RELEASE OF INORGANIC NITROGEN AND PHOSPHORUS FROM POULTRY LITTER AMENDED WITH ACIDIFIED BIOCHAR

by

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(Under the Direction of Miguel Cabrera and KC Das)

ABSTRACT

This study aimed to 1) evaluate the effect of acidified biochar on the release of NH_3, CO_2 and inorganic N and P from surface-applied (SPL) or incorporated poultry litter (IPL), and 2) investigate the sorption and desorption of NH_4^+ and ortho-P on acidified biochar. SPL or IPL with or without acidified biochar was incubated for 21 d. Acidified biochars reduced NH_3 losses by 24 to 67% and CO_2 evolved by 9 to 22% from SPL. Also, it decreased NH_3 volatilized by 55 to 60% but increased CO_2-C emission by 0.5 to 45% from IPL. Acidified biochars generally did not affect leachable inorganic P and N or extractable inorganic P and NH_4^+ from SPL and IPL. It did not affect extractable NO_3^- from SPL (except PC600) and from IPL (except for PC600 and PH600). The biochars could sorb NH_4-N but not ortho-P. Acidified biochars could reduce NH_3 losses but could not address the problem on P loading in runoff from poultry litter in pasture soils.

INDEX WORDS: Poultry litter, Biochar, Ammonia, Carbon dioxide, Inorganic nitrogen, Inorganic P, Sorption, Desorption

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CHAPTER 1

INTRODUCTION

Nature and Importance of the Study

Being the top-broiler producing state in the country, Georgia is estimated to generate an average of two million Mg poultry litter (PL) annually (Cabrera, M., personal communication). Consisting primarily of poultry manure, bedding material, feathers and some waste feed, PL provides both macro and micronutrients to crops. As a way of utilizing its nutrient value, much of this PL is surface applied to pastures and no-till fields or incorporated into the soil in conventional-till fields. While this material offers a cheaper fertilizer source particularly for nitrogen (N) and phosphorus (P), its N value decreases when N is lost as ammonia (NH_3) gas, especially from surface applications. This process, known as NH_3 volatilization, could account for 4 to 60% of the total N lost from the litter under laboratory condition (Brinson et al., 1994; Cabrera et al., 1993; Cabrera and Chiang, 1994). Ammonia loss from poultry litter is important not only agronomically, but also environmentally. Deposition of NH_3 from the atmosphere could potentially lead to N loading to lakes, acidify soils of low buffering capacity and damage sensitive crops such as tomato, cucumber and conifer (Gay and Knowlton, 2005; Pearson and Stewart, 1993; ApSimon et al., 1987; Van Breemen and Van Dijk, 1988). One possible way of minimizing NH_3 loss from poultry litter is by mixing it with biochar, a carbon (C) residue that comes as a byproduct in bioenergy production.

When biomass residues are converted to liquid and gaseous fuel through pyrolysis, biochar is also produced. Biochar is composed primarily of carbon (C) (Onay, 2007; Encinar et al., 2000; Demirbaş, 2001; Demirbas, 2006;). Biochar C is polyaromatic which suggests high resistance against decomposition (Swift, 2001; McLauchlan, 2006; Lützow et al 2006; Glaser et al., 2002). Biochar has gained increasing interest as one of the means for sequestering CO_2 from the atmosphere. Lehmann (2007) argues that when combined with bioenergy production, heating plant biomass can be a clean technology while at the same time storing up carbon in biochar. When applied to soils, this byproduct has an estimated residence time which ranges from hundreds to thousands of years (Skjemstad et al., 1998; Lehmann, 2007; Lützow et al., 2006). Adding to its refractory nature towards microbial breakdown, chars are also reported to increase the cation exchange capacity of soils (Liang et al. 2006; Cheng et al., 2006). The presence of chars has been associated with the enhanced nutrient retention of Terra Preta soils that were formed originally from nutrient-poor, leaching-prone soils in the Central Amazonia (Glaser et al., 2002; Liang et al., 2006). Such a remarkable retentive property of chars is also one of the major factors ascribed for better crop production with inorganic or organic fertilizer plus char combinations over inorganic or organic fertilization alone (Glaser et al., 2002; Lehmann et al., 2002; Lehmann et al., 2006; Steiner et al., 2007a).

Considering the environmental and economic benefits of renewable bioenergy over conventional burning of fossil fuels (Guo et al., 2007; Lehmann, 2007; Demirbas, 2007; Cook and Beyea, 2000; Demirbas, 2008), it is anticipated that thermochemical generation of bio-fuel will be one of the alternatives to petroleum. In view of the anticipated increase in the supply of biochars in the future, it would be practical to utilize this byproduct as a means of increasing the stable organic C pool in soil (Gaskin et al., 2008), while at the same time improving N fertilizer efficiency of poultry litter. When acidified, biochar may be able to reduce NH_3 volatilization by lowering the pH of the litter and by providing more exchange sites for ammonium (NH_4^+), which could otherwise volatilize to the atmosphere. However, its effect on carbon dioxide (CO_2) evolution and on the release of inorganic N and P are areas which have not been well investigated. Evolution of CO_2 from organic fertilizers, such as poultry litter, is important because it may contribute significantly to global warming (Ajwa and Tabatabai, 1994; McLauchlan, 2006; Franzlaubbers, 2005). Some studies have shown chars to stimulate respiration (Pietikäinen et al., 2000; Hamer et al., 2004; Steiner et al., 2007b; Steiner et al., in press) and have raised questions recently on stability of C pools in soils with biochar application. Assessment of release of potentially available N and P is also important for the resulting impact of acidified biochar on the nutrient-supplying capacity of poultry litter to plants. Although the reported synergistic effect of combined application of charcoal and inorganic fertilizer resulted to improved growth or yield of cereals and legume, foliar nutrient analysis of these crops did not differ from the inorganically fertilized plants in their N or P contents (Lehmann et al., 2003; Steiner et al., 2007a). It is then speculated that NH_4-N and orthophosphate (ortho-P) may have been held strongly by biochar, limiting their release to soil solution. With regard to PL management, sorption of NH_4-N and ortho-P by biochars may be deemed favorable as a way of controlling the NH_4-N substrate for NH_3 volatilization and controlling ortho-P in runoff from pasture soils. Understanding the role of biochar in retaining NH_4-N and ortho-P is limited by little information on sorption and desorption of these ions on biochar in soil.

Objectives

This study therefore aimed to evaluate the effect of biochar on NH_3 volatilization, CO_2-C evolution, and release of inorganic N and P from surface-applied or incorporated poultry litter. This study also aimed to investigate the sorption and desorption of NH_4-N and ortho-P on biochar.

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CHAPTER 2

REVIEW OF RELATED LITERATURE

Charcoal and Its Properties

Charcoal is mainly comprised of polyaromatic C which suggest high resistance against decomposition (Swift, 2001; McLauchlan, 2006; Lützow et al., 2006; Glaser et al., 2002). It is widely used in several purification processes. These applications range from cleaning up waste gases and filtering water.

The sorptive property of charcoal is considered to be related with its porous nature (Shimada et al., 2004; Ioannidou and Zabaniotou, 2007; Pulido-Novicio et al., 2001; Asada et al., 2002). Shimada et al., (2004) classified these pores as micropores (<1 nm), mesopores (1 to 25 nm), and macropores (>25 nm) based on their radius. In addition, equally important in determining the sorptive capacity of charcoal is its surface chemistry.

Charcoal surface contains acidic and basic functional groups. These acidic groups include carboxyl, lactonic, carbonyl, and phenolic species, while the basic groups include ketone, pyrone, and chromene (Goldberg, 1985; Chun et al., 2004b; Lahaye, 1998; Boehm, 2002). In most industrial applications, a low density of these oxygen-containing groups is advantageous in removing hydrophobic impurities in aqueous solutions (Mohan et al., 2007). However, in agricultural interests, the acidic groups are of particular importance as they impart the cation exchange behavior of charcoal (Liang, et al., 2006; Lahaye, 1998; Cheng, et al., 2006; Glaser et al., 2002).

The physical and chemical properties of charcoal differ widely depending on the kind of organic precursors from which they are produced. For instance, in terms of surface density of acidic groups, wheat char is more reactive than pinewood char (Chun et al., 2004b). Chars prepared from the same organic material also differ in their sorptive properties by the effect of the charring conditions. Among these factors, temperature appears to exert the greatest influence. Generally, surface density of acidic functional groups decreases as pyrolysis temperature is raised. From this thermal influence, low-temperature chars appear to have greater cation retention capacity than high-temperature chars.

Charcoal Effect on NH_3 Volatilization

Charcoal may have the potential for reducing NH_3 loss by its capacity to sorb NH_3 in both gaseous and aqueous phases. Ammonia sorption has been shown to be greater in charcoal produced at lower (400 and 500°C) than at higher temperature (Asada et al., 2002; Asada et al., 2006). This corresponds to the generally observed greater density of acidic functional groups in low-temperature than in high-temperature chars. Interestingly, Iyobe et al. (2004) reported a much higher removal efficiency (90%) of an untreated wood charcoal for this gas compared to that of commercial activated carbon (<20%) after 24 h of exposure which has been attributed to the less polar surface of the latter (Iyobe et al., 2004; Asada et al., 2006; Mohan et al., 2007).

In aqueous solutions, low-temperature char also removed greater NH_3 compared to those produced at high temperature (Asada et al., 2006). However, better sorption was achieved when charcoal was treated with sulfuric acid (Asada et al., 2006). Better sorption with sulfuric acid treatment was attributed to the reduction in the amounts of metals eluted by the charcoal itself, thereby decreasing the amounts of other cations that could compete with NH_3 for the sorption sites in charcoal (Asada et al., 2006). Oya and Iu (2002) also reported improved deodorization performance for NH_3 of wood-prepared charcoal when it was loaded with orthophosphoric acid (H_3PO_4). Oya and Iu (2002) suggested H_3PO_4 reacting with NH_3 to form $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$.

For agricultural application, although these studies demonstrated the promising effect of charcoal in reducing NH_3 volatilization, there is still a need to investigate such potential particularly when combined with animal waste. Adding an acidified charcoal to poultry litter, for instance, may bring up the problem of competing ions coming from the poultry litter itself. Secondly, chars also contain some metals that may be difficult to remove. These competing metals may interfere with the sorption sites in the chars, thereby making these sites ineffective for NH_4^+ sorption – one of the speculated mechanisms for reducing NH_3 volatilization.

Charcoal Effect on CO_2 Evolution

The inert nature of carbon in charcoal has gained increasing interest in terms of its significance in sequestering CO_2 from the atmosphere. Lehmann (2007) argues that when combined with bioenergy production, heating plant biomass can be a clean technology while at the same time locking up carbon in charcoal. When applied to soils, this byproduct has an estimated residence time which ranges from hundreds or thousands of years (Skjemstad et al., 1998; Lehmann, 2007; Lützow et al., 2006). Such a refractory nature of charcoal towards decomposition has been observed in a longterm field experiment (Steiner et al. 2007). In their study, soils added with charcoal lost only 4% while soils added with compost or chicken manure lost 27% of the initial soil organic C.

Contrary to these findings, however, a number of recent studies have shown an increase in CO_2 evolution from charcoal obtained from certain types of biomass. Pietikäinen et al. (2000) observed an increased basal respiration from a charred twig of *Empetrum nigrum* L. and activated charcoal overlying some humus in a laboratory simulation of forest soil after a forest fire. The authors attributed this response to the high pH of these chars which resulted to a pH increase in humus and the consequent rise of the respiration activity. Similarly, adding increasing levels of charcoal (made from a secondary forest wood) to an acidic agricultural soil caused a linear and significant increase of respiration even without any added substrate (Steiner et al., in press). Even more surprising is the surge in respiration when an easily decomposable C source such as glucose was added (Steiner et al., in press; Hamer et al., 2004). While Steiner et al. (in press) suggested the substrate-induced respiration to be caused by the degradation of the pyroligneous acid fraction of freshly produced chars, Hamer et al. (2004) demonstrated the positive priming effect of glucose on the mineralization of the charred materials themselves.

These observations have raised some uncertainty on the role of charcoal in global C sequestration. However, although the radio-labeled experiment of Hamer et al. (2004) is convincing, it still needs to be verified in the field. Additionally, the degradation of charcoal in this experiment may not be conclusive to all types of soil since the microorganisms decomposing the charcoal in this study may not be dominant in other locations and under certain climatic conditions. Furthermore, the priming effect of glucose on charcoal in this study may not be observed when charcoal is combined with other C source of heterogeneous compositions (that has some non-readily mineralizable fractions in it) such as the case for poultry litter.

