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Effects of biochars and hydrochars produced from lignocellulosic and animal manure on fertility of a Mollisol and Entisol

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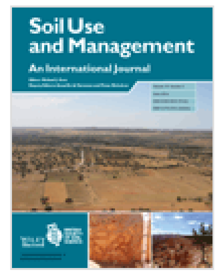

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Abstract

Biochar and hydrochars (HC) are emerging soil fertility amendments; however, their ability to improve fertility levels in soils possessing vastly different pedogenic characteristics has not been well investigated. In this study, several plant and manure biochars and two blended HC applied at 3.84 g/kg (ca.10 t/ha) were incubated in pots containing a highly fertile-Mollisol (Waukegan series; Sandy-skeletal, mixed, superactive, mesic Typic Hapludoll) and an infertile Entisol (Margate series; Siliceous, hyperthermic, Mollic Psammaquent). During the 124–125 day laboratory incubations, pots were leached four times with deionized H_2O with the leachates analysed for the concentrations of dissolved phosphorus (DP) and potassium (DK). After the incubations, both soils were analysed for fertility characteristics (i.e. pH, cation-exchange capacity (CEC), and extractable P and K). In both soils after biochar additions, there were mixed pH and CEC responses. Both the Mollisol and Entisol treated with swine solid biochar had greater plant extractable P and K contents, which was reflective of the elevated P and K contents in the swine solid biochar. However, most biochars and HC additions to the Mollisol and Entisol had minimal impact on soil fertility characteristics indicating a low direct fertilization potential. These nutrient contents could be altered through feedstock blending to target a particular fertilizer requirement.

Introduction

In the South-eastern Coastal Plain region of the USA, the concentration of confined animal feeding operations has made animal manures readily available for fertilizer use (Kellogg *et al*., 2000). Repeated applications of animal manures to some Coastal Plain soils has resulted in high to excess soil P concentrations (Kellogg *et al*., 2000), which has caused water quality impairment concerns (Sharpley, 1999).

An alternate management strategy is being investigated for its use as a bioenergy source through thermochemical processing (Cantrell *et al*., 2007) and hydrothermal carbonization (Libra *et al*., 2011). Thermochemical processing of animal manures produces bioenergy in the form of gasses and a solid residual by-product called biochar (Antal & Grønli, 2003). Hydrothermal carbonization of animal manures also produces bioenergy gasses under high temperature and pressure, but the process can also produce a by-product called hydrochars (HC; Libra *et al*., 2011).

Biochar and HC have gained global attention as soil amendments to potentially improve soil quality (Sohi *et al*., 2009; Libra *et al*., 2011) because they contain a variety of organic structures (Amonette & Joseph, 2009) and inorganic elements (Novak *et al*., 2013a). The quantity and distribution of organic and inorganic constituents are related to feedstock selection (Kwapinski *et al*., 2010), biochar and HC processing conditions (Novak *et al*., 2013a; Zheng *et al*., 2013), and postproduction handling and storage. Biochar and HC can improve the SOC content (Lehmann *et al*., 2009; Libra *et al*., 2011), while their functional groups can increase the CEC of soils (Laird *et al*., 2010; Libra *et al*., 2011). The inorganic constituents in biochars and HC can also bolster the plant nutrient content of soils (Jeffery *et al*., 2011; Bargmann *et al*., 2013).

Recently, Jeffery *et al*. (2011) reported that biochar improved the fertility of highly weathered sandy soils, but there are few studies that have compared the effects of biochar and HC on soils possessing inherently different fertility and parent material characteristics. The biochars and HC used in this investigation are unique in the literature because they were produced from a variety of lignocellulosic feedstocks, manures and their blends. Moreover, there is minimal information on the impact of HC as a soil amendment and sparse results in the literature utilizing HC produced using blends of feedstocks. The objectives for this study were to (i) quantify the impact of biochars produced using pyrolysis and hydrothermal extraction on modifying the soil fertility characteristics of both a Mollisol and an Entisol, and to (ii) quantify dissolved P (DP) and dissolved K (DK) concentrations in leachates collected from these soils amended with biochars and HC.

