Biochar impact on nutrient leaching from a Midwestern agricultural soil

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ABSTRACT

Application of biochar to highly weathered tropical soils has been shown to enhance soil quality and decrease leaching of nutrients. Little, however, is known about the effects of biochar applications on temperate region soils. Our objective was to quantify the impact of biochar on leaching of plant nutrients following application of swine manure to a typical Midwestern agricultural soil. Repacked soil columns containing 0, 5, 10, and 20 g-biochar kg^{-1}-soil, with and without 5 g kg^{-1} of dried swine manure were leached weekly for 45 weeks. Measurements showed a significant decrease in the total amount of N, P, Mg, and Si that leached from the manure-amended columns as biochar rates increased, even though the biochar itself added substantial amounts of these nutrients to the columns. Among columns receiving manure, the 20 g kg^{-1} biochar treatments reduced total N and total dissolved P leaching by 11% and 69%, respectively. By-pass flow, indicated by spikes in nutrient leaching, occurred during the first leaching event after manure application for 3 of 6 columns receiving manure with no biochar, but was not observed for any of the biochar amended columns. These laboratory results indicate that addition of biochar to a typical Midwestern agricultural soil substantially reduced nutrient leaching, and suggest that soil–biochar additions could be an effective management option for reducing nutrient leaching in production agriculture.

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1. Introduction

Leaching of nutrients from agricultural soils depletes soil fertility, accelerates soil acidification, increases fertilizer costs for farmers, reduces crop yields, and adversely affects the quality of surface and ground water. Problems of nutrient leaching vary substantially with both rainfall intensity and soil properties. The problem is particularly acute for the highly weathered Oxisols of the Amazon basin because these soils are dominated by low activity clays that have little capacity to retain nutrients and both soil organic matter and organic residues decompose rapidly releasing organically bound nutrients in warm humid environments (Juo and Manu, 1996). Ancient Amerindian farmers solved this sustainability problem by incorporating large amounts of biochar (also known as charcoal, char, black carbon, and agrichar) along with manure, bones and other organic residues into the soils of the Amazon transforming the native Oxisols into Anthrosoils, known as Terra Preta (Glaser et al., 2001). Today, over 500 years after cessation of the practices that led to their creation, the Terra Preta soils are the prize agricultural and horticultural soils of the Amazon region.

The Terra Preta soils of the Amazon contain significantly more C, N, Ca, K and P and have higher cation-exchange capacities, pH values and base saturations than the surrounding soils (Zech et al., 1990; Glaser et al., 2000; Lima et al., 2002). However, the capacity to retain and apparently recycle these nutrients during prolonged periods of cultivation is the outstanding feature that distinguishes the Terra Preta soils from the surrounding Oxisols (Lehmann et al., 2003). The presence of biochar either as a legacy of ancient Amerindian practices or added during modern scientific investigations appears to play a critical role in increasing retention of nutrients and thereby reducing nutrient leaching (Lehmann et al., 2003; Steiner et al., 2007; Steiner et al., 2008a; Novak et al., 2009). The high surface charge density of biochar enables the retention of cations by cation exchange (Liang et al., 2006), and the high surface area, internal porosity, and the presence of both polar and non-polar surface sites enable biochar to adsorb organic molecules and associated nutrients. Biochar also appears to stimulate soil microbial activity (Steiner et al. 2008b) particularly mycorrhizal fungi (Ishii and Kadoya 1994), which are critically important for nutrient cycling (Lambers et al., 2008). The reason biochar stimulates microbial activity is not fully known although several hypotheses have been put forward (Warnock et al., 2007). Thus a combination of physical, chemical, and biological processes all appears to contribute to the reduced leaching of nutrients observed for the studied highly weathered soils amended with biochar.

Leaching of N and P from Midwestern agricultural soils, due to the inability of soils to fully retain these nutrients under annual cropping systems and to excessive manure and synthetic fertilizer use on vulnerable soils has been shown to contribute to the annual development of a large hypoxic zone in the Gulf of Mexico (Dagg and Breed,

2003; Nangia et al., 2008) and eutrophication of water in regional streams and lakes (Carpenter et al., 1998). Midwestern farmers have relatively few management options for reducing nutrient leaching in conventional corn (Zea mays L.) and soybean [Glycine max (L.) Merr.] cropping systems (Dinnes et al., 2002). One option is to amend soils with slow release forms of nutrients, such as sparingly soluble or coated fertilizer materials (Shaviv and Mikkelsen, 1993). Another is to use multiple fertilizer applications throughout the growing season, timed to supply nutrients during periods of maximum crop uptake. A third strategy is to use cover crops that maintain integrated root systems during the off season when soils under annual cropping systems are typically fallow and vulnerable to nutrient leaching (Logsdon et al., 2002). All of these options are temporary solutions to the problem of nutrient leaching and can increase production costs or reduce yield. Based on the limited evidence, primarily from research on highly weathered soils, application of biochar may provide a new management option with the potential to increase the long-term capacity of soils to retain and recycle nutrients.