Charcoal Amendment and Crop Productivity

Amending soil with charcoal in soil is not a new agricultural practice. However, how charcoal improves soil fertility has received attention among scientists only recently. Enriching soils with charcoal improves crop productivity and various soil properties (Glaser et al., 2002). In central Amazon, a prolonged prehistoric input of charcoal may be responsible for the high soil organic matter contents and improved fertility of the anthropogenic soils popularly known as Terra Preta (Glaser et al., 2002). In these soils, biomass production of cowpea and rice increased by 38 to 45% even without fertilization (Lehmann et al., 2003). Likewise, deliberate addition of charcoal to infertile soils increased total biomass production of oats by a factor of 1.27, rice by 1.20 and cowpea by 1.50 and even up to two times greater than the control when the rate of charcoal application was further raised (Glaser et al., 2002). Direct nutrient addition from single application of charcoal to plants has been attributed to some nutrients contained in it (Tryon, 1948).

Nutrients in the ash fraction of charcoal are not bound by electrostatic forces and are present as soluble salts (Glaser et al., 2002). Among the salts present in ash, calcium, magnesium, and potassium are the most common (Tryon, 1948). As these salts are released and dissolved into the soil solution, available nutrients are readily supplied to plants. Additionally, as these salts are released, soil pH is increased. Oguntunde et al. (2004) observed a change in soil pH by a factor of almost two units higher in charcoal site (pH 7.6) than in adjacent field soils (pH 5.8). In addition, highly significant difference in soil pH also exists between soil mixtures containing different kinds of charcoal. Tryon (1948) found hardwood charcoal more effective in increasing soil alkalinity than conifer charcoal. Hardwood char-soil combinations raised soil pH from 5.15 to 6.15, while conifer char-soil mixtures measured only up to pH 5.55 (Tryon, 1948). As the soil nears neutral pH, nutrients in the soil become available. In contrast, concentrations of acid-forming cations, such as aluminum, iron and manganese in the soil solution are lowered (Troeh and Thompson, 2005). Reducing aluminum availability is desirable as aluminum toxicity commonly limits crop and microbial growth by interfering with the physiological processes of the organisms (Troeh and Thompson, 2005).

The nutrient supplying capacity of ash is short-lived. For this reason, charcoal as a fertilizer may not be sustainable. Although plain charcoal amendment increased biomass production of rice over un-amended soils, N uptake of the crop had been poor because of typically wide C:N ratio of charcoal (Lehmann et al., 2002). Similarly, in a long-term experiment with various types of cereals, Steiner et al. (2007) found only minor effect on total cumulative stover production from lone charcoal application.

However, charcoal enhances crop performance when it is applied together with inorganic or organic fertilizers. In rice, stover production increased by 29% and grain yield by 73% when charcoal was applied with mineral fertilizer compared to charcoal or inorganic fertilization alone (Steiner et al., 2007). Similarly, cowpea had significantly greater shoot biomass production when charcoal was added with manure compared to manure-fertilized soil alone (Lehmann et al., 2003). In this study, however, combined charcoal-manure application did not produce greater shoot biomass of cowpea than plain charcoal.

Nutrient Retention and Release in Charcoal-Amended Soil

The role of charcoal in increasing crop productivity is an integrated effect of enhanced soil physical, chemical and biological properties (Steiner et al., 2007). Among the factors enhanced by charcoal in soil, Glaser et al. (2002) emphasized stronger nutrient retention capacity. Highly charcoal-enriched soils of Brazilian Anthrosols possess CEC which is 1.9 times higher than the surrounding un-amended soils of the same kaolinitic mineralogy (Liang et al., 2006). High specific surface area of these soils attributable to the presence of charcoal gives much greater negative charge density (potential CEC per unit surface area) compared to adjacent soils (Liang et al., 2006). As proposed by Liang et al. (2006) these charges are created through oxidation on the edges of the aromatic backbone and by sorption of other organic matter on charcoal surfaces. High retentive capacity is important in holding nutrients applied in the soil. Surprisingly, however, application of inorganic N fertilizers in these soils resulted to a cumulative amount of nearly 80 kg ha^{-1} leached ammonium after 38 days of lysimeter study with rice (Lehmann et al., 2003). Such an amount of leached ammonium even exceeded the one obtained from fertilized Ferralsol without any charcoal amendment at all (Lehmann et al., 2003). Conversely, applying charcoal (20% by weight of soil) with synthetic nitrogen fertilizer to Ferralsol largely reduced ammonium leaching from around 50 kg ha^{-1} to 20 kg ha^{-1} (Lehmann et al., 2003). Mixing the same amount of charcoal with either cattle or chicken manure, however, did not significantly affect leaching results (Lehmann et al., 2003). From these findings, it appears that charcoal has better retention capacity for manure-derived ammonium than from ammonium sulfate. However, comparison on desorbability of ammonium from manure and inorganic fertilizer could not really be drawn from this study since the quantity of released ammonium from these two fertilizer sources differs. Thus, the insignificant leaching of ammonium from manure may have only been largely due to the slow N mineralization.

The conflicting results on the retention and leaching of ammonium between the charcoal-rich Anthrosol and the charcoal-amended Ferralsol when both were fertilized with inorganic N fertilizer may have been due to the quality (or kind) and the quantity of charcoal applied in these two soils. Different kinds of charcoal exert different effect on CEC of soils. In his early works, Tryon (1948) observed an increased CEC with addition of hardwood (oakwood) but not with conifer (pinewood) charcoal. In the case the above comparison between the Anthrosol and the charcoal-amended Ferralsol, however, no direct information on the quality of charcoal can be drawn since the nature of the organic materials, from which the pyrogenic carbon of the Anthrosol and the added charcoal to Ferralsol originated, is unknown. Moreover, it is most likely that these charcoal came from a combination of different organic precursors rather than from a single wood type or biomass. This further complicates the nature of the contrasting effect of pyrogenic carbon and the freshly added charcoal used in the above lysimeter study on ammonium retention.

The influence of charcoal on CEC is also affected by the quantity used in amending the soil. Most of the reported increase in CEC has been achieved from large addition of charcoal from a range of 10 to 20% by weight of soil (Glaser et al., 2002; Lehmann et al., 2003). In contrast, a lower charcoal application rate at 0.8% (11,000 kg ha^{-1} at 10 cm soil depth) was ineffective in raising the CEC even when in combination with inorganic and various organic fertilizers (Steiner et al., 2007). These studies suggest that applying large amounts of charcoal may be desired to achieve greater nutrient retention capacity of the soil. However, at this point, it is important to note that such high rates of charcoal application (10 to 20%) used in the above studies were based on charcoal yields if the aboveground woody biomass of forests were to be charred, as an alternative to widespread slash and burn nutrient management in the tropics. In comparison, charcoal yield from bio-fuel production may not be as much as what would be obtained from slash and char. Thus, applying charcoal as byproduct from bio-fuel production at similarly high rates as 10 to 20% may be impractical. The potential of different kinds of charcoal produced from bio-fuel processing for nutrient retention capacity at relatively smaller application rates in soil therefore has to be investigated.

In addition to CEC, charcoal also exhibits AEC. Fujita et al. (1991) estimated the AEC of non-activated pure wood charcoal to be 88.2 cmol kg^{-1}. Such an AEC for charcoal would therefore mean sorption of anionic nutrients such as phosphate. However, sorption of these anions has not been investigated because these nutrients come in higher supply with charcoal addition (Lehmann et al., 2002). The ash fraction of charcoal releases considerable amounts of phosphorus together with other nutrients. As a result, these nutrients showed higher concentrations in the equilibrium solution than the amount added (Lehmann et al., 2002). In their sorption experiment, however, Lehmann et al. (2002) used wood charcoal (obtained from black locust). To evaluate the potential of charcoal to adsorb added nutrients, the soluble salt fraction may have to be removed. Aside from the effect of ash in releasing some nutrients, Shinogi and Kanri (2003) suggested removing the ash as its presence decreases the surface area of charcoal by plugging the pores with residue and render its surface more alkaline than it actually is. Evaluation of the adsorptive power of charcoal requires isolation of the char fraction by chemical procedures that do not cause alteration of the charcoal surface properties (Chun et al., 2004a). Acid demineralization has proven effective enough in removing soluble salts and minerals of charcoal (Chun et al., 2004a). Although this procedure may reduce the char surface area to a certain degree, it only causes little, if any, variation in the surface acidity (Chun et al., 2004a).

Charcoal Influence on the Release of Retained Nutrients for Plants

Combining charcoal with inorganic or organic fertilizers often leads to better crop production over inorganic or organic fertilization alone. This has been assumed to be partly due the enhanced nutrient retention capacity of the soil (Glaser et al., 2002; Lehmann et al., 2002; Lehmann et al., 2006; Steiner et al., 2007). Although Lehmann et al. (2003) has shown sorption of added ammonium in charcoal-amended soil, their lysimeter experiment did not show how charcoal aid in retaining ammonium and phosphorus. Among the mechanisms suggested for the retention are direct electrostatic sorption of nutrients and indirect retention by the attraction of soil water containing dissolved nutrients in it (Glaser et al., 2002; Lehmann et al., 2003). In addition to the unclear mechanism of retention, the question on how strongly the added nutrients are held for release to plants is also unknown.

Improved crop productivity is generally related to improved nutrition of the crops. This trend may be expected from the synergistic effect of combined application of charcoal and NPK fertilizers which increased cumulative grain yield of tested cereal crops for four cropping seasons (Steiner et al., 2007). However, foliar nutrient analysis of crop residues obtained from these treatments did not show any difference at all in terms of their N and P contents (Steiner et al., 2007). In this study, only foliar K contents of crop residues originating from plots receiving charcoal and mineral fertilizer were greater than those on plots with mineral fertilizer alone.

Similar findings were obtained by Lehmann et al. (2003) from combining charcoal with either animal manure or triple superphosphate (TSP) of equal amounts of available P. Mixing charcoal with either of the two fertilizers significantly increased shoot biomass production of cowpea. However, in terms of foliar P contents, combining charcoal with either animal manure or TSP did not significantly differ from single application of either animal manure or TSP (Lehmann et al., 2003). According to Troeh and Thompson (2005), P uptake is influenced by the availability of N by some physiological processes of the plant. This appears to coincide with the lack of differences in foliar N of cowpea between the charcoal-amended TSP and the TSP fertilized soil and between the charcoal plus manure and the plainly manured soil (Lehmann et al., 2003). The lack of difference in foliar N may be expected since TSP-fertilized soil did not supply other inorganic nutrients other than P while the manure-fertilized soil received both N and P inputs together from the manure itself. However, even when the complete recommended rate of NPK fertilizers was applied, adding charcoal together with these inorganic fertilizers still did not improve N nutrition and foliar P in rice (Lehmann et al., 2003). Since mixing charcoal with inorganic or organic fertilizer increased nutrient retention capacity, it is speculated that ammonium and phosphate retained by charcoal-amended soil may be held strongly which limits its release to the soil solution. However, as for the reason of improved biomass production despite low foliar N and P, Steiner et al. (2007) only cited the effect of charcoal in decreasing aluminum availability in acid soil.

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CHAPTER 3

RELEASE OF INORGANIC NITROGEN AND PHOSPHORUS FROM POULTRY LITTER AMENDED WITH ACIDIFIED BIOCHAR[1]

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Abstract

Georgia generates an average of two million Mg poultry litter (PL) annually. While this material is used as a fertilizer, its nitrogen (N) value could decrease considerably due to ammonia (NH_3) volatilization. One possible way of minimizing NH_3 volatilization from PL is by mixing it with acidified biochar, a by-product from bio-fuel production. This study aimed to evaluate the effect of acidified biochar on NH_3 volatilization, CO_2 evolution, and on the release of inorganic N and P from surface-applied or incorporated PL. It also aimed to investigate the sorption and desorption of ammonium and orthophosphate on biochar. Poultry litter with or without acidified biochars was surface-applied or incorporated into the soil. During the 21-d incubation, volatilized NH_3 and CO_2 evolved were determined over time. Inorganic N and P were determined by leaching the soil with 0.01 M of $CaCl_2$ followed by a N- and P-free nutrient solution at 14 and 21 d of incubation. In addition to leaching, the treatments were extracted with 1 M KCl at the end of the experiment.