Materials and methods

Study sites, soil sampling and characterization

Two soil series were chosen based on forming under different weathering regimes, from contrasting parent materials and possessing different fertility characteristics. The first soil was a fertility-poor Margate series classified as a Siliceous, hyperthermic, Mollic Psammaquents is a poorly drained, sandy Entisol, underlain by coarse textured sandy marine sediments. The sampling site was located in Hendry County (26°42′N, 81°02′W), approximately 12 km SW from Clewiston, Florida, USA. The nearly level (0 to 1% slope) field was under sugarcane (a complex hybrid of *Saccharum* spp.) production. Bulk soil samples were collected from the Ap horizon between 0 and 15 cm depth. Samples were air-dried and then 2-mm sieved. The Margate Ap horizon had a pH of 7.2 (1:2 soil:H_2O), a soil organic carbon content of 0.6%, an inorganic carbon content of <0.05% and a total N content of 0.05%. The soil texture was sand with a particle size analysis of 96.5% sand, 3.5% silt and 0% clay.

The second soil chosen was a highly fertile, Waukegan series. The Waukegan is a well-drained Mollisol that formed in loess over glacial outwash. The soil has been in a long-term (>10 yrs) rotation of corn (*Zea mays*) and soybean (*Glycine max*). Bulk samples were collected from a nearly level (<2% slope) field at the University of Minnesota Research and Outreach Station in Rosemount, Minnesota (44°45′N, 93°04′W). The Waukegan soil is classified as a fine-silty over skeletal mixed, super active, mesic Typic Hapludoll (Soil Survey of Dakota County, Minnesota, **1983**). The Ap horizon was sampled from the 0 to 10 cm soil depth, air-dried and then 2-mm sieved. Particle size analysis revealed that it was a silt loam with 22% sand, 55% silt and 23% clay. The Waukegan topsoil pH was 6.4 (1:1 H_2O) and contained 2.6% total organic carbon (TOC; organic + inorganic carbon).

Feedstock selection, biochar production and characterization

The feedstocks chosen for biochar and HC production reflect their accessibility to application sites, their availability for plot research, or availability as a biochar source that has been produced for other purposes. From the Florida location, the feedstock's consisted of milled bagasse (residual material after sugarcane production), pine chips (*Pinus tadea* spp.) and swine solids. For the Minnesota soil-sampling site, commercially available biochars selected were produced from corn stover (Chip Energy, Goodfield, Illinois), wood pellets (Best Energy, Mantria Industries, Sequatchie Co., TN) and macadamia nut shell (*Macadamia* spp.) processing (EternaGreen™, Pacific Pyrolysis, Somersby, Australia).

Biochars from air-dried flakes/solids of sugarcane bagasse, pine chips and swine solids were produced by pyrolysis using a Lindburg oven with a retort at 350 °C as outlined by Cantrell & Martin (**2012**). Biochars produced from production by Best Energy, Chip Energy and EternaGreen™ were created at pyrolysis temperatures ranging between 500 and 600 °C. More specific production details for these three biochars are proprietary.

Two designed hydrochars were prepared by blending citric acid (HOAc)-washed 10% swine manure solids hydrochar with 90% sugar beet HC (HC-1) or 90% pine bark HC (HC-2). Washing swine solid feedstock with HOAc reduced its P content thus yielding blending ratios considered optimal in plant-available P contents when applied to soil at 3.84 g/kg w/w (see next section). The swine manure HC was obtained by mixing appropriate amounts of HOAc-wash swine manure solids with deionized H_2O to obtain a 20% solid solution for hydrothermal carbonization at 250 °C for 20 h (Cao *et al*., **2011**). The sugar beet and pine bark mulch HC were prepared using the patented hydrothermal carbonization in steam process (Revatec GmbH, DE 10 2009 010 223.7) carried out in a 70-L stainless steel reactor. The raw feedstock (chipped sugar beet 1.0–1.5 cm and shredded bark mulch <5 cm) was placed in the reactor and hydrothermally carbonized at 200 °C (16 kPa) for 3 h (Libra *et al*., **2011**). As noted above, these three HC provided blending material to produce HC-1 and HC-2. All biochars and HCs were then air-dried, ground to <0.25 mm and stored in a dessicator until used in the soil incubation experiment.