In recent years, the production of renewable fuels from cellulosic biomass has attracted much attention in the Midwest. However, many farmers, scientists and conservationists are concerned about adverse impacts of sustained biomass harvesting on soil and environmental quality (Lal, 2004; Wilhelm et al., 2004; Lal and Pimentel, 2007). The harvesting of biomass removes substantial amounts of plant nutrients from soils and unless these nutrients are replaced by synthetic fertilizers, manure, or other soil amendments, soil productivity will decline. Even if the nutrients are replaced, the sustained removal of biomass without compensating organic amendments can cause a decline in soil organic matter and cation-exchange capacity, both of which further decrease the ability of soils to retain nutrients. Recently the pyrolysis platform has been proposed as a potentially sustainable means for processing cellulosic biomass to produce renewable energy products (Lehmann, 2007; Laird, 2008). Pyrolysis transforms biomass into bio-oil and syngas, which may be used as energy products, and a co-product (biochar) that could be used as a soil amendment. Application of biochar is hypothesized to increase soil organic C levels, return most of the nutrients harvested with the biomass to the soil, and increase the soil's capacity to retain and recycle nutrients. As noted above, most of the biochar research on nutrient leaching have been conducted on highly weathered tropical and subtropical soils. Our research is focused on determining whether using biochar as a soil amendment on Midwestern agricultural soils will enhance the sustainability of biomass harvesting by improving soil quality, sequestering carbon, and increasing nutrient retention and recycling. The specific objective for this study was to quantify the impact of soil–biochar amendments on nutrient leaching following a swine manure application for a typical Midwestern agricultural soil. A companion paper (Laird et al., 2010) reports the impact of these treatments on various indicators of soil quality for the same soil and biochar system.

2. Materials and methods

2.1. Soil and charcoal

Clarion (fine-loamy, mixed, superactive, mesic Typic Hapludolls) soil collected from a fallow strip between field plots on the Iowa State University Agronomy and Agricultural Engineering Research Farm in Boone County Iowa was used for this study. Surface soil (0 to 15 cm) was collected and stored at field moisture content in plastic buckets with tight closing lids until it could be used within one month of collection.

Lump charcoal >1 cm was obtained from a commercial producer who uses mixed hardwood [primarily oak (Quercus spp.) and hickory (Carya spp.)] and slow pyrolysis (traditional kilns) to produce charcoal primarily for the steel industry. The lump charcoal was ground in a hammer-mill and the <0.5 mm fraction was separated by dry sieving

(the <0.5 mm fraction is referred to as biochar hereafter). Basic properties of the biochar (moisture, volatiles, fixed carbon and ash content) were determined by proximate analysis (ASTM standard 1762-84(2007)). Total C and N in the biochar and freeze-dried swine manure were determined by dry combustion using a Carlo-Erba NA1500 NSC elemental analyzer (Haake Buchler Instruments, Paterson, NJ). The elemental composition of biochar and manure was determined by ashing the samples at 700 °C, digesting the ash in aqua regia and analyzing the elemental composition of the digest by inductively coupled plasma–atomic emission spectroscopy.

2.2. Preparation of soil columns

Batches of field moist soil (15 kg) were tumbled in a rotary cement mixer for 20 min. During the tumbling treatment a predetermined amount of biochar was slowly added to the soil to bring the final biochar content to 0, 5, 10, or 20 g kg^{-1} of oven dry soil. The tumbling treatments produced roughly spherical soil aggregates ~1 cm diameter, and based on visual observation, the added biochar was dominantly concentrated on the external surfaces of the aggregates. Soil treated with biochar was noticeably darker than the control soil.

Soil columns (7.7 cm i.d. by 25 cm length = 1164 cm^3 volume) were constructed of PVC tubing and fitted with PVC end caps on the bottoms. A hole was drilled through the end caps and drain tubes (3 mm i.d.) were attached to the bottom of each column. A small amount of fiberglass was inserted into the drain opening at the base of the columns and then 100 g of coarse sand (2–5 mm) was placed in the bottom of each column. The sand filled the concave portion of the end cap which protruded below the base of the PVC column. The soil columns were packed with 1 kg (oven dry weight equivalent) of soil by tamping the columns as the soil was added. All columns were packed to an initial bulk density of 1.1 g cm^{-3}.

