THE FATE OF AMENDED PHOSPHORUS AND SORPTION OF CIPROFLOXACIN IN SOILS

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Abstract: Environmental contamination from natural and anthropological sources is receiving increased attention due to risks to human and ecological health. Manure from concentrated animal feeding operations is generally applied to fields as a cost-efficient way of disposal. Antibiotics are used in animal feeding operations to prevent disease and promote growth. The heavy and continuous application of manure can negatively impact the environment due to the release of excess nutrients such as phosphorus and antibiotics which contribute to increasing rates of eutrophication and the emergence of resistant microorganisms. Soil samples from a century-long continuous winter wheat (*Triticum aestivum* L.) experiment was used to determine the fate of added phosphorus from manure and chemical fertilizers in soil. Comparing data from the years of 1998, 1999, 2000, 2006, and 2018 found that 100% of added phosphorus was accounted in all treatments. The added chemical fertilizer phosphorus in 89 consecutive years was either removed in the harvested wheat grain or remained in the top 0-30 cm of the soil, while about 40% of the added manure-phosphorus was found in the subsurface 30-90 cm of the soil profile. Following 119 years of manure application, manure-phosphorus did not reach deeper than 90 cm of soil, suggesting that leaching to groundwater is not a concern at this study site. Based on evaluation on sorption of ciprofloxacin in 20 diverse soils, sorption capacity ranged from 8 to 141 g kg^{-1}; distribution coefficient (K_d) ranged from 23 to 200 mL kg^{-1} soil; and organic carbon-water partition coefficient (K_{oc}) ranged from 54 to 2146 mL g^{-1} organic carbon. Clay content and cation exchange capacity influenced sorption capacity and K_d values significantly, while little influence was observed from soil pH. Cultivation led to changes in the quality of soil organic matter, resulted in a significant relationship between sorption of ciprofloxacin and soil organic carbon content. Soils are effective in restraining the mobility of ciprofloxacin through adsorption and the effectiveness increases with clay content.

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CHAPTER I

INTRODUCTION

Environmental contamination from anthropological and natural sources are receiving increased attention due to the negative impact that certain pollutants have on human and ecological health. Some of the widespread contamination is associated with improper handling and/or disposal of animal and human wastes. Disposal of animal manure generated from animal feeding operations to nearby fields is the most cost-efficient means of disposal. In waste, excess nutrients such as phosphorus (P) and antibiotics such as ciprofloxacin can accumulate and be released into the soil when manure is repeated applied in large quantity and cause adverse effects on the ecosystem. It is, therefore, crucial to understand what soil properties govern the fate and interactions of these contaminants in soils and what management practices can hinder their release.

Phosphorus loading in the environment is contributed by the heavy and continuous application of animal manure as a source of P for crop production and as an economical waste disposal (Kleinman, 2000; Schindler, 2006; Carpenter, 2008). Generally, the application of manure was based on the crop nitrogen (N) demand, regardless of the P content of the manure and the soil in the past. The general N to P ratio for animal manure is 3.3:1, while a majority crops require a ratio of 8:1 (Gilbertson et al., 1979; White and Collins, 1982; Zhang et al., 2004). If the application rate is not adjusted based on P levels, the over application of P beyond crop requirement occurs, and this can increase the risk of P loss through leaching and runoff

(Barker and Zublena, 1994; Mikkelsen, 1997; Chang et al., 2005). Phosphorus can be transported from farmland to water bodies, resulting in eutrophication and consequently algal bloom and oxygen depletion (Sharpley, 2000)

Animal waste also contains antibiotics that are used for disease prevention and for growth promotion in animal feeding operations. Antibiotics could reach the environment through rough excrement application, the direct release of wastewater and the use of wastewater as an irrigation source, and the application of sludge or biosolids as a fertilizer source (Wang and Wang, 2015). It is estimated that 90% of an administrated dose of antibiotics are excreted in human and animal waste unmetabolized (Tambosi et al., 2010). The accumulation of antibiotics in the ecosystem has led to the development of resistant strains of microorganisms, which in turn can negatively affect human and environmental health. One of the challenges that limits the study of the fate of antibiotics in the environment is that antibiotic usage is not always reported accurately, especially in the agricultural industry and in developing countries. Current available methods for quantification and the poor reproducibility of results have led to an underestimation of antibiotic use worldwide. (Dodgen and Zheng, 2016; Singer et al., 2016).

