



## Leachate water quality of soils amended with different swine manure-based amendments



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### HIGHLIGHTS

- Swine manure based pyrochar, compost, and hydrochar improved soil fertility.
- Pyrochar and compost amended soils released high concentrations of P and K.
- Only small amounts of P, K, and N were leached from hydrochar amended soil.

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### ABSTRACT

In the face of the rising level of manure production from concentrated animal feeding operations (CAFOs), management options are being sought that can provide nutrient recycling for plant growth and improved soil conditions with minimal environmental impacts. Alternatives to direct manure application are composting and thermochemical conversion which can destroy pathogens and improve handling and storage. The effect of four forms of swine manure-based soil amendments (raw, compost, hydrochar, and pyrochar) on soil fertility and leachate water quality characteristics of a sandy soil were investigated in soil incubation experiments. All four amendments significantly increased soil carbon, cation exchange capacity and available nutrient contents of the soil. However, hydrochar amended soil leached lower amounts of N, P, and K compared to the other amendments including the control. On the other hand, pyrochar amended soil leached higher concentrations of P and K. Subsequent tests on the hydrochar for K and N adsorption isotherms and surface analysis via XPS suggested that these nutrients were not sorbed directly to the hydrochar surface. Although it is still not clear how these nutrients were retained in the soil amended with hydrochar, it suggests a great potential for hydrochar as an alternative manure management option as the hydrochar can be soil applied while minimizing potential environmental issues from the leaching of high nutrient concentrations to water bodies.

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### 1. Introduction

Traditionally raw swine manure has been used to provide nutrients for plant growth and to improve soil conditions. However, the increase in concentrated animal feeding operations (CAFOs) results in high levels of nutrients in the proximal crop and pasturelands due to production of more manure than required to meet the local plant nutrient demand (Ro et al., 2014). Soil runoff and leaching of land applied nutrients can enrich surface and ground water with nitrogen and phosphorus compounds leading to eutrophication

and hypoxia (Rabotyagov et al., 2014). In addition, over application of animal manure can spread pathogens, release hormones and other pharmaceutically active compounds, and emit ammonia, greenhouse gases, and odorous compounds (Stone et al., 1998; DeSutter and Ham, 2005; Gerba and Smith, 2005). Recently, the potential of thermochemical conversion of animal manures blended with other agricultural residuals to produce energy and/or biochar have been reviewed (Ro et al., 2010, 2014). Although thermal pyrolysis of raw manure alone does not produce enough energy to support the conversion process, blending with other feedstocks with high energy density such as dried biomass or agricultural plastics can increase energy output enough for both

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biochar and power production (Ro et al., 2010, 2014). Conversion of CAFO' surplus manures into biochar via pyrolysis is an alternative for manure management may offer multitudes of environmental benefits (He et al., 2000). Pyrolyzing manures destroys pathogens and substantially reduces odor and the volume of manure for easy handling, storage, and transportation (Pham et al., 2013). In addition, manure-based biochar may be used as a soil amendment to improve soil quality as other plant-based biochars (Uzoma et al., 2011).

The renaissance of research on soil application of biochar was initiated by the postulation of its role in the sustained fertility of Amazonian soils known as "Terra preta" and the recognition of its stability in soil, which results in a net reduction of atmospheric CO<sub>2</sub> (Lehmann, 2007). A range of agricultural and organic materials can be used to generate biochars with different characteristics (Spokas et al., 2011). Feedstock characteristics and thermal conditions affect the biochars' physical and chemical characteristics (Antal and Gronli, 2003; Singh et al., 2007; Cao et al., 2011; Cantrell et al., 2012; Novak et al., 2014). Generally higher the thermal conditions, higher the inorganic nutrient contents except for N (Novak et al., 2012). Furthermore, manures are nutrient-rich feedstock materials and the pyrolysis of manures produces more nutrient-rich biochar than plant-based biochars (Sheth and Bagchi, 2005; Chan et al., 2008; Gaskin et al., 2008; Ro et al., 2010; Cantrell et al., 2012). However, environmental impacts such as potential water pollution from adding these manure-based biochars to soil are not clear at this time.

Numerous research studies exist in the literature on the leaching characteristics of soils amended with biochar made from traditional dry (or thermal) pyrolysis of biomass (pyrochar). In dry pyrolysis, dried biomass undergoes pyrolytic reactions from added heat, while in hydrothermal carbonization (HTC) or wet pyrolysis organic matter in slurry is decomposed in the presence of subcritical, liquid water under pressure. The major advantage of HTC is that it can convert wet feedstock biomass into carbonaceous solids called hydrochar at relatively high yields without the need for an energy-intensive drying step before or during the process (Libra et al., 2011). Potential HTC feedstock includes wet animal manures, sewage sludge, and municipal solid waste streams, as well as aquaculture residues (Berge et al., 2011). Various applications exist for hydrochar including energy production and storage, CO<sub>2</sub> sorption, catalysis, generation of nanostructured materials, environmental sorbents, and soil application (Xue et al., 2012; Abel et al., 2013).

