



## 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.

### ARTICLE INFO

#### Article history:

Received 18 December 2014

Received in revised form 25 April 2015

Accepted 8 May 2015

Available online 27 May 2015

#### Keywords:

Hydrochar

Swine manure

Leachate water quality

Soil amendment

Soil fertility

### 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.

Published by Elsevier Ltd.

### 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

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