Ciprofloxacin is classified as a fluoroquinolone (FQ) antibiotic and is commonly used as a broad-spectrum agent in both humans and animals (Aristilde and Sposito, 2013; Wang and Wang, 2015). Ciprofloxacin binds and inhibits bacterial DNA gyrase, type II topoisomerase, and topoisomerase IV, which are all essential for DNA replication. Ciprofloxacin use in poultry production had been banned in 2005 by the United States Food and Drug Administration (FDA) and 2006 by the European Union (EU) due to an emergence of resistant strains of microorganisms that infect humans. However, the use of ciprofloxacin in agricultural production in developing countries continues and has led to increased concentrations in the environment that contributes to resistance (Kümmerer, 2004). Ciprofloxacin also enters the environment and wastewater treatment systems from sewage. Additionally, the use of ciprofloxacin is in the forefront in the fight of bioterrorism in the U.S.

The objectives of this study were (1) to determine P concentrations in different soil layers following long-term cattle manure and chemical fertilizer application; (2) to evaluate the fate and distribution of the added manure P and fertilizer P in soils that were under long-term continuous wheat production; (3) to determine the sorption capacity of ciprofloxacin in 20 soils with diverse properties and vegetation; and (4) to reveal difference in soil properties and the nature of soil organic carbon (SOC), as well as the ciprofloxacin sorption behavior in soils of different cultivation/vegetation history.

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CHAPTER II

REVIEW OF PHOSPHORUS LITERATURE

Introduction

Phosphorus (P) is an essential macronutrient for all forms of life and is often the limiting nutrient in crop production (USDA-NRCS, 2014). P is essential for plants to store and transfer energy produced by photosynthesis for their growth and reproductive processes. P is relatively stable and thus, immobile in soil, so supplemental amounts must be added to meet crop demand, usually in the forms of chemical fertilizer or animal manure. Natural P concentrations in soil can vary, but soils typically have P levels ranging from 300 to 1200 mg kg^{-1}. The variation of P is a function of basic soil properties like parent material or soil texture, and management practices such as rate and type of P applied and cultivation (Daniel et al., 1994). Soil pH also plays a role in P-availability, with pH between 6 and 7.5 being ideal, while soils below 5.5 and above 7.5 limit P-availability due to fixation by aluminum (Al) and iron (Fe), or calcium (Ca) (USDA-NRCS, 2014).

In most soils, 50-90% of P exists in inorganic form, mostly Fe and Al phosphates in acidic soils and Ca phosphates in alkaline soils, while a major portion of soil organic P is in stable fulvic and humic form (Daniel et al., 1994). The mineralization of organic P into inorganic orthophosphates ($H_2PO_4^-$ and HPO_4^{2-}) allows for P to be available in the soil solution and, thus becoming available for plant uptake. Emsley (2000) found that only 0.01% of total P required to sustain plant growth is available in soil solution, as the optimum P concentration in soil solution for most crops is from 0.01 to 0.3 mg L^{-1} (Fox, 1981). The pathways for P uptake by crops are either through diffusion or by root interception (Barber, 1966). Adsorption of P by soil occurs due to the high binding energy between soil and P (Yang et al., 2019), effectively immobilizing the nutrient. Soil has a maximum adsorption capacity, generally dictated by surface area and clay content, in which, over this level will result in P lost to the environment through surface runoff and water and/or wind erosion (Hyland et al., 2005). Lehmann et al. (2005) reported that soil exhausted the ability to adsorb additional amounts of P when soil total P reached 1000-2000 mg kg^{-1}.

The accumulation of P in soils and the subsequent release into the environment has led to accelerated rates of eutrophication in water bodies (Carpenter et al., 1998). Eutrophication is the process of increased organic enrichment or biological productivity due to an excess nutrient that expedites plant growth and limits the amount of oxygen available in a water body (Sharpley, 2000). Sharpley and Rekolainen (1997) determined that eutrophication occurs at concentrations of 0.01 mg dissolved reactive P (DRP) L^{-1} and 0.02 mg total P (TP) L^{-1}.