2.3. Soil column incubation and leaching

The columns were incubated in a constant temperature room (25 °C and 80% relative humidity) for the duration of the study. On week 12 of the incubation 5 g of dried and ground swine manure was added to half of the columns. The manure was incorporated into the top 3 cm of the soil in the columns by "micro tillage" using a laboratory spatula. Control columns not receiving manure were also tilled in a similar manner. Once each week during the incubations, all columns were leached with 200 mL of 0.001 M CaCl$_2$. The leachate was introduced on the top of each column using a slow (~1 h) dripping technique with the aid of a syringe barrel and flow restricting needle mounted above the middle of each column. A 25 mm fiberglass filter paper was placed in the middle of each column to help diffuse water drops as they impacted on the upper surface of the columns.

Leachate from each column was collected in 250 mL polyethylene bottles for ~24 h after the start of a leaching event. The bottles had a cap with a small hole drilled through it that allowed the drain tube to be inserted into the bottle so that evaporative water loss was minimized. The amount of leachate collected weekly for each column was determined gravimetrically. Leachate samples (50 mL) were filtered (<0.45 μm nylon filter), acidified by adding 1 mL of HCl, and analyzed for NO$_3$–N using a Latchet autoanalyzer, and for Al, B, Cu, Fe, K, Mg, Mn, Na, P, Si, and Zn by inductively coupled plasma–atomic emission spectroscopy. Organic- and NH$_4$–N in the leachate were determined for samples from weeks 11, 12, and 13 using Kjeldahl digestion and steam distillation (Stevenson, 1996).

2.4. Statistical analysis

The overall experimental design included 4 biochar rates, 2 manure treatments, and 6 replications (48 columns). Leachate samples were collected from each column after leaching weekly for 45 consecutive

weeks. Mass balance analysis was used to estimate the percentage of a given element added with the manure and recovered in the leachate using:

$$R_{xi} = \frac{(X_{mci} - \overline{X}_c) * 100}{X_{mi}}$$

where R_{xi} is the percent recovery of element X for column i, X_{mci} is the mass of element X that leached from column i where m and c indicate the addition of manure and the biochar level respectively, $\overline{X}_c$ is the average mass of element X that leached from no-manure control columns for the c biochar level, and X_{mi} is the mass of element X in the manure that was added to column i. Statistical analysis was conducted using SAS 9.1 for Windows. Several statistical models were tested for describing the time-series data; however, in the end an ANOVA for total leaching during weeks 1–45 and percent recovery of elements added with the manure provided the most transparent resolution of treatment effects. Tukey's Studentized Range test was used to distinguish significant differences among treatment means.

3. Results and discussion

The hardwood biochar used in this study was 71.5% C and 0.72% N by mass, and proximate analysis indicated that the biochar contained 63.8% fixed C, 19.7% volatiles, 13.9% ash and 2.6% moisture by mass. The pH of the biochar was 7.6 when first placed in deionized water but increased to 8.2 after 7 days. Neutralization of the biochar–water slurry to pH 7.0 required a total of 1.7 mol of HCl kg-biochar^{-1} administered gradually over 39 days. The swine manure was 41.3% C and 3.51% N on a dry weight basis. The biochar amendments added substantial amounts of Ca and lesser amounts of other nutrients to the columns, whereas N and P were the dominant nutrients added with the manure (Table 1).

The weekly leaching events were designed to simulate a 1 h, 4.29 cm rainfall event. This resulted in an annual rainfall total of 223 cm or approximately 2 ½ times the amount of precipitation a Clarion soil normally receives. The columns were freely drained at all times and there was no evidence of water ponding on the surface. The average leachate volume increased from 84 (±9.0 SD) mL on week 1 to 168 (±8.0 SD) mL on week 9 and remained relatively constant thereafter. Except for week 12, the average leachate volume for weeks 9 through 45 was 166 (±8.4 SD) mL, suggesting that about 34 mL of water evaporated from each column every week. Between weeks 11 and 12, 5 g of freeze-dried swine manure was added to half of the columns, and soil in all columns was tilled to a depth of 3 cm. The tillage apparently increased evaporation and reduced the average leaching volume to 139 (±8.8 SD) mL for week 12. There was no apparent effect of either biochar or manure treatment on leaching volume.

The initial soil bulk density for all columns was 1.1 g cm^{-3}. Over time the soils in the columns consolidated due to the effects of gravity and the weekly leaching events. By the end of the study, bulk densities ranged from 1.17 to 1.42 g cm^{-3} and were significantly lower for columns receiving biochar relative to the no-biochar controls (Laird et al., 2010). Assuming an average particle density of 2.5 g cm^{-3}, the 200 mL of leachate added each week initially represented 0.39 pore volumes for the columns but increased with time as the soil consolidated to represent between 0.44 and 0.66 pore volumes by the end of the study. Any effects of pore volume and bulk density on the leaching of nutrients could not be distinguished from the biochar treatment effect.

The columns were leached with dilute CaCl$_2$ to help preserve the soil structure. Each week 8 mg or 0.2 mmol of Ca was added to each column with the leachate. Hence a total of 9 mmol of Ca was added to each column during the 45 weeks of the study. This is equivalent to 8.8% of the average cation-exchange capacity for the soil in the columns. The weekly addition of Ca undoubtedly accelerated leaching of other elements from the columns.