Both pyrochar and hydrochar additions may improve soil quality. Abel et al. (2013) found that both pyrochar and hydrochar increased water retention capacity of sandy soil. The effect of char on nutrient retention and availability in soil is dependent on the initial char properties as well as on the chemical and microbial interactions as the char weathers (Berge et al., 2013). For instance, hydrochar from N-poor feedstock was found to initially induce nitrogen deficiency in sugar beets, potentially by N-immobilization (Gajic and Koch, 2012). The use of manure-based chars, which have very high nutrient contents compared to other plant biomass-based chars, may provide a reliable source of nutrients. Pyrolyzing already nutrient-rich manures further concentrates these nutrients, especially P and K (Cantrell et al., 2012). However, Novak et al. (2014) reported that the leachate from the sandy soil amended with swine pyrochar contained very high concentrations of dissolved P and K. In contrast, the leachate from the soil amended with a blended hydrochar (90% sugar beet: 10% swine manure) significantly reduced P leaching (Novak et al., 2014) due to low P contents in 90% sugar beet. However, in that study there was no direct comparison of the P leaching characteristics between entirely manure-based pyrochar and hydrochar. Since high concentrations of leachate P from manure-based soil amendments is of serious environmental concern as it may promote algal blooms and hypoxia in receiving water

bodies, this study investigates soil fertility and leachate water quality from sandy soils amended with different forms of swine manure-based amendments: raw swine manure, swine compost, swine pyrochar and hydrochar. This study utilized both soil incubation and soil leaching experiments.

## 2. Materials and methods

### 2.1. Soil amendments

Fresh dewatered swine solids were obtained from a 5600-head finishing swine operation in Sampson County, NC, which were further dried and stored in a refrigerator until needed. Swine hydrochars were prepared by hydrothermally carbonizing swine solids at 250 °C. Dried and ground (less than 2 mm) swine solids were added along with distilled water to obtain slurry of 20% (w w<sup>-1</sup>) solids. This slurry was placed into a 1-L non-stirred T316 stainless steel reactor with an external heater (Parr Instruments, Moline, Illinois). The reactor was heated to 250 °C with a heating rate of 7 °C min<sup>-1</sup>. The reactor temperature was maintained at 250 °C under its autogenic pressure of about 7 MPa for 20 h. Afterwards, the reactor was cooled to room temperature before the reaction products were filtered and dried at 100 °C. Some of the filtered hydrochars were mixed with about 200 mL acetone and agitated for 2 h in order to remove labile compounds sorbed on the hydrochar surface (Spokas et al., 2011). For clarity, the hydrochar without acetone treatment is called hydrochar (W) and with the acetone treatment as hydrochar (A). For comparative analyses, pyrochar made from traditional dry pyrolysis of the same swine solid feedstock was prepared using a skid-mounted pyrolysis system which heated the dried swine solids to 620 °C in a low oxygen environment for two hours (Ro et al., 2010). In addition, commercial swine compost was obtained from Terra Blue, Inc., Clinton, NC.

### 2.2. Incubation experiments

A 50/50 mixture of the Ap and E horizon was used as a control soil to simulate mixing of subsoil into topsoil due to deep tillage and loss of topsoil due to erosion. Triplicate sets of small pots were filled with the following contents: (1) control soil (CS) and the control soil amended with (2) raw swine solid to provide agronomic rate of 4.3 g kg<sup>-1</sup> (i.e., 178 kg ha<sup>-1</sup>) (RS), (3) pyrochar at 20 g kg<sup>-1</sup> (PC), (4) hydrochar (W) at 20 g kg<sup>-1</sup> (HW), (5) hydrochar (A) at 20 g kg<sup>-1</sup> (HA), and (6) swine compost at 20 g kg<sup>-1</sup> (SC). The soil pot incubation experiment was conducted mostly in open-top flower pots measuring 10.3 cm (i.d.) by 8.5 cm tall (series with CS1). In the last incubation experiments (i.e., the incubation conducted during 2/11/14 to 4/15/14), smaller pots made of PVC pipe (3.8 cm id × 8.5 cm tall) were used due to the limited amount of available control soil (incubation series with 2; CS2 and HA2). Pot drainage holes were covered with a nylon mesh fabric to retain soils in the pots. The durations of soil pot incubation experiments and the designations for each soil pot types are shown in Table S1.

The soil moisture content was maintained gravimetrically at 10% (w w<sup>-1</sup>) by replenishing with deionized (DI) water from mass loss measurement every 1–5 days. After 18–42 days of incubation (Table S1), ~1.3 pore volumes of deionized H<sub>2</sub>O were added to the pots (single addition) to simulate rainfall and the drainage water was collected in a container as a single composite sample. For the last incubation experiment (i.e., CS2, HA2, and SC), a second infiltration event was simulated on day 63. These leachate samples from each pots were collected until free-drainage ceased over a 30 h period and later weighed. All leachate samples were analyzed for electrical conductivity, pH, nutrients and metals (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Ni, P, and Zn) and inorganic nitrogen and phosphorus species (NH<sub>4</sub>-N, NO<sub>2</sub>-N, NO<sub>3</sub>-N, PO<sub>4</sub>-P). The leachate samples

except for the first incubation conducted during 8/7/09 to 9/30/09 were also analyzed for chemical oxygen demand (COD). Soil samples from the initial set up of each pot along with the samples at incubation termination were analyzed for pH, cation exchange capacity (CEC), and plant-available nutrients. The surface chemical compositions of both virgin and incubated pyrochar and hydrochar were also analyzed with X-ray photoelectron spectroscopy (XPS).

### 2.3. $\text{KNO}_3$ adsorption isotherm experiments

Sorption capacity of hydrochar (A) for  $\text{NO}_3\text{-N}$  was determined by shaking  $\text{KNO}_3$  (20 mL) + hydrochar (0.5 g) mixtures for 24–48 h. Initial concentration of  $\text{KNO}_3$  ranged from 0.35 to 3464  $\text{mg-N L}^{-1}$ , providing 0 to 138.6  $\text{mg NO}_3\text{-N g}^{-1}$  hydrochar. These rates were designed to represent the range of  $\text{mg-N g}^{-1}$  in the amended soils. For example, the total N in the soil was about 56.1  $\text{mg-N g}^{-1}$  hydrochar in incubation HA1.