Loss of P through Erosion, Leaching, and Runoff

P loss is mainly associated with wind and water erosion and surface runoff and leaching (USDA-NRCS, 2014). P loss from soil is primarily influenced by both natural and anthropological processes, such as the P source and chemical form used , tillage and P placement, rate and timing of application, intensity and timing of rainfall events, and soil P levels (Khaleel et al., 1980; Baker and Laflen, 1982; McLeod and Hegg, 1984; Mueller et al., 1984; Mostaghimi et al., 1992; Edwards and Daniel, 1993; Sharpley et al., 1993; Nichols et al., 1994; Sharpley, 1995; Pote et al., 1996; Sharpley and Sisak, 1997; Ginting et al., 1998; Smith et al., 1998 Eghball and Gilley, 1999; Bundy et al., 2001; Kimmell et al., 2001; Withers et al., 2001).

Leaching losses have historically been considered insignificant due to the strong adsorption capacity of clay minerals that adsorb inorganic phosphates (Lehmann et al., 2005). These phosphates are able to form binuclear bridges with hydroxyl (OH) surface groups on minerals, which allows for a low P concentration in the soil solution (Brady and Weill, 2002). However, several studies have concluded that the continual application of manure will create situations in which leaching occurs (Behrendt and Boekhold, 1993; Heckrath et al., 1995; Eghball et al., 1996; Holford et al., 1997; Hountin et al., 2000; Novak et al., 2000; Whalen and Chang, 2001). Leaching can affect groundwater if the soil has a shallow water table or the soil is prone to preferential flow (Eghball, 2003), and affect surface waters if P is both be vertically leached and laterally transported as runoff (Kleinman et al., 2011). Leaching can occur in soils that are over enriched with P, courser in texture, as in sandy, organic or peaty soils; soils with low P adsorption capacities; and in soil with substantial preferential flows pathways (Sharpley and Syers, 1979; Sims et al., 1998; Kleinman et al., 2007; Kleinman et al., 2009).

The loss of soil P in the environment through runoff or erosion occurs in both the dissolved and sediment-bound forms of P (Daniel et al 1994). Sediment P includes P adsorbed to soil particles and organic matter eroded from soil during runoff and constitutes the major portion of P transported from conventionally tilled land (75-95%), while runoff from grass or forest land is dominate by dissolved P (Daniel et al., 1994). Dissolved P is generally comprised of mostly orthophosphates (H_2PO4^{-}, HPO_4^{2-}, and PO_4^{3-}). As dissolved P is immediately available for algal uptake, the loss of P will have a greater impact on the biological productivity of a water body leading to eutrophication then that of particulate or sediment-bound P (Walton and Lee, 1972; Peters, 1981). The movement of dissolved P in runoff involves the desorption, dissolution, and extraction of P from soil, crop residues, fertilizer, and manure (Daniel et al., 1994). This process occurs as rainfall interacts with a thin layer of surface soil before leaving the field (Sharpley, 1985). Rainfall that does not runoff the soil surface percolates through the soil profile and is adsorbed by P-deficient subsoils, resulting in low dissolved P concentrations in subsurface flow.

P loss from runoff depends on application rate, method, and rainfall intensity compared to other natural or anthropological factors (Edwards and Daniel, 1993; Sauer et al., 2000; Sharpley and Tunney, 2000). Runoff can occur in soils where the application rate of manure or fertilizer has exceeded crop demand (Lehmann et al., 2005). Romkens and Nelson (1974) and Baker and Laflen (1982) both showed a significant relationship between P application rate and application method to the amount of P transported in the runoff. Timing of application also influences the amount of P loss with one or two runoff events, such as heavy rainfall immediately following application, accounting for the majority of the P lost in runoff (Edwards et al., 1992; Preedy et al., 2001).