The biochars and HCs were characterized for their pH, ash, C, N, P and K contents (Table 1). The pH value of each sample was estimated in triplicate at 1% (w/v) using deionized H_2O after shaking for 24 h at 200 rpm. Single estimates for the ash, C, and N contents of each biochar/HC were measured on an oven-dried basis by Hazen Research, Inc., (Golden, Colorado) following ASTM D 3172 and 3176 standard methods (ASTM (American Society for Testing & Materials), **2006**). The P and K contents of each biochar and both HCs were determined using a single measurement on an oven-dried weight basis using the USEPA method 3052 (available at http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/3052.pdf). Their concentrations were quantified using inductively coupled plasma emission spectroscopy (Novak *et al*., **2009**).

Table 1. Biochar and hydrochar (HC) chemical properties

Biochar (°C)	pH	Ash	Total elemental (dry basis)			
			C	N	P	K
		g/kg			mg/kg	
Sugarcane bagasse (350)[a]	5.5	37.6	752	6.6	496	3777
Best energy (500)[b]	5.0	47.7	711	1.1	168	906

Chip energy (600)[b]	9.8	64	734	2.1	184	4747
Macadamia nut shell (600)[b]	8.2	19.2	932	6.7	406	6497
Pine chips (350)[a]	4.4	15.3	747	4.5	206	1927
HC-1[c]	4.4	12.2	495	22.7	4213	2310
HC-2[d]	4.0	29.7	624	9.0	3334	2318
Swine solids (350)	9.1	331	508	3.7	40250	19274

a some results published previously in Novak *et al* . (**2013a**).

b some results published previously in Spokas *et al* . (**2011**).

c 90/10 sugar beet + swine HC.

d 90/10 pine bark + swine HC.

Biochars incubation in soils and H_2O leaching

Two soil pot incubation experiments were conducted approximately 1 month apart. The Margate and Waukegan soil pot incubation experiment was set up in late June 2010 and conducted using methods outlined in the study described by Novak *et al* . (**2009**). Briefly, biochar was applied to triplicate pots of both the Margate and the Waukegan soils at 3.84 g/kg, which is equivalent to approximately 10 t/ha. Sufficient deionized H_2O was added so that each pot containing the Margate and Waukegan soil + biochar would be at 10 and 20% moisture content (w/w), respectively. Triplicate pots containing soil without biochar served as controls. All pots were then laboratory incubated for 125 days with soil moisture contents adjusted to their respective water contents twice per week using deionized H_2O.

Pots containing the Margate and Waukegan soils treated with biochars and controls were leached four times over 125 days of incubation (on days 34, 62, 91 and 125) using 1.2–1.3 pore volumes of deionized H_2O. The leachates were collected and filtered through a 0.45-μm size filter. Leachate DP and DK concentrations were measured using ICP. The pot experiment for the Margate and Waukegan soils treated with HC and their controls (no HC) were set up in late July 2010 in a similar manner as described previously. During their laboratory incubation, these pots were leached in a similar manner, except the incubation period was 124 total days and the leaching occurred on days 34, 62, 90 and 124 of incubation. Both DP and DK concentrations were measured in the leachates as described earlier.

At termination, all soils were examined for their pH values, CEC and plant-available P and K concentrations by contract laboratories using chemical extractants typical for soils in their regions. For the Margate soils, the Clemson University Soil Testing Laboratory (http://www.clemson.edu/agsrvib/interest.htm) was contracted to measure pH using deionized H_2O and to extract plant-available nutrients (including P and K) using Mehlich-1

($HCl + H_2SO_4$) extracting solution. Cations in the extraction solution were measured using ICP, and the CEC was determined by summation. For the Waukegan soil, Midwest Laboratories (http://www/midwestlabs.com) was contracted to measure pH using deionized H_2O, and a strong Bray (4× acid concentrations as Bray 1) solution was used as an extractant for plant-available K and the readily available P, and part of the sorbed P fractions. The CEC was determined using the NH_4OAc (pH 7.0) displacement method and then by summing the quantity of extractable cations.

