Phosphorus release behaviors of poultry litter biochar as a soil amendment

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HIGHLIGHTS

- The predominant portion of P in poultry litter biochar is water insoluble.
- Poultry litter P was immobilized by forming Ca/Mg (pyro)phosphates in biochar.
- Release of P from biochar was slower and steadier than from raw poultry litter.
- Soil pH greatly influenced the P release patterns of poultry litter biochar.
- Soil amendment with biochar instead of poultry litter would reduce P runoff risks.

ARTICLE INFO

ABSTRACT

Phosphorus (P) may be immobilized and consequently the runoff loss risks be reduced if poultry litter (PL) is converted into biochar prior to land application. Laboratory studies were conducted to examine the water extractability of P in PL biochar and its release kinetics in amended soils. Raw PL and its biochar produced through 400 °C pyrolysis were extracted with deionized water under various programs and measured for water extractable P species and contents. The materials were further incubated with a sandy loam at 20 g kg^{-1} soil and intermittently leached with water for 30 days. The P release kinetics were determined from the P recovery patterns in the water phase. Pyrolysis elevated the total P content from 13.7 g kg^{-1} in raw PL to 27.1 g kg^{-1} in PL biochar while reduced the water-soluble P level from 2.95 g kg^{-1} in the former to 0.17 g kg^{-1} in the latter. The thermal treatment transformed labile P in raw PL to putatively Mg/Ca phosphate minerals in biochar that were water-unextractable yet proton-releasable. Orthophosphate was the predominant form of water-soluble P in PL biochar, with condensed phosphate (e.g., pyrophosphate) as a minor form and organic phosphate in null. Release of P from PL biochar in both water and neutral soils was at a slower and steadier rate over a longer time period than from raw PL. Nevertheless, release of P from biochar was acid-driven and could be greatly promoted by the media acidity. Land application of PL biochar at soil pH-incorporated rates and frequency will potentially reduce P losses to runoffs and minimize the adverse impact of waste application on aquatic environments.

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1. Introduction

The U.S. poultry industry generates more than 11 million tons of litter wastes annually (Gollehon et al., 2001). Poultry litter (PL) contains high levels of organic carbon (OC), nitrogen (N), phosphorus (P), potassium (K), and other plant nutrients and is commonly applied to cropland as a soil amendment (Guo et al., 2009). In concentrated poultry production regions such as Delmarva Peninsula, however, repeated and excess application of PL to limited acreage of land has resulted in severe nutrient accumulation in soils and subsequent runoff and leaching losses to water bodies, causing water eutrophication and quality degradation (Boesch et al., 2001; DNREC, 2006).

Poultry litter has an average P:N ratio of 1:2, far greater than the typical crop removal rate of 1:6 (MSU Extension, 2011). Land application of PL at rates based on crop N requirements would furnish vastly excessive P and increase the risk of P input to natural waters (Harmel et al., 2004). Studies have indicated that losses of P from land-applied animal manure are determined primarily by the content of water-soluble P (Shreve et al., 1995; Hart et al., 2004). As an example, 12–20% of the P in PL

was water-soluble and was lost within five rain events following land application (Guo et al., 2009). It would be advantageous to reduce the rate of P losses by converting PL into a more stable, slow-release source of nutrients. This would be an effective strategy to maintain a more constant and longer-term supply of nutrients in soil, preventing rapid nutrient losses in runoff and hence reducing the risk of eutrophication.

A potential approach to implement this strategy is to transform PL through pyrolysis and use the biochar produced as a soil additive. In recent years, biochar prepared from excess biomass has been suggested as a stable medium for long-term carbon storage (Lehmann, 2007), a beneficial by-product of bio-oil and syngas production (Ro et al., 2010; Guo et al., 2012), a feasible means to reduce volume and mass of organic wastes (Cantrell et al., 2007), and a soil amendment to not only improve soil quality and crop yield but potentially decrease emissions of greenhouse gases from soil (Lehmann and Joseph, 2009; Chintala et al., 2014a). For PL, conversion to biochar may also slow down nutrient release and thus minimize the environmental impacts of the poultry industry. As suggested by a recent study by Song and Guo (2012), conversion of PL into biochar through slow pyrolysis at ≥ 350 °C decreased the fraction of water-soluble P from 19.5% to below 6.9%. Pyrolysis of cattle manure (9.1 g P kg^{-1}) at ≥ 350 °C reduced this fraction from 10.2% to 0.21% (Cao and Harris, 2010). Thermal treatments of sewage sludge (26 g P kg^{-1}) at 400–800 °C in the presence of N_2, CO_2, or air altered the fraction from 20.7% in the feed to <2.5% in the resulting char/ash products (Qian and Jiang, 2014). Chintala et al. (2014b) found that merely 0.34–0.51% of the total P (1.9–2.0 g kg^{-1}) in biochars derived from corn stover and switchgrass was 0.5 M NaHCO$_3$-extractable. Due to the richness of Ca^{2+} and Mg^{2+} (12–13 g kg^{-1}) in the ash components, the corn stover and switchgrass biochars even demonstrated significant sorption capacities for P in aqueous solutions.

While the above result is encouraging, the overall lability and release dynamics of P in PL biochar as a soil amendment – which determine the rates of P supply for crops and the risk to contaminate water following land application – has not been well-characterized. This study was undertaken to evaluate the P water extractability of PL biochar, to characterize the P release kinetics of the material as a soil amendment, and to explore the mechanism for P immobilization during pyrolysis.