Runoff losses can also be contributed to grazing practices and pasture-land usage (Kleinman et al., 2011). Runoff losses from dung can account for 20-40% of total P loss from pasture land but will decrease with time as a crust forms over the excrement and prevent interactions with runoff water (McDowell, 2006). James et al. (2007) estimated fecal P contributes to streams and found that cattle was more likely to defecate in streams, as around 30% of deposits fell on land within of 40 m of the stream while 7% fell directly into the stream. Around 20% of P loss is contributed to grazing practices where runoff extracts P from the vacuoles of freshly grazing plants or plants that have been trampled upon or are in a state of natural decay (Kleinman et al., 2011). Variation of P loss from grazing can occur due to trampling and the physical disturbance of surface in particulate P losses, though usually only occurring from cattle and deer (Curran-Cournane et al., 2011). Grazing management practices can also affect P loss, as Olness et al. (1975) found that P loss was greater in continuously grazing pastures compared to rotationally grazed pastures.

Tillage practices can affect erosion potential of P from the soil surface, with no-till and other reduced tillage practices used to minimize erosion. However, while conservative tillage practices are key to controlling erosion, they can exacerbate dissolved P losses with time due to the aggravation of the stratification of soil and residual fertilizer P in the soil profile (Sharpley et al., 1993; Holanda et al., 1998; Selles et al., 1999; Vu et al., 2009). This will concentrate the applied P at soil surface, leaving the dissolved P prone to runoff risk (Sharpley, 1985). As P is adsorbed by soil particles, erosion determines sediment P movement. Sources of sediment P in streams include eroding surface soil, plant material, stream banks, and channel beds. Size of soil particles also influences the P content and reactivity in the environment as finer-sized fractions of sediment are preferentially eroded (Sharpley et al., 2002). Conflicting reports have detailed how tillage affects runoff P concentrations. Scheld et al. (2006) found that tillage exacerbates P loss by enhancing particulate P transfers to drainage waters, while others have found lower subsurface losses due to lesser solute transfer with tillage (Shipitalo et al., 2000; Djodjic et al., 2002; Kleinman et al., 2009).

Differences in Fertilizer and Manure P Concentrations

While some studies have found that livestock manures were equivalent to chemical fertilizers in P availability to soil (Eghball et al., 2005; Sikora and Enkiri, 2005; Zvomuya et al., 2006; Sneller and Laboski, 2009), others have reported results that indicate that manure P was generally less available than fertilizer P (Gracey, 1984; Motavalli et al., 1989; Sharpley and Sisak, 1997; Griffin et al., 2003). In comparing forms of P found in both fertilizers and manure, Withers et al. (2001) found that soil amended with triple superphosphate and liquid cattle manure both increased Olsen P (OP) and water extractable P (WEP) concentrations, but the increases were much larger in fertilizer plots. Reddy et at. (1999) compared increases in soil test P (STP) from applying synthetic fertilizers to manured and non-manured soils and found that it takes syntenic fertilizer 5.6 kg P ha^{-1} to raise OP by 1 mg kg^{-1} in manured soils, compared to 17.9 kg P ha^{-1} in non-manure soils. Withers et al. (2001) found that concentrations of dissolved P in runoff from soils amended with mineral fertilizer, cattle manure, and biosolids were proportional to the concentration of WEP of the different amendments, showing a positive correlation between dissolved P and WEP. Greater dissolved concentrations with fertilizers compared to manure is likely due to much larger proportion of P in water soluble forms. Lehmann et al. (2005) found that Mehlich-3 (M3) reactive P concentrations were significantly higher in soils that received manure applications for long periods of time. The capacity of the soils to adsorb additional fertilizer P decreased with increasing duration of manure applications. Dissolved P fraction of total P in runoff is inversely related to sediment loss as a function of soil surface cover in the form of vegetation or crop residue (Sharpley et al., 1992). Goss and Stewart (1979) found that plants remove higher percent of added P in superphosphate, while Sikora and Enkiri (2003) found no significant difference between poultry litter and chemical fertilizer in plant uptake. Therefore, choice of fertilizer and reagents for extraction can have various concentrations of P recovered.

