1 Introduction

There is growing concern about the large amounts of manure being generated by large animal feeding operations and the potential hazard for water eutrophication and air quality. In many cases there is insufficient land available for spreading the manure at agronomic rates and the increasing scale of animal feeding operations which has caused accumulation of excess nutrients. The poultry industry in the US produces 576,436 t of nitrogen (N) and 276,932 t of phosphorus (P) representing an excess of 483,646 and 252,493 t respectively (Gollehon et al. 2001).

Thermochemical conversion (pyrolysis) might be one option to process poultry litter for renewable energy (synthesis gas and hydrocarbon fuels) and biochar (Cantrell et al. 2007; Schnitzer et al. 2007; Tagoe et al. 2008). Biochar is the residue and consists of minerals and fixed carbon (C). In comparison to common biological treatments like composting, pyrolysis of poultry litter is faster; requires less space and; destroys potential pathogens and most pharmaceutically active compounds and reduces gaseous emissions (Cantrell et al. 2007).

During the pyrolysis process important plant nutrients (P, K+, Ca2+, and Mg2+) are concentrated in the biochar (Gaskin et al. 2008). This might facilitate a more efficient nutrient recovery by reducing the costs associated with land application and transportation. But depending on pyrolysis temperature, some nutrients susceptible to volatilization such as N are partially lost during the process (Gaskin et al. 2008).

Research on biochar as a soil improver have shown beneficial effects on soil fertility apart from its nutrient content (Glaser et al. 2002; Lehmann et al. 2003; Steiner et al. 2007). Biochar has also received attention as a potential sink for atmospheric CO2 (Lehmann et al. 2006; Steiner 2007; Gaunt and Lehmann 2008), due to its recalcitrance against decomposition (Kuzyakov et al. 2009; Smith et al. 2010).

However, this recalcitrance seems to have implications to nutrient availability. Knicker et al. (2005) have shown that fire and carbonization can increase the N content.
of soil organic carbon, but the alterations in chemical structure have long-term consequences for N availability (Knicker and Skjemstad 2000). Yet Tagoe et al. (2008) found no difference in N uptake by crops if fertilized with carbonized or un-carbonized chicken manure. Soybean seed yield was higher on soils fertilized with carbonized chicken litter (based on equal N applications) due to the higher P content of carbonized chicken manure.

The extent to which the retained or concentrated elements in biochar are available for plants is unclear. A better understanding of biochar’s properties and how it affects soil fertility is needed before it can be more widely accepted for use in agriculture. Our objectives were to compare soil fertilization efficiency of carbonized chicken litter with both un-carbonized chicken litter and mineral fertilizer. We hypothesize that a large proportion of P, K⁺, Mg²⁺, and Ca²⁺ present in carbonized chicken litter are readily available to plants whereas N uptake is reduced in comparison to un-carbonized chicken litter and mineral N fertilization.

2 Materials and methods

2.1 Soil and soil amendments

Unfertilized sandy topsoil was collected at a farm near Athens (GA, USA). The soil was screened through 4 mm mesh into three separate bins. A subsample from each bin was analyzed for cation exchange capacity (CEC), pH, total and available nutrient (Mehlich I) and C content (shown in Table 1).

Poultry litter was obtained from a broiler house and carbonized in a batch reactor at a constant 500°C carbonization temperature for 0.5 h using N₂ carrier gas. Both un-carbonized (PL) and carbonized poultry litter (PLc) were analyzed for total C and nutrient contents as above (Table 2).

2.2 Treatment preparation

Pots with a volume of 4 L were filled with 3,600 g (3,044 g dry weight) soil. First 1,200 g of soil was placed on the bottom of the pot and the remaining 2,400 g was mixed with the fertilizers (either PL, PLc or mineral fertilizers s. below). The organic soil enrichments (PL and PLc) were applied at the rates of 1.5, 3.0, and 6.0 t/ha. By coincidence the N content of PL (35.2 g/kg) was very close to that of PLc (35.0 g/kg). The concentrations of other elements such as P, K⁺, Ca²⁺, and Mg²⁺ were approximately twice as high in PLc than PL (Table 2).

An increasing concentration of these elements and a loss of N by volatilization are common for this type of feedstock (Gaskin et al. 2008). The three application rates and the nutrient concentrations should allow a direct comparison of available nutrients. For the mineral fertilized controls, we mixed ammonium nitrate (NH₄NO₃), potassium chloride (KCl), calcium phosphate (CaHPO₄), and magnesium sulfate (MgSO₄) in a ratio to match the nutrient contents of each litter treated soil (PL and PLc) and designated MF and MFc, respectively. One
unfertilized control was also established. All treatments were arranged in a randomized complete block design with four replicates as detailed in Table 3.

