Nutrient Availability from Poultry Litter Co-Products

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Abstract

Phosphorus (P) is a nutrient of concern in the Chesapeake Bay watershed due to nutrient imbalances in areas with confined animal feeding operations. By converting poultry litter to an ash via thermal conversion, nutrients are concentrated and are economical to ship out of nutrient surplus watersheds to nutrient deficient regions, such as the corn-belt. We initiated incubation and field studies on sandy loam soils to test P and potassium (K) availability from poultry litter ash (PLA). Four PLA products, derived from different sources using different combustion techniques, and 2 biochar products were characterized. Poultry litter (PL) co-products were compared to a no-fertilizer control and inorganic P (triple super phosphate; TSP) and inorganic K (muriate of potash; KCl) fertilizer at similar rates. In the incubation study, standard fertilizers (TSP and PL) had the greatest initial availability for P (55.50% TSP; 9.13% PL) and K (97.99% PL), respectively. The PL co-products varied in availabilities based on thermo-conversion system from 1.60- 8.63% for P to 8.14- 88.10% for K. One ash co-product (ASH4) produced similar availabilities to the industry standard fertilizers after 56 days. In conclusion, co-products from combustion thermo-conversion systems were found be superior to gasification and pyrolysis systems when the desire was to produce the most plant available P and K dense PL co-products. In the field studies, yield, Mehlich-I extractable soil nutrients, plant tissue and grain samples, and organic matter content was used to compare treatments. Poultry litter ash co-products were highly variable due to the thermo-conversion system and feedstock of formation. If all ideal combustion criteria are met, then PL co-products are feasible to use as fertilizer

sources, but will need to be individually analyzed for nutrient content before making application recommendations. A greater amount of the co-products will have to be applied to meet the same nutrient availability of the standards due to their lower availability. Fresh PL tends to be the better fertilizer due to its added N content, which is lost in thermo-conversion systems and would have to be supplemented with the ash co-products. Biochars tend to be less available than their ash counter parts. More research using the water soluble availabilities instead of the total concentration nutrients of the co-products are needed to be able to identify stronger relationships with standard fertilizers.

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1. Literature Review
1.1 Introduction

The Chesapeake Bay has one of the largest watersheds in the United States and spans six different states and the District of Columbia. The Cheseapeake Bay's estuarine system provides services to nearly 15 million people (Boesch et al., 2001). The bay is a complicated system spread over 166,000 square kilometers that contains a variation of land uses, nutrient sources, soil, climate, and weather conditions (Ator et al., 2011). One of the main areas of concern is the Delmarva Peninsula; which is situated on the east coast of the U.S. and is comprised of three different states: Delaware, Maryland, and Virginia. According to the 2012 US Agricultural Census, Maryland was ranked #7 in the country for broiler [*Gallus gallus domesticus* (L.)] production with 64,192,426 birds and $922,999,000 in sales, followed closely by Delaware at #11 with 43,206,514 birds and $811,301,000 in sales, and Virginia at #14 with 38,386,310 birds and $1,161,564,000 in sales (NASS, 2012). Also, farmers in these states are large fertilizer consumers for their agricultural crop lands: Maryland has 612,213 hectares, Delaware has 220,838 hectares, and Virginia has the most with 1,097,656 hectares of cropland (NASS, 2012). For example, in 2007, Virginia used 76.4 million total lbs of P with at net mass balance of 42.7 million lbs of P, Maryland used 32.8 million lbs of P with a net mass balance of 12.8 million lbs of P, and Delaware used 12.2 million lbs of P with a net mass balance of 5.8 million lbs of P (Mid-Atlantic Water Program, 2007).

One of the water quality issues with the greatest concern in the Chesapeake Bay is eutrophication. Eutrophication occurs when an overload of nutrients contributes to algae growths, which are then decomposed by microbes, resulting in a lack of oxygen called hypoxia. The low dissolved oxygen ultimately contributes to fish kill. Over the years, many sources that

cause eutrophication were identified and reduced to prevent pollution, but phosphorous (P)

inputs remain a nutrient of concern (Boesch et al., 2001). On the Delmarva, many sources of

non-point-source P inputs include manure applications, fertilizer, sediment, and runoff from

cropping systems, livestock operations, and populated areas.

Exporting excess manure out of the watershed has been attempted, but was found to be

uneconomical. Poultry litter has a low nutrient density due to its water content and bedding

material, although it remains a good source of nutrients. Due to low nutrient density, fresh

poultry litter has shipping limitations and it is not homogenous enough to serve as marketable

fertilizer for farmers a significant distance from the source location. A solution to the low

nutrient density material may be to combust the fresh poultry litter into an ash product.

Combustion homogenizes the fresh poultry litter by mixing and condensing the nutrients into the

ash or biochar co-product. In the long term, ash could be transformed into a marketable and

useful product through granulation and different formulations of nutrients.

The objective of this project is to analyze the composition of the ash and determine its

relationship in the soil and availability to plants. This project evaluated removing some of the

watershed's excess P by repurposing certain co-products of the poultry industry into a

marketable fertilizer that can be exported out of the watershed and used by farmers in the P

deficient areas of the country or used within the watershed where fresh poultry litter use is not an

option

1.2 The Problem

Phosphorous and nitrogen (N) are both nutrients of concern to water quality (USEPA,

1988) and are most often connected with eutrophication (Levine and Schinder, 1989; Pote et al.,

1996). Areas of intensive animal production often have the greatest potential for eutrophication

due to non-point nutrient sources (Pote et al., 1996; Duda and Finan, 1983). Phosphorus is also an important nutrient because it is a valuable agronomic nutrient and is considered a non-renewable resource. Current research estimates within 50-100 years we will have mined our current known P supplies (Lynch et al. 2013). Phosphorous is present in PL in solid phase organic P as well as inorganic P and is normally present in the acid soluble fraction ($H_2PO_4^-$ and HPO_4^{2-}), but can vary widely due to husbandry and diet practices.

Traditionally, animal waste products were added to agricultural crop lands at a rate that correlated with N requirements of crops, which typically lead to an over application of P (Maguire et al., 2007; Sims et al., 1998). Over application of P is often due to fresh poultry litter's N:P ratio. Manure P is typically higher than the ratio that plants require, leaving a surplus of P (Pote et. al 1996). The average N:P ratio plants require is 8:1 (Zhang et al., 2002; Bryson et al., 2014) and the average PL ratio is 1:1 (Zhang et al., 2002). For example, when applying PL to meet the N requirements of a crop, you will be providing 8 times more P than required. In a study by Sharpley (2007), the effects of PL applications on bermudagrass [*Cynodon dactylon* (L.]) found that by applying PL to meet the N requirements resulted in an excess of 365 kg P ha^{-1} that was not removed by the bermudagrass.

Soil testing is used to categorize soil nutrient concentrations. In Virginia, soil test calibrations are completed using the Mehlich-I extract for P. Soil is divided into nutrient categories as low= 0 to 12 mg P kg^{-1}; medium = 13 to 24 mg P kg^{-1}; optimum/high = 25 to 50 mg P kg^{-1}; very high/excessive = > 50 mg P kg^{-1} and potassium (K): low= 0-38 mg K kg^{-1}; medium= 38-88 mg K kg^{-1}; optimum = 88-150 mg K kg^{-1}; high/excessive= >150 mg K kg^{-1} (Maguire et al., 2014; Sims and Gartley, 1996). Soils tend to strongly hold P due to clay, Fe-oxide, and Al-oxide contents, so in soils with low, medium, and high P testing soils there is little to no risk of

leaching (Sims et al., 1998). However, under long-term applications of P in excess of crop removal rates, the rising soil P rates will increase the chance of leaching and runoff (Maguire and Sims, 2002; Kleinman et al., 2000; Reiter et al., 2013).

A study by Ator et al. (2011), estimated that 1.32×10^8 kg of N and 9.74×10^6 kg of P enter the Chesapeake Bay Watershed from sources that include fertilizer and manure applications in agricultural areas, undifferentiated urban activities, point sources, atmospheric deposition and direct fixation by crops, and mineral sources. Sharpley et al. (2007) reviewed the economic and environmental impact of eutrophication in the Chesapeake Bay Watershed and found that the Delmarva lost an estimated $1 billion in the last two decades due to water quality issues directly related to eutrophication. Industries damaged were tourism, fishing, and natural resource based economies (Goodman, 1999; Howarth et al., 2000). To combat water quality problems, many regulations have moved towards a P-based nutrient management system in areas of high soil P with intensive animal operations and manure surpluses (VA DCR Nutrient Guidelines, 2014; Maguire et al., 2007; Maguire and Sims, 2002; Sims, 1999; Sims and Coale, 2002).

1.3 Fresh Poultry Litter

Poultry litter is primarily composed of three different components: the bedding, feathers, and manure (Bolan et al., 2010; Kelley et al., 1996; Tasistro et al., 2004) Fresh poultry litter has been well documented over the years as a valuable source of plant nutrients (Bolan et al., 2010; Kelley et al., 1996; Williams et al., 1999; Chan et al., 2008; Harmel et al., 2009; Reiter et al., 2014). Chemically, PL contains the macronutrients: N, P, K, and the secondary macronutrients: calcium (Ca), magnesium (Mg), and Sulfur (S), micronutrients: copper (Cu), zinc (Zn), and molybdenum (Mo), pesticide residuals, pharmaceuticals, and microorganisms (Bolan et al. 2010). The nutrient concentration of PL can vary greatly due to its heterogeneity, the bedding

used, feed use efficiency of the broilers and PL management practices of the farmer (Edwards and Daniel, 1992; Sims and Wolf, 1994). Average nutrient concentrations of fresh poultry litter were compiled in a review by Bolan et al. (2010) on a dry weight basis: N= 25.7 g kg^{-1}, P= 6.7 g kg^{-1}, K= 10.1 g kg^{-1}, Ca= 16.2 g kg^{-1}, Mg= 3.5 g kg^{-1} and S= 5.2 g kg^{-1}.

Despite the heterogeneity, it is common practice to use PL as a fertilizer for agronomic crops. When sourced locally, PL is a relatively inexpensive fertilizer. Poultry litter typically contains two to four times more P per ton of manure than other livestock types (Kleinman et al., 2005; Sharpley and Moyer 2000; Sharpley et al., 2007) and is one of the drier manures produced in intensive agriculture with an average of 25% moisture (Lynch et al., 2012). Not only is PL a valuable source of nutrients, it is also a good soil amendment that enhances the physical, chemical, and biological fertility of soils (Friend et al., 2006; McGrath et al. 2010) by increasing the organic matter content, water holding capacity, oxygen diffusion rate, and the aggregate stability (Mahimairaja et al., 1995; Adeli et al., 2009; Bolan et al., 2010).

Despite being drier than other livestock manures, a significant problem with PL is bulkiness (Sharpley et al., 2007; Lynch et al., 2012). Poultry litter bulkiness makes transportation problematic. The bulkiness imposes economical limits from a nutrient value standpoint, often making it infeasible to ship out of the watershed; which leads to the PL application to fields for agronomic production near its source (Figure1.1 and Figure 1.2). The 5-year price average of nutrients N, P, K, and S were computed using the fertilizer price list compiled by USDA-ERS (2014) and equaled $1.26 per kg N based on urea, $1.50 per kg P_2O_5 based on TSP, $1.17 per kg K_2O based on KCl, and $0.84 per kg S based on ammonium sulfate. Using the shipping costs per loaded km of $1.55 (Weaver, 2015) and $2.48 (DeVuyst and Burton, 2008) and the total value of the fertilizers (N-P-K-S) the distance per metric ton (Mg) was calculated (Table 1.1). When

factoring in the average load weight allowed on a commercial tractor trailer in Virginia, approximately 21.79 Mg, the added value of the ash co-product becomes clear (Table 1.2) (VDOT, 2015). When graphed against a map of the United States PL is only economical transported to the Ohio/Indiana boarder and the PLA can feasibly be shipped anywhere in North America.

There are many state regulations and best management practices (BMPs) like tax credit incentives, transport incentive programs, educational training, and nutrient planning (VADCR, 2005) to help curb and control the amount of non-point source P runoff that enters sensitive watersheds and waterways (Maguire et al., 2007; Maguire and Sims, 2002; Sims, 1999; Sims and Coale, 2002).

Other environmental concerns regarding the land application of PL is often based on trace elements (As, Cu), pesticide residuals, pharmaceuticals (antibiotics, coccidiostats, larvicides, endocrine disruptors), and microbial pathogens [*Clostridium* (L.)*, E. Coli* (L.)*, Salmonella* (L.)*, Enterobacter spp*(L.)] (Bolan et al. 2010). The soil, via Fe-oxides and soil organic matter, has the ability to adsorb and chelate the majority of trace metal containments, residuals and pathogens can be reduced by composting, combustion, and adjusting the timing of chemical applications (Gupta and Charles, 1999; Sims and Wolf 1994; Powers and Angel, 2008)

1.4 Fresh Poultry Litter Utilization Techniques

A review by Kelleher et al. (2002) discussed the advances in PL conversion technologies by analyzing the most common techniques: composting, anaerobic digestion, direct combustion, and pyrolysis. The goals of utilizing these technologies are to make the PL co- products safer for land application, reduce the total volume, increase the nutrient density, and increase the value of the product.

The process of composting is an aerobic process that occurs relatively quickly (4-6 weeks) and produces a material that is odorless, fine-textured, and has a low moisture content (Kelleher et al., 2002). Moisture content is an important factor in composting. During the process the moisture should be between 40-60% to allow for evaporation during the metabolic heating process (Kelleher et al., 2002; Rynk et al., 1991), higher moisture rates during composting will inhibit the process resulting in higher ammonia volatilization rates and lower moisture rates will inhibit the decomposition rate (Kelleher et al., 2002). At the end of the composting process, the composted material will be granular with moisture content of 20% or less (Elwell et al., 1998). The composted material will be pathogen free and easy to handle, but disadvantages include loss of N (47-62%), odor, P is not reduced or concentrated, and there is a cost for equipment and labor inputs (Kelleher et al., 2002; Sweeten, 1988).

Anaerobic digestion is commonly used around the world as a way to dispose of numerous agricultural and industrial waste products. Anaerobic digestion has two basic stages. The first stage is acid fermentation and the organic material is broken down into organic acids, alcohols and bacterial cells. The second stage involves the conversion of the hydrolysis products to gases (CO_2 and methane) (Kelleher et al., 2002; Williams, 1999). The gas mixture (60% methane) produced by this process is collected and used in bioreactors, as fuel, as a natural gas replacement, or used in generators to create electricity (Kelleher et al., 2002). Many disadvantages to digestion include high equipment costs, added volume without concentrating P, and the need for added nutrients (N) to correct for the C: N ratio as N is needed to drive microbial metabolism and reactions. Other added costs include measures taken to enhance the digestion because PL has a high pH and ammonia content which inhibits methane production (Krylova et al., 1997; Kelleher et al., 2002).

Direct combustion, a high oxygen thermo-conversion technique, is the most promising new technology available to farmers. Numerous studies showed that thermo-chemical conversion of poultry litter to a bio-fuel is possible through multiple techniques including combustion (>1100ºF and high O_2), gasification (700-1000ºF and minimal O_2), liquefaction, and pyrolysis (350-650ºF and depleted O_2) (Mante and Agblevor, 2010; Çaglar and Demirbas, 2000; McKendry, 2002; Cantrell et al., 2007; Farm Manure-to-Energy Initiative, 2015). Direct combustion tends to be most feasible for the farm-scale conversion of PL. Some models employ a technique called localized fluidized bed combustion units (FBC) to gasify the PL at 700-1000°F with moisture around 25% (Kelleher et al., 2002; Williams, 1999). The advantages of combustion are the concentration of nutrients (P, K, S, etc.) to 6 or 7 times that of the original feedstock and an increase of 1.5 to 2.5 times the bulk density of the PL (Bock, 2004). The main disadvantage of an ash product is the loss of N during the combustion process, but if combusted at a much lower temperature some N losses can be avoided (Faridullah et al., 2009; Steiner et al., 2010). The majority of N from the fresh poultry litter is released from the systems in the form of non-reactive nitrogen gas (N_2) but the reactive forms may also be released in the forms of nitrogen oxides (NO_x) and ammonia (NH_3) (Farm Manure-to-Energy Initiative, 2015). The emissions differ system to system but the reactive emission typically range from less than two to less than one percent due to the presence of NH_3 and organic N in PL, at higher temperatures they will react with NO_x to form the non-reactive N_2 gas and water vapor minimizing the reactive N emissions (Farm Manure-to-Energy Initiative, 2015). In general it is known that the land application of fresh poultry litter results in much higher emissions of atmospheric N, around 50 to 90%, so the thermo-conversion of PL may actually reduce atmospheric emissions of reactive N (Farm Manure-to-Energy Initiative, 2015).

Pyrolysis is the thermal decomposition of biomass in a depleted oxygen environment. It also uses a fluidized bed reaction at around 450°C (Mante and Agblevor, 2010), but differs from direct combustion by using lower heat and low oxygen. The lower temperature helps prevent N losses, but a substantial amount of N is still lost or converted to pyrogenic N (Knicker, 2007). Pyrolysis technology also concentrates the amounts of nutrients from the original substrate including P and K, while reducing the total mass by around 60%, which increases the nutrient density (Kim et al., 2009; Revell et al., 2012).

Poultry litter has the potential to be used to produce heat and electricity at large centralized facilities as well as smaller on farm options depending on the techniques used (Szogi and Vanotti, 2009; Kelleher et al., 2002; Zering, 2006; Turnell et al., 2007; Fibrowatt, 2008). Utilization of PL as a fuel compared to other biomass currently used (wood-based) is more complex and challenging regarding emissions because of high concentrations of nutrients and metals in ash such as, N, S, Cl, and alkali metals (Mante and Agblevor, 2010).