Application methods of both fertilizer and manure can lead to different concentrations of P in soil and P loss in runoff. Fertilizers and manure are usually applied to soil through several different application methods including surface or incorporated broadcast, banding, injection, fertigation, foliar application, sidedress or topdress, and seed placement (Jones and Jacobsen, 2003). Several studies have determined P concentrations in runoff comparing application methods. Daniel et al. (1994) found that concentrations of dissolved P in runoff from areas receiving broadcast application of P fertilizer averaged 100x higher than the runoff from areas receiving similar rates of P that were point injected. Tabbara (2002) found that dissolved reactive P and total dissolved P concentrations were higher in fertilizer and manure amended soil that were surface broadcasted compared to incorporated broadcast, with broadcasted fertilizer higher than broadcasted manure. Total dissolved P concentrations losses were 10-17% from manure and 20-35% from fertilizer; bioavailable P (BAP) losses were reduced on incorporation by 62 to 70% for fertilizers and 42 to 68% for manure; and TP losses were 15-17% from broadcasted fertilizer and 9% from broadcasted manure. Tabbara (2002) concluded that incorporation reduces surface P concentrations and increases that potential for P to bind with soil, which will decrease TP and bioavailable P losses. Lower enrichment ratios found in manure compared to fertilizer plots, attest to the ability of soil aggregates to absorb liquid manure, causing less erosion and retaining more added P, resulting in a lower enrichment ratio (Bhatnagar et al., 1985; Tabbara, 2002;).

Characteristics of P-Fertilizers

Fertilizers are usually applied to soil in either $H_2PO_4^-$ or HPO_4^{2-} form. Through soil processes, P is quickly fixed to soil particles after application, resulting in decreased concentration of plant available P. In general, only 15-20% of P that is adsorbed by the plant is obtained from fertilizer (Zhang et al., 2008). Poorly managed applications can lead to increased P concentrations and cause soil to lose the ability to adsorb P, increasing the risk of loss to the environment. Generally synthetic fertilizer often results in greater increase in soil test P (STP) than manure (Withers et al., 2001; Zheng et al., 2001; Kashem et al., 2004; Jiao et al., 2007). Fertilizers allow the consumer the flexibility to cater to their individual crop needs, reducing the risk of overapplication (Daniel et al., 1994).

The manufacturing process of P fertilizers begins with the treatment of rock phosphate through either a dry or wet process, resulting in the production of phosphoric acid (Diaz et al., 2011). In the dry process, phosphate rock is heated by an electric furnace and produces a more pure and expensive form of phosphoric acid, while in the wet process, in which phosphate rock is treated with sulfuric acid, produces an impure form phosphoric acid. P fertilizers are made in both liquid and granular form, with water soluble preferred due to the fact that P is immediately available in the soil solution to plants.

Characteristics of P Manure

The proportion of organic and inorganic P solubility depends on manure type and animal diet (Barnett, 1994). A greater proportion of inorganic P than organic P appears to be retained in manure soils, though some forms of organic P can adsorb more strongly to soil than inorganic phosphates (Lehmann et al., 2005). Blake et al. (2000) found that manure P availability is dependent on climate, soil, and other plant-available nutrients, while Ca content has been identified as important determinant of manure P availability (Siddique and Robinson, 2003; Leytem and

Westermann, 2005). Manure applications tend to be based on N content, with neglect to P content, resulting in excess amounts of P in soil. Animal manures have a N:P ratio of 3:1 (Gilbertson et al., 1979), while a majority of crops require a N:P ratio of 8:1 (White and Collins, 1982).

Kleinman et al. (2002b) found that manure applications resulted in large temporary increases of WEP in manure at soil surface, indicting a higher risk of runoff loss. Manure WEP and runoff dissolved P concentrations were greatest in swine slurry and lowest in dairy manure (Kleinman et al., 2002a). Kleinman et al. (2002b) found that WEP concentrations decreased as manure weight increased, indicting a dilution effect on P concentrations. Soil properties can influence the adsorption of P in manure to soil. Kumaragamage et al. (2011) studied WEP concentrations on two soil types; Newdale Clay Loam (Orthic Black Chernozem) and Lone Sand (Gleyed Eluviated Dystric Brunisol) and determined that Lone Sand had higher WEP concentrations, because of the ability of Newdale Clay Loam to retain added P in labile but not water-soluble forms. Newdale had greater concentrations of clay, organic carbon, exchangeable Ca and Mg would provide greater P retention. WEP constituted 18% of TP in the inorganic and 5% in organic fractions while 55% of inorganic P was hydroxide soluble.