Statistics

Mean values for soil pH, CEC, extractable P and K concentrations were compared for significant differences using a Fisher least significant difference (LSD) pairwise multiple comparison procedure at a $P = 0.05$ level of significance. A minimum and maximum value for the leachate DP and DK concentrations were reported to express their ranges. The cumulative masses of DP and DK in the four leachates were then determined. Next, the total mass of P and K (from soil + biochar) in each pot was calculated. Then, cumulative estimates of mass of %DP and %DK solubilized was compared with the total P and K pools in each system. The mean cumulative %DP and cumulative %DK in leachates were then tested for significant differences between treatments as determined previously.

Results and discussion

Biochar and hydrochar characteristics

The biochars produced from sugar cane bagasse and pine chip feedstocks using low pyrolysis temperatures (ca.350 °C) had low pH values and ash contents (Table 1, <40 g/kg). Low-temperature pyrolysis commonly results in biochars with low ash contents and pH values (Amonette & Joseph, **2009**). In contrast, two of the three biochars produced from wood and macadamia nut shell feedstocks were pyrolysed at higher temperatures (500–600 °C) and had alkaline pH values and higher ash contents (>50 g/kg). Higher pyrolysis temperatures (≥500 °C) results in biochars with higher concentrations of alkali-earth metals (Novak *et al*., **2009**). The exception was Best Energy biochar, produced from wood wastes, which had an acidic pH and < 50 g/kg ash content.

There were no common trends among biochars and HCs for C, N, P and K contents. Biochar made from swine solids had alkaline pH values, and the highest ash, P and K contents, which are typical traits for this biochar-type (Cao *et al*., **2011**). Biochar produced from macadamia nut shells possessed the highest C content. The highest N content was in the HC-1 biochar, the mixture of sugar beet + swine manure.

The relatively high total P content in swine manure-based biochar justified the blending with HC produced from pine bark mulch and sugar beets (Table 1). Total P content was reduced through blending relative to swine solid biochar. Acid washing of the swine manure may have caused both HCs to be strongly acidic (pH ≤ 4.4). However, HCs are typically more acidic because they have higher H contents than their corresponding dry thermal processed biochar from the same feedstock (Libra *et al*., **2011**).

Biochar incubation in soils

The untreated Margate soil (control) had an alkaline pH, and medium CEC and K levels (Table 2). In general, amending the Margate soil with these biochars caused variable improvement in its fertility status. While some biochars produced from bagasse and swine solid feedstocks caused small, but significant increases in soil pH; application of HC-2 appreciably lowered the pH to 7.20. The low pH in the Margate soil that resulted from the addition of HC-2 corresponded to a low pH of the HC-2 (Table 1, 4.0) and the low buffer capacity of the Margate soil (0.6% SOC content).

Table 2. Margate soil fertility characteristics after 124–125 d incubation with 10 t/ha of biochar and hydrochars (HC; mean of n = 3)[a]

Biochar treatment (°C)	pH	CEC (cmol/kg)	Mehlich 1 extractable (mg/kg)	
			P	K
Margate control	7.50ac	6.2ac	48.7b	7.8b
Sugarcane bagasse (350)	7.77b	5.3a	46.5b	9.8b
Pine chip (350)	7.63ab	5.6ac	45.2b	9.0b
HC-1[b]	7.40c	5.2a	48.3b	9.6b
HC-2[c]	7.20d	4.7b	45.4b	8.7b
Swine solids (350)	7.70b	6.8c	150.3a	19.5a
LSD (0.05)	0.16	0.8	17.9	2.6

a means in the same column followed by a different letter are significantly different based on the LSD at a P = 0.05.
b 90/10 sugar beet + swine HC.
c 90/10 pine bark + swine HC.