Lynch et al. (2013) discussed the utilization and viability of PL as an energy source in response to the growing demand for animal protein. Many farming operations have converted to confined animal feeding operations, allowing farmers to significantly lower their operational costs while maximizing profits. Another positive is that it has been estimated that using poultry litter as fuel could save 283 million gallons of liquefied petroleum gas (LPG) equivalent fossil fuel energy (Singh et al., 2007; Codling, 2013). A study by Kelleher et al. (2002) found that poultry litter has a typical caloric value of 13.5 GJ/ton, which is about half that of coal. Depending on the bedding material and moisture content, PL has been rated at 8 to 15 GJ/ton (Perera et al., 2010; Martin, 2006). Burning PL is a viable approach to energy generation and

also reduces the total volume into an easily transportable ash that remains high in key crop nutrients P and K (Sharpley et al., 2007; MacDonald, 2007)

1.5 Poultry Litter Ash

After combustion or gasification, the resulting product is poultry litter ash (PLA), with a reduction in the original feedstock material by 90% by weight, is sterile, and is a powder like material with high concentrations of macro and micronutrients (Table 2) (Lynch et al., 2013; Kelleher et al., 2002). The PLA reduced in total volume contains concentrated amounts of macronutrients P and K (Sharpley et al., 2007; Codling et al., 2002). In a study by Lynch et al. (2013), the elemental content of PLA was determined using ICP Spectroscopy and showed high concentrations of P (110 g kg^{-1}), K (170 g kg^{-1}), S (26 g kg^{-1}) and Ca (160 g kg^{-1}). The co-product, PLA is a condensed and homogenized form of PL creating potential as a viable fertilizer for farmers. The reduced weight, homogeneity, and sterility of ash are solutions to many of the problems of utilizing straight PL as a land applied fertilizer. But there are negatives to the ash product. Combusting PL can lead to the potential release of N, S, CO_2, and Cl as gaseous containments. The bulk density of the PL (400 kg m^{-3} at 35% moisture), when compared to coal (900 kg m^{-3}) is low, translates PL into a low energy dense fuel, which effects how economical the PL is to ship to processing facilities (Lynch et. al 2013). Densification would serve as a new form of income if found to be a viable fertilizer source.

There is significant research describing the analysis of wood-based ash co-products, but very few of manure ash products. Instead of actual figures, manure ash is generally reported to be a satisfactory source of P for agronomic crops (Crozier, 2009). Crozier (2009) studied a granulated manure ash in three different experimental systems (greenhouse low-P soil, long-term P research sites with established P gradients, and agricultural fields with prior P fertilization at

agronomic rates) and found when compared to triple super phosphate (TSP), source differences were infrequent and relativity minor. Codling (2002) compared the effectiveness of PLA as a fertilizer with an industry standard fertilizer, potassium phosphate (KP) as a P source for wheat. The two fertilizers were applied at three rates (0, 39, and 78 kg P ha^{-1}) in a wheat [*Triticum aestivum* (L.)]-based trial. No significant difference was found between the two fertilizers. A study by Reiter et al. (2004) comparing PLA to traditional fertilizer in a rice [*Oryza sativa*(L.)], wheat, and soybean[*Glycine max*(L.)] rotation found that the PLA had slightly less short-term availability but increased the residual soil P. In studies by Pagliari (2006; 2008), turkey [*Meleagris gallopavo*(L.)] manure ash was found to have no statistical differences in plant yield and uptake when compared with TSP in corn [*Zea mays*(L.)] and alfalfa [*medicago sativa*(L.)] trials. These studies are a step in proving that PLA co-products have a similar value to farmers as traditional fertilizers. Research indicates that ash could be a viable P source, but needs further testing to explore the optimum application rates. Ash applications act not only as fertilizers but also as soil amendments. Demeyer et al. (2001) found that ash worked as a liming agent increasing the pH of the soil, stimulated the microbial activities, increased the calcium carbonate equivalent (CCE) and increased the water holding capacity (WHC) by decreasing the aeration of the soil.

1.6 Biochar

Biochar is a pyrolysis co-product of fresh PL. There is interest in biochar for a multitude of uses including bioenergy, C sequestration, as a soil amendment, and fertilizer (Maguire and Agblevor, 2010). Biochar is voluntarily regulated by the International Biochar Institute; which established regulations for the creation, sampling, testing, and usage of biochar worldwide. Biochar is defined by the International Biochar Institute (2015), as the C rich product when

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biomass is heated with little or no available oxygen. After pyrolysis, the inorganic components of

PL is significantly concentrated, although less concentrated than ash, it gives the co-product

value as an agronomic nutrient source (Revell et al., 2012b; Agblevor et al., 2010). The main

difference between a biochar product and an ash is the temperature at which it is created.

Variations in temperature during production will have an impact on the quantity and quality of

the end product (Maguire and Agblevor, 2010). Biochar is the product pyrolysis which occurs at

a much lower burning temperature (400-500°C) than combustion or gasification (Gaskin et al.,

2008).

Studies proposed that biochar can be used to improve soil productivity and sequester

carbon (Atkinson et al., 2010; Laird, 2008). It has been found, mainly by scientists in the tropics,

that biochar and charcoal created from the pyrolysis process will improve soil health and

productivity of crops (Chan et al., 2007; Lehmann et al., 2003; Oguntunde et al., 2004; Steiner et

al., 2007; Yamato et al., 2006). By increasing the active surface area of the soil, its capacity to

retain nutrients and water increases improving the WHC and nutrient uptake (Maguire, 2010). In

a study by Revell et al. (2012b), biochar was found to decrease the bulk density of the soil, the

WHC increased linearly, at rates of (0, 4.5, and 9 Mg ha^{-1}), pH was increased, and the cation

exchange capacity (CEC) of the soil increased. It is important to note that the positive changes

occurred only when applied above agronomic nutrient rates. Increased WHC is one of the major

benefits to using biochar, as drought is a major reason for decreased crop production in non-

irrigated lands (Revell et al., 2012a; Havelin et al., 2005).

A study by Schomberg et al. (2012), reported that improvements greatly depended on the

quality of the substrate, the temperature and speed of pyrolysis, and the soil type of the area.

Laboratory incubations with various biochar amendments were conducted in the long and short

term to explore the effects of biochar on changes in soil pH, ammonia losses, and soil C effects. The addition of biochar resulted in a reduction of N leaching and large increases in mineralizable N were not observed, meaning most soil C in the biochar was not available to microorganisms. The study suggested that development of standards and guidelines would allow better usage of biochar by matching the biochar to specific soils and land use situations (Schomberg et al., 2012).

1.7 Summary

The literature lacks information and studies on PLA. With this project we will create a sustainable cycle that lessens our dependence on mining P by utilizing P from PL where it is needed. Better matching P mass balances will provide a sustainable way to serve agronomic fertilizer needs while assisting water quality improvement. By creating a sustainable cycle, we can effectively move P wastes out of concentrated areas and into P deficient areas of the country. This will greatly reduce occurrences of elevated P concentrations in watersheds and possibly create a new source of income for the animal protein producer.

1.8 Research Objectives

Objective 1: Compare volume and nutrient concentrations of fresh poultry litter going in with poultry litter ash coming out of demonstration combustion units.

Objective 2: To determine the availability of P and K in PLA through incubation studies.

Objective 3: To determine the effect of PLA on crop productivity through crop yields.

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Tables

Table 1.1: Fertilizer worth versus transport distance for PLA†, fresh PL‡, and standard fertilizers.

	Fertilizer Worth§	High Mileage Estimate¶	Low Mileage Estimate#
	$ Mg^{-1}	--------------------km Mg^{-1}--------------------	
PLA	384.98	248	155
PL	58.46	37.6	23.5
KCl	700.44	451	282
TSP	688.98	444	277

†Based on average nutrient concentrations of PLA (Lynch et al., 2013).
‡Based on average nutrient concentrations of PL (Bolan et al., 2010).
§Based on 5-year price average of nutrients computed using fertilizer use and price list compiled by USDA-ERS (2014).
¶Calculated using the shipping costs per loaded km of $1.55 (Weaver, 2015).
#Calculated using the shipping costs per loaded km of $2.48 (DeVuyst and Burton, 2008).

Table 1.2: Fertilizer worth versus transport distance with trucking estimation for PLA†, fresh PL‡, and standard fertilizers.

	Fertilizer Worth§	Fertilizer Worth per truck load¶	High Mileage Estimate#	Low Mileage Estimate
	----------$ Mg^{-1}--------	-------------------$ load^{-1}------------------	----------------------------------km load^{-1}--------------------------	
PLA	384.98	8388.71	5412	3383
PL	58.46	1273.84	822	514
KCl	700.44	15262.59	9847	6154
TSP	688.98	15012.87	9686	6054

†Based on average nutrient concentrations of PLA (Lynch et al., 2013).
‡Based on average nutrient concentrations of PL (Bolan et al., 2010).
§Based on 5-year price average of nutrients computed using fertilizer use and price list compiled by USDA-ERS (2014).
¶Calculated using the average load weight allowed on a commercial tractor trailer in Virginia of 21.79 Mg (VDOT, 2015)
#Calculated using the shipping costs per loaded km of $1.55 for high mileage (Weaver, 2015) and using the shipping costs per loaded km of $2.48 for low mileage (DeVuyst and Burton, 2008).

Figures

Figure 1.1: High distance estimate transport radius map based on average nutrient (N, P, K, and S) concentrations of PLA†, fresh PL‡, and standard fertilizers§
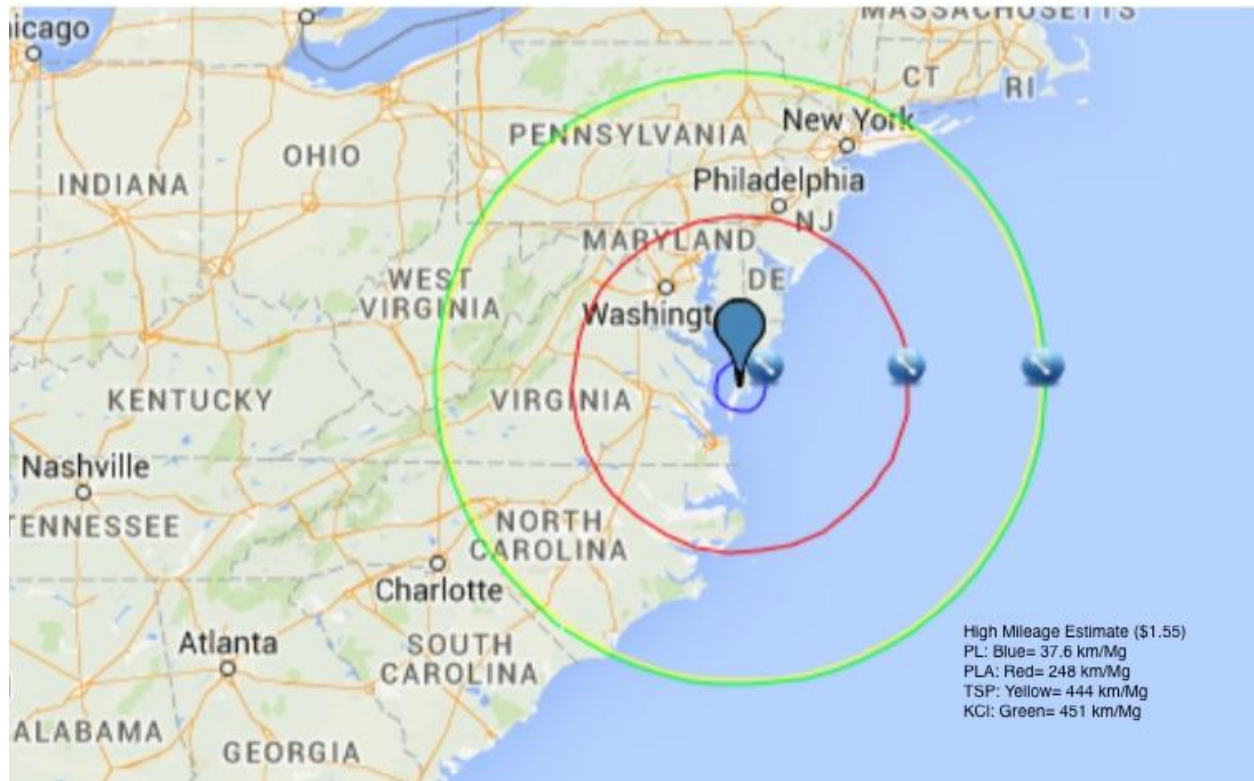
†Based on average nutrient concentrations of PLA (Lynch et al., 2013).
‡Based on average nutrient concentrations of PL (Bolan et al., 2010).
§Calculated using the shipping costs per loaded km of $1.55 (Weaver, 2015). Based on 5-year price average of nutrients computed using fertilizer use and price list compiled by USDA-ERS (2014) and .the average load weight allowed on a commercial tractor trailer in Virginia of 21.79 Mg (VDOT, 2015).

Figure 1.2: Low distance estimate transport radius map based on average nutrient (N, P, K, and S) concentrations of PLA†, fresh PL‡, and standard fertilizers§

†Based on average nutrient concentrations of PLA (Lynch et al., 2013).
‡Based on average nutrient concentrations of PL (Bolan et al., 2010).
§Calculated using the shipping costs per loaded km of $2.48 (DeVuyst and Burton, 2008). Based on 5-year price average of nutrients computed using fertilizer use and price list compiled by USDA-ERS (2014) and the average load weight allowed on a commercial tractor trailer in Virginia of 21.79 Mg (VDOT, 2015).

2. Characterization of Poultry Litter Ash Co-Products

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2.1 Abstract

Phosphorus (P) is a nutrient of concern in the Chesapeake Bay watershed due to nutrient imbalances in areas with confined animal feeding operations. By converting poultry litter to an ash via thermal conversion, nutrients are concentrated and are economical to ship out of nutrient surplus watersheds to nutrient deficient regions, such as the corn-belt. We initiated a study to characterize the chemical of poultry litter co-products as compared to industry standard fertilizers. Seven poultry litter ash (PLA) products, derived from different sources using different combustion techniques, and two biochar products were characterized and compared to fresh poultry litter (PL), inorganic P (triple super phosphate; TSP) and inorganic K (muriate of potash; KCl) fertilizer. There was variability between all ashes and biochars based on their thermo-combustion system and the composition of the original feedstock PL. On an elemental level, the inorganic fertilizers had the highest concentrations for their nutrient, the ash products were the best complete fertilizers and the biochars were less available than the ashes. Nutrient densification varied between systems: P concentration fell within a range of 4-10 times concentrated, K concentration ranged 2.5-5 times concentrated, and S ranged 2-3 times concentrated. Additional, water soluble based extractions found deceased solubility of the ash and biochar products compared to the fertilizer standards. In conclusion, the PLA and biochar sources derived from PL are suitable and comparable P and K fertilizer sources based on the nutrient concentrations although further testing is needed to determine plant availability and nutrient uptake.

2.2 Introduction

Phosphorous (P) and nitrogen (N) are both nutrients of concern to water quality (USEPA, 1988) and are most often connected with eutrophication (Levine and Schinder, 1989; Pote et al., 1996). Areas of intensive animal production often have the greatest potential for eutrophication due to non-point nutrient sources (Pote et al., 1996; Duda and Finan, 1983). Phosphorus is also an important nutrient because it is an extremely valuable agronomic nutrient and it is considered a non-renewable resource. Current research estimates that within 50-100 years we will have mined all of our current known supplies (Lynch et al. 2013).

Poultry litter (PL) has been well researched and vetted as a satisfactory fertilizer source (Reiter et al., 2013; Sharpley et al., 2007; Revell et al., 2012). Although, in regions with intensive animal production land application of PL is not a viable option due to high residual nutrient levels in the soil. Due to nutrient management regulations (VA-DCR, 2014), this often leads to the transport of PL off of the farms. Poultry litter has a low nutrient density making it difficult for farmers to ship it out of nutrient rich areas. A solution to low nutrient concentration is the thermochemical conversion of PL into co-products poultry litter ash (PLA) and biochar. The combustion of PL is a viable approach to alternative energy generation, while at the same time reducing the total volume of the product into an easily transportable ash that remains high in key crop nutrient P and potassium (K) (Sharpley et al., 2007; MacDonald, 2007).

A review by Kelleher et al. (2002) discussed the advances in poultry litter conversion technologies by analyzing the most common techniques: composting, anaerobic digestion, direct combustion, and pyrolysis. The goals of utilizing these technologies are to make the products safer for land application, reduce the total volume, increase the nutrient density, and increase the value of the product.

The process of composting is an aerobic process that occurs relatively quickly (4-6 weeks) and produces a material that is odorless, fine-textured, and has a low moisture content (Kelleher et al., 2002). Moisture content is an important factor in composting. During the process the moisture should be between 40-60% to allow for evaporation during the metabolic heating process (Kelleher et al., 2002; Rynk et al., 1991), higher moisture rates during composting will inhibit the process resulting in higher ammonia volatilization rates and lower moisture rates will inhibit the decomposition rate (Kelleher et al., 2002). At the end of the composting process, the composted material will be granular with moisture content of 20% or less (Elwell et al., 1998). The composted material will be pathogen free and easy to handle, but disadvantages include loss of N (47-62%), odor, P is not reduced or concentrated, and there is a cost for equipment and labor inputs (Kelleher et al., 2002; Sweeten, 1988).

Anaerobic digestion is commonly used around the world as a way to dispose of numerous agricultural and industrial waste products. Anaerobic digestion has two basic stages. The first stage is acid fermentation which breaks down the organic material into organic acids, alcohols and bacterial cells. The second stage involves the conversion of the hydrolysis products to gases (CO_2 and methane) (Kelleher et al., 2002; Williams, 1999). The gas mixture (60% methane) produced by this process is collected and used in bioreactors, as fuel, as a natural gas alternative, or used in generators to create electricity (Kelleher et al., 2002). Many disadvantages to digestion include high equipment costs, added volume without concentrating P, and the need for added nutrients (N) to correct for the C: N ratio, nitrogen is needed to drive microbial metabolism and reactions. Other added costs include measures taken to enhance the digestion because PL has a high pH and ammonia content which inhibits methane production (Krylova et al., 1997; Kelleher et al., 2002).