Soil and manure P solubility likely control dissolved reactive P (Mcdowell and Sharpley, 2001) and the variation in dissolved reactive P loss in runoff a function of manure type (Sharpley et al., 1998; Westerman and Overcash 1980). Kleinman et al. (2002b) found that in manure-amended soils, dissolved reactive P accounted for 51-73% of runoff TP concentration, while in unamended soils, only 13% of runoff TP concentrations is contributed by dissolved reactive P. Olsen, M3, Bray-1 are effective in predicting dissolved reactive P loss in runoff (Vadas et al., 2005). Andraski et al. (2003) found there was no difference in dissolved P concentration between the control and plots treated with manure applied every third year, and found that dissolved P and BAP loads in runoff were significantly higher where manure was annually applied due to higher runoff concentrations of these P compared with other treatments.

Andraski et al. (2003) found a significant linear relationship occurred between soil test P and runoff concentrations of dissolved P and BAP but not TP among manure treatments. The poor relationship between soil test P levels and TP can be attribute to the fact that TP is primarily a function of sediment content. Manure reduces sediment loss in runoff while increasing soil test P levels, concluding the indication of the value of using soil P testing for predicting potential dissolved P and BAP. Significant correlations between dissolved reactive P and total dissolved P in runoff and available P have been observed using a variety of STP methods but the comparison have yielded contradictory results. Soil test P ranging from 20-60 mg kg^{-1} is considered adequate for crop production, this is the critical value, as crops would not respond to additional P fertilizer when STP is over that point (Sharpley et al., 2007). Chang et al. (2005) determined that STP was 38% of the TP pool in animal manure amended fields, with STP increasing every time animal manure was applied

Concentrated Animal Feeding Operations

To meet the demands of growing population, agricultural production has shifted to large-scale animal operations that allow for numerous animal units in a confined space (Evans et al., 1996). Concentrated animal feeing operations (CAFOs) are defined and categorized by the United States Department of Agriculture-National Resources Conservation Service (UDSA-NRCS) in terms of animal units, in which a large CAFO is classified as ≥1000 head of cattle, 2500 swine over 25kg, 10000 swine under 25kg, 125000 chicken, 82000 laying hens, or 55000 turkeys (USDA-NRCS, 2009). Land application and direct discharge into water ways are two of the most economical ways to dispose of animal waste (Graham et al., 2010). Land application of manure generated from livestock production can improve soil fertility and tilth but can result in elevated P concentrations (Sharpley et al., 1994b). These feeding operations designated as CAFO must acquire a National Pollution Discharge Elimination System (NPDES) permit for direct discharge into waterways in special circumstances (EPA, 2019). CAFO generates large amounts of waste that are mostly applied to fields nearby as soil amendments to supply water, nutrients and organic matter. Unfortunately, repeated heavy application of animal waste can lead to accumulation of nutrients and other associated chemicals in soils (Kleinman, 2000; Schindler, 2006; Carpenter, 2008). Some CAFOs are located on rivers and stream flood plains and a generally are distributed within a few US states (Burkholder et al., 1997; Mallin et al., 1999; Mallin 2000; Wing et al., 2002).

Effects of Manure Type on P Concentrations

Swine Manure: Forms of swine manure is classified either as a solid, liquid (<4% solids), or slurry (4-10% solids) depending on storage and handling (Tabbara, 2002). Slurry application can lead to P loss compared to other forms of manure, due to the fact that P availability and solubility in runoff is greater compared with solid manure since seal the soil surface resulting in increased runoff and erosion rates (Ross et al., 1979; Haraldsen and Sveistrup, 1996; Withers et al., 2000). The nutrient content in swine manure varies depending on the age of the animals, ration, temperature, methods used to collect and store manure, and the moisture content (Chastain et al., 1999). Due to the amount of water used, moisture content can increase due to dilution of liquid and slurry manures.