The experiment was conducted in a heated greenhouse. Five plants of ryegrass (*Lolium perenne*) were established from seeds. Two to three seeds were planted in five locations in each pot on November 11th. After germination, the plants were thinned to five plants per pot. Above-ground biomass was sampled for the first time 72 days after planting (January 22nd) and thereafter once a month for three consecutive harvests (February 19th, March 19th and April 23rd). Water supply was regulated by an automatic trip irrigation system and slightly modified according to variations in demand and to avoid leaching of nutrients.

### 2.3 Analysis of litter enrichments, soil, and plant samples

Aboveground biomass was dried at 60°C and ground before analysis. The soil samples were sieved (2 mm) and ground in a ball mill before nutrient analysis. Soil samples were taken at treatment preparation and at the end of the experiment. Total nutrient content of the soil, PL, and PLc, and aboveground plant biomass were digested with nitric acid (USEPA Method 3050B, USEPA, 1996) in HP500 microwave vessels and a CEM Mars Express microwave digestion system and analyzed by Inductively Coupled Plasma (ICP – Thermo Jarrell-Ash model 61E Thermo Fisher Scientific, Waltham, MA, USA). Plant available nutrients in the soils were measured using Mehlich I extraction (0.05 M HCl + 0.0125 M H₂SO₄) (Mehlich, 1953) and ICP analysis. The pH in soil was measured in 0.01 M CaCl₂ in a 1:1 soil solution ratio using a digital pH meter (AR15, Thermo Fisher Scientific, Waltham, MA). Total C and N in soil, PL, and PLc were measured by dry combustion (LECO CNS-2000, St. Joseph, MI, USA).

### 3 Results

Our results show that the N contained in carbonized poultry litter (PLc) is not available for plants and thus clearly limited by N (Figure 1a). Increasing N fertilization did increase N uptake of the crops except for plants growing in pots fertilized with PLc. At the lower fertilization rates, plant biomass was higher on PLc at the first harvest than on PL, but they had the lowest N concentrations in plant tissues (Figure 1a). There was still residual N available in the soil to support plant growth. The P and K uptake of plants fertilized with PLc did slightly increase with increasing application rates, but the growth was most likely limited by N (Figure 1b and c).

This is corroborated by the finding that plants grew larger when fertilized with PLc than the plants growing on the control, but their N concentration in plant tissue was the lowest of all treatments. The biomass production (Figure 2) and the N concentration in the tissue did not increase with increasing fertilization rates.

The treatments had no significant influence on total C and nutrient contents of the soil at the end of the study. The soil fertilized with mineral fertilizer had the lowest pH.
The nitrogen contained in carbonized poultry litter is not plant available.

**Figure 1:** Regressions of nutrients (N, P, and K) fertilized and cumulative uptake up by ryegrass (*Lolium perenne*) per kg of soil after 4 consecutive harvests. CO = control, PL = poultry litter, MF = mineral fertilizer, PLc = carbonized poultry litter, MFc = mineral fertilization based on PLc, means and standard errors, n = 4.

<table>
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<tr>
<th>Harvest</th>
<th>Co</th>
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<th>MF</th>
<th>PLc</th>
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**Legend and linear regressions**

- **A:** CO
  - $y = 0.279x + 97.89, R^2 = 0.958$
  - $y = 0.772x + 86.87, R^2 = 0.999$
  - $y = 0.016x + 102.4, R^2 = 0.999$
  - $y = 0.747x + 96.75, R^2 = 0.998$

- **B:** PL
  - $y = 0.097x + 6.767, R^2 = 0.965$
  - $y = 0.093x + 7.259, R^2 = 0.969$
  - $y = 0.022x + 8.953, R^2 = 0.988$
  - $y = 0.088x + 7.360, R^2 = 0.962$

- **C:** MF
  - $y = 0.589x + 130.9, R^2 = 0.808$
  - $y = 1.119x + 125.8, R^2 = 0.972$
  - $y = 0.083x + 147.1, R^2 = 0.593$
  - $y = 0.604x + 144.0, R^2 = 0.988$

**Figure 2:** Cumulative biomass yields (DM g/pot) of 4 consecutive harvests (I-IV) of ryegrass (*Lolium perenne*) at 3 fertilization levels (1.5, 3 and 6 t/ha) and an unfertilized control CO = control, PL = poultry litter, MF = mineral fertilizer, PLc = carbonized poultry litter MFc = mineral fertilization based on PLc, means and standard errors, n = 4, MSD indicates the minimum significant difference (p ≤ 0.05, Student-Newman-Keuls test).
Table 4: Soil nutrient contents after 4 harvests of Lolium perenne. Different letters in the same column indicate significant differences (p<0.05) between treatments (Student-Newman-Keuls test, means, n = 4)