Direct combustion, a high oxygen thermo-conversion technique is the most promising new technology available to farmers. Numerous studies showed that thermo-chemical conversion of poultry litter to a bio-fuel is possible through multiple techniques including combustion (>1100ºC and high O_2), gasification (700-1000ºC and minimal O_2), liquefaction, and pyrolysis (350-650ºC and depleted O_2) (Mante and Agblevor, 2010; Çaglar and Demirbas, 2000; McKendry, 2002; Cantrell et al., 2007; Farm Manure-to-Energy Initiative, 2015). Direct combustion tends to be most feasible for the farm-scale conversion of PL. Some models employ a technique called localized fluidized bed combustion units (FBC) to gasify the PL at 700-1000°C with moisture around 25% (Kelleher et al., 2002; Williams, 1999). The advantages of combustion are the concentration of nutrients (P, K, S, etc.) to 6 or 7 times that of the original feedstock and an increase of 1.5 to 2.5 times the bulk density of the PL (Bock, 2004). The main disadvantage of an ash product is the loss of N during the combustion process, but if combusted at a much lower temperature some N losses can be avoided (Faridullah et al., 2009; Steiner et al., 2010). The majority of N from the fresh poultry litter is released from the systems in the form of non-reactive nitrogen gas (N_2) but the reactive forms may also be released in the forms of nitrogen oxides (NO_x) and ammonia (NH_3) (Farm Manure-to-Energy Initiative, 2015). The emissions differ system to system but the reactive emission typically range from less than two to less than one percent due to the presence of NH_3 and organic N in PL, at higher temperatures they will react with NO_x to form the non-reactive N_2 gas and water vapor minimizing the reactive N emissions (Farm Manure-to-Energy Initiative, 2015). In general it is known that the land application of fresh poultry litter results in much higher emissions of atmospheric N, around 50 to 90%, so the thermo-conversion of PL may actually reduce atmospheric emissions of reactive N (Farm Manure-to-Energy Initiative, 2015).

Pyrolysis is the thermal decomposition of biomass in a depleted oxygen environment which uses a fluidized bed reaction between 350-650°C (Farm Manure-to-Energy Initiative, 2015; Mante and Agblevor, 2010), but differs from direct combustion by using lower heat and lower oxygen concentrations. The lower temperature helps lower N losses, but a substantial amount of N is lost or converted to atmospheric N (Knicker, 2007). Pyrolysis technology also concentrates the amounts of nutrients from the original substrate including P and K, while reducing the total mass by around 60%, which increases the nutrient density (Kim et al., 2009; Revell et al., 2012).

The majority of research for manure based fertilizers has been related to N availability because N is typically the most yield-limiting nutrient in row crops (Slaton et al., 2013). The plant availability of N, P, and K are all vital to plant health and growth and interrelated in their respective cycles (Brady and Weil, 1996). A study by Sharpley and Sisak (1997) proposed that the bioavailability of P from manure sources may differ from traditional inorganic fertilizer and suggested that application recommendations be tailored to the unique fertilizer source. Studies have shown the P in manure is generally found to be 60-100% of the availability of commercial fertilizers depending on the source over multiple years (Barbazan et al., 2009), the first year P bioavailability was similar to inorganic fertilizer (Sneller and Laboski, 2009) and most K is highly water soluble and plant available (Jackson et al., 1975).

Phosphorous is present in PL in the solid phase as organic P as well as inorganic P and is normally present in the acid soluble fraction. Although, nutrient levels can vary widely due to husbandry and diet practices like type of bedding material, number of birds in a flock, and number of flocks between clean outs (Lynch et al., 2012). Soils tend to strongly hold P due to clay, Fe-oxide, and Al-oxide contents so in low P testing soils there is little to no risk of leaching

(Sims et al., 1998; Brady and Weil, 1996). Phosphorous fixation occurs at both ends of the pH spectrum, in acidic low pH soils (<5.0) and basic, high pH soils (>8.0) (Brady and Weil, 1996). In the low ranges, P will react to Al, Fe, and Mn oxides and in the high ranges P will react to Ca fixing the P into insoluble compounds (Brady and Weil, 1996). But under long-term applications of P, in excess of crop removal rates, the soil P concentrations will rise (Maguire and Sims, 2002). When soil test P levels reach high or excessive, an increased chance of nutrient leaching and agricultural runoff can be expected (Moore and Edwards, 2007; Maguire and Sims, 2002). Another factor that affects P availability in the soil system is the soil pH.

Traditionally in Virginia, the primary test for soil P has been Mehlich-I, which is also known as the dilute double acid method (Sims, 2000; Mehlich, 1953). Other methods discussed in literature pertaining to the Mid-Atlantic are water extraction and dilute salt extraction at varying ratios of 1:10 and 1:100 (Aslyng, 1964; Olsen and Sommers, 1982; van Diest, 1963). Many phosphates in the soil have formed insoluble compounds that are no longer plant available (Brady and Weil, 1996). There is some criticism that the Mehlich acid based extraction is too harsh and extracts more than the plant available P (Self-Davis and Moore, 2000), which leads to unreliable P recommendations. Leading many to recommend water or dilute salt extractions over the traditional Mehlich-I extraction (Self-Davis and Moore, 2000; Pote et al., 1996; Luscombe et al, 1979).

While there is no single recommended protocol for measuring water extractable P (WEP), there are some commonly recommended protocols (Self-Davis and Moore, 2000; Kleinman et al., 2007). The dilute salt (0.1M $CaCl_2$) and water extractions (1:10 and 1:100) are tests that extract the readily available portions of the nutrients that will be available for plant uptake. These tests produce lower concentrations of nutrients as compared to acid extractions

and are used in the industry to make recommendations for P-based management systems on farms (Self-Davis and Moore, 2000). The dilute salt extraction is used in place of water to obtain a clearer filtrate, but the amount of soluble P will be smaller due to Ca^{2+} ions enhancing P sorption in the soil (Aslyng, 1964). Water extraction ratios have been discussed in the literature since the mid-1980s. A study by Kleinman et al. (2007) looked at WEP extraction ratios with help from 10 laboratories across the country. They compared extracts at 3 different ratios (soil: extractant): 1:10, 1:100, and 1:200. They found the 1:10 level was the most problematic out of the 3 ratios of soil to extractant. At the 1:10 ratio, the results were inconsistent, they had trouble obtaining sufficient extract for analysis, and the extracts were relatively dark in color causing many problems for colorimetric analysis including the clogging of instrumentation tubing (Kleinman et al., 2007). They also found a consistent trend, with greater quantities of WEP being recovered as the extraction ratio increased. However, due to the experimental variability no proportional relationship could be determined between the ratios. The study recommended the usage of the 1:100 ratio as the middle ground because it offered the most reasonable balance of precision and practicality (Kleinman et al., 2007).

This project evaluated removing excess P by repurposing certain co-products of the poultry industry into a marketable fertilizer that can be exported out of the watershed and used by farmers in the P deficient areas of the country or used within the watershed where fresh poultry litter is not an option. The objective of this project was to analyze poultry litter co-product composition and characterization as compared to traditional inorganic fertilizer and fresh poultry litter.

2.3 Materials and Methods

        A study was initiated to evaluate the chemical characteristics of PL co-product

sources (Table 2.1) compared to triple super phosphate (TSP) and muriate of potash (KCl). The

fertilizers were arranged in a randomized complete block design (RCBD) with 4 replications.

2.3.1 Elemental Analysis

        Fertilizer samples (0.5 g) were digested in nitric acid and hydrogen peroxide using

method 3050B (USEPA, 1996), and then analyzed using ICP-OES (Spectro Analytical

Instruments, Kleve, Germany) at the Virginia Tech Soil Testing Laboratory (Maguire and

Henkendorn, 2011). Using dilute salt and water extraction testing protocols for 0.1M $CaCl_2$

(Aslyng, 1964), 1:10 water (Olsen and Sommers, 1982), and 1:100 (van Diest, 1963) the correct

ratio of sample to solution was placed in 60 ml straight-walled plastic extracting beakers. The

samples were shaken for 1 hour on a reciprocating shaker (Eppindorf, Enfield, CT, 06082) set at

200 oscillations per minute (opm). The extracts were filtered through Whatman no. 2 filter paper

into plastic vials and then analyzed using ICP-OES (Spectro Analytical Instruments, Kleve,

Germany) at the Virginia Tech Soil Testing Laboratory (Maguire and Henkendorn, 2011). A

total N, C, and S combustion procedure was conducted for the samples using the Dumas method

with a Vario EL Cube (elementar Americas, Mt. Laurel, NJ, USA) (Bremner, 1996).

2.3.2 Balance Comparison

        Balance comparisons of the poultry litter going in and ash coming out of poultry litter

burners took place as litter burners began running at the farm locations. Each thermo-conversion

system was unique to the farm location in its physical construction, operating conditions;

residence time and initial feedstock (PL) (Table 2.2); individual system sampling methods are

listed below. Samples were tested for percent moisture (Wolf and Haskins, 2003), calcium

carbonate equivalent (CCE) (Wolf and Haskins, 2003), and elemental concentration using the

EPA method 3050B. Densification was calculated by taking the ash nutrient concentration percentage and dividing by its corresponding feedstock PL nutrient concentration percentage. (Times Concentrated= Ash nutrient %/ PL nutrient %)

Wayne Combustion Global Refuel: ASH3 and ASH6

Samples were taken at three sampling locations in accordance to the residence time of the system: fresh PL going in, the main bulk ash auger, the fly ash auger from the side at the heat exchanger. The residence time was observed to be 30 minutes from the start to the main bulk ash auger and the fly ash auger. The time and temperature of the combustion chamber was recorded for each sampling.

Total Energy Blue Flame Stoker: ASH4

Samples were taken at three sampling locations in accordance to the residence time of the system: fresh PL entering the system, the main ash auger, and the end ash auger. The residence time was observed to be 60 minutes from start to the main bulk ash auger and 70 minutes from start to the end auger with the bulk ash and fly ash mixture. The time, stack temperature, and water heating set point was recorded for every sample, the combustion temperature was not available on this system.

Enginuity Energy: Energy Ecoremedy Gasifier: ASH7

Samples were taken at two sampling locations in accordance to the residence time of the systems: fresh PL entering the system and the bulk ash auger at the end of the system. The residence time was observed to be 157 minutes from the start to the end of the system. The time and chamber temperature was recorded at two locations within the system at a residence time of 55 minutes (Gas burner #1) and 147 minutes (Gas burner #2). The water boiler set temperature was also recorded for each sample.

2.3.3 Total Carbon Content

Total carbon content of the ash co-products were determined using a total N, C, and S dry combustion procedure was conducted for the samples using the Dumas method with a Vario EL Cube (elementar Americas, Mt. Laurel, NJ, USA) (Bremner, 1996).

2.3.4 Statistical Analysis

Statistical analysis was conducted using analysis of variance (ANOVA), SAS PROC MIXED procedures and Fisher's LSD with an alpha level of 0.10 using SAS 10.1 statistical software (SAS Institute, 2007).

2.4 Results and Discussion

2.4.1 Elemental Analysis

Acid Digestion

The nitric acid/hydrogen peroxide digestion is a complete elemental digestion that quantified the total concentrations of elements (Table 2.3a; Table 2.3b). The industry standard TSP had the highest P concentration (201.81 g kg^{-1}) and a significant concentration of Ca (168.22 g kg^{-1}). The KCl had the highest K concentration (493.11 g kg^{-1}) as expected. When comparing the ash co-products to each other, ASH3 was the superior fertilizer because it had the highest concentrations of nutrients across the board, which was followed by ASH4 as a close second (Table 2.3a). The BIOCHAR3 had the worst concentration of micro nutrients; meaning although it has a significant concentration of macro elements (P, K, and S) it was lacking in the micro, which would make it the least complete fertilizer (Table 2.3a). The biochar co-products had the lowest concentrations of nutrients across the board. The ASH5 fertilizer was superior for K, but low as a complete fertilizer (Table 2.3a).

When compared to the industry fertilizer standards no co-product was similar to TSP for P concentration (Table 2.3a, 2.4, 2.5, 2.6). For K concentration, no co-products were similar to KCl, but all co-products had concentrations greater than or similar to the fresh PL standard (Table 2.3a, 2.6). In the dilute salt extraction and the 1:10 water extraction the BIOCHAR1 co-product had a concentration less than both KCl and PL (Table 2.4, 2.5). For S concentration, the fresh PL had the greatest concentration, and all co-products had significant less S but were similar to each other (Table 2.3a)

Micro nutrients or trace elements were present in all of the co-product samples (Table 2.3a; Table 2.3b) with the exception of ASH5 all of these concentrations were below the level of environmental concern according to the fertilizer law (USDA-NRCS, 2015). Micro-nutrients such as boron (B), manganese (Mn), Copper (Cu), and Zinc (Zn) are vital to health growth in plants, in highly managed and high yielding farming systems farmers are looking to supplement these nutrients to crops. By using a PL co-product these farmers will get the extra benefit of these nutrients not normally found in inorganic fertilizers. The ASH5 fertilizer had the highest concentration of trace elements (Table 2.3b) and was over the threshold to be applied as a commercial fertilizer due to its arsenic (As) concentration levels. This is most likely due to being created from an older PL, over 10 years old. Since, there have been many regulation and pharmaceutical changes that have significantly reduced the trace elements in PL. The biggest change has been in residual As concentration, which was prevalent with the usage of the pharmaceutical known as Roxersone. Roxersone was used in poultry production to help prevent coccidiosis, a parasitic disease that infects the intestinal tracts in poultry and can lead to death in poultry (US-FDA, 2015). After a FDA study in 2009 found significant concentrations of As in

the poultry meat, the industry voluntarily shifted away from the use of Roxersone (US-FDA, 2015).

<u>Dilute Salt and Water Extractions</u>

While there is no single recommended protocol for measuring WEP, we analyzed our sources using three of the most recommended protocols (Kleinman et al., 2007). The dilute salt extraction is used in place of water to obtain a clearer filtrate, but the amount of soluble P will be smaller due to Ca^{2+} ions enhancing P sorption in the soil (Aslyng, 1964). Our results found known significant differences between the three extractions for P concentration. There was a significant difference for K concentration; the 1:100 water extractions produced higher concentrations than the others. Trends show that although no significant differences were produced from our data the 1:10 $CaCl_2$ extraction concentrations (Table 2.4) were tended to be slightly less than the 1:10 water extract concentrations (Table 2.5).

The results from the WEP testing reaffirmed our results from the complete acid extractions in terms of which system produced superior fertilizer products although it showed they were potentially less plant available. The ash co-products were all similar in their nutrient concentrations (Table 2.4, 2.5, 2.6). The ASH5 co-product, the only fly ash tested, had the highest K and S concentrations. Potassium and S are likely to volatilize and exit the system through the exhaust stack (Kelleher et al., 2002); therefore would likely be present in the fly ash. The BIOCHAR1 co-product had the lowest nutrient concentration and the other biochar, BIOCHAR2 was similar.

2.4.2 Balance Comparison

The characterization of PL from four different farms showed many differences between location in moisture, CCE, and its elemental concentrations (Table 2.6), which was

expected. The composition of poultry litter varies greatly from location to location depending on the practices of the individual poultry producer (Bolan et al., 2010; Kelley et al., 1996; Tasistro et al., 2004). Thus, the resulting ash from the different thermo-combustion systems is influenced by not only the unit, but by the starting material (Table 2.7). The ASH7 system had much higher moisture concentrations than the other locations, thus produced an incomplete burn (Table 2.8). The incomplete burn of the ASH7 system resulted in the lowest densification of nutrients (Table 2.9). The ASH4 location had the highest concentration of nutrients from the densification across the board; this system had the superior mix of burn temperature (1000ºC), oxygen levels, and feedstock moisture content (25.24 %). This is supported by the literature which stated that the ideal conditions for combustion are at 700-1000°C with moisture around 25% (Kelleher et al., 2002; Williams, 1999). The literature also states that the typical concentration factor is 6 or 7 times that of the original feedstock nutrients (P, K, and S) of the PL (Bock, 2004). Our study found that this varied between systems based on moisture, but falls well within our range of 4-10 concentration for P (Table 2.9). The systems tested in our balance comparison trials were not equipped with cyclones or bagging units, so the majority of K and S escaped the systems through the exhaust (Kelleher et al., 2002) and resulted in lower concentrations 2.5-5 for K (Table 2.9), and 2-3 for S (Table 2.9); which vary between systems.

2.4.3 Total Carbon Content

The carbon content of PL co-products also varies greatly on the thermo-conversion system and the initial PL feedstock. The ASH7 co-product had the highest carbon content, followed by ASH3 and the ASH4 (Table 2.10). The feedstock of the ASH7 had the highest moisture content thus the most incomplete burn, therefore having less carbon removed from the system.

2.5 Conclusion

Overall, our data has determined that nutrient concentrations of PL co-products are highly dependent on the conditions of their feedstock. The thermo-combustion system is the greatest variable; which includes the temperature of combustion, the fuel to oxygen ratio for combustion, the residence time of the PL, and if the system has an exhaust scrubbing system to catch fly ash. Another major factor is the PL from which the co-product is formed; the initial concentration of nutrients, the bedding material, and the moisture content of the PL impact the end co-product. Our study found that nutrient densification varied between systems: P concentration fell within a range of 4-10 times concentrated, K concentration ranged 2.5-5 times concentrated, and S ranged 2-3 times concentrated. Our comparisons between total nutrient digestions and water soluble extractions found that the ash products were significantly less plant available than the standard fertilizers (TSP and KCl). A greater amount of the co-products will have to be applied to meet the same nutrient availability of the standards. Overall, if all ideal combustion criteria are met (ie. 700-1000ºC; 25% moisture), then poultry litter co-products are feasible to use a fertilizer sources, but will need to be individually analyzed for nutrient content before making application recommendations. More research into balance comparisons are needed to be able to identify stronger relationships within the nutrients.