### 2.4. Physical and chemical analyses

The BET (Brunauer–Emmett–Teller) surface areas of amendments were measured via  $\text{N}_2$  adsorption multilayer theory using a Nova 2200e surface area analyzer (Quantachrome, Boynton Beach, FL). The total carbon and total combustible nitrogen contents of both control and amended soils were measured using either a LECO TruSpec CN analyzer (LECO Corp., St. Joseph, MI) or a vario MAX CNS analyzer (Macro Elementar Analyzer, Hanau, Germany). The volatile matter (VM) was determined using a thermogravimetric analyzer (TGA/DSC1; Mettler Toledo International Inc., Columbus, OH) following a recommended method in Cantrell et al. (2010); and fixed carbon content was determined (following ASTM D 3172) as the difference between 100% and the sum of VM and ash (ASTM, 2006). The leachate pH and electrical conductivity were measured using a standard pH and a conductivity meter. Nutrients and metals of leachate samples were determined using inductive coupled plasma atomic emission spectroscopy (ICP-AES). Inorganic nitrogen and phosphorus species,  $\text{NH}_4\text{-N}$ ,  $\text{NO}_2\text{-N}$ ,  $\text{NO}_3\text{-N}$ , and  $\text{PO}_4\text{-P}$  in the leachate samples were measured according to the Standard Method 4500- $\text{NH}_3\text{ G}$ , 4500- $\text{NO}_3\text{ F}$ , and 4500- $\text{P F}$  (APHA, 1998). The concentrations of  $\text{K}^+$  and  $\text{NO}_3\text{-N}$  of the  $\text{KNO}_3$  adsorption isotherm samples were measured with an ion chromatography (Thermo Fisher Dionex ICS 2000, Sunnyvale, CA) according to the ASTM Standards D4327-11 and D6919-09 (ASTM, 2009, 2011). Initial and final incubated soil samples were analyzed by the Clemson University Soil Testing Laboratory (<http://www.clemson.edu/agsrvib/interest.htm>). The Clemson laboratory measured the pH of the soil samples using deionized  $\text{H}_2\text{O}$  and determined plant-available nutrients using Mehlich-1 ( $\text{HCl} + \text{H}_2\text{SO}_4$ ) extracting solution. Cations in the

extraction solution were measured by ICP and the cationic exchange capacity (CEC) was determined by summation. Surface elements of the virgin and weathered (after incubation) pyrochar and hydrochar samples were determined using XPS. All XPS spectra were collected on a ThermoScientific ESCALB 250 instrument at the University of Oregon. Pass energy was 150 eV for survey scans and 20 eV for “multiplex” (composition) scans using monochromatized Al X-ray source and a 500  $\mu\text{m}$  spot size. Binding energy scales were adjusted in spectra plots (Hydrocarbon C1s = 284.8 eV) and an electron flood source used for charge neutralization.

### 2.5. Statistics

Statistical results included means, standard deviations, analysis of variance (ANOVA), and least significant difference at a 0.05 probability level ( $\text{LSD}_{0.05}$ ) for multiple paired comparisons among means using statistical software GraphPad Prism (GraphPad Software, Inc., La Jolla, CA).

## 3. Results and discussion

### 3.1. Soil amendment characteristics

A significant portion of volatile matter (VM) of the raw swine solids was removed by HTC (Table S2). This processing decreased VM from 68.5% to 38.0% due to a decrease in carbohydrates and proteins/peptides (Cao et al., 2011, 2013). Washing the hydrochar with acetone further decreased the VM to 28.6%, reflecting a decrease in sorbed organic compounds present on the hydrochar (Spokas et al., 2011) as well as decreases in the abundances of O-alkyls, NCH, and  $\text{COO/N-C=O}$  moieties (Cao et al., 2011). Traditional dry pyrolysis produced pyrochar with the lowest VM (16.3%). As the severity of carbonization condition increased, VM contents decreased with an increase in fixed carbon and ash contents. Interestingly, the commercial swine compost had higher VM than hydrochar, but the lowest total C content (Table S2). A slight decrease in N was observed for all soil amendments compared to the raw swine solids. The BET surface areas ranged from 0.7 to 4.2  $\text{m}^2/\text{g}$  amendment. These low BET surface areas are typical in non-activated chars. The slightly higher BET surface area for the hydrochar (A) was probably due to the loss of surface labile carbon from acetone washing, which freed up some pore space.

### 3.2. Soil fertility

The addition of swine manure-based amendments increased soil pH, CEC, C, and N in all treatments as shown in Table 1a.

**Table 1a**  
Initial soil fertility.

Sample	Soil pH	%		C/N	mg/kg					CEC ( $\text{cmol kg}^{-1}$ )	
		C	N		P	K	Ca	Mg	Zn		Mn
CS1	5.2 (0.1)	0.55 (0.02)	0.06 (0.00)	9.17 (0.04)	33 (0)	47 (1)	200 (8)	44 (1)	3.3 (0.1)	9.5 (0.1)	3.1 (0.0)
HW1A	5.9 (0.2)	1.50 (0.05)	0.11 (0.00)	13.64 (0.03)	607 (31)	77 (3)	830 (40)	364 (11)	16.3 (0.1)	34.7 (0.6)	9.0 (0.5)
CS1*	5.0	0.61 (0.02)	0.06 (0.00)	10.17 (0.03)	52	54	279	68	4.5	11.0	3.7
HW1B	5.5	1.39 (0.06)	0.12 (0.00)	11.58 (0.04)	610	72	841	353	19.4	36.0	9.0
PC	6.7	1.36 (0.06)	0.10 (0.00)	13.60 (0.04)	867	420	852	569	22.2	37.0	11.5
RS	5.6	0.62 (0.03)	0.06 (0.01)	10.33 (0.17)	118	93	303	101	10.4	13.5	4.3
HA1	7.0	1.01 <sup>#</sup>	0.11 <sup>#</sup>	9.18 <sup>#</sup>	1153	115	1369	632	33.9	54.5	13.5
CS2	5.0	0.56 (0.04)	0.05 (0.00)	11.20 (0.07)	38	60	288	64	4.6	12.5	4.1
HA2	5.6 (0.0)	1.45 (0.12)	0.11 (0.01)	13.18 (0.12)	957 (6)	103 (0)	1266 (3)	523 (4)	18.0 (0.1)	49.3 (0.4)	12.8 (0.1)
SC	5.7 (0.0)	0.94 (0.04)	0.11 (0.01)	8.55 (0.10)	610 (23)	166 (4)	1042 (29)	350 (13)	48.1 (1.0)	20.8 (0.4)	10.6 (0.3)
$\text{LSD}_{0.05}$	0.4	–	–	0.16	45	7	59	19	0.4	0.9	0.8