Acidified biochars reduced NH_3 losses by 24 to 67% from surface-applied poultry litter. Similarly, it decreased NH_3 volatilized from incorporated poultry litter by 55 to 60%, with the exception of PL+PC600. In terms of CO_2-C evolved, acidified biochars decreased it by 9 to 22% when PL was surface-applied but increased it by 0.5 to 45% when PL was incorporated with soil. Acidified biochars generally did not affect leachable and extractable inorganic P from surface-applied or incorporated PL, except for surface-applied PL+PC600. It did not also affect leachable inorganic N from surface-applied and incorporated PL. Combining acidified biochars with surface-applied or incorporated PL did not have an effect on extractable NH_4^+. In terms of extractable NO_3^- under surface-

applied incubation, char-amended PL treatments were comparable to unamended PL except for PL+PH600. Under incorporated incubation, char-amended PL treatments were also comparable to unamended PL except for PL+PC600 and PL+PH600. Contrary to the findings from both surface and incorporated incubation studies, batch sorption and desorption experiments have shown biochars to have a capacity to sorb NH_4-N. However, none of the biochars have demonstrated capacity to sorb inorganic P. Acidified biochars indeed have the potential to reduce NH_3 loss from PL. However, its lack of capacity to sorb ortho-P suggests that it could not control P loading in runoff from PL in pasture soils.

Introduction

As the top-broiler producing state in the country, Georgia is estimated to generate an average of two million Mg poultry litter (PL) annually. Consisting primarily of poultry manure, bedding material, feathers and some waste feed, PL provides both macro and micronutrients to crops. As a way of utilizing its nutrient value, much of this PL is surface applied to pastures and no-till fields or incorporated into the soil in conventional-till fields. While this material offers a cheaper fertilizer source particularly for nitrogen (N) and phosphorus (P), its N value decreases when N is lost as ammonia (NH_3) gas, especially from surface applications. This process, known as NH_3 volatilization, could account for 4 to 60% of the total N lost from the litter under laboratory condition (Brinson et al., 1994; Cabrera et al., 1993; Cabrera and Chiang, 1994). Ammonia loss from poultry litter is important not only agronomically, but also environmentally. Deposition of NH_3 from the atmosphere could potentially lead to N loading to lakes, acidify soils of low buffering capacity and damage sensitive crops such as tomato, cucumber and conifer (Gay and Knowlton, 2005; Pearson and Stewart, 1993; ApSimon et al., 1987; Van Breemen and Van Dijk, 1988). One possible way of minimizing NH_3 loss from poultry litter is by mixing it with biochar, a carbon (C) residue that comes as a byproduct in bioenergy production.

When biomass residues are converted to liquid and gaseous fuel through pyrolysis, biochar is also produced. Biochar, or char, is composed primarily of carbon (C) (Onay, 2007; Encinar et al., 2000; Demirbaş, 2001; Demirbas, 2006;). Biochar C is polyaromatic which suggests high resistance against decomposition (Swift, 2001; McLauchlan, 2006; Lützow et al 2006; Glaser et al., 2002). Biochar has gained increasing interest as one of the means for sequestering CO_2 from the atmosphere. Lehmann (2007) argues that when combined with bioenergy production, heating plant biomass can be a clean technology while at the same time storing up carbon in biochar. When applied to soils, this byproduct has an estimated residence time from hundreds to thousands of years (Skjemstad et al., 1998; Lehmann, 2007; Lützow et al., 2006). Adding to its refractory nature towards microbial breakdown, chars are also reported to increase the cation exchange capacity of soils (Liang et al. 2006; Cheng et al., 2006). The presence of chars has been associated with the enhanced nutrient retention of Terra Preta soils that were formed originally from nutrient-poor, leaching-prone soils in the Central Amazonia (Glaser et al., 2002; Liang et al., 2006). Such a remarkable retentive property of chars is also one of the major factors ascribed for better crop production with inorganic or organic fertilizer plus char combinations over inorganic or organic fertilization alone (Glaser et al., 2002; Lehmann et al., 2002; Lehmann et al., 2006; Steiner et al., 2007a).

Considering the environmental and economic benefits of renewable bioenergy over conventional burning of fossil fuels (Guo et al., 2007; Lehmann, 2007; Demirbas, 2007; Cook and Beyea, 2000; Demirbas, 2008), it is anticipated that thermochemical generation of bio-fuel will be one of the alternatives to petroleum. In view of the anticipated increase in the supply of biochars in the future, it would be practical to utilize this byproduct as a means of increasing the stable organic C pool in soil (Gaskin et al., 2008), while at the same time improving N fertilizer efficiency of poultry litter. When acidified, biochar may be able to reduce NH_3 volatilization by decreasing the pH of the litter and by providing more exchange sites for ammonium (NH_4^+), which could otherwise volatilize to the atmosphere. However, its effect on carbon dioxide (CO_2) evolution and on the release of inorganic N and P are areas which have not been well investigated. Evolution of CO_2 from organic fertilizers, such as poultry litter, is important because it may contribute significantly to global warming (Ajwa and Tabatabai, 1994; McLauchlan, 2006; Franzlaubbers, 2005). Some studies have shown chars to stimulate respiration (Pietikäinen et al., 2000; Hamer et al., 2004; Steiner et al., 2007b; Steiner et al., in press) and have raised questions recently on stability of C pools in soils with biochar application. Assessment of release of potentially available N and P is also important for the resulting impact of acidified biochar on the nutrient-supplying capacity of poultry litter to plants. Although the reported synergistic effect of combined application of charcoal and inorganic fertilizer improved growth or yield of cereals and legume, foliar nutrient analysis of these crops did not differ from the inorganically fertilized plants in their N or P contents (Lehmann et al., 2003; Steiner et al., 2007a; Gaskin, unpublished data). It is then speculated that NH_4^-N and orthophosphate (ortho-P) may have been held strongly by biochar, limiting their release to soil solution. With regard to PL management, sorption of NH_4-N and ortho-P by biochars may be deemed favorable as a way of controlling the NH_4-N substrate for NH_3 volatilization and controlling ortho-P in runoff from pasture soils. Understanding the role of biochar in retaining NH_4-N and ortho-P is limited by little information on sorption and desorption of these ions on biochar in soil.

This study therefore aimed to evaluate the effect of acidified biochars on NH_3 volatilization, CO_2 evolution, and release of inorganic N and P from surface-applied or incorporated poultry litter. It also aimed to investigate the sorption and desorption of ammonium and orthophosphate on biochar.

Materials And Methods

Biochar Production and Acidification

Biochars were produced from pine chips (PC) and pelletized peanut hull (PH) residues by slow pyrolysis at peak temperatures of 400 and 600°C. These pyrolysis conditions generated four types of biochar: PC400, PC600, PH400, and PH600, with the numbers indicating the temperatures at which the biochars were produced. The biochars were ground and sieved through 53-µm diameter mesh. The ground and sieved samples were acidified by taking two 25-g subsamples. Each subsample was added with 250 mL of 0.5 N HCl and shaken for 30 min. After letting the suspension stand for 24 h, it was filtered through 0.45-µm membrane (GE Water and Process Technologies, Trevose, PA) and the collected biochars were oven-dried at 65°C for 48 h. The two subsamples of each biochar were thoroughly mixed and a representative sample was taken for analysis of the following tests: pH in water (1:30 biochar-water ratio), total C (dry combustion), total P (kjehldahl digestion), total N (Kjehldahl digestion), and CEC in 1 M NH_4OAc at pH 7 using the procedure described by Gaskin et al. (2008).

Soil and Poultry Litter Sampling and Characterization

Soil samples were collected from a pasture near Eatonton, GA, which had received many years of poultry litter application. The dominant soil series in that pasture was Cecil (fine, kaolinitic, thermic Typic Kanhapludult). The samples were air-dried and passed through a 2-mm sieve. The sieved soil was mixed with acid-washed sand at a 1:1 (w/w) ratio to facilitate leaching of inorganic N and P at certain periods during the incubation experiments. The mixture was analyzed for pH, total C, total N, total P, and CEC using the same procedures used for the characterization of the acidified biochars.

Poultry litter samples were collected from a poultry litter stack remaining from a load of poultry litter applied in Spring of 2008 to the sampled pasture soil used in this experiment. These samples were characterized for pH, total C, total N and total P using the same procedures used for biochars and soil. Chemical properties of the acidified biochars, soil and poultry litter are reported in Table 2.1.

Incubation Experiment

A wet mixture of acid-washed sand and soil (77.43 g, 200 g kg^{-1} moisture content) was packed to a depth of 1 cm in 7.4-cm diameter plastic funnels lined with a 0.45- μm filter membrane at the bottom. The one-cm depth of packing was selected to achieve a bulk density of 1.5 g cm^{-3}, which is typical of soils in the sampled pasture (Perkins, 1987). Eighteen funnels were prepared to accommodate three replications of six treatments in a completely randomized design. The six treatments were: T0 (control), T1 (2.78 g of poultry litter (PL) (327.8 g kg^{-1} moisture content), T2 (PL + 2.09 g PC400), T3 (PL + 2.09 g PC600), T4 (PL + 2.09 g PH400), and T5 (PL + 2.09 g PH600). These treatments were tested in two separate conditions, as surface-applied and incorporated. Under surface-applied incubation, the treatments were directly applied on the surface of the packed soil. Under incorporated incubation, the treatments were thoroughly mixed with soil before packing the whole mixture in the funnel. Other than the manner of application of the treatments, the two incubation studies were conducted using the same procedures throughout the incubation period.

Each funnel (experimental unit) was incubated at 20°C for 21 days in a flow-through system that circulated humidified air through each funnel at a rate of 0.86 L min^{-1}. Ammonia lost from each treatment was trapped by bubbling the air through 50 mL of 0.1 N H_2SO_4. The acid traps were replaced at 1, 3, 5, 7, 10, 14 and 21 days after incubation. Carbon dioxide was measured at 1, 3, 5, and 7 days after incubation with a CO_2 analyzer (LICOR, Inc., Lincoln, NE) that was inserted in the air stream flowing from each experimental unit. Moisture gained or lost from each treatment was monitored by weighing each funnel every time the NH_3 traps were replaced.

On the same day the incubation started, separate samples of the soil-sand mixture, PL, and the different acidifed biochars were extracted with 1 M KCl at a ratio of 1 g:10 mL. These extracts were characterized for the initial inorganic P, NH_4^+-N, and NO_3^--N.

On the 14th day, each funnel was taken out of the incubator and leached with 150 mL of 0.01 M $CaCl_2$, in 30 mL increments every 1.5 h. After the last addition of 0.01 M

$CaCl_2$, 50 mL of N- and P-free solution (66.81 mg L^{-1} Ca, 39.22 mg L^{-1}, Mg, 21.72 mg L^{-1} S, and 119.70 mg L^{-1} K) was added at the same rate and collected in the same container used for the 0.01 M $CaCl_2$ leachate. Samples of the leachates were collected and analyzed for inorganic P, NH_4^+-N, and NO_3^--N. After leaching, the funnels were weighed and incubated again at the same temperature and airflow rate. On the 21st day, the funnels were leached again with the same solutions in the same manner. After leaching, the funnel contents were extracted with 1 M KCl at a 1:10 soil-solution ratio (Mulvaney, 1996). These final KCl extracts were analyzed for inorganic P, NH_4^+-N and NO_3^--N.

All of the ammonia traps, NH_4-N samples in the leachate, and 1 M KCl extracts were analyzed colorimetrically (Mulvaney, 1996) at 667 nm using a UV spectrophotometer (Shimadzu Corp., Kyoto, Japan). Inorganic P, and NO_3^--N analyses were also done colorimetrically with an autoanalyzer (Alpkem Corp., College Station, TX) following the ascorbic acid method for P described by Kuo (1996) and nitrate reduction by Mulvaney (1996). Carbon dioxide evolved, inorganic P, and inorganic N released were reported as the total amounts obtained from each experimental unit (funnel) per g of the sand-amended soil. The amounts of NH_3 volatilized was calculated by subtracting the amounts of NH_3 volatilized from T0 from the rest of the treatments and expressing the results as percent of total N in the poultry litter. Ammonia losses, CO_2–C evolved and release of inorganic P and inorganic N in the leachates were statistically analyzed as repeated measures using appropriate covariate structure in PROC MIXED in SAS, and using the percent moisture gained or lost from each funnel as a covariable. Treatment mean comparisons were done based on a set of orthogonal contrasts as follows: T1 vs (T2+T3+T4+T5)/4, T2 vs T3, T4 vs T5, and (T2+T3)/2 vs (T4+T5)/2.

Significant differences were considered at p-value <0.05. Inorganic P and inorganic N determined from the final 1 M KCl extractions were analyzed as one-way ANOVA using PROC GLM. Treatment mean comparisons of these data were based on LSMEAN differences at 0.05 level of significance.