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Tables

Table 2.1: Descriptions of PL co-product sources used in all studies.

Source	Co-Product Type	Farm Name	Thermo-Conversion System
Ash1	Bulk Ash	BHSL	Gasification
Ash2	Bulk Ash	MOO	Gasification
Ash3	Bulk Ash	RHO	Combustion
Ash4	Bulk Ash	ZIM	Combustion
Ash5	Fly Ash	MOK	Combustion
Ash6	Bulk Ash	ROR	Combustion
Ash7	Bulk Ash	HEL	Gasification
Ash8	Bulk Ash	WVR	Combustion
Biochar1	Biochar	NCB	Pyrolysis
Biochar2	Biochar	JFB	Pyrolysis
Biochar3	Biochar/Ash	FPPC	Combustion

Table 2.2: Source information and background information for poultry litter co-product thermo-conversion systems.

Source	Location	System	Burn Temp	Residence Time	Mode of Energy Dispersal	PL Type	Co-Product Type
ASH1	Limerick, Ireland	Bhsl-Ireland Fluidized bed system	85ºC water set temp	N/A†	Hot Water	Broiler	Ash
ASH2	Lancaster County, PA	Enginuity Energy: Energy Ecoremedy Gasifier	593ºC at beginning of bed 204ºC at end of bed	157 min	Forced Air	Broiler	Ash
ASH3§	Port Republic, VA	Wayne Combustion Global Refuel	593ºC in chamber	30 min	Forced Air	Turkey	Ash
ASH4§	Lancaster County, PA	Total Energy Blue Flame Stoker	82ºC water set temp 171ºC exhaust temp	60 min	Hot Water	Organic Broiler¶	Ash
ASH5	Lancaster County, PA	Enginuity Energy: Energy Ecoremedy Gasifier	593ºC at beginning of bed 204ºC at end of bed	167 min	Forced Air	Broiler	Fly Ash
ASH6§	Lancaster County, PA	Wayne Combustion Global Refuel	593ºC in chamber	30 min	Forced Air	Broiler	Ash
ASH7§	Lancaster County, PA	Enginuity Energy: Energy Ecoremedy Gasifier	593ºC at beginning of bed 204ºC at end of bed	157 min	Forced Air	Organic Broiler	Ash
ASH8	Pendleton County, WV	Wayne Combustion Global Refuel	593ºC in chamber	30 min	Forced Air	Broiler	Ash
BIOCHAR1	North Carolina State University	Coaltec Unit	400ºC in chamber	5 min	Forced Air	Broiler	Biochar
BIOCHAR2	Hardy County, WV	Westfiber by PHG Energy	450ºC	360 min	Forced Air	Broiler	Biochar
BIOCHAR3‡	Cheraw, SC	BGP	871ºC in chamber	60 min	Forced Air	Broiler	Biochar/Ash

†N/A- information not available at this time.

‡When the system capacity is overload with feedstock, unit will produce biochar (our sample) but is designed to produce ash.

§Thermo-Conversion systems used in the balance comparison study.

¶Organic broiler operations clean the PL out the poultry house with every flock, meaning fewer nutrients will be present in the PL feedstock.

Table 2.3a: Total elemental concentration of ash co-products, fresh PL and standard fertilizers.

	P	K	S	Ca	Mg	Mn	Na	Fe	Al	B	Zn	Cu
	--g kg^{-1}--									--------------------mg kg^{-1}------------------		
ASH1	81.89d†	114.30e	24.33b	138.42c	37.19b	3.12b	31.55b	9.56cde	10.56c	249.19c	2670.55b	1222.61d
ASH2	52.72f	71.27f	13.59b	77.33d	27.48d	2.16e	33.74a	9.11de	9.52d	139.41e	1510.43d	1089.3e
ASH3	104.90b	129.77d	28.42b	162.58a	36.59b	4.60a	25.24c	16.88b	2.15f	220.56d	2888.41a	3429.68a
ASH4	90.22c	145.78c	16.95b	131.82c	46.42a	2.94c	23.57d	14.98b	17.94b	383.45b	2515.92b	1861.01c
ASH5	9.40i	202.35b	41.49b	51.86e	8.93f	0.86g	13.98g	70.95a	2.53ef	98.10f	2879.72a	809.23f
ASH8	77.21e	116.57e	34.20b	133.04c	34.26c	2.45d	31.36b	13.24bc	19.82a	242.27c	1793.99c	3252.34b
BIOCHAR1	34.37g	32.03g	9.20b	147.19b	10.18f	0.86g	6.56i	6.01ef	9.31d	38.21g	948.90e	84.10hi
BIOCHAR2	30.81h	67.15f	13.64b	45.80e	14.92e	1.19f	17.22f	10.28cd	8.85d	108.81f	1081.55e	1848.22c
BIOCHAR3	37.08g	66.30f	9.06b	47.82e	7.36g	0.58h	21.81e	4.81f	2.82ef	45.39g	39.35g	155.80h
KCl	0.03j	493.11a	0.25b	0.72g	0.88i	NDi‡	15.01g	0.22g	0.07h	0.73h	0.15g	0.16j
PL	12.51i	29.06g	370.92a	23.64f	174.73g	1.39h	9.38h	0.04g	1.02g	43.66g	588.35f	519.43g
TSP	201.81a	1.70h	247.95a	168.22a	4.54h	0.11i	3.03j	2.55fg	3.08e	643.96a	425.41f	22.56ij
LSD$_{0.10}$	3.44	9.62	166.85	8.44	1.84	0.14	1.13	3.96	0.77	16.84	173.78	79.84

† A different letter within the column designates significance at the 0.10 level.

‡ ND= Non-detectable, below the detectable limit of the instrumentation (<.0001 mg L^{-1}).

Table 2.3b: Total elemental concentration of ash co-products, fresh PL and standard fertilizers.

	As	Be	Cd	Co	Cr	Hg	Mo	Ni	Pb	Sb	Se	Si
						---mg kg^{-1}---						
ASH1	2.87ef†	0.92c	NDc	9.21d	41.96cd	ND‡	37.08c	37.60def	9.48b	1.21d	2.77c	44.09bc
ASH2	15.07c	0.34e	NDc	12.00c	169.69ab	ND	25.51d	108.86ab	7.18c	1.87c	1.88cd	29.59cde
ASH3	13.51c	0.12h	NDc	8.97d	15.45d	ND	48.84a	50.00cde	5.58d	1.07de	4.59b	35.04bc
ASH4	4.48de	1.37b	NDc	19.68b	33.11d	ND	25.14d	67.17cd	5.14d	1.60cd	2.51c	56.51ab
ASH5	51.87a	0.17g	4.91b	27.05a	237.07a	ND	36.32c	146.33a	56.89a	4.26a	20.29a	24.15cdef
ASH8	3.79de	0.44d	NDc	6.98f	31.09d	ND	42.20b	60.82cde	5.88d	0.35f	1.33de	32.63bcd
BIOCHAR1	0.87fg	0.45d	NDc	7.59ef	13.33d	ND	4.52g	7.47f	5.14d	0.22f	NDf	22.68cdef
BIOCHAR2	19.46b	0.31f	NDc	6.37f	12.86d	ND	21.37e	22.72ef	6.21d	0.38f	2.03cd	8.77def
BIOCHAR3	1.83efg	0.35e	NDc	3.46g	104.11bc	ND	13.90f	86.38bc	2.54e	0.54ef	NDf	4.07ef
KCl	0.27fg	NDi	NDc	0.04i	0.05d	ND	NDh	0.24f	NDf	NDf	NDf	19.64cdef
PL	NDg	0.14gh	NDc	1.25hi	4.83d	ND	1.19h	3.35f	2.02e	NDf	0.67ef	NDf
TSP	5.99d	1.59a	8.28a	1.71h	159.13b	ND	4.57g	26.58ef	3.08e	2.53b	NDf	81.92a
LSD$_{0.10}$	2.81	0.03	0.67	1.50	69.94	---------	1.59	38.17	1.25	0.65	0.92	25.59

† A different letter within the column designates significance at the 0.10 level.

‡ ND= Non-detectable, below the detectable limit of the instrumentation (<.0001 mg L^{-1}).

Table 2.4: Weak Salt (0.1 M CaCl$_2$) Extraction of ash co-products, fresh PL and standard fertilizers.

	P	K	S	Mg	Mn	Zn	B
	--g kg^{-1}-------------------------------------			---mg kg^{-1}---			
ASH1	0.054b†	60.29e	28.94c	679.47de	0.02c	ND‡c	29.65c
ASH2	0.06b	48.25f	27.45d	1865.64b	0.22c	0.32c	10.75fg
ASH3	0.08b	72.81d	30.06c	646.97e	0.17c	NDc	21.10e
ASH4	0.02b	60.15e	19.95e	4.42g	NDc	NDc	50.13a
ASH5	0.01b	211.95b	50.35a	1287.03c	0.73c	1.35c	10.06g
ASH8	0.01b	88.64c	39.21b	218.03fg	0.05c	NDc	26.13d
BIOCHAR1	0.14b	13.25i	2.44i	259.99f	0.73c	0.30c	4.39h
BIOCHAR2	0.26b	42.32g	10.14h	927.81d	7.05c	12.01c	13.82f
BIOCHAR3	11.64b	74.74d	11.71g	5.17g	NDc	NDc	1.73hi
KCl	0.28b	483.89a	0.27j	563.96e	0.28c	NDc	0.90i
PL	0.82b	26.07h	13.11f	567.07e	21.43b	79.93b	25.00d
TSP	219.57a	1.64j	3.09i	5138.78a	112.70a	443.26a	38.74b
LSD$_{0.10}$	16.56	3.89	1.13	250.89	8.07	20.65	3.29

† A different letter within the column designates significance at the 0.10 level.

‡ ND= Non-detectable, below the detectable limit of the instrumentation (<.0001 mg L^{-1}).

Table 2.5: Water Extraction (1:10) of ash co-products, fresh PL and standard fertilizers.

	P	K	Ca	S	Mg	Mn	Zn	B
	--g kg^{-1}--------------------------------------				--mg kg^{-1}----------------------------------			
ASH1	0.13c†	62.60e	0.12c	25.53c	150.16e	0.02d	ND‡d	30.63c
ASH2	0.10c	48.06f	0.19c	23.21d	1293.29b	0.95d	1.35d	11.12g
ASH3	0.27c	70.31d	0.12c	25.23c	167.43e	0.29d	0.05d	20.85e
ASH4	0.11c	63.95e	0.05c	17.48e	8.81f	NDd	NDd	42.86a
ASH5	0.03c	194.39b	6.72b	44.25a	1243.33b	0.56d	0.91d	8.54h
ASH8	0.06c	89.54c	0.34c	33.16b	136.86e	NDd	NDd	23.45d
BIOCHAR1	0.59c	11.39i	0.08c	1.98i	90.92ef	0.37d	0.76d	3.86i
BIOCHAR2	0.40c	37.85g	0.18c	8.47g	436.85cd	5.72c	16.14c	13.53f
BIOCHAR3	11.82b	67.90de	0.02c	9.83f	6.17f	NDd	NDd	1.42j
KCl	0.02c	516.14a	0.30c	0.23j	503.46c	0.03d	NDd	1.49j
PL	0.82c	22.52h	0.48c	10.94f	346.69d	16.78b	77.39b	23.50d
TSP	209.68a	1.80j	132.40a	3.37h	4158.25a	108.80a	294.95a	38.96b
LSD$_{0.10}$	5.23	5.40	3.40	1.24	109.58	4.41	3.90	1.17

† A different letter within the column designates significance at the 0.10 level.

‡ ND= Non-detectable, below the detectable limit of the instrumentation (<.0001 mg L^{-1}).

Table 2.6: Water Extraction (1:100) of ash co-products, fresh PL and standard fertilizers.

	P	K	Ca	S	Mg	Mn	Zn	B
	--g kg^{-1}--------------------------------------				--mg kg^{-1}--------------------------------			
ASH1	1.95d†	72.52def	0.23c	27.04c	1189.50c	0.32e	ND‡e	31.49c
ASH2	1.43de	57.15fg	0.50c	24.43c	2080.35b	2.42de	2.42e	14.28f
ASH3	1.97d	86.56cd	0.35c	28.40bc	1063.69c	2.94de	NDe	25.26d
ASH4	0.77def	70.02ef	0.21c	18.48d	603.55de	NDe	NDe	48.88a
ASH5	0.21ef	265.59b	18.31b	65.73a	1871.13b	5.44d	32.93c	17.77ef
ASH8	0.26ef	92.93c	1.03c	32.03b	487.48e	0.15e	NDe	26.19d
BIOCHAR1	1.36de	28.80hi	0.37c	5.21f	535.72c	5.45d	9.59de	8.49g
BIOCHAR2	1.52d	44.93gh	0.63c	8.35ef	893.33cd	11.66c	18.68d	14.31f
BIOCHAR3	12.61b	77.70cde	0.08c	10.60e	134.29f	0.04e	NDe	NDh
KCl	0.06f	479.70a	0.41c	0.23g	571.76de	0.67e	0.28e	1.06h
PL	3.55c	27.23i	0.85c	11.44e	990.78c	25.93b	74.21b	22.08de
TSP	190.42a	1.54j	133.86a	12.01e	4571.50a	118.17a	359.51a	43.20b
LSD$_{0.10}$	1.25	16.53	3.40	4.27	344.82	4.40	13.28	5.09

† A different letter within the column designates significance at the 0.10 level.

‡ ND= Non-detectable, below the detectable limit of the instrumentation (<.0001 mg L^{-1}).

Table 2.7: Characterization of fresh poultry litter samples from four different thermo-conversion systems in the Mid-Atlantic.

	Moisture	CCE†	N	P	K	S	Mg	Ca	Na	Fe	Al	Mn	Cu	Zn	B	K_2O‡	P_2O_5‡
	---%---								-------------------------------------mg kg^{-1}-----------------------------							----------%-------	
ASH3	22.56d§	0.29d	4.58b	1.70a	2.19c	0.88a	0.59b	2.64b	5696c	678	116c	749a	616a	620b	57c	2.02c	3.04
ASH4	25.24c	1.78c	3.91d	0.76d	2.26c	0.38c	0.53b	1.65b	3769d	231	308b	420d	175c	565c	52c	2.03c	3.61
ASH6	28.9b	2.36b	4.04c	1.20c	3.00b	0.81b	0.64b	2.02b	6220a	665	603a	540c	226b	423d	706a	2.57b	1.97
ASH7	40.35a	3.46a	5.54a	1.41b	5.14a	0.86a	2.09a	5.14a	6018b	808	312b	663b	146d	909a	636b	3.67a	1.93
LSD$_{0.10}$	1.25	0.66	0.17	0.13	0.30	0.03	0.60	1.47	176	NS	72	37	23	36	24	0.20	NS

† CCE- Calcium Carbonate Equivalent.

‡Available fertilizer equivalent.

§A different letter within the column designates significance at the 0.10 level.

Table 2.8: Characterization of Poultry litter ash samples from three different thermo conversion systems in the Mid-Atlantic.

	Moisture	CCE†	N	P	K	S	Mg	Ca	Na	Fe	Al	Mn	Cu	Zn	B	K_2O‡	P_2O_5‡
	---%---								-------------------------------------mg kg^{-1}-------------------------------------							---------%----------	
ASH3	0.20b§	22.54c	0.30b	10.70a	11.04b	2.32a	3.83	17.68a	33980a	10320b	1806d	4102a	3262a	2170b	261c	13.26	24.50a
ASH4	0.09b	31.13a	0.15c	7.20b	11.52b	1.24c	3.93	11.77b	20211c	12600a	18622a	2751b	1115b	2099b	316c	13.83	16.50b
ASH6	0.50b	28.90b	0.35b	6.09c	11.30b	2.30a	3.11	9.76c	28000b	9780b	13200b	2330c	1060c	1620c	2590a	13.40	13.90c
ASH7	17.76a	12.71d	2.36a	5.46d	12.47a	1.85b	5.96	7.29d	17400d	5336c	4036c	2177c	396d	2496a	1770b	12.33	10.27d
LSD$_{0.10}$	1.28	1.96	0.20	0.40	0.63	0.11	NS	1.22	1518	610	617	220	52	143	87	NS	0.80

† CCE- Calcium Carbonate Equivalent.

‡Available fertilizer equivalent.

§A different letter within the column designates significance at the 0.10 level.

Table 2.9: Concentration of nutrients from the densification of poultry litter entering the thermo-conversion unit and poultry litter ash exiting the unit from four different units in the Mid-Atlantic.

	N	P	K	S	Mg	Ca	Na	Fe	Al	Mn	Cu	Zn	B	K_2O	P_2O_5
	---Times Concentrated†---
ASH3	0.07b‡	6.41b	5.04a	2.63b	6.62b	6.93b	5.98a	22.93b	15.71c	5.54b	5.36b	3.52b	4.61b	6.55b	8.26b
ASH4	0.04c	10.22a	5.12a	3.26a	7.49a	7.25a	5.41b	55.54a	65.44a	6.63a	6.48a	3.79a	6.05a	6.83a	11.36a
ASH6	0.09b	5.08c	3.77b	2.84b	4.86c	4.83c	4.50c	14.71c	21.89b	4.31c	4.69c	3.83a	3.67c	5.21c	7.06b
ASH7	0.43a	4.07c	2.48c	2.15c	3.12d	2.44d	2.90d	14.53c	16.58c	3.30d	2.80d	2.74c	2.77d	3.41d	5.54c
$LSD_{0.10}$	0.04	1.22	0.21	0.21	0.51	0.76	0.41	5.39	7.09	0.48	0.46	0.28	0.28	0.25	1.78

†Times Concentrated= Ash nutrient Concentration %/ Feedstock PL nutrient concentration %).