\* Incubation of control soil (CS1) with HW1B;  $\text{LSD}_{0.05}$  = least significant difference value for comparison of any two means (except single values) within the same column.

<sup>#</sup> Calculated using C and N contents of hydrochar (A) in Table 2.

**Table 1b**  
Final soil fertility.

Sample	Soil pH	%		C/N	mg/kg						CEC (cmol kg <sup>-1</sup> )
		C	N		P	K	Ca	Mg	Zn	Mn	
CS1	5.4 (0.0)	0.55 (0.02)	0.05 (0.00)	11.00 (0.04)	34 (6)	33 (1)	161 (6)	34 (3)	3.2 (0.4)	9.0 (0.5)	2.4 (0.0)
HW1A	6.4 (0.1)	1.55 (0.04)	0.11 (0.01)	14.09 (0.09)	696 (25)	64 (2)	966 (38)	395 (16)	43.0 (0.9)	36.8 (1)	9.3 (0.6)
CS1*	5.2 (0.1)	0.56 (0.03)	0.05 (0.01)	11.20 (0.21)	43 (15)	42 (2)	247 (21)	52 (8)	4.8 (0.8)	7.5 (1.0)	3.5 (0.1)
HW1B	6.3 (0.0)	1.26 (0.07)	0.09 (0.01)	14.00 (0.12)	769 (47)	75 (2)	1059 (49)	444 (21)	46.8 (2.4)	37.5 (2.3)	10.5 (0.5)
PC	6.9 (0.1)	1.34 (0.09)	0.10 (0.01)	13.40 (0.12)	853 (27)	290 (25)	889 (19)	535 (21)	32.2 (0.8)	37.3 (0.3)	10.8 (0.4)
RS	5.4 (0.1)	0.61 (0.05)	0.06 (0.00)	10.17 (0.08)	114 (3)	57 (3)	277 (3)	80 (3)	11.9 (0.5)	10.2 (0.8)	3.6 (0.2)
HA1	6.4 (0.1)	1.32 (0.08)	0.10 (0.00)	13.20 (0.06)	1077 (41)	108 (7)	1256 (42)	619 (26)	62.2 (0.2)	47.5 (2.2)	13.0 (0.4)
CS2	5.3 (0.1)	0.52 (0.01)	0.04 (0.00)	13.00 (0.02)	36 (2)	29 (1)	220 (11)	36 (2)	4.3 (0.2)	7.5 (0.7)	3.1 (0.1)
HA2	6.7 (0.1)	1.30 (0.06)	0.09 (0.01)	14.44 (0.12)	1071 (18)	73 (1)	1411 (15)	560 (6)	53.6 (1.6)	49.5 (0.7)	13.3 (0.1)
SC	5.9 (0.1)	0.94 (0.03)	0.09 (0.00)	10.44 (0.03)	469 (21)	81 (2)	933 (42)	207 (8)	46.5 (1.7)	15.5 (0.7)	8.4 (0.0)
LSD <sub>0.05</sub>	0.2	–	–	0.27	78	28	86	44	3.5	2.7	0.9

\* Incubation of control soil (CS1) with HW1B; LSD<sub>0.05</sub> = least significant difference value for comparison of any two means within the same column.