Sorption and Desorption Experiment

Washing of Acidified Biochars

For this study, the acidified biochars were washed with deionized water (DIw) to remove soluble salts. Briefly, three subsamples of 8 g of each of the acidified biochars were added to 800 mL in 1-L glass jars, shaken for 5 min, placed in a water bath at 65°C for 1 h and filtered. This washing cycle was done two more times. After the last filtration, the biochars were transferred to 50-mL beakers and dried at 65°C. The three subsamples of each biochars were mixed together, representing one sample for each char.

Sorption Study

Three replications of 200 mg of each of the washed biochars were placed into 50-mL round-bottom centrifuge tubes and 20 mL of inorganic matrix containing 0, 1, 2, 5, 10 or 20 ug mL^{-1} NH_4-N and 0, 0.1, 0.2, 0.5, 1.0 or 2.0 ug mL^{-1} ortho-P was added to each tube. The inorganic matrix was prepared with 5.06 mmol/L NaCl (adjusted to pH 7 using 12.64 mmol/L organic buffer beta-morpholino-ethansulfosäure (MES) (Acros Organics, NJ, USA) and 1 M NaOH) in 0.005 mmol/L $HgCl_2$. The suspensions were shaken at low speed for 24 h and centrifuged at 10,000 rpm for 20 min. Ten milliliters of supernatants were taken for NH_4-N and ortho-P analysis. Sorption isotherms were drawn based on the difference between the initial and final NH_4-N and ortho-P concentrations. Sorption parameters for each biochar were obtained by calculating the sorption maxima, and sorption strength from the linearized Langmuir equation: $C/q = 1/Kb + C/b$, where C is the sorbate equilibrium concentration in solution (ug mL^{-1}), q is the sorbed sorbate concentration (ug g^{-1}), K is the Langmuir constant, and b is the sorption maxima (ug g^{-1}) (Sparks, 2003). Statistical analyses of these parameters were done using a one-way ANOVA. Treatment mean comparisons between biochars were done by the following contrast: PC400 vs PC600, PH400 vs PH600, and PCs vs PHs.

Desorption Study

Because the biochars did not sorb any ortho-P, only the desorption of NH_4-N was investigated in this study. Residual samples (from the sorption study) that initially received 10 ug mL^{-1} NH_4-N were brought back to their original weight with inorganic matrix only (no additional NH_4-N added). The centrifuge tubes were again shaken for 24 h at low speed. The process of centrifuging, pipetting out 10 mL of the supernatant, and adding inorganic matrix was done four more times. The supernatants were further filtered through 0.45-um membrane (GE Water and Process Technologies, Trevose, PA) to remove floating biochar particles. Based on prior testing, these floating biochars were only less than 1% of the weight of the biochars placed in the centrifuge tubes. Thus, such a source of error was considered negligible. Desorption isotherms were drawn by subtracting the amounts of NH_4^+ that was desorbed from the amounts of NH_4^+ that was sorbed during the sorption experiment. Remaining NH_4-N sorbed after the last desorption step for each biochar was statistically analyzed in one-way ANOVA using LSMEAN differences of the same contrasts used for the sorption maxima.

Results and Discussion

Incubation Experiment

Surface-applied PL volatilized 16 % of its total N while PL amended with acidified biochars lost only 5 to 12 % (Fig. 2.1). PC400 performed better than PC600 (F=20.92; p=0.0132) for reducing NH_3 loss but there was no difference between PH400 and PH600 (F=2.12; p=0.2293). Incorporated PL lost 7% while most of the char-amended PL lost only 3% of the total N in the PL (Fig 2.1). Statistical findings observed between char-amended litters compared under surface incubation also held true under incorporated incubation. The difference between PC biochars may be explained by the lower pH and higher CEC of PC400 compared to that of PC600 (Table 2.1). Volatilization of NH_3 is a highly pH-dependent process. In general, the conversion of aqueous NH_4^+ into NH_3 starts around pH 7 and accelerates at higher pHs (Court et al., 1964). In this study, the acidified biochars had reduced the initial pH of PL from 8.55 to a pH range of 7.16 to 7.65 (data not shown). Similarly, it had brought down the starting pH of the mixture of soil and PL from 6.94 to a pH range of 6.47 to 6.73. However, because these are only initial pH measurements, treatment differences in initial pH measurements among PL+chars or PL+char+soil mixtures do not necessarily coincide with their differences in reducing the amounts of volatilized NH_3 (data not shown). In the work of Ferguson et al. (1984), their findings showed that the greater the amount of the H^+ buffering capacity between a soil's initial pH to a pH of 7.5, the lesser is the likelihood for serious losses of NH_3. Although in this experiment the buffering capacity of the acidified biochars or the soil with the acidified biochars was not determined, PC400 may have imparted a good H^+ supplying capacity to the PL and to the soil.

Aside from lowering the pH of the PL, the biochars may have kept the amounts of volatilized NH_3 at lower levels by retaining some of the NH_4^+ on their exchange sites. Based on the CEC of the biochars, the theoretical reduction in NH_3 volatilization under surface incubation could have only ranged from 6 to 36%. However, the actual reduction ranged from 24 to 67% when compared to the unamended surface-applied PL.

The CEC values for low-temperature biochars (Table 2.1) are close to the initial value of 140 mmol kg^{-1} (14 cmol kg^{-1}) obtained by Cheng et al. (2006) for black carbon (BC) from black locust (*Robinia pseudoacacia* L.). Cheng et al. (2006) demonstrated adding manure led to a 64% and a 39% increase in potential CEC of BC and BC – soil mixtures. This was attributed to the oxidation of the BC itself and to the sorption of non-BC organic matter to the BC particles (Cheng et al., 2006). Considering the fact that their experiment was incubated under a different condition (30°C for 120 d), it could not be ascertained if the biochars in this study had increased their CEC to a similar extent, if it had indeed increased. Nevertheless, it is possible that the observed greater reduction of lost NH_3 from surface-applied char-amended PL (than theoretically expected from the biochars' CEC) was mainly due to a pH effect rather than to a CEC effect. This is even more apparent under incorporated incubation where some NH_3 were still volatilized even though the soil's CEC alone is more than enough to retain what was volatilized from surface-applied PL.

Adding acidified biochars to PL depressed CO_2-C evolved in the surface incubation (F=9.24; p=0.0083) by as much as 9 to 22% of those evolved from unamended PL (Fig. 2.2). Conversely, when char-amended PL was mixed with soil, total CO_2-C were greater by 0.5 to 45% compared to unamended PL (F=6.88; p=0.0255) (Fig. 2.2). Biochars have been reported to enhance microbial activity and growth either directly by providing some labile C or indirectly by providing an environment (or habitat) conducive to microbial growth (Kolb et al., 2009; Steiner et al., 2007; Steiner et al., in press; Pietikäinen et al., 2000). Because heterotrophic microorganisms require C to build up tissues, release of respired CO_2-C is expected to increase when microbial growth is stimulated. This may have been the reason for the increased CO_2-C released when PL+char mixtures came in good contact with soil in the incorporated incubation. Considering that biochars are known to be relatively resistant to microbial decomposition and considering that they did not increase CO_2-C evolved from surface-applied PL, it appears that such a surge of CO_2 evolved from char-amended incorporated PL may have been due to the priming of soil organic carbon by biochars. Adding biochar to soils has been observed to increase losses of soil organic carbon (Steinbeiss et al., 2009; Wardle et al., 2008). Furthermore, in the incorporated incubation, PL+PC600 and PL+PH600 released more CO_2-C than PL+PC400 (F=5.86; p=0.0360) and PL+PH400 (F=6.01; p=0.0341), respectively. Litters amended with PCs were also found to liberate more CO_2-C than those with PHs. This suggests that high-temperature biochars may have enhanced microbial activity more than low-temperature biochars and that PCs may have been preferred more than PHs by soil microbes.

Regardless of the time of leaching, inorganic P in the leachate was not different among treatments for both surface (F=0.68; p=0.6270) and incorporated (F=1.08; p=0.4227) incubations (Fig. 2.3). Likewise, the unamended PL did not differ from the rest in terms of the amount of 1 M KCl-extractable inorganic P at the end of both experiments (Fig. 2.4), except for surface-applied PL+PC600.

Most of the inorganic P in PL is bound in salts of Ca, Mg, Na and K (Tasistro et al., 2004). After one month of surface application to soil, PL changes pH from 8 to 6, causing some of the salt-bound P to dissolve (Tasistro et al., 2004). In this experiment, since the acidified biochars did not generally affect the release of inorganic P from PL, it could be speculated that char-amended PL had lowered its pH to the same level as that of the unamended PL after 15 and 21 days of incubation (the days when the leaching events and extraction were performed to the experimental units). If these speculations are true, the observed difference in the amounts of inorganic P extracted between surface-applied PLs amended with PC600 and those with PC400 or with the other biochars may be associated with their difference in retaining P. Novak et al. (2009) found decreasing amounts of inorganic P with increasing pecan shell biochar application to sandy soils and suggested P sorption on biochar as one of the possible reasons. In contrast, Kolb et al. (2009) reported increasing inorganic P with increasing levels of charcoal added to four soils of different physical and chemical properties. Kolb et al. (2009) attributed such increase to direct addition and slow mineralization of P from the charcoal itself. In this study, the inorganic P released is most likely derived from the PL and the soil rather than from biochars because of the small amount of total P in the biochars compared to those in the PL and the soil combined.

In terms of N release, surface-applied PL with acidified biochars had comparable amounts of inorganic N leached as unamended litter (F=3.05; p=0.1146) (Fig. 2.5) regardless of whether it was on the 14 or 21 d. For PC-amended litters, PL+PC400 had more inorganic N leached than PL+PC600 (F=9.06; p=0.0142). As discussed above, PC400 reduced NH_3 losses from PL better than PC600. This may have contributed to keeping more of the PL-released NH_4^+ in solution by the PC400 instead of volatilizing it to the air. In addition, PL+PHs led to greater inorganic N leached compared to PL+PCs (F=6.74; p=0.0289). The greater inorganic N leached from PL+PHs suggests increased soluble inorganic N from PL or from PHs. The possibility that some of the soluble inorganic N may be coming from PHs may be excluded as total amounts of released inorganic N from char-amended PL were not different from unamended PL under surface incubation (F=2.65; p=0.1123) (Table 2.2). Similarly, Gaskin et al. (2008) reported that biochar N from PHs or PCs do not mineralize in soil. Under incorporated incubation, no difference in leachable inorganic N among treatments were observed (F=2.56; p=0.1093) (Fig. 2.6). This lack of difference among char-amended litters in their amounts of inorganic N leached under incorporated incubation may be due to the possibility that inorganic N released in solution by char-amended litters may have been immobilized by the soil microorganisms. This agrees with the fact that unamended PL itself did not mineralize under the incorporated incubation. In addition, the total amount of released inorganic N from unamended PL was no different from those of the char-amended PL under incorporated incubation (F=0.49; p=0.7470) (Table 2.2). In terms of the amounts of leached NH_4^+ or NO_3^-, no significant differences were observed among treatments under surface or incorporated incubations (Fig. 2.5 and 2.6).

Char-amended PL had insignificantly different amounts of extractable NH_4^+ as unamended PL under surface (F=2.54; p=0.1134) and incorporated incubations (F=2.16; p=0.1551) (Fig. 2.7). This implies lack of retention of NH_4^+ by biochars. In contrast, combining acidified biochars with surface-applied or incorporated PL had variable effect on extractable NO_3^-. Under incorporated incubation, adding PL with PC600 and PH600 had higher amounts of extracted nitrate compared to PL with PC400 and PH400, respectively. The increased amounts of NO_3^- extracted from PL amended with the high-temperature biochars could either mean increased retention or increased nitrification. However, this experiment could not ascertain either of these two possible mechanisms. In forest soils, charcoal has been reported to increase nitrification when added with glycine, a readily mineralizable N source (Gundale and DeLuca, 2007; DeLuca et al., 2006; MacKenzie and DeLuca, 2006; Berglund et al., 2004). These reports attributed such an observation to the capacity of charcoal to sorb phenolic compounds that inhibit nitrification (Zackrisson et al., 1996; DeLuca et al., 2002; Gundale and DeLuca 2007; DeLuca et al., 2006). In this study, the observed difference in extracted NO_3-N between the high-temperature and the low-temperature biochars could not be easily related to their capacity to sorb these nitrification-inhibiting compounds since this was not explored. If the high-temperature biochars had indeed enhanced nitrification, they may have simply provided a physical environment more conducive for microbial growth away from predation (Pietikainen et al., 2000). This appears to coincide with the greater CO_2-C released from PL amended with high-temperature than from those amended with low-temperature biochars (Fig 2.4) under incorporated incubation. Under surface incubation, difference in the amounts of extracted NO_3^- was only observed between PH biochars and no longer between PC biochars (Fig. 2.9). The reason for the insignificant difference of NO_3^- released between surface-applied PL+PC400 and PL+PC600 with surface incubation is not clear. Surface-applied char-amended PL did not increase the amounts of extractable nitrate, except for those amended with PH600.