After adding these amendments, there was no significant improvement in the Margate's soil CEC. Addition of HC-2, in contrast, significantly lowered the mean soil CEC level by almost 1.5 cmol/kg. Hydrochar-2 may have chelated basic cations, possibly causing resistance to extraction using Mehlich 1 reagent. The CEC reduction for HC-2 may also be related to residual exchangeable H from the HOAc pretreatment. After adding four of the five biochars/HC, there was no modification in the extractable P and K contents of the Margate soil relative to the control. With respect to extractable P, addition of biochars pyrolysed from sugarcane bagasse, pine chips and both HCs probably caused P binding by inorganic and/or organic structures, thereby reducing extraction efficiencies. These declines were similar to results observed for digested sugar beet biochar, postulated due to Mg in sugar beet tissues (Yao *et al*., **2011**).

Additions of swine solid biochar, in contrast, dramatically increased the Mehlich 1 extractable P and K contents (Table 2). Compared with the other treatments, this biochar caused a 2-fold increase in K and a 3-fold increase in Mehlich-1 P, which is consistent with this biochar containing the highest total P and K contents (Table 1). Therefore, considering P leaching potential, biochar produced from swine solids that have high total P contents should be applied to sandy soils at rates 10 t/ha.

Blending the swine solid HC with the other HC (sugar beet and pine bark mulch) reduced its P contents. Blending feedstocks can be a protocol to design a biochar without causing unbalanced plant-available P (or possibly other nutrient) contents in the soil as outlined by Novak *et al*. (**2013b**). The additional pretreatment of feedstocks and/or blending of multiple feedstocks to balance P contents will probably raise biochar and HC production costs.

All five biochars added to the Waukegan soil had no significant impact on pH and CEC (Table 3). Potentially, this could be due to the higher buffering capacity from the elevated SOC content and more acidic pH compared with the Margate soil. This means that base cations entrained within the biochars were tied up and did not participate in reactions measuring CEC or pH. This is a plausible explanation considering the insignificant modifications (near similar mean values) between the untreated control and biochar-treated Waukegan soils (Table 3).

Table 3. Waukegan soil fertility characteristics after 124–125 days of incubation with 10 t/ha of biochars produced under different pyrolysis temperatures (mean of $n = 3$)[a]

Biochar treatment (°C)	pH	CEC (cmol/kg)	Strong Bray extractable (mg/kg)	
			P	K
Waukegan control	5.60a	16.7a	39c	252c
Best energy (500)	5.70a	16.9a	49b	271ab
Chip energy (600)	5.77a	16.0a	50b	269abc
Macadamia nut shell (600)	5.60a	16.6a	47b	258bc
Pine chip (350)	5.63a	16.7a	46b	259bc
Swine solids (350)	5.70a	16.8a	124a	279a
LSD (0.05)	0.19	1.4	5	17

a means in the same column followed by a different letter are significantly different based on the LSD at a $P = 0.05$.

Extractable P concentrations from the Waukegan soil were significantly increased (compared with the control) by additions of biochar produced from pine chip and macadamia nut along with biochars produced by Best Energy and Chip Energy (Table 3). After these four biochars were applied to the Waukegan soil, in general, their Strong Bray extractable P content increased between 7 and 11 mg/kg. In contrast, the Strong Bray soil extractable P concentration after additions of the swine solids biochar rose 3-fold compared with the control (Table 3; 124 vs. 39 mg/kg). The extractable P concentration in the Waukegan soil was a few fold higher than the optimum concentrations range for corn production in the Midwestern USA Corn Belt region (>25–30 mg/kg, Dodd & Mallarino, 2005).

Leaching of DP and DK from soils

Leaching the treated and untreated Margate and Waukegan soil multiple times with deionized H_2O revealed differences in DP (Table 4) and DK (Table 5) mass losses. In the Margate soil treated with bagasse or pine chip biochar, and both HC, leachate DP concentrations ranged between 0.68 and 2.39 mg/L. Less DP was released from HC-1 (90:10 sugar beet + swine solid HC) compared with HC-2 (90:10 pine bark mulch + swine solid HC). There were significant differences in the cumulative percentage of DP lost in the treated Margate soil. Margate soil treated with HC-1 had the lowest %DP lost (0.62%) due to leaching, while the soil treated with HC-2 had a relatively higher %DP lost (1.85%). Overall, these two biochars and two HC amendments accounted for cumulative DP losses of <2% of the total TP mass in the Margate system. The highest minimum (9.75) and maximum (15.65 mg/L) DP concentrations measured in all four leachates from the Margate soil occurred after additions of swine solid biochar (Table 4). Likewise, the highest cumulative% DP released (6.03%) occurred after incubating the swine solids biochar in the Margate soil.