Leachate from the columns was clear or nearly so for all events except for those receiving manure but no biochar (C0M columns) on week 12; the first leaching event after the manure addition. The color

Table 1

Mass of elements added with the manure and biochar treatments to the soil columns. Total mass of elements leached during weeks 1–45 of the experiment. Percentage of elements added with the manure recovered in the leachate based on mass balance calculations. The percent recovery for each element was calculated by subtracting the average mass of each element recovered in the leachate for columns that did not receive manure from the mass recovery for columns that did receive manure, multiplying by 100, and then dividing by the mass of the element added with the manure to the column.

Mass of elements added to the columns with the manure and biochar (mg per column)											
Component	P	Cu	K	Mg	Mn	Na	Zn	B	Si	Ca	Total N[a]
5 g manure	102	1.93	46	30	1.66	20.8	5.97	nd[b]	14	93	195
5 g biochar	1.3	0.042	9	3.3	2.8	0.9	0.10	nd	13	166	36
10 g biochar	2.5	0.083	17	6.7	5.7	1.9	0.19	nd	25	332	72
20 g biochar	5.0	0.167	35	13.4	11.4	3.7	0.39	nd	50	663	144

Total mass of elements leached during weeks 1–45 (mg per column)											
Treatment	P	Cu	K	Mg	Mn	Na	Zn	B	Si	Ca	Total N
C0	4.7 E[c]	0.040 B	31 E	56 D	0.034 A	3.1 B	0.32 C	0.24 AB	68 C	364 E	70 D
C5	4.7 E	0.044 B	38 D	60 CD	0.035 A	3.8 B	0.36 C	0.25 AB	71 BC	406 D	71 CD
C10	4.7 E	0.051 AB	42 D	60 CD	0.030 A	5.0 B	0.36 BC	0.23 B	63 C	433 D	68 D
C20	5.1 DE	0.056 AB	54 CB	64 C	0.035 A	4.2 B	0.41 AB	0.29 AB	64 C	493 C	88 C
C0M	33.7 A	0.140 A	51 C	81 A	0.044 A	24.0 A	0.45 A	0.29 AB	84 A	492 C	186 A
C5M	19.9 B	0.057 AB	54 CB	78 AB	0.036 A	23.5 A	0.45 A	0.25 AB	79 AB	512 BC	175 AB
C10M	15.4 BC	0.062 AB	58 B	77 AB	0.044 A	24.1 A	0.44 A	0.28 AB	73 ABC	542 AB	167 B
C20M	10.3 CD	0.054 AB	68 A	76 B	0.035 A	22.2 A	0.44 A	0.33 A	67 C	562 A	165 B

Percentage of elements added with the manure recovered in the leachate (mass:mass)											
Treatment	P	Cu	K	Mg	Mn	Na	Zn	B	Si	Ca	Total N
C0M	29 A	5.2 A	44 A	81 A	0.6 A	101 A	2.1 A	nd	118 A	138 A	60 A
C5M	15 B	0.6 A	36 AB	58 B	0.0 A	94 AB	1.5 A	nd	62 AB	114 A	53 A
C10M	11 BC	0.6 A	35 B	56 B	0.9 A	92 AB	1.2 AB	nd	72 AB	118 A	51 A
C20M	5 C	−0.1 A	29 B	37 C	0.0 A	86 B	0.5 B	nd	28 B	74 B	40 B

[a] Total N is the sum of NO$_3$–N and Kjeldahl–N. Kjeldahl–N was determined for weeks 11, 12, and 13 only.

[b] Not determined.

[c] Numbers followed by the same letter within a column are not significantly different at the $P<0.05$ level based on Tukey's Studentized Range test.

of the C0M 12-week leachate indicated that dissolved organic C (DOC) from the recently applied manure leached through the C0M columns without being retained by the soil. By contrast, only a very slight tint of color was evident in the 12-week leachate from the columns receiving both manure and biochar (C5M, C10M and C20M columns). Leachate recovered during all other weeks (weeks 1–11 and 13–45) was nearly clear. This visual observation suggests that biochar amendments were an effective means of reducing DOC leaching, although no quantitative measurements were attempted.

A summary of elemental leaching from the various columns is given in Table 1. Among control columns receiving biochar but no manure, total amounts of K, Mg, Zn, and Ca and total N that leached during weeks 1–45 increased significantly ($P < 0.05$) with level of biochar added to the columns. This trend reflects increasing amounts of these elements added to the columns with increasing amounts of biochar, and demonstrates that nutrients added with the biochar are at least partly mobile. Among columns receiving manure, there was a significant decrease in total amounts of P, Mg, Si, and total N that leached with increasing levels of biochar, despite the fact that the biochar treatments added substantial amounts of these nutrients to the columns (Table 1). By contrast, total amounts of K and Ca that leached increased with the level of biochar added for the manure-amended columns. Table 1 also shows percentages of elements added with the manure that were recovered in the leachate. For all elements except Mn and Cu, there is a significant decrease in leaching of nutrients added with the manure as the level of biochar increased. The mass balance analysis is a means of isolating the effect of nutrients added with the manure from those added with the biochar.