Sorption-Desorption Study

Experimental sorption and desorption isotherms show sorption and desorption behavior of biochars for NH_4-N (Fig. 2.8). Sorption of NH_4-N is characterized by its high affinity on biochars when present at lower concentrations, continues to progress as concentrations increase, and levels off after a certain point. Desorption of this ion from biochars indicates hysteresis, a phenomenon implying capacity of biochars to hold its sorbed NH_4-N when subjected to disequilibrium. Linearized Langmuir isotherm parameter in Table 2.3 suggests PC400 and PH400 to have relatively greater sorption maxima than PC600 and PH600, respectively, although difference among biochars were not significantly different (F=2.94; p=0.0989). Greater sorption maxima suggest greater sorption capacity. Additionally, after the last desorption step, PC400 and PH400 retained more than PC600 (p=0.0004) and PH600 (p=0.0005), respectively.

These findings appear to contradict the lack of significant retention of NH_4-N (1 M KCl-extractable) in char-amended PL treatments for surface (F=2.54; p=0.1134) and incorporated (F=2.16; p=0.1551) incubations after two leaching events. This is even more unexpected considering the fact that chars have been shown to adsorb dissolved organic matter (DOM) (Miura et al., 2007; Miura et al., 2008) and that poultry litter could have been a good source for this. Adsorbed organic matter could have provided additional sorption sites for NH_4^+. However, it should also be noted that poultry litter also contains substantial amounts of salts. Moreover, the acidified biochars used in the incubation studies were unwashed unlike those tested in the batch sorption-desorption experiment. The soluble salts from the poultry litter and biochars may have released competing polyvalent ions in solution that would have stronger affinities than NH_4^+ for sorption sites on the biochar zsurface or on the adsorbed organic matter (such as divalent cations as Ca^{2+}, Mg^{2+}, etc.).

Contrary to their capacity to sorb NH_4-N, the biochars did not sorb inorganic P even at very low concentrations. This does not agree with the implied difference in inorganic P extracted between litters with PC400 and those with PC600 in surface incubation. It is possible then that the observed difference in the amounts of inorganic P extracted in soil and PL with these two biochars at the end of the surface incubation was merely due to pH effect. It has been discussed earlier that PC400 may have better H^+ supplying capacity than PC600. This may have caused more of the inorganic P from the poultry litter to solubilize. On the other hand, the lack of difference in the amounts of extracted P between these two biochars under incorporated incubation may be due to its thorough mixing with the soil which caused their initially different pHs to be overwhelmed by that of the soil.

Conclusion

Amending PL with acidified biochars reduced NH_3 loss from PL by 24 to 67% under surface incubation and by 55 to 60% under incorporated incubation. It also decreased CO_2 evolved from surface-applied PL by as much as 9 to 22% but it increased

CO_2 evolved from incorporated PL by as much as 0.5 to 45%. In terms of nutrient release, amending PL with acidified biochars did not generally affect the release of both leachable and extractable inorganic P from both surface-applied and incorporated poultry litter. Similarly, it did not affect the release of leachable inorganic N from poultry litter under both surface and incorporated incubations. Extractable NH_4^+ from char-amended PL were not different from unamended PL under both surface and incorporated incubations. Extractable NO_3^- from char-amended PL were comparable to unamended PL under surface incubation, except for PL+PH600. Under incorporated incubation, extractable NO_3^- from char-amended PL were also similar to unamended PL except those PL with the high-temperature biochars. Contrary to the findings from the incubation experiments, the biochars have shown capacity to sorb NH_4-N. However, in terms of ortho-P, the biochars did not show capacity to sorb this ion at all.

Overall, the acidified biochars have indeed shown potential to reduce NH_3 losses from PL. The fact that it did not affect the release of leachable inorganic N and P suggests that acidified biochars do not withhold potentially available N and P from PL for the plants. However, from an environmental perspective, the lack of effect of acidified biochars on the release of inorganic P could render acidified biochar an unsuitable amendment especially to surface-applied PL as P loading in runoff is also a major problem in pasture soils.

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Table 2.1. Selected chemical properties of soil, poultry litter, and acidified biochars.

Sample	pH	Total C, %	Total P, ug g^{-1}	Total N, ug g^{-1}	CEC, cmol kg^{-1}
Soil	6.69	2.2	724	2,027	6.4
Poultry litter	8.62	35.3	16,238	41,200	ND
PC400	2.54	60.8	18	1,372	17.4
PC600	2.63	74.4	110	1,484	3.2
PH400	2.55	62.5	126	1,835	15.7
PH600	2.55	67.8	1,294	19,730	5.4

Note: PC and PH refer to biochar from pine chips and peanut hulls, respectively; 400 and 600 refer to the peak pyrolysis temperature. ND means not determined

Table 2.2. Total N released from surface-applied or incorporated poultry litter (PL) with or without acidified biochars.

	Total N released, % of Total N in PL	
Treatments	Surface-applied*	Incorporated*
PL	37.4	26.7
PL+PC400	35.6	28.0
PL+PC600	26.3	24.1
PL+PH400	38.8	30.6
PL+PH600	39.6	26.9

Note: PC and PH refer to biochar from pine chips and peanut hulls, respectively; 400 and 600 refer to the peak pyrolysis temperature. Within each column, * means treatments are not significantly different at p-values <0.05.

Table 2.3 Linearized Langmuir sorption isotherm parameters calculated from linearized Langmuir equation: C/q = 1/Kb + C/b, where C is the sorbate equilibrium concentration in solution (ug mL^{-1}), q is the sorbed sorbate concentration (ug g^{-1}), K (mL ug^{-1}) is the Langmuir constant, and b is the sorption maxima (ug g^{-1}).

Biochar	b*, ug g^{-1}	K*, mL ug^{-1}	R^2
PC400	1,229	0.12	0.96
PC600	692	0.18	0.87
PH400	981	0.14	0.97
PH600	456	0.45	0.98

Note: PC and PH refer to biochar from pine chips and peanut hulls, respectively; 400 and 600 refer to the peak pyrolysis temperature. Within each column, * means treatments are not significantly different at p-values <0.05.

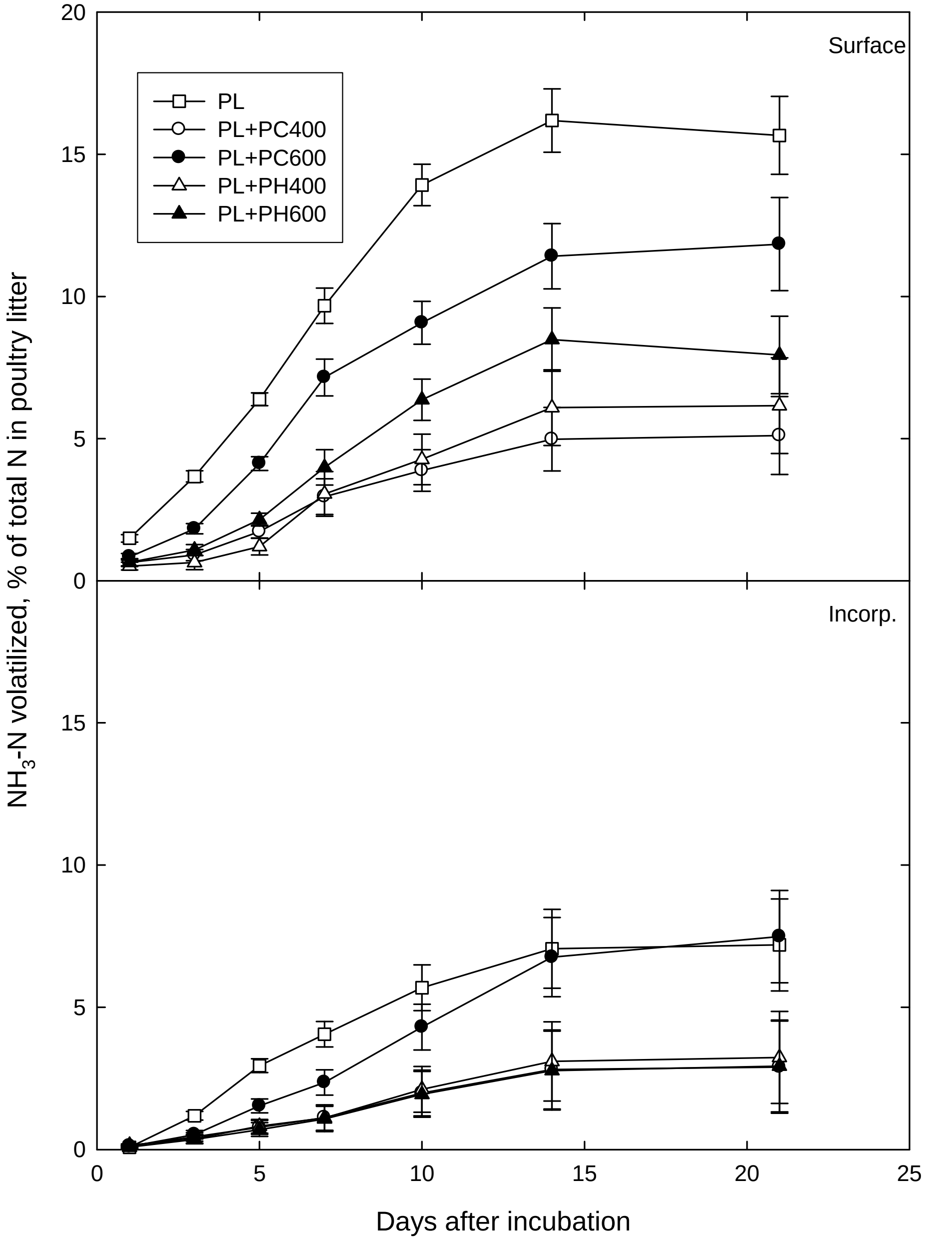

Figure 2.1. Cumulative NH_3-N lost (20°C) from poultry litter (PL, 2.1 g) with or without acidified biochars (PC400, PC600, PH400, PH600, 2.1 g) surface-applied or incorporated. (Error bars are standard errors.)

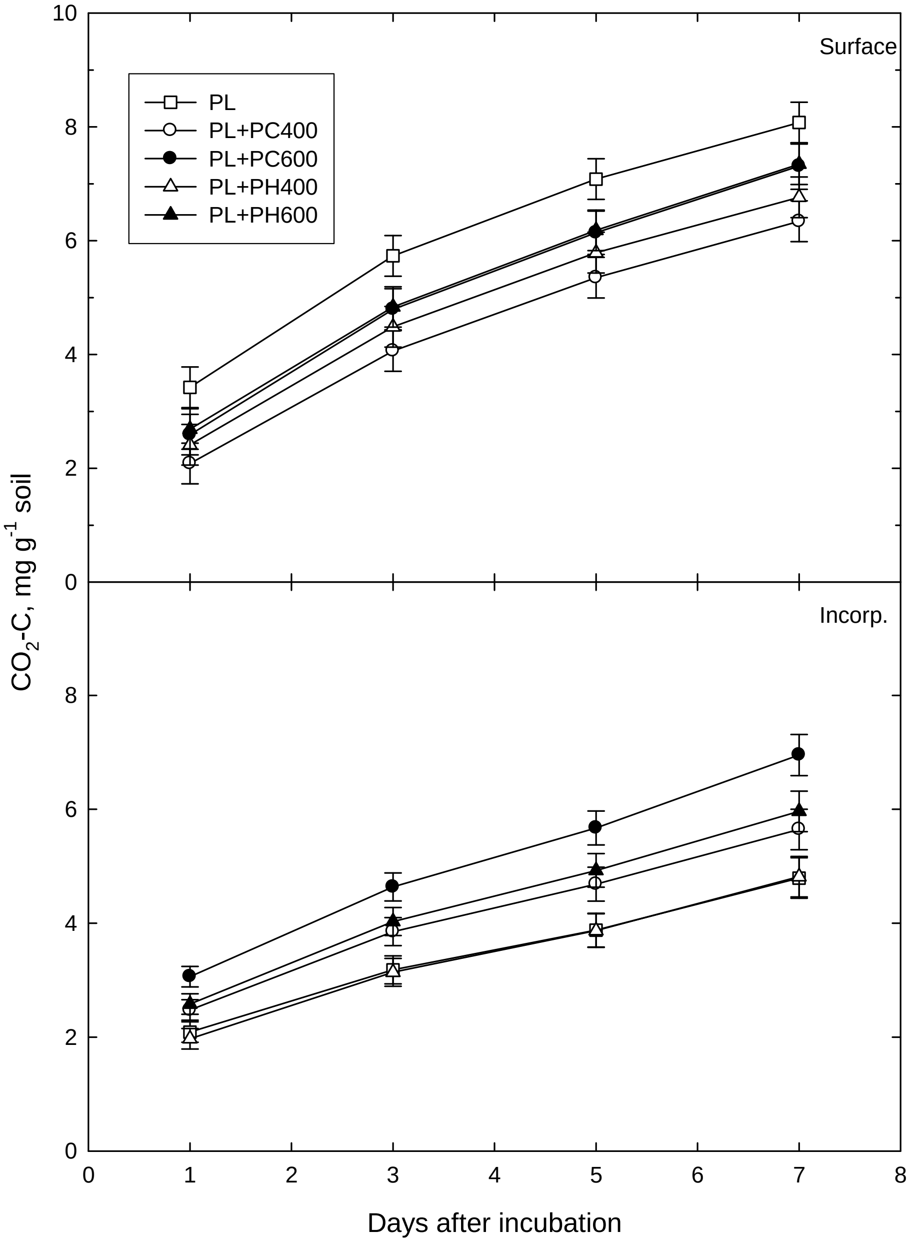

Figure 2.2. Cumulative CO_2-C lost (20°C) from soil (64.5 g) and poultry litter (PL, 2.1 g) with or without acidified biochars (PC400, PC600, PH400, PH600, 2.1 g) surface-applied or incorporated. (Error bars are standard errors.)