**Table 2**  
Nutrients in leachate samples.

	Leaching (days)	pH	EC * 1000 dS m <sup>-1</sup>	Standard methods (mg L <sup>-1</sup> )					ICP-AES (mg L <sup>-1</sup> )			
				PO <sub>4</sub> -P	NH <sub>4</sub> -N	NO <sub>2</sub> -N	NO <sub>3</sub> -N	COD	K	P	Ca	Mg
CS1	15	4.8 (0.0)	784 (36)	ND	13.3 (0.6)	ND	76.5 (3.4)	–	34.9 (0.5)	0.6 (0.1)	44.2 (1.7)	23.0 (0.7)
HW1A	15	5.9 (0.1)	486 (111)	14.0 (4.4)	ND	ND	18.5 (3.2)	–	25.9 (6.0)	14.9 (4.7)	11.4 (2.2)	34.2 (8.2)
CS1*	18	5.1 (0.0)	1058 (58)	ND	9.1 (1.0)	ND	82.9 (2.9)	116 (8)	40.6 (1.7)	0.4 (0.1)	66.2 (1.8)	34.6 (0.8)
HW1B	18	5.5 (0.2)	304 (84)	4.4 (1.1)	0.2 (0.3)	ND	6.0 (4.5)	153 (48)	16.4 (2.6)	7.5 (1.2)	8.0 (2.0)	20.0 (4.8)
HA1	38	7.1 (0.1)	130 (30)	9.6 (1.7)	ND	ND	2.4 (1.2)	20 (0)	15.0 (3.5)	9.7 (1.8)	1.7 (0.2)	8.8 (2.0)
PC	34	7.3 (0.0)	3064 (139)	104.7 (6.0)	21.6 (1.4)	ND	74.9 (10.5)	690 (172)	447.8 (17.3)	96.5 (5.5)	10.5 (0.6)	83.3 (3.2)
RS	34	6.0 (0.1)	1137 (26)	9.0 (0.7)	12.5 (0.3)	ND	86.0 (2.8)	400 (35)	84.8 (2.1)	9.8 (0.6)	49.3 (1.3)	61.5 (2.1)
CS2	42	5.7 (0.2)	1100 (26)	0.6 (0.0)	24.9 (1.1)	ND	135.1 (4.2)	138 (17)	53.4 (1.8)	0.4 (0.2)	85.6 (1.8)	44.4 (1.3)
HA2	42	6.8 (0.0)	520 (88)	17.3 (1.3)	1.8 (0.1)	0.4 (0.1)	37.3 (7.0)	195 (28)	42.8 (6.0)	19.2 (2.3)	10.1 (1.7)	48.2 (8.1)
SC	42	5.3 (0.0)	2573 (70)	96.2 (3.7)	2.4 (1.2)	ND	294.6 (10.6)	330 (21)	159.6 (4.6)	100.3 (1.2)	140.5 (1.5)	225.6 (4.5)
CS2 <sup>#</sup>	63	5.2 (0.0)	157 (40)	0.9 (0.1)	1.9 (0.7)	ND	17.8 (5.6)	45 (10)	10.5 (1.6)	1.1 (0.1)	16.0 (4.0)	7.5 (2.1)
HA2 <sup>#</sup>	63	6.7 (0.1)	457 (45)	25.4 (1.3)	0.6 (0.1)	ND	25.0 (5.0)	160 (22)	35.2 (2.3)	29.6 (1.6)	10.0 (0.9)	50.3 (2.9)
SC <sup>#</sup>	63	5.8 (0.0)	329 (20)	77.6 (2.3)	ND	ND	13.2 (2.7)	173 (34)	44.8 (2.0)	80.2 (2.9)	24.0 (1.2)	32.6 (2.0)
LSD <sub>0.05</sub>	–	0.2	191	5.2	1.9	–	16.1	157	16.4	7.1	5.4	11.8

\* Incubation of control soil (CS1) with HW1B.

<sup>#</sup> Second leachate samples; LSD<sub>0.05</sub> = least significant difference value for comparison of any two means within the same column.

Among these, raw swine solid (RS) increased soil CEC the least (from 3.1 to 4.3 cmol kg<sup>-1</sup>), while pyrochar (PC), swine compost (SC), and both hydrochars (HW1, HW2, HA1, and HA2) significantly increased CEC. These amendments also increased C and N contents of soil. Addition of these swine manure-based amendments also dramatically increased Mehlich-1 extractable nutrients P, K, Ca, Mg, Zn, and Mn. There was a somewhat benign increase in nutrients (N, P, Ca, Mg, Zn, and Mn) with the RS soil amendment because the amount of raw swine solid applied was only 4.3 g kg<sup>-1</sup>, one fifth that of the other amendments as shown in Table 1a. The CEC and the high nutrient contents of these soils treated with swine manure-based amendments were mostly maintained even after incubation except for the RS amendment (Table 1b). These results demonstrate that the swine manure-based amendment should improve soil fertility. Besides increasing the plant macro nutrients (N, P, and K), these amendments also increased soil micro nutrients such as Zn. More importantly, these amendments increased the Norfolk CEC capability almost 3-fold. This is especially important for the Norfolk soil, which is a highly weathered ultisol commonly used for crop production in the coastal plain region of the South East of U.S. (Busscher et al., 2007).

### 3.3. Leachate water quality

The leachate sample concentrations of most heavy metals (i.e., Cd, Cr, Cu, Ni, Pb) regulated under the Code of Federal Regulation Title 40 part 503 (40 C.F.R. §503) were below detection limits for

all treatments. A low concentration of Zn was detected in the control soil CS2 (0.3 mg/L). Most amended soils produced leachates with Zn concentration below detection level. Chemical oxygen demands (COD) of leachate samples ranged from 20 to 690 mg/L: Leachates from pyrochar amended soils (PC) showed the highest COD while hydrochar amended soils (HA1) produced leachates with the lowest COD. Except with HA2 with slightly higher COD, both controls (CS1\* and CS2) and hydrochar amended soils (HW1B and HA1) produced statistically similar COD values in their respective leachates. In terms of oxygen demanding characteristics, the leachates from hydrochar amended soils were cleaner than other amended soils.

The nutrient concentrations in the leachate samples revealed some interesting differences among different swine manure-based amendments (Table 2 and Fig. 1). Similar to the study by Novak et al. (2014), the P concentration in the PC (pyrochar) leachate was very high, almost an order of magnitude higher than that from control soil (CS1). In contrast, the hydrochar amended soils (HW1A, HW1B, HA1, and HA2) showed only moderate increases in P concentration in the leachates despite the fact that both swine pyrochar and hydrochars showed very high Melich-1 extractable P of similar magnitude (Fig. 1). The mass percentage of P leached (i.e., mass of P in the leachate sample/total mass of P in the soil) from hydrochar amended soils were significantly lower than that from pyrochar amended soils (Table S3). Swine compost amended soil showed the highest P leaching potential. This finding suggests that the swine manure-based hydrochar