‡A different letter within the column designates significance at the 0.10 level.

Table 2.10: Differences in carbon content of PLA and fresh PL by thermo-conversion system.

	Bulk PLA	Fresh PL
	---C---
	---%---
ASH3	5.30b†	37.95b
ASH4	2.31c	38.43a
ASH7	13.03a	36.98c
$LSD_{0.10}$	1.11	0.39

†A different letter within the column designates significance at the 0.10 level.

3. Incubation of Poultry Litter Co-Products for Phosphorous and Potassium Availability

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3.1 Abstract

Phosphorus (P) and nitrogen (N) are nutrients of concern in the Chesapeake Bay watershed due to nutrient imbalances in areas with confined animal feeding operations. By converting poultry litter to an ash via thermal conversion, nutrients are concentrated and can be shipped further from the source to nutrient deficient regions, such as the corn-belt. A non-leached aerobic incubation study was conducted on a Bojac sandy loam soil to test P and potassium (K) availability from poultry litter ash (PLA). Four PLA products, derived from different sources using different combustion techniques, and 2 biochar products were surface broadcast applied at a rate of 85 mg P kg^{-1} and the corresponding K rate was recorded. Poultry litter co-products were compared to a no-fertilizer control and inorganic P (triple super phosphate; TSP) fertilizers at similar rates. A dilute salt extraction (P and K) was used to analyze the characteristics and availabilities of the PL co-products under a controlled soil incubation environment to determine how they compare to the current industry standards in terms of potential bioavailability. Overall, standard fertilizers (TSP and PL) had the greatest initial availability for P (55.50% TSP; 9.13% PL) and K (97.99% PL) respectively. The PL co-products varied in availabilities based on thermo-conversion system from 1.60- 8.63% for P to 8.14- 88.10% for K. One ash co-product (ASH4) produced similar availabilities to the industry standard fertilizers after 56 days. In conclusion, co-products from combustion thermo-conversion systems were found to be superior to gasification and pyrolysis systems when the desire was to produce the most plant available P and K dense PL co-products. As new thermal conversion systems are designed, the ash co-products will need further evaluation as temperature and oxygen during the combustion process significantly alters water soluble nutrient availability.

3.2 Introduction

Phosphorous (P) and nitrogen (N) are both nutrients of concern to water quality (USEPA, 1988) and are most often connected with eutrophication (Levine and Schinder, 1989; Pote et al., 1996). Areas of intensive animal production often have the greatest potential for eutrophication due to non-point nutrient sources from manure (Pote et al., 1996; Duda and Finan, 1983). Phosphorus is also an important nutrient because it is valuable agronomically and is considered a non-renewable resource. Current research estimates that within 50-100 years we will have mined all of our current known P supplies (Lynch et al. 2013).

Poultry litter has been well researched and vetted as a satisfactory fertilizer source (Reiter et al., 2013; Sharpley et al., 2007; Revell et al., 2012). Although, in regions with intensive animal production, land application of PL is not a viable option due to the high residual nutrient levels in the soil. For example, most manure applications were historically applied to agricultural crop lands at a rate that correlates with the N requirements of the crops, which typically leads to an over application of P (Maguire et al., 2007; Sims et al., 1998). The over application of P is often due to the N:P ratio. The P content of manure is typically higher than the ratio that plants require leaving a surplus of P (Pote et. al 1996). The average N:P ratio plants require is around 8:1 (Zhang et al., 2002; Bryson et al., 2014) and the average range of PL is 1:1 (Zhang et al., 2002). For example, when applying PL to meet the N requirements of a crop, you will be providing 8 times more P than required. In a study by Sharpley (2007), the effects of PL applications on bermudagrass [*Cynodon dactylon* (L.] found that by applying PL to meet the N requirements resulted in an excess of 365 kg P ha^{-1} that was not removed by the bermudagrass.

Due to nutrient management regulations (VA DCR, 2014), this often leads to transport of PL off of the farms. Poultry litter has a low nutrient density, making it difficult for farmers to ship out of nutrient rich areas. A solution to this issue is the thermo-chemical conversion of PL into nutrient dense co-products (PLA and biochar). Combustion of PL is a viable approach to alternative energy generation, while at the same time reducing the total volume into an easily transportable ash that remain high in key crop nutrients P and K (Sharpley et al., 2007; MacDonald, 2007). Direct combustion, a high oxygen thermo-conversion technique is the most promising new technology available to farmers. Numerous studies showed that thermo-chemical conversion of poultry litter to a bio-fuel is possible through multiple techniques including combustion (>1100ºC and high O_2), gasification (700-1000ºC and minimal O_2), liquefaction, and pyrolysis (350-650ºC and depleted O_2) (Mante and Agblevor, 2010; Çaglar and Demirbas, 2000; McKendry, 2002; Cantrell et al., 2007; Farm Manure-to-Energy Initiative, 2015). Direct combustion tends to be most feasible for the farm-scale conversion of PL. Some models employ a technique called localized fluidized bed combustion units (FBC) to gasify the PL at 700-1000°C with moisture around 25% (Kelleher et al., 2002; Williams, 1999). The advantages of combustion are the concentration of nutrients (P, K, S, etc.) to 6 or 7 times that of the original feedstock and an increase of 1.5 to 2.5 times the bulk density of the PL (Bock, 2004).

Phosphorous is present in PL in its solid organic P phase as well as its inorganic P and is normally present in the acid soluble fraction ($H_2PO_4^-$ and HPO_4^{2-}), but can vary widely due to husbandry and diet practices. (Lynch et al., 2012). In soils with low P testing soils there is little to no risk of leaching because Soils tend to strongly adsorb P due to reactions with clay, iron (Fe)-oxide, and aluminum (Al)-oxide (Sims et al., 1998; Brady and Weil, 1996). Although, under long-term applications of P in excess of crop removal rates, the soil P concentrations will rise

increasing the likelihood of leaching or runoff as the P sorption capacity of the soil is surpassed (Maguire and Sims, 2002). When soil test P levels reach high or excessive, an increased chance of nutrient leaching and agricultural runoff can be expected (Moore and Edwards, 2007; Maguire and Sims, 2002). Another factor that affects P availability in the soil system is the soil pH. Phosphorous fixation occurs at both ends of the pH spectrum, in acidic low pH soils (<5.0) and basic high pH soils (>8.0) (Brady and Weil, 1996). In the low pH ranges, P will react with Al, Fe, and manganese (Mn) oxides and in the high pH ranges P will react with calcium (Ca) fixing the P to form insoluble compounds (Brady and Weil, 1996).

The majority of research into manure based fertilizers has been into N availability because N is typically the most yield-limiting nutrient in row crops (Slaton et al., 2013). The plant availability of N, P, and K are all vital to plant health and growth and interrelated in their respective cycles (Brady and Weil, 1996). A study by Sharpley and Sisak (1997) proposed that the P bioavailability from manure sources may differ from traditional inorganic fertilizers. They suggested that application recommendations needed to be tailored to the unique fertilizer source. Studies have shown the P in manure is generally found to be 60-100% bioavailable depending on the source (Slaton et al., 2013; Barbazan et al., 2009; Sneller and Laboski, 2009) and most K is highly water soluble and plant available (Jackson et al., 1975). The N content of PL existing in several forms organic N and inorganic N (ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-)) and constantly changes form based on microbial activity, temperature, pH, moisture and oxygen concentration (Bremner, 1996; Kelleher et al., 2002). The majority of N in PL (60-80%) is found in organic N form urea and proteins and 40-90% of the organic N will be converted to the volatile ammonia gas (NH_3) within a year (Keheller et al., 2002).

The primary disadvantage of an ash product is the loss of N during the combustion process, but if combusted at a much lower temperature some N losses can be avoided (Faridullah et al., 2009; Steiner et al., 2010). It is known that the land application of fresh poultry litter results in much higher emissions of atmospheric N, around 50 to 90%, so the thermo-conversion of PL may actually reduce atmospheric emissions of reactive N (Farm Manure-to-Energy Initiative, 2015).The majority of N from the fresh poultry litter is released from the systems in the form of non-reactive nitrogen gas (N_2) but the reactive forms may also be released in the forms of nitrogen oxides (NO_x) and NH_3 (Farm Manure-to-Energy Initiative, 2015). The emissions differ system to system but the reactive emission typically range from less than two to less than one percent due to the presence of NH_3 and organic N in PL, at higher temperatures they will react with NO_x to form the non-reactive N_2 gas and water vapor minimizing the reactive N emissions (Farm Manure-to-Energy Initiative, 2015).

The objective of this study is to analyze the characteristics and availabilities of the PL co-products under a controlled soil incubation environment to determine how they compare to the current industry standards in terms of potential bioavailability.

3.3 Materials and Methods

3.3.1 Experimental Design

A non-leached aerobic incubation study was conducted with a Bojac sandy loam soil (Table 3.1) (Coarse, loamy, mixed, semiactive, thermic, Typic Hapludult) (USDA-NRCS, 2012) with a bulk density of (1.14 g cm^{-3}) (Table 3.2) to evaluate the P and K mineralization characteristics of PL co-products. To evaluate the P and K mineralization of 4 PLA (ASH1, ASH2, ASH3, and ASH4) and 2 biochar sources (BIOCHAR1 and BIOCHAR2) (Table 3.3) compared to TSP and KCl applied at a rate of 85 mg P kg^{-1} and the amount of K applied per

source was recorded. The fertilizers were arranged in a randomized complete block design (RCBD) with 4 replications and incubated for 0, 3, 7, 14, 28, 56, 84, 112, and 140 days as described by (Reiter et al., 2014). The Fertilizers were mixed in 50 g of air-dried soil in 500 ml plastic bottles. Bottles were then raised to approximately 60% water-filled pore space (0.15 g water g soil^{-1}; Schomberg et al., 2011) with double de-ionized water. Final weights were taken so the water content could be adjusted on an as needed basis. Uncapped bottles were placed into incubation chambers at 80% humidity and 25°C.

3.3.2 Sample Analysis

At each sampling day, four replications were extracted per treatment source. For extraction, each bottle was filled with 500 mL of 0.01 M CaCl$_2$ solution (Aslyng, 1964) and shook for 1 hour at 200 opm (Kuo, 1996). The suspension settled for an hour and the supernatant was decanted and filtered through Whatman 42 filter paper into 25 mL scintillation vials and stored at 4°C until analyzed. Samples were analyzed for P and K concentration using ICP-OES (Spectro Analytical Instruments, Kleve, Germany) at the Virginia Tech Soil Testing Laboratory (Maguire, R. O. and S. E. Henkendorn, 2011). The P and K concentrations of the untreated control soil samples were averaged and subtracted out. The percent remaining in the sample was calculated by the concentration of the sample divided by the original amount of fertilizer added and multiplied by 100. ($\frac{\text{Sample Concentation}}{\text{Original Amount Added}} \times 100 = \%$ remaining)

3.3.3 Statistical Analysis

Statistical analysis was conducted using analysis of variance (ANOVA), SAS PROC MIXED procedures and Fisher's LSD with an alpha level of 0.10 using SAS 10.1 statistical software (SAS Institute, 2007).

3.4 Results and Discussion

Overall availability of soil P from fertilizer sources was low due to the acidic nature of the soil. Water pH readings from the incubation soil averaged 5.4 (Table 3.2); which would decrease overall recoverable P. Phosphorous fixation occurs rapidly in the acidic pH ranges reacting with Al, Fe, and Mn ions and oxides to form insoluble compounds that are not plant available (Brady and Weil, 1996). When comparing the percentage P recovered/ P fertilizer applied over time for each fertilizer source (Figure 3.1), a significant P interaction between fertilizer source and incubation sampling day (Table 3.5) was observed. As expected the standard fertilizer TSP was initially the most available and water soluble at 0 d (55.50%), followed by fresh PL (9.13%). Triple super phosphate became less available over time as Fe-oxides and Al-oxides in the soil absorbed P (Sims et al., 1998; Brady and Weil, 1996). Fresh PL decreased in availability until day 28 (4.35%) and began significantly increasing in availability, 56 d (6.36), until peak availability at 112 d (7.19%). The increase in availability over time is likely from microbial activity, as the fresh material releases the P from PL organic matter (Sharpley et al., 2007). Fresh PL was found to be far less available (9.13%) than the 60-100% bioavailability range the literature field studies suggested (Slaton et al., 2013; Barbazan et al., 2009; Sneller and Laboski, 2009)

Comparing ash co-products, ASH4 ash has the highest water soluble P, (5.84 % at 0 d) and experienced a similar increase in availability to PL at 14 d (5.95%) and 56 d (8.63%). The remaining co-products remained at a consistent solubility across time and had a range of around 2-4% available P; which was lower than the TSP and fresh PL standards. Trends showed that the ASH2 ash product and the biochars had the least P availability.

The characteristics and solubility of the ash co-products vary due to the differences in their formation. All of the sources were derived from different thermo-conversion systems and

were combusted at different temperatures and had varying oxygen rates (Table 2.2). It seems that the ASH4 system had the optimal ratio of temperature to oxygen for soluble P availability in a growing season and the ASH2 system would lead to the lowest solubility. The ASH2 system was gasified at higher temperatures for a longer period of time than the ASH4 system. The biochars were found to have a lower P availability rate, which was expected as biochars are formed in low heat with the intention of creating a slow release product resulting in a product where, the full nutrient release may not be seen for years (Maguire and Agblevor, 2010).

When comparing the percentage K recovered/ K fertilizer applied over time by each of the sources (Figure 3.2) a significant K interaction between fertilizer source and incubation sampling day (Table 3.6) was observed. Fresh PL had the greatest initial K availability at 0 d (97.99%). Our results for K availability were closer to the estimated availability in the literature; which stated that K should be highly soluble and should be 100% plant available (Jackson et al., 1975; Slaton et al., 2013). At 56 d, the K availability of the ASH4 product (88.19%) became similar to PL (88.19%) and remained consistent until then end of the study. Also at 56 d there was a significant increase in K availability for 4 of the co-products ASH1 (46.37%), BIOCHAR2 (78.65%), ASH3 (54.54%), and ASH4 (81.04%). Out of all the co-products, the ASH2 had the least water soluble K at 0 d (10.89%).

Fresh PL was by far the highest supplier of water soluble K, which was expected as the standard unprocessed material, but over time the ASH4 co-product produced similar K availabilities after 56 d. Similar to the P release, the ASH2 co-product had the lowest nutrient availability which did not change over time and remained within a range of 8.14-12.63%. The difference in these sources can once again be explained by differences in initial feedstock and system of thermo-conversion (temperature and oxygen ratios). The K availability results further

reiterate the ASH4 system's optimal conditions for creating a nutrient dense and plant available fertilizer.

3.5 Conclusion

The industry inorganic standard fertilizer (TSP) and fresh PL had the greatest initial availability for P and K. Overtime, some of the ash co-products reached similar availabilities comparable to the standards but differed due to the variability in their systems of formation. The ASH4 thermo-conversion system produced an ash co-product that was the most similar to the standards and provided an ideal fertilizer that was both nutrient dense and plant available. The ASH2 system converted the feedstock at higher temperatures and had longer residence times creating a nutrient dense product that was not readily water soluble. The biochar co-products were among the least available of the fertilizers in the study; which was expected because the biochars are specifically formed with a slow release product in mind to strongly hold and remove nutrients and carbon from the soil system for many years. Further ash research will be needed for each thermo-conversion system and feedstock as the burning process significantly alters the overall nutrient water solubility over time.

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Tables

Table 3.1: Mehlich-I background analysis of nutrients of the Bojac sandy loam soil (coarse, loamy, mixed, semiactive, thermic, Typic Hapludult) used in the incubation studies.

	P	K	Ca	Mg	Zn	Mn	Cu	Fe	B
	----------------------------kg ha^{-1}------------------------				---------------------------------------mg kg^{-1}--------------------------------				
Soil	194	146	832	95	1.4	25.4	1.3	25.0	0.2

Table 3.2: Chemical and physical properties of the Bojac sandy loam soil (coarse, loamy, mixed, semiactive, thermic, Typic Hapludult) used in the incubation studies.

	pH	Buffer Index	Estimated CEC†	Bulk Density	Acidity	Base Saturation
			---meq 100 g^{-1}---	g cm^{-3}	----------------------%--------------------	
Soil	5.4	6.14	3.9	1.136	39.5	60.6

†CEC- Cation exchange capacity

Table 3.3: Nutrient content of PL co-products, fresh PL and standard fertilizer for P and K incubation study.

Source	N	P	K	S
	--%--			
ASH1†	0.256	1.08	12.77	2.98
ASH2†	0.542	6.07	33.13	3.18
ASH3†	0.280	10.39	11.25	2.29
ASH4†	0.141	6.38	8.40	1.45
BIOCHAR1‡	1.44	2.29	1.71	0.40
BIOCHAR2‡	2.51	2.59	4.87	1.25
PL	3.55	1.08	1.91	1.10
TSP	0.00	20.09	0.00	0.00

Table 3.4: Phosphorus availability as a percentage of total P recovered or total P applied over a 140 d incubation study with a Bojac sandy loam soil (coarse, loamy, mixed, semiactive, thermic, Typic Hapludult) for PL co-products and fresh PL and standard P fertilizer.

	0	3	7	14	28	56	84	112	140
				-Incubation Day-					
				-% P Recovered-					
ASH1	3.69†	4.43	3.89	3.30	4.13	3.48	3.89	3.85	4.33
ASH2	1.89	2.58	2.32	1.78	2.71	2.29	2.78	2.29	2.20
ASH3	2.44	3.40	3.24	2.72	2.72	3.12	3.75	3.95	3.45
ASH4	5.84	6.74	5.99	5.95	6.45	8.01	8.63	7.75	7.51
BIOCHAR1	1.60	2.19	2.04	1.76	2.69	1.74	2.25	2.11	2.11
BIOCHAR2	3.28	3.34	3.23	2.75	3.70	3.50	3.17	3.51	3.95
PL	9.13	4.50	5.21	4.64	4.35	6.36	6.65	7.19	5.25
TSP	55.50	15.12	12.32	11.31	11.36	7.43	6.68	5.25	5.88

† Phosphorus source x incubation time interaction $LSD_{0.10}=1.99\%$.