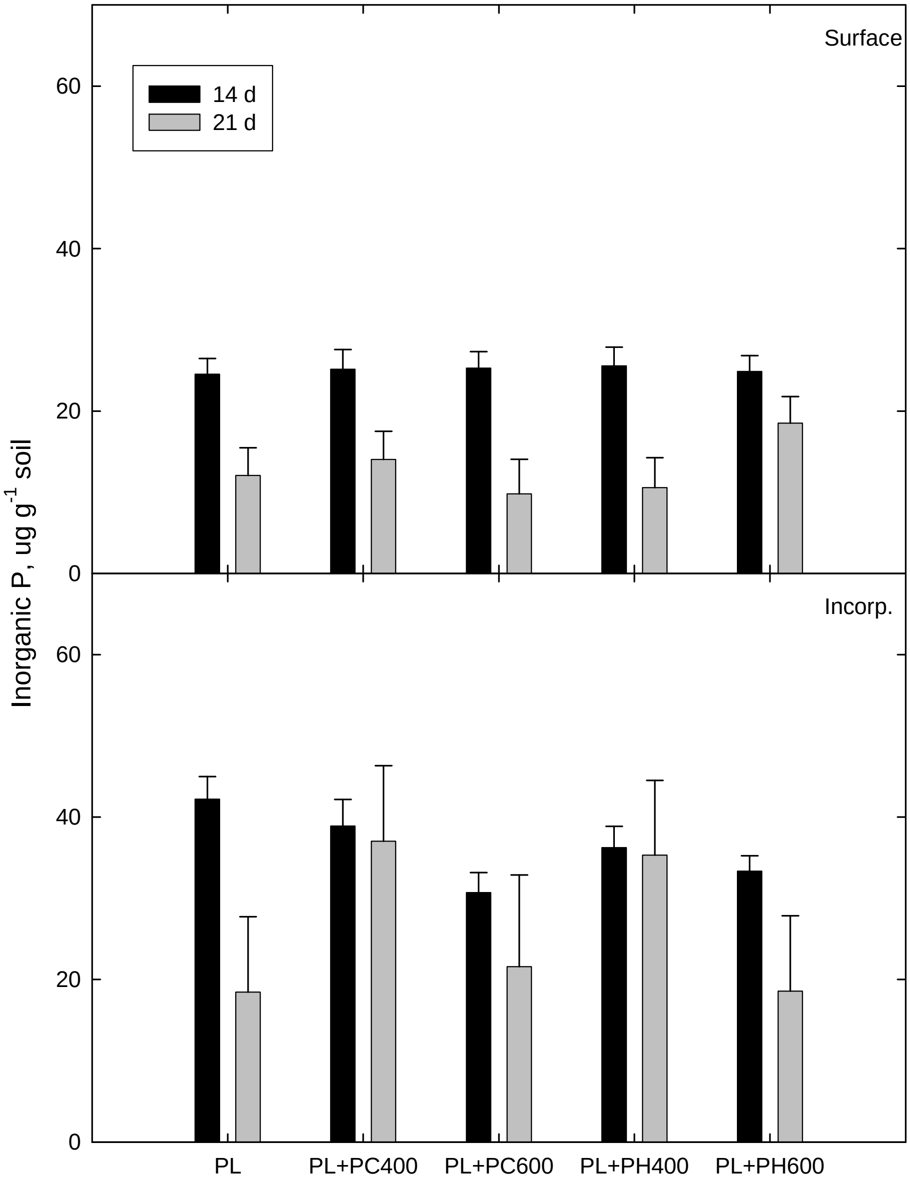

Figure 2.3. Inorganic P leached with 0.01 M $CaCl_2$ at 14 and 21 d of incubation of soil (64.5 g) and poultry litter (PL, 2.1 g) with or without acidified biochars (PC400, PC600, PH400, PH600, 2.1 g) surface-applied or incorporated. (Error bars are standard errors.)

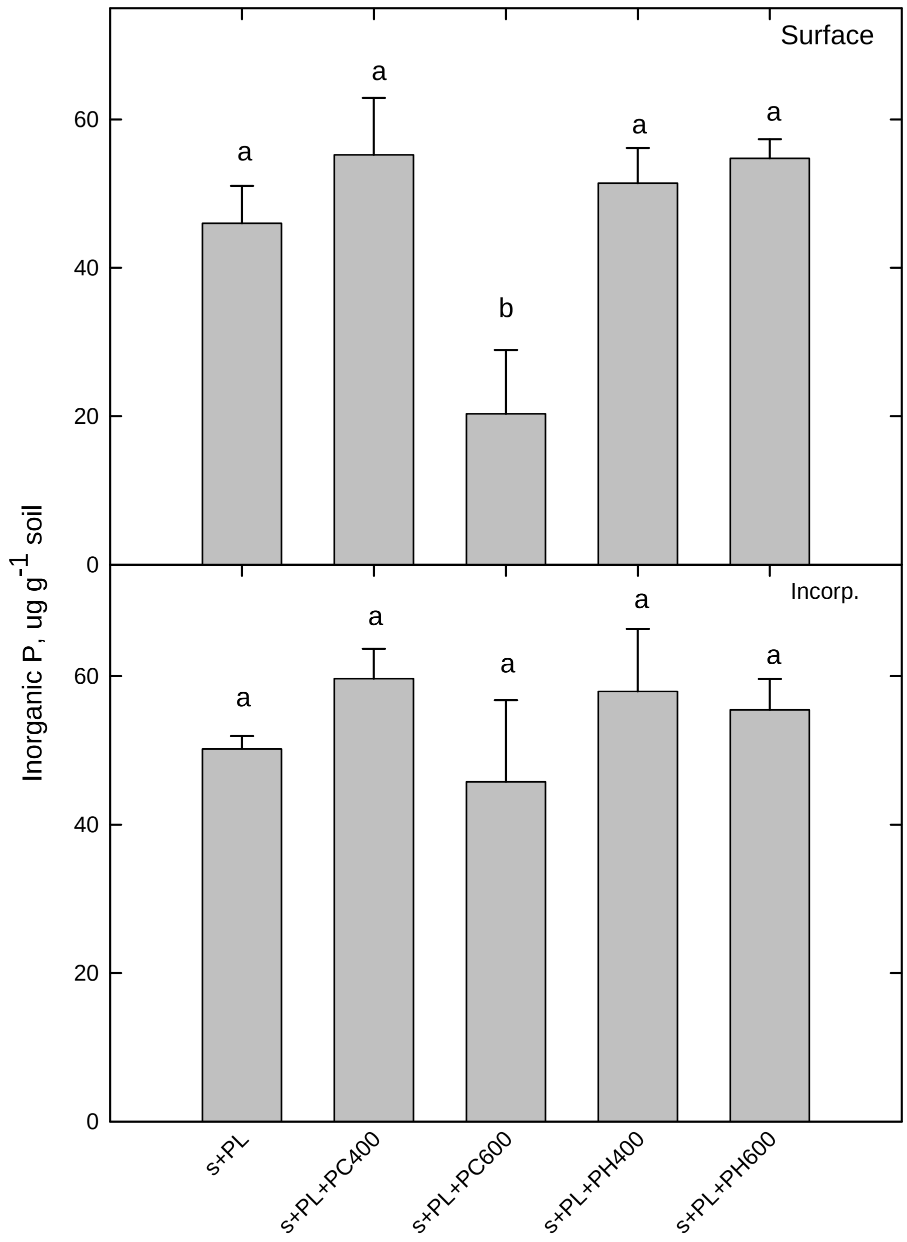

Figure 2.4. Final (21d) inorganic P extracted with 1 M KCl from soil (64.5 g) and poultry litter (PL, 2.1 g) with or without acidified biochars (PC400, PC600, PH400, PH600, 2.1 g) surface-applied or incorporated. (Error bars are standard deviations.
Treatments indicated by a common letter are not significantly different at p-value <0.05)

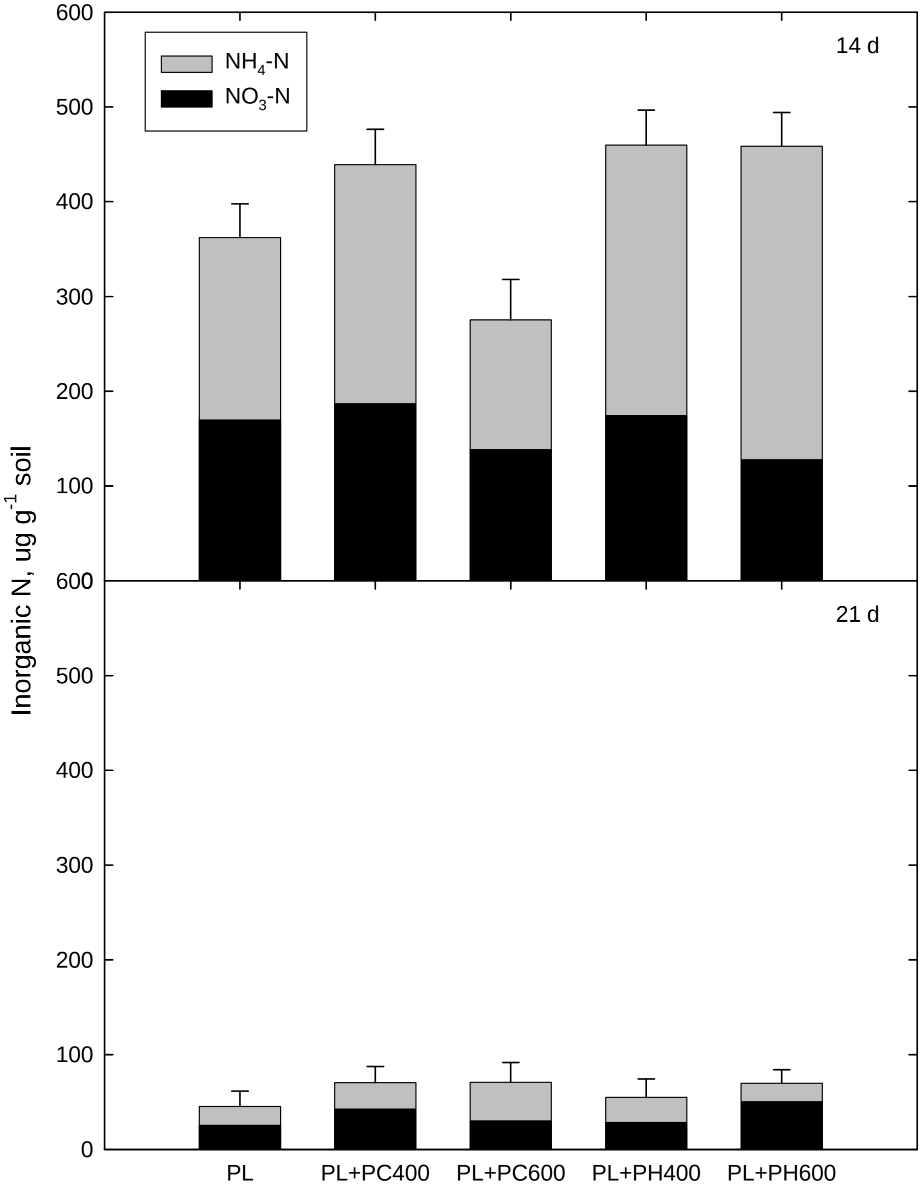

Figure 2.5. Inorganic N leached with 0.01 M $CaCl_2$ at 14 and 21 d of incubation of soil (64.5 g) and surface-applied poultry litter (PL, 2.1 g) with or without acidified biochars (PC400, PC600, PH400, PH600, 2.1 g). (Error bars are standard errors.)