Table 4. Mean minimum and maximum dissolved P (DP) concentrations along with cumulative DP mass as a percentage of total mass (soil + biochar/hydrochar; HC) contained in the Margate and Waukegan soils incubated with biochars and HC ($n = 3$; standard deviation in parentheses)

Biochar treatment (°C)	Leachate DP (mg/L)		Cumulative%DP in leachates[a]
	Minimum	Maximum	
Margate			
Control (no biochar)	1.48 (0.04)	1.68 (0.02)	1.44d
Sugarcane bagasse (350)	1.65 (0.06)	1.86 (0.04)	1.61c
Pine chip (350)	1.47 (0.07)	1.82 (0.05)	1.48d

HC-1[b]	0.68 (0.04)	0.82 (0.05)	0.62e
HC-2[c]	1.87 (0.04)	2.39 (0.11)	1.85b
Swine solids (350)	9.75 (0.21)	15.65 (0.33)	6.03a
LSD (0.05)			0.12
Waukegan			
Control (no biochar)	0.23 (0.14)	0.65 (0.18)	0.30b
Best energy (500)	0.21 (0.08)	0.68 (0.03)	0.07c
Chip energy (600)	0.23 (0.13)	0.67 (0.10)	0.07c
Macadamia nut shell (600)	0.25 (0.13)	0.58 (0.07)	0.08c
Pine chip (350)	0.22 (0.10)	0.66 (0.05)	0.08c
Swine solids (350)	3.37 (0.58)	4.67 (0.28)	0.61a
LSD (0.05)			0.03

a means within the same column followed by a different letter are significantly different based on the LSD at a $P = 0.05$.
b 90/10 sugar beet + swine HC.
c 90/10 pine bark + swine HC.

Table 5. Mean minimum and maximum dissolved K (DK) concentrations along with cumulative DK mass as a percentage of total mass (soil + biochar/hydrochar; HC) contained in the Margate and Waukegan soils incubated with biochars and HC ($n = 3$, SD; standard deviation in parentheses)

Biochar treatment (°C)	Leachate DK (mg/L)		Cumulative%DK in leachates[a]
	Minimum	Maximum	
Margate			
Control (no biochar)	1.68 (0.02)	1.89 (0.11)	6.10e
Sugarcane bagasse (350)	2.10 (0.28)	6.32 (0.02)	15.58b
Pine chip (350)	3.42 (0.19)	13.76 (0.12)	9.05d
HC-1[b]	3.15 (0.20)	14.64 (0.75)	9.75 cd
HC-2[c]	2.99 (0.13)	15.94 (0.64)	10.41c

Swine solids (350)	19.92 (0.65)	86.47 (4.70)	34.19a
LSD (0.05)			0.73
Waukegan			
Control (no biochar)	21.20 (3.10)	72.00 (6.53)	0.88a
Best energies (500)	17.82 (1.00)	87.1 (9.31)	0.89a
Chip energies (600)	20.83 (0.81)	88.84 (7.10)	0.91a
Macadamia nut shell (600)	21.60 (1.65)	51.77 (8.7)	0.86a
Pine chip (350)	20.47 (1.29)	69.50 (8.80)	0.79b
Swine solids (350)	20.67 (1.77)	66.00 (5.12)	0.74b
LSD (0.05)			0.06

a means in the same column followed by a different letter are significantly different based on the LSD at a *P* = 0.05.
b 90/10 sugar beet + swine HC.
c 90/10 pine bark + swine HC.