Although, Na is not an essential plant nutrient, the leaching of Na (Fig. 1) illustrates the general effect of biochar on the leaching of cations. Sodium is a strongly hydrated monovalent cation and hence is relatively mobile in soils. The soil in each column contained 5.55 mg of extractable Na, the biochar added up to 3.72 mg of Na to columns receiving 20 g kg^{-1} biochar (proportionally less for columns receiving less biochar), and the manure added 20.8 mg of Na to all columns receiving manure. Among columns receiving manure but no biochar (C0M columns) a sharp spike in Na leaching occurred on the first leaching event after manure addition (week 12). Furthermore, there was a wide range in the amount of Na that leached from individual C0M columns on week 12 (0.43 to 7.59 mg per column). This sharp spike in Na leaching and the high column-to-column variability in the mass of Na leached for the week 12 event, suggests that Na added with the manure was able to move through some of the columns with minimal interaction with the soil matrix (by-pass flow). By contrast, peaks for Na leaching among columns receiving biochar and manure (C5M, C10M, and C20M) occurred 5 to 7 weeks after the manure

addition and there was no evidence of by-pass flow for any of the biochar treated columns (standard deviations for Na leaching from the C5M, C10M, and C20M columns were all less than 0.83 for all leaching events between weeks 12 and 45 versus a standard deviation of 2.75 for Na leaching from the C0M columns on week 12). The total amount of Na recovered in the leachate relative to the amount of Na added with the manure (based on the difference in mass of recovered Na leached from columns with and without manure additions at each biochar level) decreased from 101% to 86% as the biochar concentration increased from 0 to 20 g kg^{-1} (Table 1). The amount of Na recovered in leachate for no-manure control columns that received biochar (C5, C10, and C20 columns) was not significantly different from the amount of Na in the leachate for the C0 columns. The results suggest that soil–biochar additions reduced the leaching of Na added with the manure by reducing by-pass flow and by increasing the ability of the soil to retain Na.

Substantial amounts of Ca, Mg and K were present as exchangeable cations in the soil, and as components of the biochar and the manure. Furthermore, the water used to leach the columns contained Ca. In general, leaching of Ca, Mg and K (Figs. 2–4, respectively) was influenced by the combined effects of the multiple sources of these elements, properties of the elements, and the influence of the biochar on the mobility of the elements. Before the manure addition (weeks 1–11), the amount of Ca, Mg and K in the weekly leachate increased with the level of biochar addition, suggesting that the bases added with the biochar were at least partially mobile. Spikes in leaching for all three elements on week 12 for the C0M columns are attributed to by-pass flow. By contrast, no evidence of by-pass flow was observed for the columns receiving both biochar and manure (C5M, C10M, and C20M). Average peaks for leaching of Ca, Mg and K occurred on week 17, 5 weeks after the manure was applied. Mass balance analysis (Table 1) indicates that the biochar treatments significantly reduced leaching of all three elements induced by the manure addition. Addition of the manure induced leaching of more Ca (138%) than was added with the manure for the C0M columns (Table 1). This result suggests that other cations added with the manure, including Mg, K, Na, and H, accelerated the leaching of Ca that was already present in the soils.

Only trace concentrations of the Cu, Zn and B were detected in the leachates. Most of the Cu that leached on week 12 came from a single C0M column and is attributed to by-pass flow. Because of the high column-to-column variability, the effect of biochar on Cu leaching was not significant. The recovery of Zn added with the manure in leachate for the C20M columns was significantly lower than the recovery of Zn in the leachate for the C0M columns. No evidence of by-pass flow was
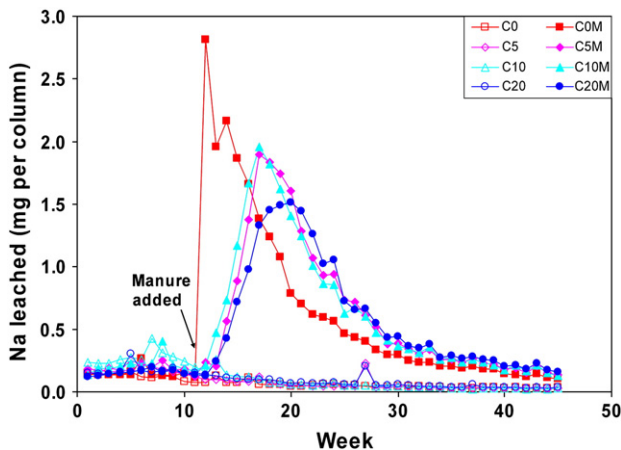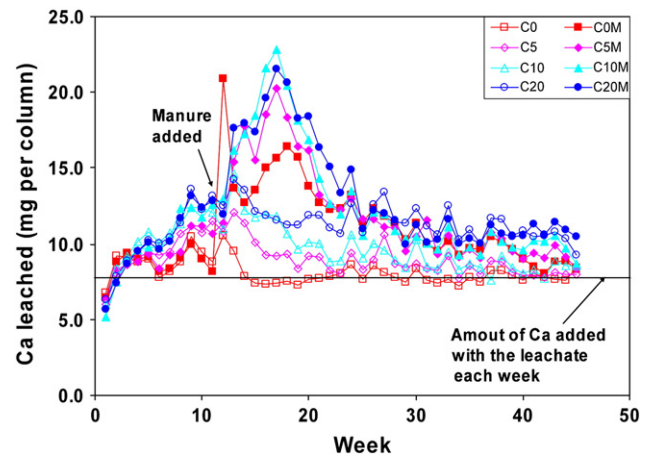