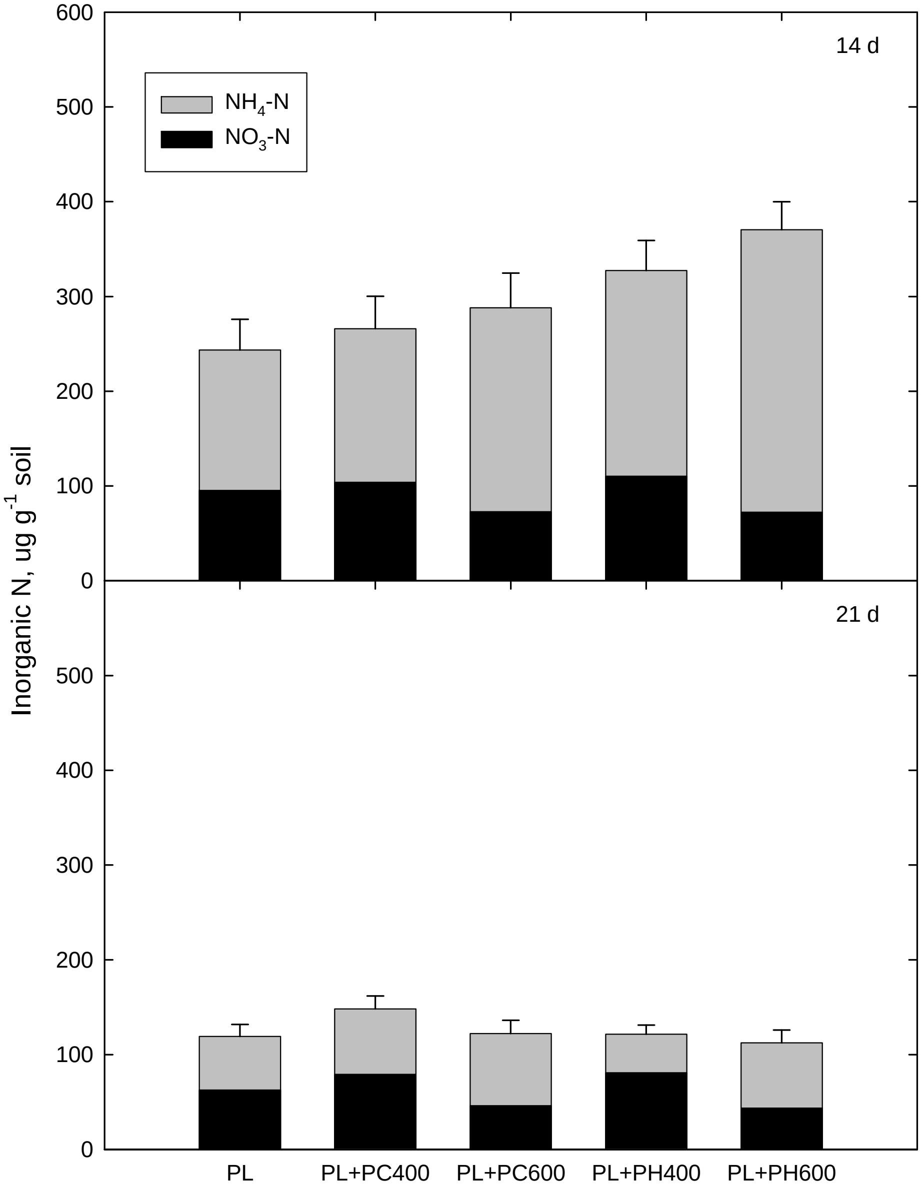

Figure 2.6. Inorganic N leached with 0.01 M $CaCl_2$ at 14 and 21 d of incubation of soil (64.5 g) and incorporated poultry litter (PL, 2.1 g) with or without acidified biochars (PC400, PC600, PH400, PH600, 2.1 g). (Error bars are standard errors.)

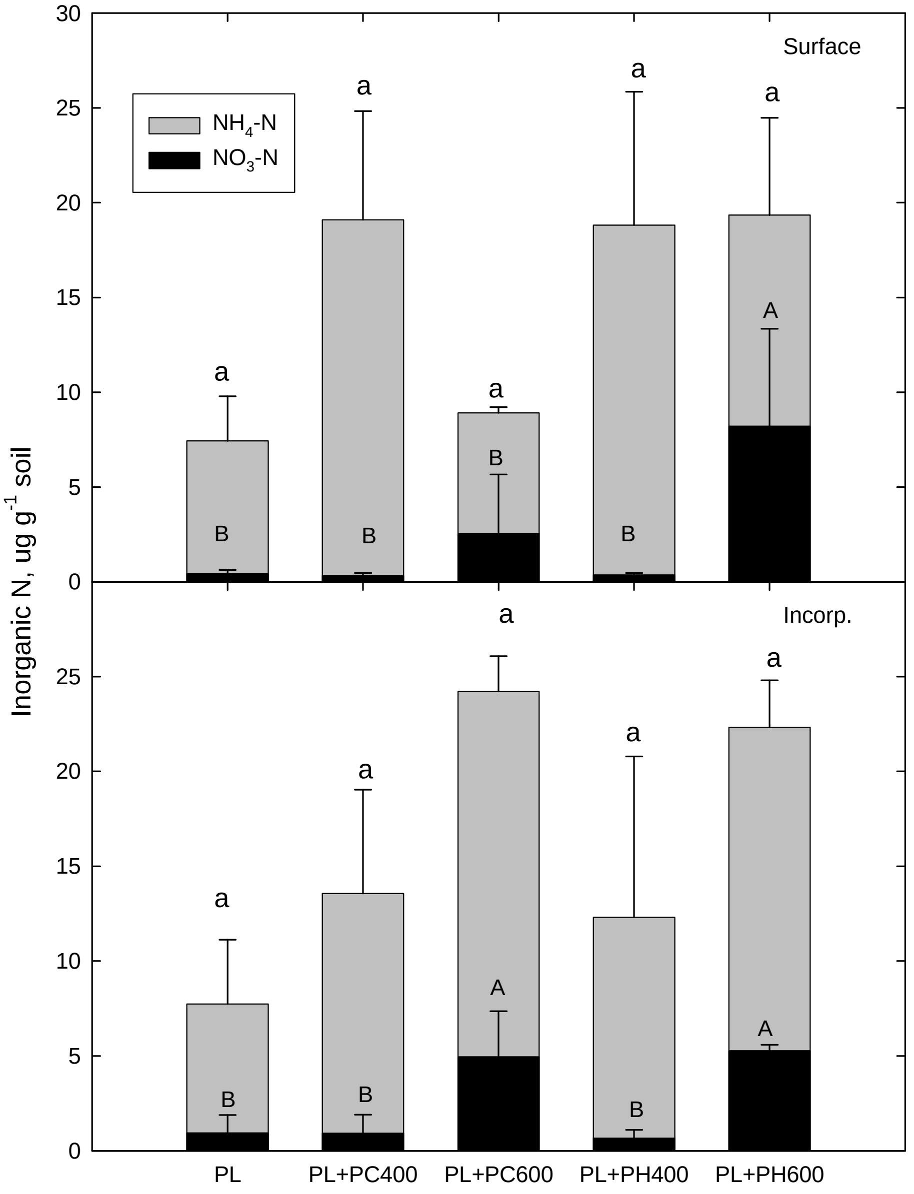

Figure 2.7. Final inorganic N extracted with 1 M KCl at 21 d after incubation of soil (64.5 g) and poultry litter with or without acidified biochars (PC400, PC600, PH400, PH600, 2.1 g) when surface-applied or incorporated. (Error bars are standard deviations. Treatment means having a common letter are not significantly different at p-value <0.05. Lower case letters denote mean comparisons for NH_4-N. Upper case letters denote mean comparisons for NO_3-N.)

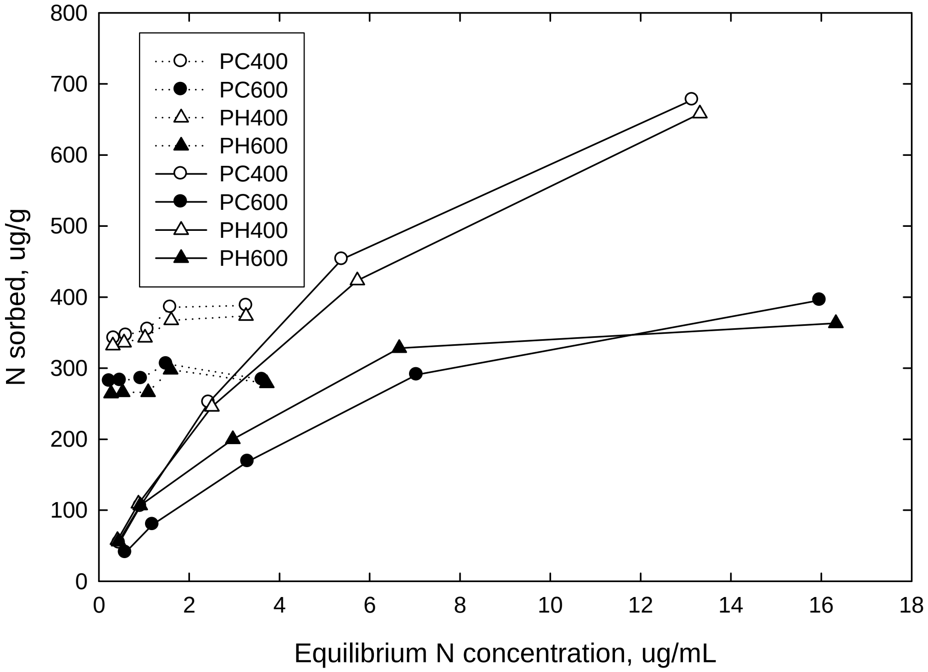

Figure 2.8. Sorption and desorption isotherms for NH_4-N on washed biochars in inorganic matrix (I=5.06 mmol L^{-1} NaCl at pH 7). Solid lines are sorption while dotted lines are desorption isotherms.

CHAPTER 4

SUMMARY AND CONCLUSION

As the top broiler-producing state in the United States, Georgia generates an average of two million Mg poultry litter (PL) annually. Much of this waste is surface applied to pastures, no-till fields or incorporated into the soil in conventional-till farms. While this material provides a good nutrient source particularly for nitrogen (N) and phosphorus (P), its N value could decrease considerably due to ammonia (NH_3) volatilization. One possible way of minimizing NH_3 volatilization from PL is by mixing it with biochar (or char). Biochar, consisting mainly of polyaromatic C, is a by-product from thermochemical bio-fuel production. When acidified, it may reduce NH_3 losses from PL. This study aimed to evaluate the effect of acidified biochar on NH_3 volatilization, CO_2 evolution, and release of inorganic N and P from surface-applied or incorporated PL. This study also aimed to investigate the sorption and desorption of ammonium and orthophosphate on biochar. It is speculated that the biochars have the capacity to sorb NH_4-N and ortho-P from poultry litter. Sorption of NH_4-N by biochars is deemed favorable as another way of controlling the NH_4-N substrate for NH_3 volatilization. Sorption of ortho-P by biochars is also considered desirable as a way for controlling ortho-P in runoff especially from fields surface-applied with poultry litter. Poultry litter with or without acidified pine chips or peanut hull biochars produced at 400 or 600C was surface-applied or incorporated into the soil. Volatilized NH_3 was trapped in

0.1 N H_2SO_4 while CO_2 evolved was estimated with the use of a CO_2 analyzer. Release of inorganic P and N was analyzed by leaching the soil with 0.01 M of calcium chloride followed by a N- and P-free nutrient solution. By the end of the incubation period, each of the treatment was extracted with 1 M KCl to extract inorganic P and N from surface-applied and incorporated poultry litter with the different acidified biochar treatments. Acidified biochars reduced NH_3 losses by 24 to 67% from surface-applied poultry litter. Similarly, it decreased NH_3 volatilized from incorporated poultry litter by 55 to 60%, with the exception of PL+PC600. PC400 consistently reduced NH_3 losses from both surface-applied and incorporated PL. In terms of CO_2-C evolved, acidified biochars decreased it by 9 to 22% when PL was surface-applied but increased it by 0.5 to 45% when PL was incorporated with soil. No significant differences were observed in terms of CO_2-C evolved among char-amended surface-applied PL. However, incorporated PL amended with high temperature biochars lost greater CO_2-C compared to their respective low-temperature biochars. In addition, incorporated litters amended with PCs were found to have released more CO_2-C compared to those amended with PHs. Acidified biochars generally did not affect leachable and extractable inorganic P from surface-applied or incorporated PL, except for surface-applied PL+PC600 which released lower amounts of extractable inorganic P than the unamended PL. It did not also affect leachable inorganic N from surface-applied and incorporated PL. However, among surface-applied char-amended PL, PL+PC400 had greater inorganic N leached compared to PL+PC600. In addition, PL+PHs led to greater leached amounts of inorganic N compared to PL+PCs. In contrast, none of these char-amended treatment differences in leachable inorganic N was observed under incorporated incubation. Combining acidified biochars with surface-applied or incorporated PL did not have an effect on extractable NH_4^+. In terms of extractable NO_3^-, char-amended PL were comparable to unamended PL except for PL+PH600. Under incorporated incubation, char-amended PL were also comparable to unamended PL except for PL+PC600 and PL+PH600.