Poultry Manure: Sharpley et al. (2007) determined that there are several factors that make poultry litter more difficult to manage than dairy and swine manure. First, poultry operations have higher confined animal units per hectare available for land application (Kellogg et al., 2000). Secondly, poultry manure has two-four times more P per ton of manure than other livestock types (Sharpley and Moyer, 2000; Kleinman et al., 2005).Thirdly, The combination of higher animal units and high levels of P in poultry production result in greater amount of P per land area for poultry than other livestock (Kellogg et al., 2000). Finally, Poultry litter is bulkier than other manures leading to greater challenges with application, treatment, and transport. Kleinman et al. (2005) determined that turkey manure had the greatest WEP concentrations in all livestock manures, and was 1.9 times that of broiler chicken manures, while Moore et al. (1995) observed WEP concentrations 2.4 times that of broiler chicken manure. Differences in WEP within and between the two chicken manures were related to manure dry matter content and TP (Kleinman et al., 2005). Mechanisms of P solubility are somewhat independent between species. Differences in manure P between broiler and layer chickens appear to be a function of bird metabolism, rather than dietary intake of P. Less than one-third of feed P is utilized by poultry with the remainder excreted in manure and applied to land for crop use (Patterson et al., 2005). Rapidly growing broilers have greater efficiency in metabolism P, and recommended dietary P intake is higher for broiler chickens than for layer chickens (NRC, 1994). Ca phosphates may control availability and mobile P in soils with large amounts of poultry manure. Intensified poultry operations are exacerbated by their close proximity to P-sensitive waters in these regions (Lander et al., 1998: Kellogg et al., 2000)

Phytate

Much of the concern about manure P is related to the compound phytate. Phytate is the main P storage form in plant seed, composing approximately 60-70% (Angel et al., 2005). The release of P from phytate requires the enzyme phytase, which is ineffective or absent in monogastric animals, so undegraded phytate can be released into environment as a component of manure (Yi and Kornegay, 1996; Correll, 1998; Smith et al., 1999). Phytase can present in four ways for the utilization in animals: endogenous mucosal, gut microfloral phytase, plant phytase and exogenous microbial phytase (Humer et al., 2014). Phytate is unavailable in monogastric animals and other forms of P must be supplemented in order to provide adequate amounts of P for animals such as pigs and chickens. Mineral phosphate supplements are commonly added to diets to prevent P deficiencies, but can lead to an accumulation of P concentrations in manure and an increase risk of release into the environment (Leytem et al., 2004a). The development of commercially available phytases, in the form of plant or exogenous microbial phytase, can reduce the requirements for inorganic P supplementation in pig diets. With each additional unit of phytase, P release diminishes until additional supplementation leads to no further response (Kornegay, 2001).

The availability of phytate P is influenced by the location and chemical association of phytate within the seed (O'Dell et al., 1972; O'Dell and de Boland, 1976). Several factors are responsible for the inhibitory bioavailability of phytate including pH, content of minerals and phytate, solubility of phytates and concentration of enhancers or inhibitors (Humer et al., 2014). Since the endogenous mucosal phytase enzyme in monogastric organisms appears incapable of hydrolyzing sufficient amounts of phytate-bound P, supplementation of exogenous microbial phytase in diets is a common method to increase mineral and nutrient absorption of P (Humer et al., 2014). These enzymes are isolated from numerous bacteria, yeast and fungi (Harland and Morris, 1995). The variability of enzyme efficiency can be contributed to differences in species digestive conditions and different structural and kinetic characteristics between broilers and pig (Augspurger et al., 2003). Plant phytase is less active than microbial phytase in the gut (Eeckhout and de Paepe, 1991) due to the acidic pH found in the gut (Phillippy, 1999). Phytase activity varies greatly among species of plant. As a result, diets including ingredients with high phytase activity, such as wheat bran, wheat, triticale or rye, promote greater absorption of phytate P (Pointillart, 1991).