Fig. 1. Leaching of Na from columns amended with biochar and manure and leached weekly with 200 mL of 0.001 M CaCl$_2$. Column soils were treated with 0, 5, 10, and 20 g kg^{-1} biochar (C0, C5, C10, and C20 respectively: the M indicates manure added).
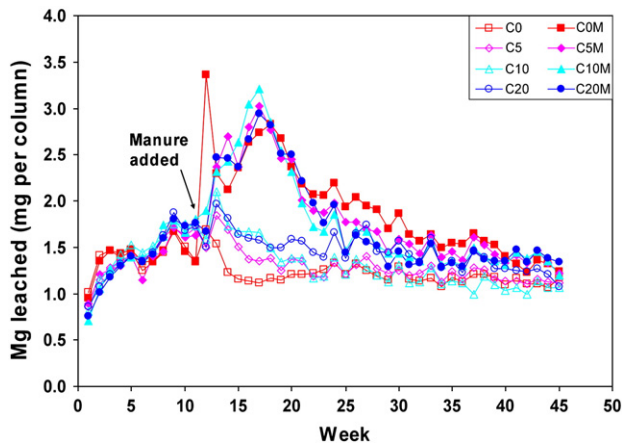

Fig. 2. Leaching of Ca from columns amended with biochar and manure and leached weekly with 200 mL of 0.001 M CaCl2. Column soils were treated with 0, 5, 10, and 20 g kg^{-1} biochar (C0, C5, C10, and C20 respectively: the M indicates manure added).

Fig. 3. Leaching of Mg from columns amended with biochar and manure and leached weekly with 200 mL of 0.001 M CaCl₂. Column soils were treated with 0, 5, 10, and 20 g kg⁻¹ biochar (C0, C5, C10, and C20 respectively: the M indicates manure added).

detected in the leaching data for Zn and B. The results confirm that all three elements are tightly retained by soils.

The soil used in the column study contained 20.5 g kg⁻¹ C and 1.74 g kg⁻¹ N and had a C:N ratio of 11.8. There was no evidence of free carbonates and the soil pH before biochar amendment was 6.4 (± 0.3 SD). Thus we infer that all of the C in the soil was associated with the soil organic matter or microbial biomass. The freeze-dried swine manure contained 3.9% total N. The chemical form of N in the swine manure was not determined, but it is reasonable to assume that both organic and mineral forms of N were present (Toor et al., 2006). The NO_3^- detected in the leachate from the columns was produced through nitrification of ammonium forms of N added with the manure or produced through mineralization of organic N associated with the soil organic matter and the manure.