2. Materials and methods

2.1. Preparation of soil and PL biochar

The soil used in the experiments was Sassafras sandy loam (fine-loamy, siliceous, semiactive, mesic Typic Hapludults) collected from the top 20 cm of a Delaware cropland on which soybean, corn, and winter wheat were growing in rotation. The soil was air-dried, ground to pass a 2-mm sieve, and evaluated for fertility characteristics. It contained 55.4 mg kg^{-1} Mehlich-III extractable P and 0.22 mg kg^{-1} water soluble P. Selected physical and chemical properties of the soil are given in Table 1.

Granular PL was obtained from Perdue AgriRecycle, Inc. (Seaford, DE), where raw PL collected from local poultry houses was milled, pelletized, dried at 80–110 °C, and broken into <6 mm granules. The material contained 28.5% of mineral ash, 35.5% of organic carbon, 3.07% of N, and 1.51% of P on the dry mass basis. Detailed chemical composition of the material can be found in Table 1 of Song and Guo (2012). To produce biochar, the PL granules were packed in a 15 cm (D) × 21 cm (H) galvanized iron container and heated in a muffled furnace at 400 °C. There was a 0.5-cm hole in the center of the container lid, allowing vapors to escape but maintaining an air-absent environment in the container during pyrolysis. The continuous emission of volatile vapors from inside the container through the small hole in the lid prevented possible diffusion of air into the container, creating an oxygen-free condition for pyrolyzing the PL. The pyrolytic heating lasted for approximately 8 h until no visible smokes were emitted. After pyrolysis, the container was immediately sealed by plugging the lid hole and cooled to room

Table 1
Basic physical and chemical properties of the Sassafras loam soil. Values are dry mass-based means of triplicate measurements with coefficients of variation less than 2%.

Parameter	Value
Particle size composition	Sand 470 g kg^{-1}, silt 480 g kg^{-1}, clay 50 g kg^{-1}
pH[a]	6.5
EC[a], dS m^{-1}	0.12
Organic matter content, g kg^{-1}	32.1
CEC[b], cmol$_c$ kg^{-1}	11.6
Total N, mg kg^{-1}	88.5
Mehlich-III P, mg kg^{-1}	55.4
Water soluble nutrients[c], mg kg^{-1}	
NO$_3$-N	5.92
NH$_4$-N	0.22
PO$_4$-P	0.22
SO$_4^{2-}$	17.5
K$^+$	23.8
Ca^{2+}	18.2
Mg^{2+}	7.5

[a] Measured in 1:1 soil/water paste.
[b] Cation exchange capacity.
[c] Soil was extracted with deionized water at room temperature under shaking for 24 h.

temperature. The black charcoal-like solids in the container were PL biochar, with a yield 51.5% of the raw PL on the dry mass basis. The PL biochar was transferred into an airtight bucket and stored at 22 °C for several weeks prior to use. A more detailed description of the pyrolysis process and conditions has been provided elsewhere (Song and Guo, 2012).

2.2. Characterization of PL biochar

The PL biochar was analyzed for a variety of characteristics as a soil amendment. For comparison, the raw PL was also characterized. Both of the PL granules and biochar were ground to <2 mm to improve homogeneity. The pH and electrical conductivity (EC) of PL and biochar were measured in 24-h, 1:5 solid/water extracts with an Accumet AB15 pH meter (Fisher Scientific, Swannee, GA) and an Oakton CON510 conductivity/TDS meter (Oakton Instruments, Vernon Hills, IL). The liming capacity in CaCO$_3$ equivalency was determined following the indicator titrimetric methods (ASTM, 1999). Specific surface areas of PL and biochar (ground to <0.15 mm) were measured by the Brunauer–Emmett–Teller (BET) adsorption method with nitrogen gas, using a Nova 2000 Quantachrome Surface Area Analyzer (Boynton Beach, FL). Cation exchange capacity (CEC) was measured using the ammonium acetate extraction method (Hendershot et al., 2008). The cations (including both water soluble and exchangeable) extracted by 1.0 M ammonium acetate (pH 7.0) were analyzed by inductively coupled plasma (ICP) (IRIS Intrepid II XSP Duo View, Thermo Electron, Franklin, MA). Organic matter contents of PL and biochar were measured by the loss-on-ignition (LOI) method based on sample weight loss upon heating at 360 °C (Dean, 1974). Total organic carbon (OC) and nitrogen were determined by combustion using an Elementar Vario-Max CN Analyzer (Elementar Americas, Mt. Laurel, NJ), following procedures adopted from Peters (2003). For metal analysis, 2.0 g of PL or biochar and 20 mL of deionized (DI) water were placed in a 50-mL flask into which 0.4 mL of 12 M HCl was added. The PL and biochar samples were allowed to soak for 10 h and then heated in a muffle furnace at 425 °C for 8 h. The samples were mixed with an acidic persulfate solution and autoclave-digested at 121 °C for 45 min. The digested samples were then diluted and analyzed by ICP for Al, B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn concentrations. Water soluble OC, P, and N in the PL and biochar were measured in 72-h, 1:20 solid/water extracts. Extractable NH$_4^+$ and NO$_3^-$ were obtained by extracting the PL and biochar with 2.0 M KCl (1:10 w/v) for 15 min on a reciprocal shaker at 200 rpm, followed by colorimetric measurement using a Bran & Lubbe Technicon Auto Analyzer (Norderstedt, Germany).