The biochars have shown capacity to sorb NH_4-N. Low-temperature biochars have greater retention capacity compared to the high-temperature biochars. However, none of the biochars demonstrated capacity to sorb inorganic P.

The acidified biochars have indeed shown potential to reduce NH_3 losses from PL. The fact that it did not affect the release of leachable inorganic N and P suggests that acidified biochars do not withhold potentially available N and P from PL for the plants. However, from an environmental perspective, the lack of effect of acidified biochars on the release of inorganic P could render acidified biochars an unsuitable amendment especially to surface-applied PL as P loading in runoff is also a major problem in pasture soils.

APPENDIX A

STATISTICAL ANALYSES

Appendix Table A.1. Repeated Measure Analysis of Variance for Cumulative NH_3-N volatilized from surface-applied poultry litter with or without acidified biochars using PROC MIXED, SAS.

Source	df	F	p-value
Treatment	4	24.99	0.0072
PL vs REST	1	75.42	0.0019
PL+PC400 vs PL+PC600	1	20.92	0.0132
PL+PH400 vs PL+PH600	1	2.12	0.2293
PL+PCs vs PL+PHs	1	2.81	0.1784
Day	6	63.00	0.0041
Treatment x Day	24	43.40	0.1194
Moisture	1	33.00	<.0001

Appendix Table A.2. Repeated Measure Analysis of Variance for Cumulative NH_3-N volatilized from incorporated poultry litter with or without acidified biochars using PROC MIXED, SAS.

Source	df	F	p-value
Treatment	4	3.68	0.0433
PL vs REST	1	8.60	0.0150
PL+PC400 vs PL+PC600	1	4.13	0.0695
PL+PH400 vs PL+PH600	1	0.03	0.8726
PL+PCs vs PL+PHs	1	1.94	0.1942
Day	6	23.72	0.0007
Treatment x Day	24	13.98	0.2086
Moisture	1	0.63	0.4465

Appendix Table A.3. Repeated Measure Analysis of Variance for Cumulative CO_2-C evolved from surface-applied poultry litter with or without acidified biochars using PROC MIXED, SAS.

Source	df	F	p-value
Treatment	4	3.25	0.0409
PL vs REST	1	9.24	0.0083
PL+PC400 vs PL+PC600	1	2.35	0.1455
PL+PH400 vs PL+PH600	1	0.72	0.4086
PL+PCs vs PL+PHs	1	0.46	0.5069
Day	3	531.81	<.0001
Treatment x Day	12	1.14	0.3899
Moisture	1	5.49	0.0260

Appendix Table A.4. Repeated Measure Analysis of Variance for Cumulative CO_2-C evolved from incorporated poultry litter with or without acidified biochars using PROC MIXED, SAS.

Source	df	F	p-value
Treatment	4	6.44	0.008
PL vs REST	1	6.88	0.0255
PL+PC400 vs PL+PC600	1	5.86	0.0360
PL+PH400 vs PL+PH600	1	6.01	0.0341
PL+PCs vs PL+PHs	1	7.10	0.0237
Day	3	847.65	<.0001
Treatment x Day	12	3.26	0.0839
Moisture	1	42.90	0.0007

Appendix Table A.5. Repeated Measure Analysis of Variance for Inorganic P in the leachate from surface-applied poultry litter with or without acidified biochars using PROC MIXED, SAS.

Source	df	F	p-value
Treatment	4	0.68	0.6270
Leaching time	1	11.39	0.0059
Treatment x Leaching time	4	1.68	0.2408
Moisture	1	0.38	0.5531

Appendix Table A.6. Repeated Measure Analysis of Variance for Inorganic P in the leachate from incorporated poultry litter with or without acidified biochars using PROC MIXED, SAS.

Source	df	F	p-value
Treatment	4	1.08	0.4227
Leaching time	1	3.80	0.0694
Treatment x Leaching time	4	1.25	0.3553
Moisture	1	5.05	0.0546

Appendix Table A.7. Analysis of Variance for Inorganic P in 1 M KCl extract from surface-applied poultry litter with or without acidified biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	4	1863.72	465.93	13.94	0.0007
Error	9	300.89	33.43		
Total	13	2164.60			

Appendix Table A.8. Analysis of Variance for Inorganic P in 1 M KCl extract from incorporated poultry litter with or without acidified biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	4	326.71	81.68	2.19	0.1509
Error	9	335.31	37.26		
Total	13	662.03			

Appendix Table A.9. Repeated Measure Analysis of Variance for Inorganic N in the leachate from surface-applied poultry litter with or without acidified biochars using PROC MIXED, SAS.

Source	df	F	p-value
Treatment	4	4.49	0.0284
PL vs REST	1	3.05	0.1146
PL+PC400 vs PL+PC600	1	9.06	0.0142
PL+PH400 vs PL+PH600	1	0.08	0.7836
PL+PCs vs PL+PHs	1	6.74	0.0289
Leaching time	1	119.84	<.0001
Treatment x Leaching time	4	3.57	0.0555
Moisture	1	1.34	0.2778

Appendix Table A.10. Repeated Measure Analysis of Variance for Inorganic N in the leachate from incorporated poultry litter with or without acidified biochars using PROC MIXED, SAS.

Source	df	F	p-value
Treatment	4	2.56	0.1093
Leaching time	1	43.80	<.0001
Treatment x Leaching time	4	3.00	0.0780
Moisture	1	43.04	<.0001

Appendix Table A.11. Analysis of Variance for Nitrate-N in the leachate from surface-applied poultry litter with or without acidified biochars using PROC MIXED, SAS.

Source	df	F	p-value
Treatment	4	1.32	0.3340
Leaching time	1	32.59	<.0001
Treatment x Leaching time	4	2.72	0.1066
Moisture	1	0.01	0.9119

Appendix Table A.12. Analysis of Variance for Nitrate-N in the leachate from incorporated poultry litter with or without acidified biochars using PROC MIXED, SAS.

Source	df	F	p-value
Treatment	4	3.45	0.0575
Leaching time	1	1.74	0.2056
Treatment x Leaching time	4	0.02	0.9986
Moisture	1	5.58	0.0327

Appendix Table A.13. Analysis of Variance for NH_4-N in 1 M KCl extract from surface-applied poultry litter with or without acidified biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	4	394.83	98.71	2.54	0.1134
Error	9	350.44	38.94		
Total	13	745.27			

Appendix Table A.14. Analysis of Variance for NH_4-N in 1 M KCl extract from incorporated poultry litter with or without acidified biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	4	248.4239000	62.11	2.16	0.1551
Error	9	258.78	28.75		
Total	13	507.20			

Appendix Table A.15. Analysis of Variance for Nitrate-N in 1 M KCl extract from surface-applied poultry litter with or without acidified biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	4	138284123.3	34571030.8	4.98	0.0215
Error	9	62485242.8	6942804.8		
Total	13	200769366.1			

Appendix Table A.16. Analysis of Variance for Nitrate-N in 1 M KCl extract from incorporated poultry litter with or without acidified biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	4	59911442.11	14977860.53	13.29	0.0008
Error	9	10139854.75	1126650.53		
Total	13	70051296.86			

Appendix Table A.17. Analysis of Variance for Total N released (% TN in PL) from surface-applied poultry litter with or without acidified biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	4	249.34	62.33	2.65	0.1123
Error	8	188.23	23.53		
Total	12	437.57			

Appendix Table A.18. Analysis of Variance for Total N released (% TN in PL) from incorporated poultry litter with or without acidified biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	4	55.90	13.97	0.49	0.7470
Error	9	259.30	28.81		
Total	13	315.20			

Appendix Table A.19. Analysis of Variance for sorption maxima of biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	3	1020736.50	340245.50	2.94	0.0989
Error	8	925643.60	115705.45		
Total	11	1946380.09			

Appendix Table A.20. Analysis of Variance for NH_4-N retained by biochars after five desorption steps using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	3	16921.47	5640.49	22.70	0.0006
Error	7	1739.64	248.52		
Total	10	18661.11			

Appendix Table A.21. Analysis of Variance for individual pHs of poultry litter and biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	4	87.79	21.95	86634.90	<.0001
PL vs REST	1	87.77	87.77	346474.00	<.0001
PC400 vs PC600	1	0.01	0.01	47.96	<.0001
PH400 vs PH600	1	0.0001	0.0001	0.26	0.6191
PCs vs PHs	1	0.0044	0.0044	17.40	0.0019
Error	10	0.0025	0.00025		
Total	14	87.79			

Appendix Table A.22. Analysis of Variance for initial pHs of poultry litter and biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	4	3.77	0.94	421.30	<.0001
PL vs PL+chars	1	3.37	3.37	1504.53	<.0001
PL+PC400 vs PL+PC600	1	0.23	0.23	101.85	<.0001
PL+PH400 vs PL+PH600	1	0.08	0.08	35.42	0.0001
PL+PCs vs PL+PHs	1	0.10	0.10	43.39	<.0001
Error	10	0.0224	0.0022		
Total	14	3.80			

Appendix Table A.23. Analysis of Variance for initial pHs of soil, poultry litter and biochars using PROC GLM, SAS.

Source	df	SS	MS	F	p-value
Treatment	4	0.43	0.11	7.54	0.0045
s+PL vs s+PL+chars	1	0.32	0.32	22.31	0.0008
s+PL+PC400 vs s+PL+PC600	1	0.02	0.02	1.42	0.2602
s+PL+PH400 vs s+PL+PH600	1	0.07	0.07	4.62	0.0572
s+PL+PCs vs s+PL+PHs	1	0.03	0.03	1.82	0.2067
Error	10	0.14	0.01		
Total	14	0.58			

APPENDIX B

INITIAL CHEMICAL PROPERTIES OF SOIL, POULTRY LITTER AND BIOCHARS

Appendix Table B.1. Initial pH readings of poultry litter with or without acidified biochars.

Sample	Mean pH	Standard Deviation
PL	8.55	0.01
PL+PC400	7.26	0.07
PL+PC600	7.65	0.05
PL+PH400	7.39	0.02
PL+PH600	7.16	0.06

Appendix Table B.2. Initial pH readings of soil, poultry litter with or without acidified biochars.

Sample	Mean pH	Standard Deviation
s+PL	6.94	0.04
s+PL+PC400	6.47	0.25
s+PL+PC600	6.59	0.03
s+PL+PH400	6.73	0.09
s+PL+PH600	6.52	0.03

Appendix Table B.3. Initial inorganic P and N of soil, poultry litter and acidified biochars at the start of surface or incorporated incubation.

Sample	Initial Inorganic P, ug g-1		Initial Inorganic N, ug g-1	
	Surface	Incorp.	Surface	Incorp.
Soil	11	13	61	71
PL	340	326	10,011	13451
PC400	11	11	1	2
PC600	4	4	2	2
PH400	36	35	1	2
PH600	61	66	15	14

Appendix Table B.4. Mineral composition of washed biochars used in the sorption-desorption experiment.

Char	Elemental Composition								
	Ca	Mg	K	Na	Mn	S	Al	Fe	Si
PC400	1035.50	491.33	95.22	14.23	144.10	54.62	83.27	63.02	71.36
PC600	1837.00	744.97	72.67	18.84	254.27	86.49	152.07	80.69	93.75
PH400	1241.33	566.20	79.64	17.70	98.58	177.30	127.27	194.23	114.84
PH600	3886.33	2194.00	465.97	21.95	113.07	582.10	728.13	522.60	152.27