The biochar treatments influenced NO_3^- leaching during the first 11 weeks prior to manure addition (Fig. 5). During this early period we assume that the microbial populations were adapting to new environments. By week 14 NO_3^- leaching for most of the no-manure controls (C0, C5, and C10) decreased to approximately 1 mg of NO_3–N per column per week and remained at that level through the duration of the experiment. By contrast, approximately 2 mg of NO_3–N per column per week leached from the C20 control columns. Integrated over 45 weeks the C20 columns lost 26% more NO_3–N to leaching than the C0 columns. This significant ($P<0.05$) effect is attributed to enhanced mineralization of organic N stimulated by the high rate of
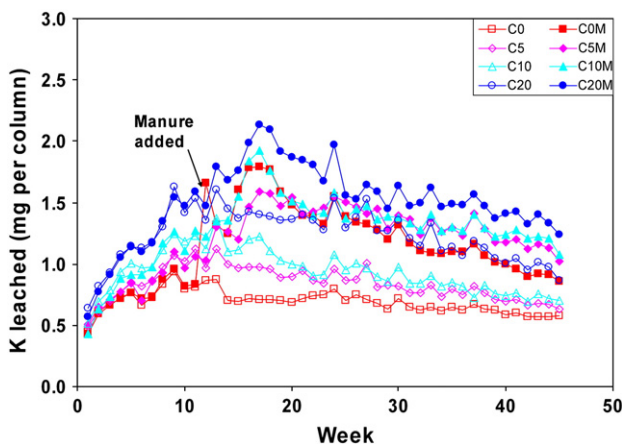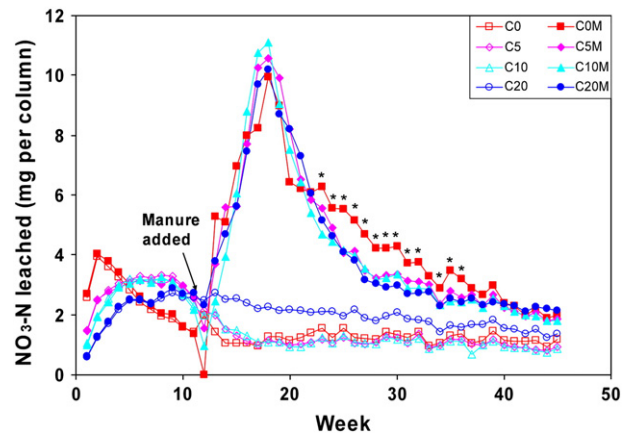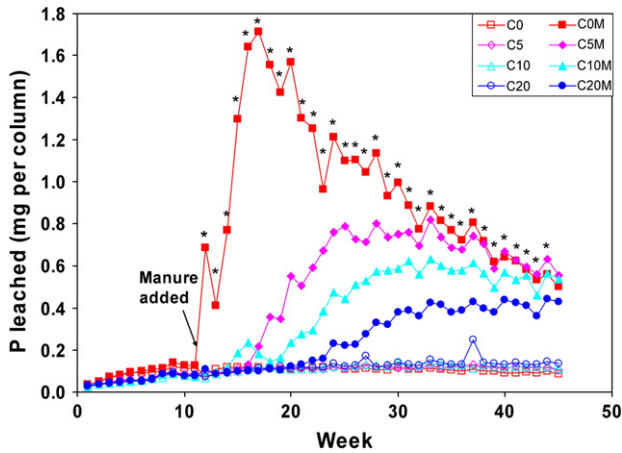

Fig. 4. Leaching of K from columns amended with biochar and manure and leached weekly with 200 mL of 0.001 M CaCl₂. Column soils were treated with 0, 5, 10, and 20 g kg⁻¹ biochar (C0, C5, C10, and C20 respectively: the M indicates manure added).

Fig. 5. Leaching of NO_3 from columns amended with biochar and manure and leached weekly with 200 mL of 0.001 M CaCl₂. Column soils were treated with 0, 5, 10, and 20 g kg⁻¹ biochar (C0, C5, C10, and C20 respectively: the M indicates manure added). The * indicates weeks after the manure treatment in which NO_3–N leaching from the C0M columns was significantly greater than NO_3–N leaching from columns receiving at least one of the other manure treatments (C5M, C10M, or C20M).

biochar addition. The interpretation is consistent with increasing respiration with increasing levels of biochar addition (Rogovska et al., 2010) and independent reports of biochar enhanced microbial respiration (Steiner et al., 2008b) and enhanced mineralization of humic material (Wardle et al., 2008).

The manure addition on week 12 resulted in a broad NO_3–N leaching peak, which reached a maximum on week 18 (Fig. 5). Between weeks 23 and 36 the biochar treatments significantly reduced NO_3–N leaching from the manure + biochar treated columns (C5M, C10M, and C20M) relative to the manure-only control columns (C0M). We speculate that the biochar adsorbed NH_4 and soluble organic compounds from the manure and decomposing microbial biomass and in so doing inhibited mineralization of organic N and/or nitrification of NH_4 for the manure-amended columns. That the effects of biochar on NO_3–N leaching are in opposite directions for the no-manure columns and the manure-amended columns is intriguing and also serves to emphasize the complexity of the N-cycle and soil–biochar by N-mineralization interactions.

On week 12, the amounts of NO_3–N in leachate from the manure-amended columns were substantially lower than in the weeks before or after. We attribute this suppression in NO_3–N leaching for the manure-amended columns on week 12 to temporary immobilization induced by the presence of high concentrations of bioavailable DOC in the soil solution. Ammonium and organic N in the leachate were quantified by determining total Kjeldahl-N for weeks 11, 12, and 13. For week 11 no Kjeldahl-N was detected in any of the leachate samples. For week 12, 4.19 (± 1.69 SD), 0.54 (± 0.22 SD), 0.72 (± 0.37 SD), and 0.37 (± 0.08 SD) mg of Kjeldahl-N were present in the leachate for the C0M, C5M, C10M, and C20M columns, respectively. For week 13, Kjeldahl-N averaged 0.43 (± 0.19 SD) for the C0M columns and was less than 0.2 mg for all of the other treatments. The Kjeldahl-N in the leachate for week 12 was 2% of the total N that leached from the C0M columns during the study (Table 1). The biochar treatments reduced the total amount of N (NO_3–N + Kjeldahl-N) that leached from the manure-amended columns by 11% relative to the manure-only control columns (Table 1).