Table 3.5: Potassium availability as a percentage of total K recovered or total K applied over a 140-d incubation study with a Bojac sandy loam soil (coarse, loamy, mixed, semiactive, thermic, Typic Hapludult) for PL co-products and fresh PL.

	---Incubation Day---							
	0	3	7	14	56	84	112	140
	---% K Recovered--							
ASH1	36.00†	43.12	40.36	33.70	46.37	45.60	47.74	43.44
ASH2	10.89	11.39	12.10	8.14	12.63	12.15	10.81	10.42
ASH3	41.29	53.59	51.17	39.48	54.54	62.74	61.77	57.59
ASH4	58.76	66.91	67.41	60.44	81.04	88.10	76.73	81.95
BIOCHAR1	63.58	72.23	73.92	49.53	71.54	76.31	66.80	59.64
BIOCHAR2	64.19	69.55	67.83	59.61	78.65	82.18	80.68	74.20
PL	97.99	88.58	88.36	87.94	88.19	93.24	92.75	87.73

†Potassium source x incubation time interaction $LSD_{0.10}$=8.99%.

Figures

Figure 3.1: Phosphorus availability as a percentage of total P recovered or total P applied over a 140 d incubation study with a Bojac sandy loam soil (coarse, loamy, mixed, semiactive, thermic, Typic Hapludult) for PL co-products and fresh PL and standard P fertilizer.
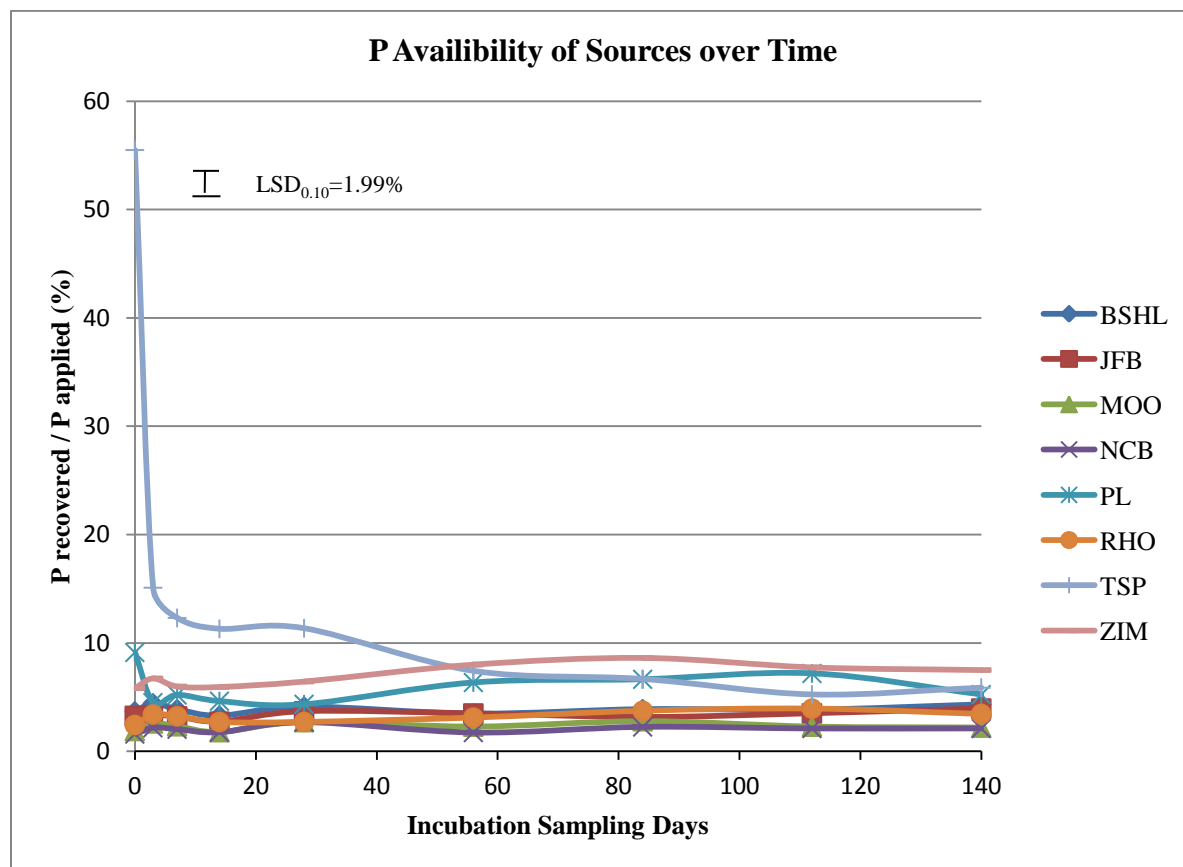
Figure 3.2: Potassium availability as a percentage of total K recovered or total K applied over a 140 d incubation study with a Bojac sandy loam soil (coarse, loamy, mixed, semiactive, thermic, Typic Hapludult) for PL co-products and fresh PL.
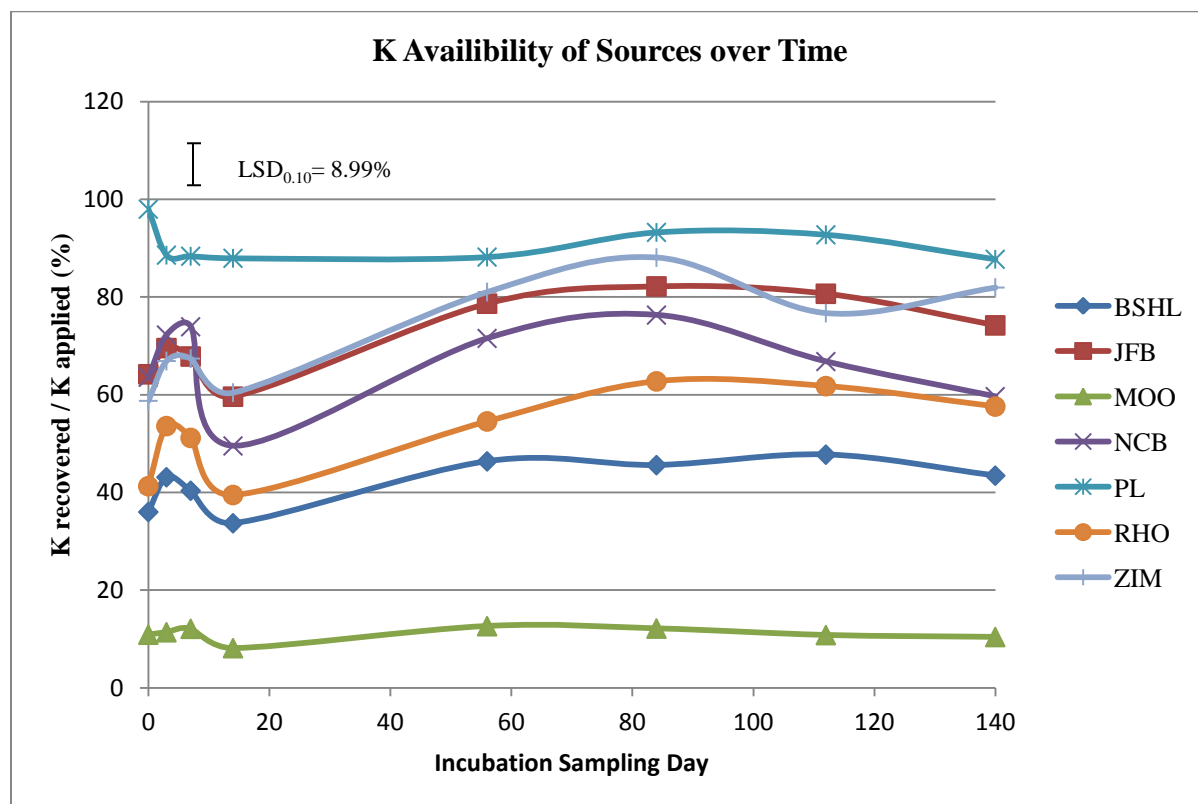
4. Nutrient Availability of Poultry Litter Co-Products in Field Trial Applications

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4.1 Abstract

Phosphorus (P) is a nutrient of concern in the Chesapeake Bay watershed due to nutrient imbalances in areas with confined animal feeding operations. By converting poultry litter to an ash via thermal conversion, nutrients are concentrated and are economical to ship out of nutrient surplus watersheds to nutrient deficient regions, such as the corn-belt. We initiated field studies (corn [*Zea mays* (L.)], soybean [*Glycine max* (L.)], and wheat [*Triticum aestivim* (L.)] on sandy loam soils to test P and potassium (K) availability from poultry litter ash (PLA). Four PLA products, derived from different sources using different combustion techniques, and 2 biochar products were surface broadcast applied at varying P and K rates. Poultry litter co-products were compared to a no-fertilizer control and inorganic P (triple super phosphate; TSP) and inorganic K (muriate of potash; KCl) fertilizer at similar rates. Yield, Mehlich-I extractable soil nutrients, plant tissue and grain samples, and organic matter content were used to compare treatments. In general, PL was the superior fertilizer source. Poultry litter ash co-products were highly variable due to the thermo-conversion system and feedstock of formation. However, when applied at the proper rate the PL co-products appear to be comparable to standard fertilizers in corn, soybeans, and wheat field studies.

4.2 Introduction

Over the years, many sources that cause eutrophication were identified and reduced to prevent pollution, but phosphorous (P) inputs are still important to water quality concerns. On the Delmarva, many sources of non-point-source P inputs include cropping systems, livestock operations, and runoff from populated areas. Exporting excess manure out of the watershed has been attempted but was found to be uneconomical. Poultry litter has a low nutrient density due to its water content and bedding material, although it remains a good source of nutrients (Reiter et al. 2013). Due to low nutrient density, fresh poultry litter has shipping limitations and is not homogenous enough to serve as marketable fertilizer for farmers a significant distance from the source location (Kelleher et al., 2002). A solution to the low nutrient density material may be to combust the fresh poultry litter into an ash product. Combustion homogenizes the fresh poultry litter by mixing and condensing the nutrients into the ash or biochar co-product. In the long term, ash could be transformed into a marketable and useful product through granulation and different formulations of nutrients.

Poultry litter ash is a co-product of the thermal conversion of fresh poultry litter to energy that has proposed agronomic value as a fertilizer. There is significant research describing the analysis of wood-based ash co-products, but very few of manure ash products. Crozier (2009) studied a granulated manure ash in three different experimental systems (greenhouse low-P soil, long-term P research sites with established P gradients, and agricultural fields with prior P fertilization at agronomic rates) and found when compared to triple super phosphate (TSP), source differences were infrequent and relativity minor. Codling (2002) compared the effectiveness of poultry litter ash (PLA) as

a fertilizer with an industry standard fertilizer, potassium phosphate (KP) as a P source for wheat. The two fertilizers were applied at three rates (0, 39, and 78 kg P ha^{-1}) in a wheat [*Triticum aestivum* (L.)]-based trial. No significant difference was found between the two fertilizers. A study by Reiter et al. (2004) comparing PLA to traditional fertilizer in a rice [*Oryza sativa*(L.)], wheat, and soybean[*Glycine max*(L.)] rotation found that the PLA had slightly less short-term availability but increased residual soil P. In studies by Pagliari (2006, 2008), turkey [*Meleagris gallopavo*(L.)] manure ash was found to have no statistical differences in plant yield and uptake when compared with TSP in corn [*Zea mays*(L.)] and alfalfa [*medicago sativa*(L.)] trials. These studies are a step in proving that PLA co-products have a similar value to farmers as traditional fertilizers. Research indicated that ash could be a viable P source, but needs further testing to explore optimum application rates. Ash applications act not only as fertilizers but also as soil amendments. Demeyer et al. (2001) found that ash worked as a liming agent increasing the pH of the soil from 4.5 to 7.0 with the highest application rate of 44 Mg ha^{-1}, stimulated the microbial activities and increased water holding capacity (WHC) by increasing soil aeration.

Biochar is another co-product of the thermal conversion of fresh poultry litter. There is interest in biochar for a multitude of uses including bioenergy, carbon sequestration, as a soil amendment, and fertilizer (Maguire and Agblevor, 2010). Biochar is voluntarily regulated by the International Biochar Institute; which established regulations for the creation, sampling, testing, and usage of biochar worldwide. Biochar is defined by the International Biochar Institute (2015), as the carbon (C) rich product when biomass is heated with little or no available oxygen. After pyrolysis, the inorganic

components of PL is significantly concentrated, although less concentrated than ash, the densification increases the co-products value as an agronomic nutrient source (Revell et al., 2012b; Agblevor et al., 2010). The main difference between a biochar product and an ash is the creation temperature as variations in temperature during production will have an impact on the quantity and quality of the end product (Maguire and Agblevor, 2010). Biochar is the product of a lower burning temperature during combustion 400-500°C compared to ashes that are produced at temperatures greater than 1000ºC (Gaskin et al., 2008).

Studies proposed that biochar can be used to improve soil productivity and sequester carbon (Atkinson et al., 2010; Laird, 2008). It has been found, mainly by scientists in the tropics, that biochar and charcoal created from the pyrolysis process will improve soil health and productivity of crops (Chan et al., 2007; Lehmann et al., 2003; Oguntunde et al., 2004; Steiner et al., 2007; Yamato et al., 2006). This process forms hydrogen and organic carbon bonds that will sequester carbon for over 100 years (International Biochar Institute, 2015). By increasing the active surface area of the soil, its capacity to retain nutrients and water increases WHC and nutrient uptake (Maguire, 2010). In a study by Revell et al. (2012b), biochar was found to decrease the bulk density of the soil by increasing aeration, the WHC increased linearly with rates of (0, 4.5, and 9 Mg ha^{-1}), pH was increased, and the cation exchange capacity (CEC) of the soil increased only when applied above agronomic rates. Increased WHC is one of the major benefits to using biochar, as drought is a major reason for decreased crop production in non-irrigated lands (Revell et al., 2012a; Havelin et al., 2005). A study by Schomberg et al. (2012) reported that soil parameter improvements greatly depended on biochar quality,

temperature and speed of pyrolysis, and the soil. Laboratory incubations with various biochar amendments were conducted in the long and short term to explore the effects of biochar on changes in soil pH, ammonia losses, and soil carbon effects. Biochar additions resulted in a reduction of NO_3^- leaching and large increases in mineralizable N were not observed, meaning most soil C in the biochar was not available to microorganisms. The study suggested that development of standards and guidelines would allow better usage of biochar by matching the biochar to specific soils and land use situations (Schomberg et al., 2012).

This project evaluated removing some of the watershed's excess P by repurposing certain co-products of the poultry industry as a P and K fertilizer source. Ideally, excess P could be exported out of the watershed and used by farmers in P deficient areas of the country or used within the watershed where fresh poultry litter is not an option. The objective of this project is to determine co-product availability to plants as compared to traditional inorganic fertilizer and fresh poultry litter sources.

4.3 Materials and Methods
4.3.1 Experimental Design

We initiated a study on sandy loam soils (Table 4.1) to test P and K availability from poultry litter ash (PLA) on corn, soybean, and wheat. Overall, three corn P studies, two full-season soybean K studies, three double-crop soybean K studies, three wheat P studies, and three wheat K studies were conducted.

Corn studies were conducted at the Virginia Tech Eastern Shore Agriculture Research and Extension Center (AREC) in Painter, Virginia (2013, 2014) and at the Virginia Tech Tidewater AREC in Suffolk, Virginia (2014). Studies consisted of 4 replications and 25 total fertilizer treatments arranged in a RCBD. Four PLA products (ASH1, ASH2, ASH3, and ASH4), derived from different sources using different combustion techniques, and 2 biochar products (BIOCHAR1 and BIOCHAR2) (Table 4.2) were surface broadcast applied at 3 P rates (22, 44, and 88 kg P_2O_5 ha^{-1}). Potassium was applied with a balanced application using KCl to ensure all plants had identical total K rates. Poultry litter co-products were compared to a no-fertilizer control and inorganic P (TSP) fertilizer at similar rates.

Full-season soybean studies were conducted at the Virginia Ag Expo location in the Land of Promise, Virginia (2013) and Lottsburg, Virginia (2014) (Table 4.1). Double-crop soybean studies were conducted on the Eastern Shore of Virginia at 2 sites in Accomack County (2014) (Table 4.1). The studies consisted of 4 replications and 10 total fertilizer treatments arranged in a RCBD. Five PLA products (ASH1, ASH2, ASH3, ASH4 and ASH5), derived from different sources using different combustion techniques, and 2 biochar products (BIOCHAR1 and BIOCHAR2) (Table 4.2) were surface broadcast applied at one K rate (67 kg K_2O ha^{-1}) and P was applied with a balanced

application using TSP. Poultry litter co-products were compared to a no-fertilizer control and K (KCl) fertilizer at similar rates.

Phosphorus wheat studies were conducted at three locations on the Eastern Shore of Virginia in Accomack County (2014) (Table 4.1). The studies consisted of 4 replications and 13 total fertilizer treatments arranged in a RCBD. One PLA product (ASH3) (Table 4.2) was surface broadcast applied at 4 P rates (34, 67, 101, and 134 kg P_2O_5 ha^{-1}) and K was applied with a balanced application using KCl. Poultry litter co-product was compared to a no-fertilizer control and inorganic P (TSP) fertilizer at similar rates.

Potassium wheat studies were conducted at three locations on the Eastern Shore of Virginia in Accomack County (2014) (Table 4.1). The studies consisted of 4 replications and 13 total fertilizer treatments arranged in a RCBD. One PLA product (ASH3) (Table 4.2) was surface broadcast applied at 4 K rates (34, 67, 101, and 134 kg K_2O ha^{-1}) and P was applied with a balanced application using TSP. Poultry litter co-product was compared to a no-fertilizer control and inorganic K (KCl) fertilizer at similar rates.