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<th>Fertilization level</th>
<th>Treatment</th>
<th>CaCl₂</th>
<th>H₂O</th>
<th>pH</th>
<th>Total C (g kg⁻¹)</th>
<th>Total N (g kg⁻¹)</th>
<th>Total Acid Digestion (g kg⁻¹)</th>
<th>Mehlich 1 mg/kg⁻¹ (ppm)</th>
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CO = unfertilized control, CL1, CL2, CL3 = poultry litter (1.5, 3, and 6 Mg ha⁻¹, respectively), CLc1, CLc2, CLc3 = carbonized poultry litter (1.5, 3, and 6 Mg ha⁻¹, respectively), MF = mineral fertilizer (N, P, K, Ca, and Mg) dosed to match CL, MFc = mineral fertilizer (N, P, K, Ca, and Mg) dosed to match CLc.
and the soil fertilized with PLc the highest. However, in particular at the highest fertilization level, the Mehlich 1 extractable nutrients (P, K⁺, and Mg²⁺) were significantly higher in pots fertilized with PLc. This again supports the conclusion that the plant growth was limited by N and not by the other nutrients.

4 Discussion

The availability of N supplied with organic fertilizers depends on the C:N ratio and mineralization rates (Probert et al. 2005). Poultry litter has a narrow C:N ratio and about 50% of the total N is reported to mineralize over the growing season after application (Sistani et al. 2008), hence it is not surprising that N uptake of plants fertilized with PL was lower than that of plants receiving mineral fertilizer.

The mineralization of biochar depends on carbonization characteristics such as pyrolysis temperature. Higher pyrolysis temperatures produce biochar more recalcitrant against decomposition but also with a lower N content (Cantrell et al. 2012; Song and Guo 2012). The hydrolysable organic N decreases with higher pyrolysis temperature (Clough et al. 2013) and thus the release of N from biochar may depend on its decomposition. However, when the purpose of biochar production is to stabilize organic matter and sequester C, then reducing the biochar’s stability to enhance its N availability seems counterproductive.

Although Chan et al. (2008) attributed yield increases to increases in N availability, this seems not to be the case in our study. Chan et al. (2008) applied 200, 500, and 1000 kg of N per ha with the carbonized poultry manure (10, 25, and 50 t/ha, respectively) and an additional mineral N fertilization of 100 kg/ha increased yields significantly independent from the rate of biochar applied. The average N concentration in plant tissue was 2.4% with, but only 1.7% without the additional mineral N fertilization. Therefore, in our view, the results of Chan and colleagues corroborate our findings that N in carbonized poultry litter is not available.

Stronger evidence that the N in carbonized poultry manure is plant available is provided by Tagoe et al. (2008). They used ¹⁵N labelled poultry manure and found a ¹⁵N recovery of 17.6% and 8.9% for carbonized poultry manure at application rates of 50 and 100 kg N per ha, respectively. The uptake of N by plants fertilized with dried manure was only slightly higher. However, this poultry manure is different from the litter (bedding) used in our study. The original C content of the manure used by Tagoe et al. (2008) was only 12.3% and did not change due to carbonization, while the original N content was 6.0% and was reduced to 2.6% after carbonization mostly as a result of the heating of the manure. While the P content quadrupled due to carbonization, the Ca²⁺ content did not change much and Mg²⁺ contents was even reduced. In our study the concentration of the non-volatile elements in the biochar were approximately twice as high as in the carbonized feedstock, which was expected as shown by Steiner (2016). In order to reduce losses of N and avoid transferring N into recalcitrant N, Steiner et al. (2010) proposed co-composting of N-rich poultry litter with biochar produced from N-poor feedstock.

The plant growth and nutrient uptake on soils fertilized with carbonized poultry litter was clearly limited by N availability. Supplementing PLc with mineral N fertilization would provide more information on the availability of P and K⁺ in carbonized poultry litter and should be considered in future studies.

5 Conclusions

Nitrogen in poultry litter carbonized at 500°C is not plant available. This has important consequences for manure management and the sustainable use of natural resources. If the immobilization of N is a desired objective, pyrolysis might be an appropriate way to achieve this goal. The limited resources, force us to find sustainable ways to recycle nutrients and sequester C. Biochar C sequestration is promising to lock up C for relatively long-time scales. However, this deceleration of mineralization which is a positive consequence for the global C cycle is less beneficial when considering the N bioavailability of biochars with a relatively high N content.

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