The Waukegan soils treated with Best Energy, Chip Energy, macadamia nut shell, and pine chip biochar had leachate minimum and maximum DP concentrations that ranged between 0.21 to 0.68 mg/L (Table 4). While the control released 0.30% cumulative DP in the system, there was a significant reduction in the cumulative DP released after adding these four biochars (≤0.08%). This may be explained by DP binding with cations in the soil matrix (i.e., Al, Fe, Ca and Mg) forming insoluble complexes due to the slightly acidic soil pH (6.4). Applications of swine solid biochar to the Waukegan soil resulted in the highest leachate DP concentration (4.67 mg/L) and the greatest cumulative %DP released (0.61%).

Variable K concentrations in leachates from the Margate soil treated with the bagasse and pine chip biochars and the two HCs ranged from 2.10 and 15.94 mg/L, (Table 5). While the Margate soil with no added treatments (control) sustained cumulative K losses of 6.10%, additions of the other four amendments caused significant increases in the cumulative K losses (<16% of total K). The most extreme K losses occurred after additions of swine solid biochar resulting in a cumulative loss of >34.19% of total K. This means that this swine solid biochar contained substantial soluble K and that four deionized H_2O leaching events caused cumulative losses of >30% of the total K from the topsoil.

The Waukegan soil with no added biochar or HCs had soluble K releases amounting to a cumulative system loss of 0.88% of total K (Table 5). Although additions of the Best Energy, Chip Energy and macadamia nut shell biochars did not significantly cause more cumulative K leaching losses, applications of pine chip and swine solid had significantly lower cumulative losses. However, these significant losses of the overall K from the Waukegan soil amounted to <1% of the total K mass present in the system.

Conclusions

For this study, distinctive biochars and HCs were produced from a variety of lignocellulosic and animal manures along with blends. The blends of the HC were specifically made based on reducing their total P content to rebalance soil plant-available P concentrations. These materials were incubated separately in both a Waukegan silt loam (highly fertile-Mollisol) and a Margate sand (nutrient-poor Entisol) showed significant differences in their ability to impact soil chemical properties and nutrient release tendencies. Addition of biochars to the highly fertile Waukegan soil did not improve its pH, CEC, or extractable K contents. This is consistent with reports that biochar as a soil fertility amendment may not be suitable for highly fertile Mollisols (Ippolito *et al*., **2012**).

Relative to the Margate control soil, biochars produced from sugarcane bagasse, pine chip and swine solids raised soil pH, while the HC application reduced pH. In the sandy Margate soil, addition of four out of five biochars did not significantly improve its CEC. In this soil, addition of HC-2 significantly lowered the soil CEC. Biochar produced from pine chip and sugarcane bagasse, along with both HCs had no impact on augmenting soil extractable P and K concentrations. The additions of HC and biochars from pine chip and sugarcane bagasse feedstocks to the Margate sand resulted in modest DP and DK releases into leachates. In contrast, biochar from swine solids was a much worse choice as a soil amendment for the Margate soil when applied at 3.84 g/kg (ca. 10 t/ha). It resulted in a substantial increase in extractable P concentrations in excess of plant needs and large cumulative losses of DP (>6%) and DK (>34%) from the system. However, we created designer HCs by blending the swine solid HC with other lignocellulosic HC in calculated ratios. Doing so resulted in HCs with reduced total P concentrations, making these custom blended HCs potentially useful for the Margate sand. Unfortunately, pretreatment of feedstocks and or/blending with other feedstocks to reduce P concentrations will probably raise both the biochars and HCs productions costs. At a field scale, the increase in biochar production costs could make it unprofitable to implement the pretreatment/blending strategy.

This study revealed that biochar produced from swine solids at the employed application rate was not a suitable amendment choice for either soil. In both the Margate and Waukegan soils, additions of swine solid biochar caused excessive plant-available P concentrations. This is a concern because sizeable DP concentrations were released into water leachates that could facilitate DP movement into shallow groundwater. Dissolved P leaching losses were more severe in the sandy Margate soil with leachate concentrations measured up to 15.6 mg/L.

Here, it was demonstrated that application of biochars inappropriately matched to a particular soil can create unwanted *post facto* fertility modifications and possible shallow ground water quality impairment. It is suggested that protocols are needed to select the appropriate biochar that can positively impact the targeted soil deficiency and this choice should take into consideration local water quality concerns.

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