochars and soils

Material	Water Extractable			Mehlich 1 Extractable		
	DOC	TKN	P	DOC	TKN	P
	$(\mu g\ g^{-1})$			$(\mu g\ g^{-1})$		
Fresh Oak-250	3065	0	569	3517	72	530
Fresh Oak-400	1522	15	285	2234	30	321
Fresh Oak-650	355	0	159	147	32	493
Fresh Pine-250	3410	28	76	2556 ± 2	47	52
Fresh Pine-400	819	14	25	668	26	80
Fresh Pine-650	259	14	11	190	15	11
Fresh Grass-250	4429	302	1536	5800	245	1270
Fresh Grass-400	3275	174	1362	4638	186	2563
Fresh Grass-650	755 ± 2	21	578	424	40	2439
Aged Oak-250	1272	102	24	874	53	49
Aged Oak-400	1127	31	54	841	28	253
Aged Oak-650	338	0	29	213	41	319
Aged Pine-250	1267	26	4	801	59	10
Aged Pine-400	783 ± 3	33	8	515	25	22
Aged Pine-650	264	17	0	186	27	5
Aged Grass-250	2692	162	42	1901	174	51
Aged Grass-400	1892	99	223	1395	138	1065
Aged Grass-650	843	63	111	366	73	1197
BY soil	438	125	24	847	192	602
GA soil	187 ± 2	15	0	1493	48	3

Supplemental Table S5. Dissolved organic carbon (DOC), total Kjeldahl Nitrogen (TKN) and total phosphorous (P) cumulative losses by fresh and 1-y field-aged biochar during five successive aqueous batch extractions (0.5 g biochar in 40 ml distilled water).

Material	Nutrient leached (μg g^{-1} biochar)		
	DOC	TKN	P
Fresh Biochar			
Oak-250	5886	29	604
Oak-650	964	23	201
Grass-250	8622	635	1640
Grass-650	2010	168	1291
Aged Biochar			
Oak-250	3224	187	36
Oak-650	1163	57	75
Grass-250	7399	487	89
Grass-650	3056	184	233

Supplemental Table S6. Predicted cumulative losses of dissolved organic carbon (DOC), total Kjeldahl Nitrogen (TKN) and total phosphorous (P) after column leaching of 5.4 L, equivalent to 1 year of average annual north FL precipitation (123 cm)

Biochar/Experiment	Nutrient leached ($\mu g\ g^{-1}$ soil or biochar)		
	DOC	TKN	P
Oak-250	9795	235	1170
Oak-650	2075	311	312
Grass-250	18502	644	4618
Grass-650	4647	167	4211
GA	245	29	1.1
GA/Grass-250	417	45	1.2
GA/Grass-650	288	30	1.1
BY	604	55	55
BY/Grass-250	740	51	112
BY/Grass-650	441	38	66

Supplemental Table S7. Linear correlation coefficients (R^2) for relationships between amounts of nutrients extracted by various methods from fresh and aged biochars. Underlined regression coefficients are significant at $p < 0.05$ level while those with asterisk are also significant at $p < 0.001$ level

		W1[a]	M1[a]	B_{cum}[b]	CL_{cum}[b]
DOC[d]	M1	*0.75			
	B_{cum}	*0.93	0.78		
	CL_{cum}	0.90	0.93	0.92	
	CL_{1-y}[c]	0.95	0.96	0.96	0.99
TKN[d]	M1	*0.87			
	B_{cum}	*0.93	*0.90		
	CL_{cum}	0.80	0.93	0.70	
	CL_{1-y}	0.89	0.88	0.77	0.76
Total P[d]	M1	*0.55			
	B_{cum}	*0.86	0.58		
	CL_{cum}	0.92	0.20	0.89	
	CL_{1-y}	0.60	0.64	0.97	0.79

Notes:
a: Nutrients released after a single 24 h water (W1) or Mehlich 1 (M1) extraction (n = 18)
b: Cumulative nutrients released after 5 successive (20 d) batch water extractions (B_{cum}, n = 8) or 1000 mL total water flushed through columns (CL_{cum}, n = 4)
c: Cumulative nutrient release predicted after a volume of column leaching equivalent to 1 y of north Florida precipitation, 5.4 L (CL_{1-y}, n = 4)
d: dissolved organic carbon (DOC), Total Kjeldahl Nitrogen (TKN) and total phosphorous (P)