4.3.2 Sample Analysis

Yield, grain moisture, and grain test weight were collected at the time of harvest. Grain weight was captured in field by the combine's software (ALMACO Seed Spector LRX, Nevada, IA). Sample moisture and grain test weight was collected using a GAC® 2100 Agri DICKEY John Moisture Tester (Churchill Industries, Minneapolis, MO). Yield was corrected for percent moisture to industry bushel standards: 25.4 kg (56 lbs) per bushel for corn at 15.5% moisture, 27.2 kg (60 lbs) per bushel for soybeans at 13%

moisture, and 27.2 kg (60 lbs) per bushel for wheat at 13.5% moisture (Murphy, 1993).

Plant tissue samples were dried until a constant weight at 55°C. Samples (corn ear leaf, corn grain, soybean tissue at V3 and V5, soybean whole plant at R2, soybean grain, wheat whole plant prior to bloom, and wheat grain) were coarse ground to pass a 2 mm sieve. Ground samples (0.5 g) were digested in nitric acid and hydrogen peroxide using method 3050B (USEPA, 1996), and then analyzed using ICP-OES (Spectro Analytical Instruments, Kleve, Germany) at the Virginia Tech Soil Testing Laboratory (Maguire and Henkendorn, 2011) for P and K.

Mehlich-I extractable nutrients were analyzed with ICP-OES (Mehlich, 1953). Soil samples were taken pre-fertilization at 3 depths: 0-15 cm, 15-30 cm, and 30-60 cm and at harvest at the 0-15 cm depth. Soils were air-dried and ground using a hammer mill to pass through a 2 mm screen. Using the Mehlich-I soil testing protocols, 8 grams of soil were extracted with 40 ml of Mehlich I solution (1:5 soil to extractant ratio) in 60 ml straight-walled plastic extracting beakers. The samples were shaken for 5 minutes on a reciprocating shaker set at 180 opm. Extracts were filtered through Whatman no. 2 filter paper into plastic vials and was then analyzed by ICP-OES for nutrient concentration.

To estimate P currently available in soil solution, 4 grams of soil were extracted with 40 ml of 0.01 $CaCl_2$ solution (1:10 soil to extractant ratio) in 60 ml straight-walled plastic extracting beakers (Aslyng, 1964; Olsen and Sommers, 1982). The samples were shaken for 1 hour on a reciprocating shaker set at 200 opm. Extracts were filtered through Whatman no. 2 filter paper into plastic vials. The solution was analyzed by ICP-OES for nutrients.

Soil organic matter samples were determined using the Loss-On-Ignition (LOI)

Method as described by Ben-Dor and Banin (1989). The sample was air-dried at 105°C

for 24 hours, cooled in a desiccator and weighed. The sample was then placed in a muffle

furnace and ignited at 400°C for 16 hours, cooled in a desiccator and weighed. Organic

matter is assumed to equal the % LOI. The LOI was determined by the equation % LOI =

(Weight$_{105}$ - Weight$_{400}$ / Weight$_{105}$) x 100 (Ben-Dor and Banin, 1989).

4.3.3 Statistical Analysis

Statistical analysis was conducted using analysis of variance (ANOVA), SAS

PROC MIXED procedures and Fisher's LSD with an alpha level of 0.10 using SAS 10.1

statistical software (SAS Institute, 2007).

4.4 Results and Discussion

4.4.1 Corn

There were significant differences between site year so data is presented

separately and the P source x P rate interaction was not significant. For the P rate main

effect, yield increased in a linear relationship with P rate in the first year (Painter 2013)

(Figure 4.1), averaged across P fertilizer sources. Phosphorus was limited in this

experiment because a plateau was not reached due to the initial low P testing soil (9 mg

kg^{-1}). Yield increased linearly in the second year (Suffolk 2014), until it reached a plateau

at 22 kg ha^{-1} (Figure 4.1). After this point, no further benefit to P fertilizer was realize due

to high initial soil P concentrations (29 mg kg^{-1}). Yield data from Painter 2014 was

omitted due to significant deer damage across all replications.

Overall, for P source, Suffolk 2014 data indicated that PL was significantly the

highest yielding source (7891 kg ha^{-1}), averaged over P rate. We speculate that heavy

rains during the early growing season leached or denitrified significant amounts of N

fertilizer and the slow release N from PL was available to the corn crop and gave a significant yield advantage. The PL ash co-products were similar to TSP but higher than the no P fertilizer control (Table 4.3). Overall, our data agrees with Slaton et al. (2013) who, found that PL provided an additional yield benefit above that of commercial fertilizer at one of their eight responsive sites and similar yields at the other sites. The cause of the yield benefit was unknown and could not be attributed to another essential nutrient present in the PL but not in the commercial fertilizer (Slaton et al., 2013). The Painter 2013 site was not significant and the average yield was 4565 kg ha^{-1}.

When averaged by site year and P fertilizer source, corn grain moisture had a significant linear response to P rate. Moisture increased with P rate at Suffolk 2014 (y= 0.0049x + 13.5; p=0.0640) and the no fertilizer control had the lowest grain moisture (15.85%). No fertilizer plots matured more quickly with lower yields and lower available nutrient concentrations, resulting in lower grain moisture concentrations at harvest.

Corn grain test weight varied with location and P source. Test weight by P source, averaged over P rate, was significantly different with one biochar co-product BIOCHAR1 (673.0 kg m^{-3}) having lower corn grain test weight than all the other treatments (Table 4.4). The lower test weight could be explained by the biochar removing nutrients from the soil system and preventing them from being immediately available to plants (Maguire and Agblevor, 2010) as BIOCHAR1 had lower grain test weight than the no fertilizer control.

There were no observed significant differences of P concentration in the corn ear leaf. The ear leaf concentrations averaged (2.2 g kg^{-1}) across all treatments and site years; which is below the optimal range of 2.5-.5.0 g kg^{-1} for tissue P (Bryson et al., 2013).

Averaged across site year, grain P concentrations varied with P rate and P source. For P rate, the highest rate 88 kg ha^{-1} had the greatest concentration; which increased linearly (y= 1.589x + 2129; p= 0.0578). For P source, the standard, TSP (2.33 g kg^{-1}) had the highest grain P concentration and was significantly similar to ASH4 co-product (2.29 g kg^{-1}) (Table 4.4). The ASH4 co-product was also comparable to TSP in yield, moisture, test weight, and grain P concentration indicating similar P availability. The BIOCHAR2 co-product tended to have the lowest yield, moisture, test weight, and grain P concentration indication that the biochar product the least available in the first growing season following application as a P fertilizer source.

4.4.2 Soybeans

Full Season Soybeans

Full season soybean yield, moisture, and test weight varied only with location and K fertilizer source was not significant. The Promise 2013 (2858 kg ha^{-1}) location had a statistically lower yielding crop than Lottsburg 2014 (5115 kg ha^{-1}).

The Lottsburg 2014 had statistically higher moisture concentrations (15.8%) than Promise 2013 (13.1%). The Lottsburg 2014 grain test weight (1839 kg m^{-3}) was statistically denser than Promise 2013 (709 kg m^{-3}). Therefore, the fertilizer ash co-products were tested under variable growing conditions around Virginia, but source did not matter. Similar data and results were seen in other Virginia studies conducted during these same years at the same locations as ample growing conditions did not necessitate additional K fertility (Stewart, 2015).

All V3 tissue concentrations averaged across all treatments and site years (27.0 g kg^{-1}) were above or within the optimal range of 17.0-25.0 g kg^{-1} for tissue K (Bryson et

al., 2013). Tissue K concentration of V5 and R2 tissue varied with location. Lottsburg 2014 (21.0 g kg^{-1} and 25.0 g kg^{-1} for V5 and R2, respectively) had statistically higher concentrations than Promise 2013 (19.0 g kg^{-1} and 14.0 g kg^{-1}, respectively). All V5 and R2 tissue concentrations were within the optimal range of 18.0-25.0 g kg^{-1} for V5 tissue K and 15.0-22.5 g kg^{-1} for R2 tissue K (Bryson et al., 2013). The only significant result from K fertilizer source occurred at the Promise 2013 site location for grain K concentration. All ash co-products were statistically similar to the fresh PL and TSP standards with the exception of ASH4 (17.5 g kg^{-1}) which had lower grain K concentrations.

Double Crop Soybeans

The Willis Wharf A site location had significant differences between K sources. The fly ash co-product ASH5 (1824 kg ha^{-1}) underperformed fresh PL, KCl and most ash co-products, averaged across K rate. Interestingly, the fly ash has the highest K concentration (202.4 g kg^{-1}) of all ash co-products (Table 2.3a) tested. The fly ash is a fine particulate that exhausts from the thermo-conversion units as they are burning PL, but appears to have lower water solubility than the bulk ash from the same thermo-conversion system and PL as those treatments yielded 2435 kg ha^{-1} (ASH2). The ASH5 fly ash yields were actually lower than the no fertilizer control plots (2222 kg ha^{-1}). Similarly, BIOCHAR1 was also lower yielding than the standard fertilizer treatments and several ash sources (Table 4.5).

For grain moisture, averaged over location, BIOCHAR1 and BIOCHAR2 were statistically similar to fresh PL and KCl and the rest of the co-products were significantly drier than the standards, with ASH4 being the driest (Table 4.6). Test weight averaged

over site year, there was a significant difference between K sources. The BIOCHAR1, ASH3, ASH4, and ASH5 were similar to applying no fertilizer at all (Table 4.6). Low test weight results were similar to yield, and K availability may not be available from the biochar and fly ash co-products compared to other technologies that produce more soluble ash sources.

The R2 tissue K concentration averaged across location, Willis Wharf B site had significant differences between K sources. Poultry litter had the highest tissue K concentration at R2 (28.0 g kg^{-1}) than other co-products. All other co-products were similar to the no-fertilizer control. However, all R2 tissue concentrations were within the optimal range of 15.0-22.5 g kg^{-1} for R2 tissue K (Bryson et al., 2013). Muriate of potash (18.4 g kg^{-1}) had the highest grain K concentrations.

4.4.3 Wheat P

Overall, there were no major differences between ash co-products for wheat yield. Average yield by location for Gospel Temple was 4133 kg ha^{-1}, Cheriton was 3722 kg ha^{-1}, and Quinby was 3360 kg ha^{-1}. Grain moisture was only significant at the Cheriton site in P rate main effect, averaged over P source. Grain moisture content increased linearly with P addition (y= 0.0025x +13.8; p= 0.0100). Similarly, grain test weight decreased linearly with the addition of P (y= -0.0712x + 766; p= 0.0351).

For tissue P concentration averaged across P rate, the Gospel Temple site had a significant P source effect. The co-product ASH3 (2.5 g kg^{-1}) was statistically similar to TSP (2.8 g kg^{-1}), but had lower concentrations than PL (3.0 g kg^{-1}). However, all tissue P samples were within the range of 2.0-5.0 g kg^{-1} for tissue P (Bryson et al., 2013). Codling et al. (2002) found that PLA treatments produced higher tissue P concentrations than the

standard, although their concentrations were below the optimum range due to initial low soil P concentrations. Overall, there were no major differences between ash co-products grain P concentration and averaged 3.9 g kg^{-1} for Quinby, 3,8 g kg^{-1} for Gospel Temple, and 3.7 g kg^{-1} for Cheriton.

4.4.4 Wheat K

Averaged across location and K fertilizer rate, PL was statistically the highest yielding (3744 kg ha^{-1}). Muriate of potash and ASH3 were similar to the no fertilizer control treatments (3398 kg ha^{-1}) (Table 4.7). Therefore, the PL provided additional yield benefit just as in a soybean study by Slaton et al. (2013) although; the source of the additional benefit was unknown. Moisture exhibited similar results to yield when averaged over K rate, as PL (13.8%) was statistically the driest source and KCl and ASH3 were statistically similar to each other and drier than the control plot (14.3%) (Table 4.7).

The tissue K concentration increased linearly with increasing fertilizer rate (y= 21.29x + 13051; p= 0.0017) (Figure 4.2); which is indicative of K availability and plant uptake from the fertilizer sources. Averaged across location and K rate, tissue K concentration from fresh PL (16.2 g kg^{-1}) was statistically higher than KCl and ASH3 (Table 4.6). Only the PL source had tissue K concentrations within the optimal range of 15.0-30.0 g kg^{-1} for tissue K (Bryson et al., 2013). Quinby had a significant difference between K fertilizer sources, averaged across K rates. The ASH3 co-product (4.3 g kg^{-1}) was statistically similar to PL (4.3 g kg^{-1}) and had higher grain K concentrations than KCl (4.1 g kg^{-1}) and the control plot (4.1 g kg^{-1}) Therefore, the co-product was equally plant available compared to the standard sources.

4.4.5 Soil Mehlich-I and Soil Organic Matter

Following harvest, the P and K concentrations in the soil increased linearly with rate of fertilizer application, averaged over fertilizer source. Soil P concentrations increased linearly with the addition of fertilizer at the Painter 2014 corn location (y= 0.0549x + 3.8; p= 0.0115) (Figure 4.3) and soil K concentration for the wheat K locations (y= 0.1873x + 81.7; p= 0.0088) (Figure 4.4).

For the Gospel Temple site year P source main effect, PL (32.5 mg P kg^{-1}) had higher P concentrations than the TSP standard (29.7 mg P kg^{-1}) most likely due to its greater residual P although not significantly different than the ASH3 ash co-product (29.7 mg P kg^{-1}) or no fertilizer control (27.7 mg P kg^{-1}). At the Painter 2014 corn location the co-product BIOCHAR2 (87.8 mg K kg^{-1}) had the greatest concentration of K in the soil while, the other sources were statistically similar (Table 4.8). This supports the yield data that the biochar sources are less plant available and will remain in the soil for future years (Maguire and Agblevor, 2010).

The vast majority of micro elements increased linearly with increasing rate of fertilizer application and was observed with Al, Ca, Cu, B, Mg, and Zn. The overall Fe concentration in the soil made it difficult to see an Fe response from the application of the fertilizers. Overall, Zn tended to be less concentrated in the soil fertilized by ash co-products leading us to believe that Zn is more plant available in the ash form. Soil B concentration trended to be higher following PL applications. Soil Cu concentrations tended to be higher following PL and ash, as Cu is typically absent from inorganic fertilizers. None of the soil applied elements exceeded concentrations that would cause environmental concern based on comparison of background concentrations in US soils

according to the elemental limit recommendation charts from the USDA-NRCS (2015).

No significant differences were found for organic matter content after a single year application of ash and biochar co-products. No significant difference was expected because at our greatest rate (88 kg ha^{-1}) we applied biochar at a rate of 1.7 Mg ha^{-1}and a study by Revell et al. (2012), found that after two years of applying biochar at a rate of 9 Mg ha^{-1}, that 3 field sites showed significant increases in soil C (0.51, 0.39, and 0.36%; respectively). More research is need for multiple year usage to know when a change in organic matter will present.

4.5 Conclusion

Overall, PL ash and biochar sources derived from PL are suitable and comparable P and K fertilizer sources for crops on sandy loam soils in the Mid-Atlantic. Poultry litter co-products vary greatly based on thermo-conversion system and initial feedstock. If all ideal combustion criteria are met, then PL co-products are feasible to use as fertilizer sources, but will need to be individually analyzed for nutrient content before making application recommendations. In our study, we found that the combustion systems seemed to have those ideal conditions and produced co-products that were highly plant available. A greater amount of the co-products will have to be applied to meet the same nutrient availability of the standards due to their lower availability. Fresh PL tends to be the better fertilizer due to its added N content, which is lost in thermo-conversion systems and would have to be supplemented with the ash co-products. Biochars tend to be less available than their ash counter parts. More research using the water soluble availabilities instead of the total concentration nutrients of the co-products are needed to be able to identify stronger relationships with standard fertilizers.

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    application of charred bark of Acacia mangium on the yield of maize, cowpea and

    peanut, and soil chemical properties in South Sumatra, Indonesia. Soil Sci. Plant

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Tables

Table 4.1 Locations, soil types, and soil characterization for all field trial site locations.

Year	Location	Crop	Texture	Classification	CEC†	pH	P	K	Ca	Mg
					---meq 100 g^{-1}---			------------mg kg^{-1}----------		
2013	Painter, VA	C‡	SL§	Typic Hapludults	5.6	5.7	9	71	641	92
2014	Painter, VA	C	SL	Typic Hapludults	5.4	6.1	5	60	686	95
2014	Cheriton, VA	W	FSL	Typic Hapludults	4.2	6.3	37	87	460	117
2014	Quinby, VA	W	SL	Typic Hapludults	4.8	5.6	36	109	473	71
2014	Willis Wharf, VA	SB/W	SL	Typic Hapludults	6.0	5.3	86	128	646	49
2014	Gospel Temple, VA	W	SL	Typic Hapludults	5.3	5.7	31	143	592	63
2014	Keller, VA	SB	LS	Typic Hapludults	4.2	6.0	14	102	569	55
2013	Land of Promise, VA	SB	L	Typic Hapludults	8.6	5.8	48	54	958	145
2014	Suffolk, VA	C	LS	Typic Hapludults	2.8	5.0	29	94	247	51
2014	Lottsburg, VA	SB	FSL	Aquic Hapludults	5.9	6.6	84	108	783	207

† CEC- cation exchange capacity

‡ C-Corn, W- Wheat, SB- Soybean

§SL- sandy loam, L- loam, FSL- fine sandy loam, LS- loamy sand

Table 4.2: Nutrient content of Ash and Biochar Treatment Sources for field studies.