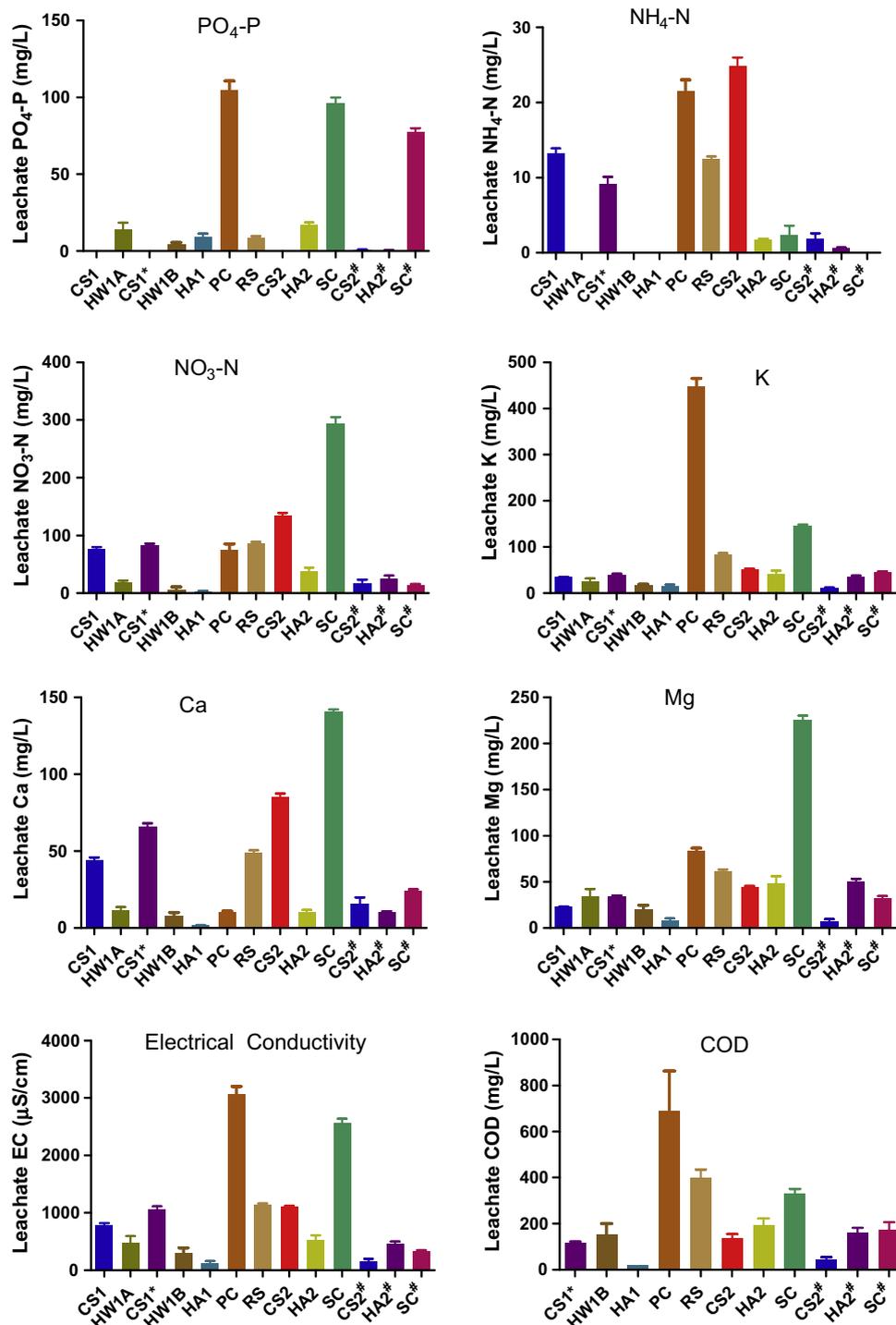


Fig. 1. Concentration of various nutrients, electrical conductivity, and chemical oxygen demands of leachate samples (sample ID corresponds to that of Table 1).

can be applied to soils proximal to CAFOs without creating environmental problems associated with biochar releasing soluble P into soil pore water and subsequently contaminating groundwater.

Nitrate is another nutrient that leached very differently from pyrochar vs. hydrochar amended soils. While similar  $\text{NO}_3\text{-N}$  concentrations were found in the leachates from the control soils and those amended with PC and RS, substantially lower  $\text{NO}_3\text{-N}$  concentrations were found in the hydrochar amended soils (HW1A, HW1B, HA1, and HA2). Interestingly, reduction in soil  $\text{NO}_3$  concentrations was reported with plant-based hydrochars (Bargmann et al., 2014). They found that the hydrochar

amendments with high C:N ratio (around 40) such as those made from beet-root chips generally reduced the crops' N content, while the hydrochars made from spent brewer's grains with low C:N ratios (less than 16) had no significant effect on the N content. In contrast, all our swine-manure based amendments had low C:N ratios (9–14). Furthermore, the HTC technology used to produce their hydrochars was different. Their hydrochars were made by the Revatec Company using the patented hydrothermal carbonization technique in a steam medium (Cao et al., 2013). Cao et al. (2013) reported that the steam-medium bark hydrochar showed significantly more biodegradability than the water-medium bark