Complex biochemical processes controlled NO_3^- leaching in the soil columns. Most of the surface charge sites on aged biochar are due to carboxylate and phenolate groups (Liang et al., 2006). These anionic surface charge sites will not retain NO_3^- and thus a priori there is little reason to anticipate NO_3^- retention by biochar in soil systems. However, biochar has a substantial capacity to adsorb both NH_4^+ and DOC from the soil solution. Thus we speculate that adsorption of NH_4^+ and organic N associated with the manure and organic compounds

Fig. 6. Leaching of total dissolved P from columns amended with biochar and manure and leached weekly with 200 mL of 0.001 M CaCl$_2$. Column soils were treated with 0, 5, 10, and 20 g kg^{-1} biochar (C0, C5, C10, and C20 respectively: the M indicates manure added). The * indicates weeks after the manure addition in which total dissolved P leaching from the C0M columns was significantly greater than total dissolved P leaching from columns receiving at least one of the other manure treatments (C5M, C10M, or C20M).

produced during mineralization of soil organic matter by the biochar reduced the rate of N mineralization and hence the rate of NO$_3$–N leaching from the manure-amended soil columns.

A major finding for the study was a large reduction in the levels of total dissolved P (TDP) in the leachate for the biochar amended columns after the manure addition (Fig. 6). Total leaching of TDP was 33.7 and 10.3 mg for the C0M and C20M columns, respectively. From mass balance analysis, we estimate that 29% of the total P added with the manure leached from the C0M columns and only 5% of the manure P leached from the C20M columns (Table 1). The effect is attributed both to adsorption of orthophosphate and to adsorption of organic P compounds by the biochar. The ability of biochar to reduce leaching of P suggests that soil–biochar amendments could be an effective tool for reducing adverse impacts of manure on water quality.

The effects of biochar on nutrient leaching clearly depend on complex chemical, physical and biological processes. Biochar substantially increased the cation-exchange capacity of the soils in the columns (Laird et al., 2010) and thus retention of alkaline and alkali earth metal cations in a manner analogous to a cation-exchange chromatographic column. Divalent cations and weakly hydrated monovalent cations (e.g., K$^+$) are more strongly retained than the strongly hydrated monovalent Na$^+$. Physical processes (e.g., by-pass flow versus matrix flow) also influenced the movement of these nutrients. Evidence of by-pass flow on week 12 for Na, Ca, Mg, K and P was observed for the same two and sometimes three C0M columns. That evidence of by-pass flow was observed for up to 3 (depending on element) of the 6 total C0M columns but none of the 18 biochar and manure treated columns (C5M, C10M, and C20M) suggest that nutrients in the water interacted strongly with biochar during the week-12 leaching event and that the biochar amendments were an effective means of reducing by-pass flow for these soil columns.

The results of this study strongly suggest that addition of biochar to Midwestern agricultural soils will increase the capacity of the soils to retain nutrients and thereby reduce leaching of nutrients. In a companion paper (Laird et al., 2010), we report that the biochar treatments significantly increased total N (up to 7%), organic C (up to 69%), and Mehlich III extractable P, K, Mg and Ca in the column soils. Increased retention of these nutrients in the soil profile should increase the probability that the nutrients will be taken up by plant roots, and thereby decrease the risk that they will be leached and transported to surface or groundwater reservoirs. The net impact of these processes should be increased nutrient use efficiency, which in turn should reduce the need for fertilizer and lime amendments in production agriculture and

improve water quality. Field work designed to test this hypothesis is underway.

A limitation of the present study is that only one biochar and one soil were used. Properties of biochars vary widely depending on the properties of the biomass that is pyrolyzed, the conditions under which it is pyrolyzed, and the extent of aging of the biochar. As biochar ages in a soil, surfaces of the biochar are anticipated to oxidize creating carboxylate groups and hence active sites for adsorption of various compounds. On the other hand, the longer biochar resides in soils the more opportunity there will be for the surfaces of the biochar particles to be saturated with metals, oxyanions, and organic compounds. Thus the function of biochar in soils will most certainly change with the length of time that it is present in soils. However, the high fertility of the Terra Preta soils and their high capacity to retain nutrients today, over 500 years after cessation of the practices that led to their development, suggest that the positive effects of biochar on soils are long-lasting.

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