Source	N	P	K	S
			%---	
ASH1†	0.256	1.08	12.77	2.98
ASH2†	0.542	6.07	33.13	3.18
ASH3‡	0.280	10.39	11.25	2.29
ASH4‡	0.141	6.38	8.40	1.45
ASH5†	0.487	0.66	37.10	8.10
BIOCHAR1§	1.44	2.29	1.71	0.40
BIOCHAR2§	2.51	2.59	4.87	1.25
PL	3.55	1.08	1.91	1.10
TSP	0.00	20.09	0.00	0.00
KCl	0.00	0.00	53.57	0.00

† Gasification
‡ Combustion
§ Pyrolysis

Table 4.3: Corn yield at the Suffolk 2014 site year comparing poultry litter co-product fertilizers to industry standard fertilizers

Source	Suffolk 2014
	--kg ha^{-1}--
ASH1	6862b
ASH2	7083b
ASH3	6476b
ASH4	6978b
BIOCHAR1	6773b
BIOCHAR2	7062b
PL	7891a
TSP	6871b
Control	5566c
LSD$_{0.10}$	834†

† A different letter within the column designates significance at the 0.10 level.

Table 4.4: Average corn grain test weight and grain P concentration across 3 site locations comparing PL co-products, fresh PL, and standard fertilizers.

Source	Test Weight	Grain P Concentration
	----------------------------kg m^{-3}------------------------	------------------------------------g kg^{-1}------------------------------------
ASH1	689.4a	2.22b
ASH2	682.5a	2.25b
ASH3	686.1a	2.16c
ASH4	685.5a	2.29a
BIOCHAR1	673.0b	2.02d
BIOCHAR2	685.3a	2.07d
PL	688.3a	2.26b
TSP	690.9a	2.32a
Control	688.9a	2.16c
LSD$_{0.10}$	8.5	0.06

†A different letter within the column designates significance at the 0.10 level.

Table 4.5: Double crop soybean yield response to K source for WWA site location comparing PL co-products, fresh PL, and standard fertilizers.

Source	Yield
	-----------------------------------kg ha^{-1}--------------------------------
ASH1	2435a
ASH2	2435a
ASH3	2397a
ASH4	2133abc
ASH5	1824c
BIOCHAR1	2020bc
BIOCHAR2	2237ab
PL	2414a
KCl	2195ab
Control	2222ab
LSD$_{0.10}$	321

†A different letter within the column designates significance at the 0.10 level.

Table 4.6: Double crop soybean moisture, test weight, and grain K concentration by source over 3 site locations comparing PL co-products, fresh PL, and standard fertilizers.

Source	Grain Moisture	Test Weight	Grain K Concentration
	------------------%----------------	----------------kg m^{-3}---------------	-----------------g kg^{-1}-------------
ASH1	12.9bcd	715.4abc	17.5cd
ASH2	12.9bcd	718.6abc	17.4cd
ASH3	12.9cd	714.7cd	17.3d
ASH4	12.8d	715.1bcd	17.6cd
ASH5	12.9bcd	712.8d	17.4cd
BIOCHAR1	12.9abc	713.7d	17.7bc
BIOCHAR2	13.0ab	718.7ab	17.8bc
PL	13.1a	718.1abc	18.0b
KCl	13.0a	721.4a	18.4a
Control	13.0a	713.8d	17.9bc
LSD$_{0.10}$	0.1	3.9	0.4

†A different letter within the column designates significance at the 0.10 level.

Table 4.7: Wheat yield, grain moisture, and tissue K concentration response to K source across 3 site locations comparing ash co-product, fresh PL, and standard fertilizers.

Source	Yield	Grain Moisture	Tissue K Concentration
	----------------kg ha^{-1}-------------	------------------%-----------------	---------------g kg^{-1}---------------
ASH3	3214b	14.0b	14.1b
PL	3744a	13.8c	16.2a
KCl	3319b	14.0b	14.2b
Control	3397b	14.3a	12.8c
LSD$_{0.10}$	222	0.1	0.7

†A different letter within the column designates significance at the 0.10 level.

Table 4.8: Soil K Concentration by fertilizer source for the Painter 2014 corn site location.

Source	Painter 2014
	--K--
	--mg kg^{-1}------------------------------------
ASH1	71.8bc
ASH2	76.5bc
ASH3	77.0b
ASH4	73.3bc
BIOCHAR1	66.8c
BIOCHAR2	87.8a
PL	74.9bc
TSP	69.4bc
Control	74.4bc
LSD$_{0.10}$	10.0

†A different letter within the column designates significance at the 0.10 level.

Figures

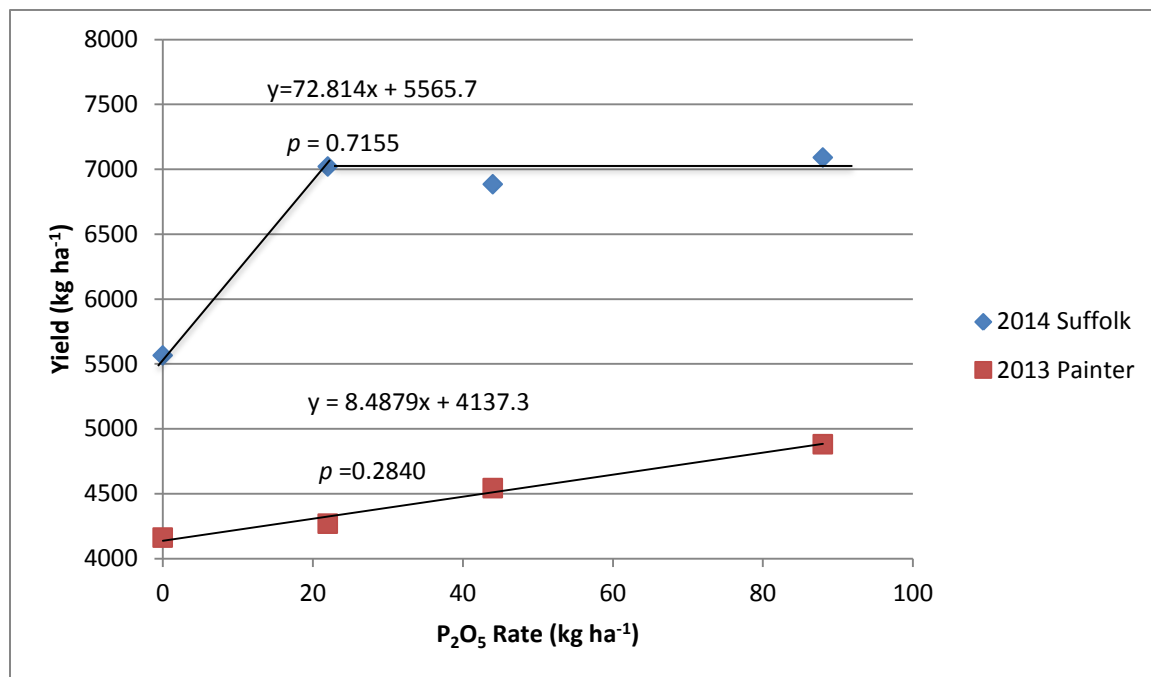**Figure 4.1: Corn yield by P rate for 2 corn site locations.**

$y=72.814x + 5565.7$

$p = 0.7155$

$y = 8.4879x + 4137.3$

$p =0.2840$

Yield (kg ha^{-1})

P$_2$O$_5$ Rate (kg ha^{-1})

◆ 2014 Suffolk
■ 2013 Painter

Figure 4.2: Wheat K tissue K concentration response to rate of K across 3 site locations.

$y = 21.287x + 13051$
$p= 0.0017$
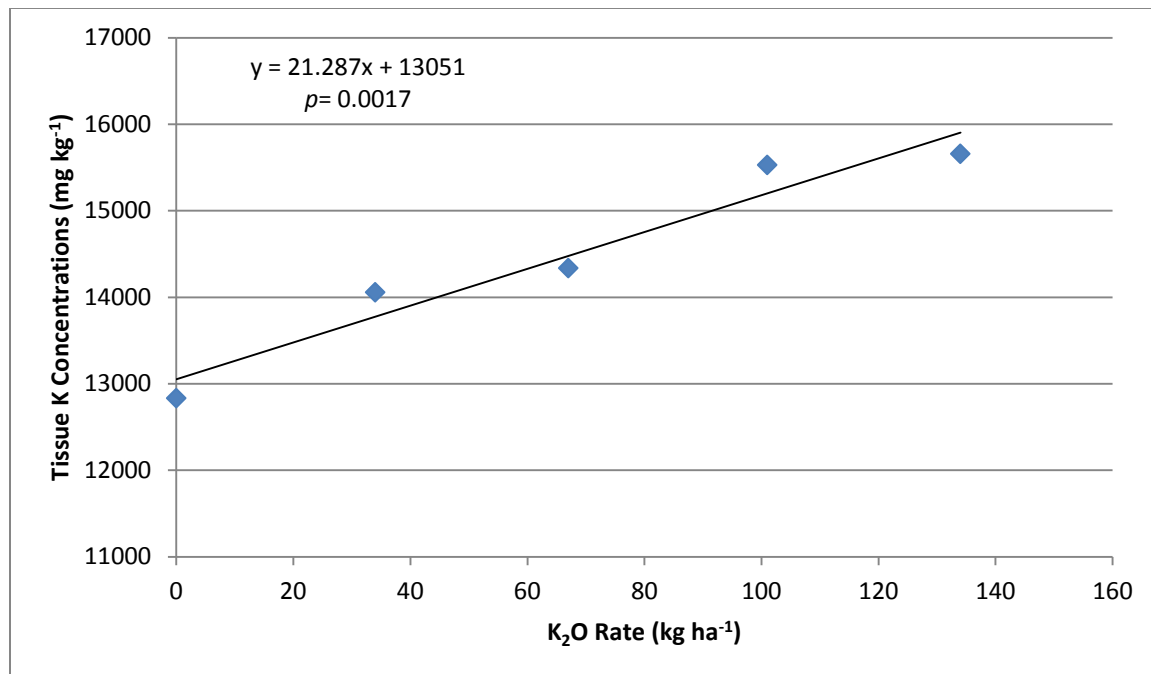
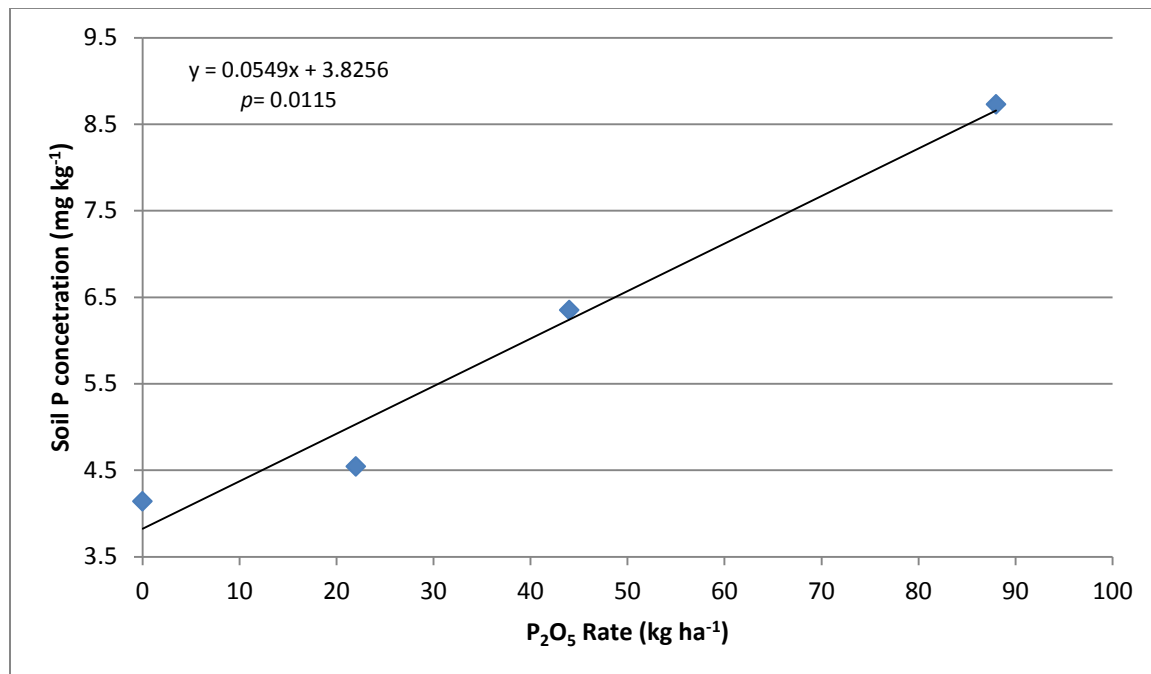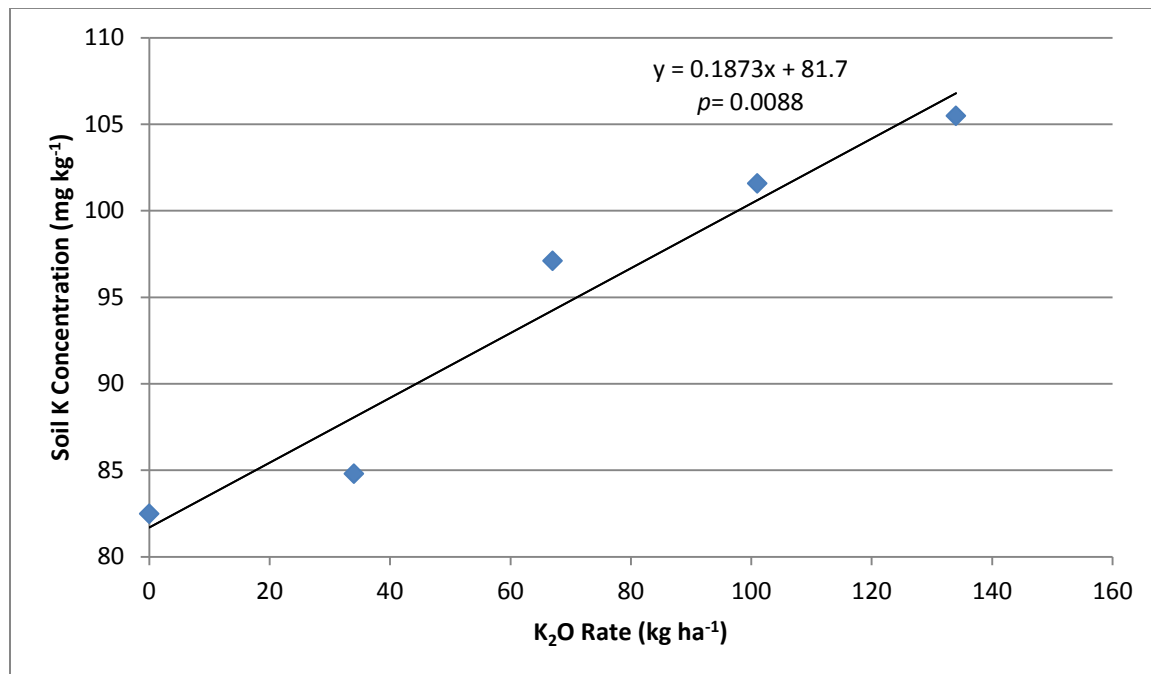**Figure 4.3: Soil P concentration by treatment rate for the Painter 2014 site location.**

Figure 4.4: Soil K concentration by treatment rate for Wheat K site locations.

5. Summary and Conclusions

   Several factors impact the overall nutrient concentrations of PL ash co-products and their resulting availability. The thermo-combustion system is one variable; which includes the temperature of combustion, the fuel to oxygen ratio for combustion, the residence time of the PL feedstock, and if the system has an exhaust scrubbing system to catch fly ash co-products. Another major factor is the PL from which the co-product is formed; the initial concentration of nutrients, the bedding material, and the moisture content of the PL impact the end co-product. Our study found that nutrient densification varied between systems: P concentration fell within a range of 4-10 times concentrated, K concentration ranged 2.5-5 times concentrated, and S ranged 2-3 times concentrated. Our comparisons between total nutrient digestions and water soluble extractions found that the ash products were significantly less plant available than the standard fertilizers (TSP and KCl). A greater amount of the co-products will have to be applied to meet the same nutrient availability of the standards. Overall, if all ideal combustion criteria are met, then PL co-products are feasible to use a fertilizer sources, but will need to be individually analyzed for nutrient content before making application recommendations. More research into balance comparisons are needed to be able to identify stronger relationships within the nutrients.

   The industry inorganic standard fertilizer (TSP) and fresh PL had the greatest initial availability for P and K. Overtime, some of the ash co-products reached similar availabilities comparable to the standards but differed due to the variability in their systems of formation. The ASH4 thermo-conversion system produced an ash co-product that was the most similar to the standards and provided an ideal fertilizer that was both nutrient dense and plant available. The ASH2 system converted the feedstock at higher temperatures and had longer residence times creating a nutrient dense product that was not readily water soluble. The biochar co-products were among the least available of the fertilizers in the study; which was expected because the

biochars are specifically formed with a slow release product in mind to strongly hold and remove nutrients and carbon from the soil system for many years. Further ash research will be needed for each thermo-conversion system and feedstock as the burning process significantly alters the overall nutrient water solubility over time.

Poultry litter ash and biochar sources derived from PL are suitable and comparable P and K fertilizer sources for crops on sandy loam soils in the Mid-Atlantic. Poultry litter co-products vary greatly based on thermo-conversion system and initial feedstock. If all ideal combustion criteria are met (ie. 700-1000°C; 25% moisture), then PL co-products are feasible to use as fertilizer sources, but will need to be individually analyzed for nutrient content before making application recommendations. A greater amount of the co-products will have to be applied to meet the same nutrient availability of the standards due to their lower availability. Fresh PL tends to be the better fertilizer due to its added N content, which is lost in thermo-conversion systems and would have to be supplemented with the ash co-products. Biochars tend to be less available than their ash counter parts. More research using the water soluble availabilities instead of the total concentration nutrients of the co-products are needed to be able to identify stronger relationships with standard fertilizers.