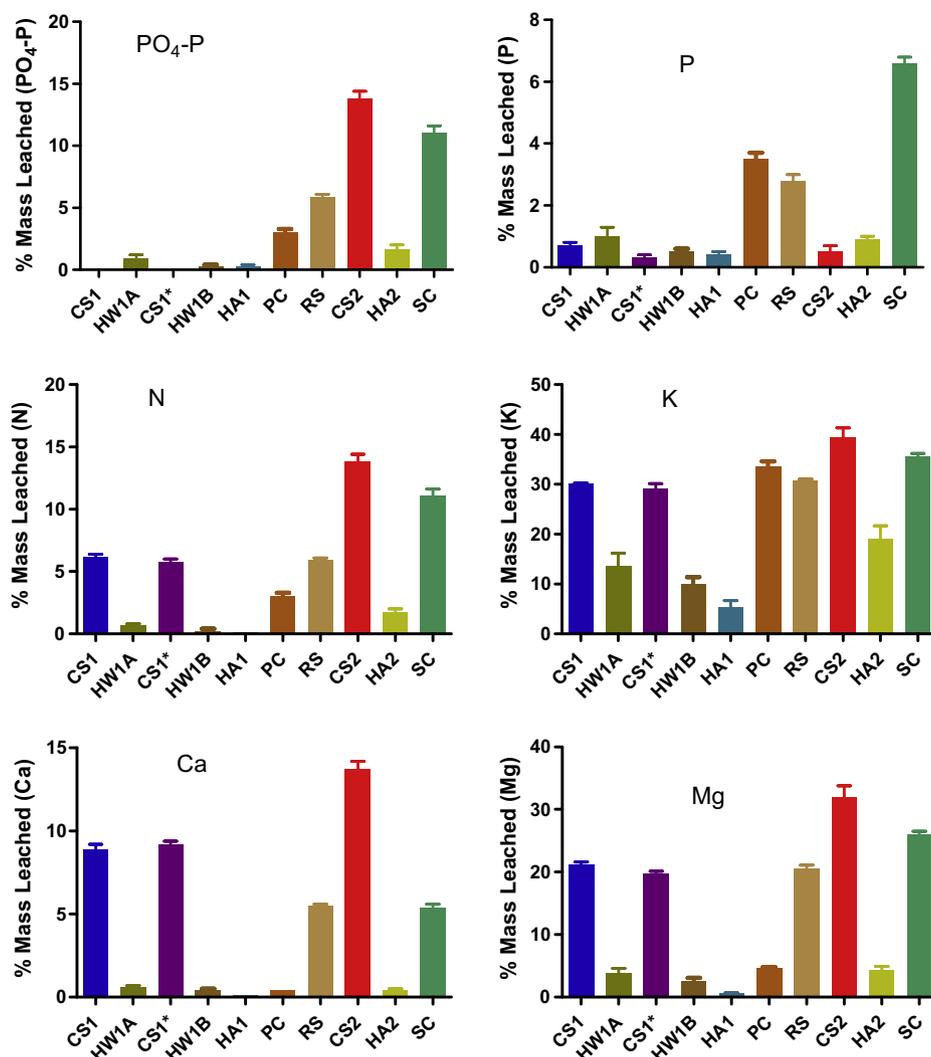


Fig. 2. % Mass recovered in the leachate samples (sample ID corresponds to that of Table 1).

Table 3

Carbon bond configurations and estimated surface chemical compositions of virgin and weathered pyrochars and hydrochars (percentage of total elements detected).

	C–C/C–H	C–O	C=O	O–C=O	Ctotal	O	Si	K	N
Hydrochar (A)	69.4	7.8	1.9	0.6	80.9	13.7	ND <sup>#</sup>	ND	2.8
Hydrochar (A) <sup>*</sup>	27.3	9.6	4.3	5.0	47.5	36.8	5.4	ND	2.6
Pyrochar	63.8	14.3	2.9	1.2	83.3	9.9	ND	0.4	2.8
Pyrochar <sup>*</sup>	28.8	8.4	4.0	4.0	46.7	36.8	4.7	ND	1.9

<sup>\*</sup> Weathered biochars.

<sup>#</sup> ND = not detected.

hydrochar due to deeper carbonization by water-medium HTC. Deeper carbonized biochars have more fused aromatic functionalities and less volatile matter. This may partly corroborate with the hypothesis of Bargmann et al. (2014) that the soil N immobilization by their hydrochar was likely caused by microbial immobilization especially with high C:N ratios.

Furthermore, microbial N immobilization alone does not explain consistently lower electrical conductivities of all our hydrochar amended soils (Fig. 1). All our hydrochars showed distinctive characteristics in increasing soil's capacity to retain both cations (K, Ca, Mg, NH<sub>4</sub>) and anions (NO<sub>3</sub>, PO<sub>4</sub>). Table S3 and Fig. 2 show such low leaching potentials of hydrochar amended soils for both cations and anions. In fact, the electrical conductivity

(EC) of the hydrochar amended soil leachates (0.130–0.520 dS m<sup>-1</sup>) were substantially lower than that from the control, PC, RS, and SC treatments (0.784–3.064 dS m<sup>-1</sup>). The EC of both control soil CS2 and swine compost (SC) were considerably lowered at the second leaching, from 1.100 to 0.157 dS m<sup>-1</sup> and 2.573 to 0.329 dS m<sup>-1</sup>, respectively, representing the loss of ionic species over the 63 days of incubation. Interestingly, only a slight reduction in EC was observed for the second leaching of hydrochar amended soil (HA2), from 0.520 to 0.457 dS m<sup>-1</sup>.

It appears that the hydrochar amended soils showed high plant available nutrients (via Mehlich-1 extraction) while the leachates still contained very low concentrations of these nutrients. These characteristics would make the swine hydrochar a good candidate

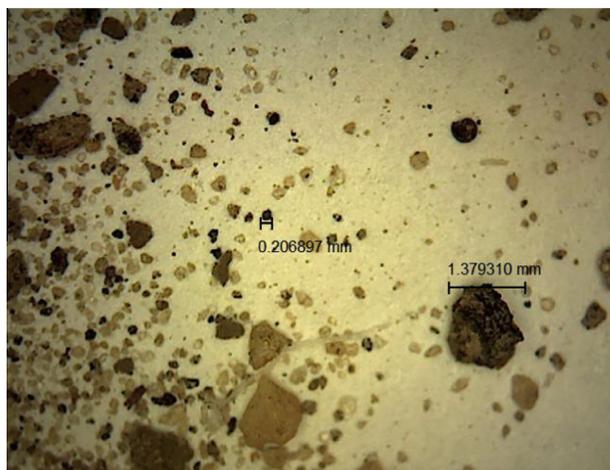


Fig. 3. Microscopic view of incubated soil HA1.

for improving soil fertility while reducing water pollution potential from leaching. Although crop yield is a commonly reported benefit of adding biochar to soils, experimental results are variable and dependent on the experimental set-up, soil properties, and conditions (Jeffery et al., 2011). More in-depth studies of the plant availability of these nutrients and crop yields are needed to further substantiate the swine hydrochar's agricultural and environmental.

#### 3.4. Adsorption of K and $\text{NO}_3$ on hydrochar's surface?

Recognition of the high  $\text{NO}_3$  and K retention characteristics of hydrochar amended soil prompted us to further investigate whether these compounds were actually adsorbed on the hydrochar's surface or not. Adsorption isotherm experiments using 0.5 g of hydrochar (A) in various concentrations of  $\text{KNO}_3$  solution were conducted. In addition, the surface concentration of these elements were analyzed using X-ray photoelectron spectroscopy (XPS). The initial  $\text{NO}_3\text{-N}$  concentrations with 0.5 g hydrochar ranged from 0.02 to  $138.6 \text{ mg NO}_3\text{-N g}^{-1}$  hydrochar (Table S4). At lower initial concentrations of  $\text{KNO}_3$  ( $<10.8 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$ ), there was no adsorption of  $\text{NO}_3\text{-N}$  on the hydrochar. Without any  $\text{KNO}_3$  in the solution, the hydrochar actually dissolved K into solution (i.e.,  $-1.34 \text{ mg-K g}^{-1}$  hydrochar). At higher initial  $\text{KNO}_3$  concentrations ( $>108 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$ ),  $\text{NO}_3\text{-N}$  sorptions were slightly negative, while K sorptions fluctuated between positive and negative numbers. However, these differences were within the uncertainty of the IC measurements as the samples had to be diluted up to 1000 times for the high  $\text{KNO}_3$  concentrations. Therefore, the uncertainties in concentration were amplified up to 1000 times. The results of this sorption experiment suggested that the hydrochar does not have any unique or specific sorption capacity for K and  $\text{NO}_3\text{-N}$ .

In addition to the sorption experiment, we investigated whether we could observe the presence of accumulated K and N on the surface of both pyrochar and hydrochar after incubation. The surface chemical characteristics of both virgin and weathered pyrochar and hydrochars were analyzed with XPS (Table 3). The weathered char particles were hand-picked from the soils after termination of incubation experiments. Fig. 3 shows the microscopic view of the HA1 soil after incubation experiment. Some of hydrochar particles were agglomerated with soil particles (the big particle with 1.38 mm diameter), while others existed as individual particles (the small particle with 0.2 mm diameter). The surface chemical compositions of both weathered pyrochar and hydrochar (Table 3) showed an increase in oxygenated carbon compounds

such as alcohols, ketones, and carboxylates, while alkyl compounds substantially decreased probably due to microbial degradation (Joseph et al., 2010). The XPS scan also revealed a significant percentage of Si that was incorporated onto weathered surfaces of the char particles. Soluble aluminosilicates and other oxides/hydroxides species exist as charge colloids into the pore water of Ultisols (Kaplan et al., 1995). These mobile colloids are electrostatically attracted to the surfaces of char particles since they are coated with negatively charged organic species such as carboxylates (Solomon et al., 2012; Joseph et al., 2013). The oxide coating can accumulate and are theorized as forming a layer that regulate further reactions on char surfaces (Joseph et al., 2013). Comparison of the surface chemical compositions of virgin and weather char particles shows no direct evidence that either K or N accumulated on the surface of weathered char particles. Based on both the adsorption experiment and the XPS analyses, it is clear that K and N were not directly sorbed on the hydrochar surface. Although it is not clear how both cationic and anionic nutrients were retained in the soil amended with hydrochar, the ability of the swine hydrochars to retain these plant-available nutrients in the soil matrix makes them environmentally and agronomically favorable soil amendments. More in-depth study of hydrochar's ability to retain nutrients in soil and the underlying mechanisms is still needed before successful field implementation is realized.

#### 4. Conclusions

Four forms of swine manure-based soil amendments (raw, compost, hydrochar, pyrochar) were evaluated for their effect on the soil fertility and leachate water quality characteristics in sandy soil. All amendments provided organic C and increased the soil CEC. Because raw swine manure contains high concentrations of nutrients such as N, P, K, all four forms of amendments substantially increased the nutrient contents of the soil. Analysis of leachate following soil incubations showed that hydrochar amended soil released much lower concentrations of soluble N, P, K. Pyrochar amended soil released over ten times more K, four times more P and double the N concentration than hydrochar. Even the control soil released more N than the hydrochar amended soil. It appeared that the hydrochar increased both CEC and AEC of the soil, but subsequent testing of K, N adsorption isotherms and surface analysis via XPS suggested that these nutrients were not accumulated on the hydrochar surface. It is not clear at this time how these were retained in the soil incubations, but the complex surface functionality of the hydrochar might interact with soil and produce conditions conducive to nutrient retention. Although it is still not clear how these nutrients were retained in the soil amended with hydrochar, it suggests a great potential for hydrochar as an alternative manure management option as the char can be applied to land nearby at high dose (in this case 2%) without creating potential environmental pollution problems from the leaching of high nutrient concentrations to water bodies.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2015.05.023>.

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