There are currently several types of technologies that improve the degradation of phytate. Phytate is quite heat stable up to approximately 100°C (Bullock et al 1993), thus thermal treatment of seeds can help the degradation of phytate. The mechanical removal and separation of phytate depends on the type of seed as well as on the morphological distribution of phytate in seeds, but will also lead to a loss of nutrients and valuable bioactive compounds (Schlemmer et al., 2009). Long-term storage of seeds can cause phytate content to decrease based on storage conditions (especially humidity and temperature) and the type and age of seeds (Larsson and Sandberg, 1995). Soaking and germination of seeds allows phytate to be transferred to the water during soaking and thus may be removed by discarding the soaked water because it is water soluble (Gustafsson and Sandberg, 1995). Fermentation of dry feeds was effectively used to degrade phytate P and improve mineral and nutrient digestibility in diets for non-ruminants (Lyberg et al 2006; Canibe and Jensen, 2012; Kraler et al., 2014). The acidification of the diet can lead to activation of endogenous plant phytase (Kozlowska et al 1996). Lactic acid bacteria are able to promote phytate degradation due to their ability to produce phytase (De Angelis et al., 2003).

Importance of P Index

Agricultural vs Environmental Soil Test: Historically, agronomic soil P tests have been used to determine critical levels in which the application of P is no longer beneficial to crops due to the inability of the crop retain additional P. Agronomic tests are based on crop response levels instead of the potential of environmental risk (Sharpley et al., 1994a), and are inadequate to address water quality concerns associated with nutrient loss (EPA, 2005). The gap between crop and environmental soil P thresholds reflects the difference in soil P removed by an acid or base extractant and by less invasive water which is soil specific (Sharpley et al., 2007). The index is a simple qualitative assessment tool to rank site vulnerability to P loss, which can identity agricultural areas or management practices that have the greatest potential to accelerate eutrophication (EPA, 2005).

Indexes differentiate between source and transport factors controlling P with source representing the pools or amount of P at a site and transport factors representing the potential to transport P from that site (Kleinman et al., 2002b). Source factors include STP, rate, method and timing of application, and the form of P applied, while transport factors mobilize P sources, creating pathways of P loss from a field or watershed including erosion, surface runoff, subsurface flow, distance of the field to stream, presence of channelized flow pathways or ditches, and existence of implemented Best Management Practices (EPA, 2005). As P-index increases in vulnerability from low to very high, the frequency of soil P testing should increase from every three years to every year and estimates of the time required to deplete soil P to optimum levels should be made. Given the strong relationship between manure P and dissolved P in runoff, a number of US states now include P source coefficient in site assessment indices (Sharpley et al 2003; Leytem et al., 2004b). Coefficients allow P source that are applied to agricultural soils to be weighted on the basis of their relative availability to enrich runoff P concentrations when applied to agricultural soils. Runoff from agricultural sources is considered a nonpoint source (NPS) of pollution. NPS is a major source of stream and lake contamination preventing attainment of the water quantity goals identified in the Clean Water Act. (EPA, 1988)

Identification of areas vulnerable to P loading refers systematic monitoring of water body tributaries. Direct monitoring can identify sub basins contributing high P loads. The advantage of this approach is that subsequent decisions regarding where to focus remedial measures will be based on data rather than subjectivity. The disadvantages are the amount of resources and time involved. It can take several years' time to obtain meaningful information. Indirect methods: the principle underlying of critical region identification is to obtain a spatial representation of some index of P export. Simple screening criteria include animal manure application rate, dilution, distance to nearest receiving water and combo of factors (Draper et al., 1979; Young et al., 1982; Motschall et al., 1984). Advances in GIS allows the linkage of spatial data on P transport factors with hydrologic/water quality simulation models (De Roo et al., 1989; Gilliland and Baxter-Potter, 1987; Wolfe, 1992).

With the increased awareness of potential negative effects of P loss to the environment, the implementation of management practices can reduce the amount of P loss from soils. The magnitude of the reduction of P losses is greater if they are implemented on targeted critical source areas in a watershed that are vulnerable to P loss in runoff (Heatwole et al., 1987; Prato and Wu, 1991). Efforts to minimize P loss in runoff involves reducing runoff and erosion by conservation tillage, buffer strips, cover crops, and contour plowing. Source controls include minimizing the build-up of surface soil P through the use of soil test P recommended to guide fertilizer and manure applications and subsurface placement where possible. Soil conservation measures such as reduced tillage, buffer strips, grassed waterways and the use of high P demand crop should be considered. The implementation of the most stringent best management practices (BMPs) can then limit P loss in watersheds of lakes that are sensitive to P loading. The next management step after determining a vulnerable critical water body that is P limited, is to identify regions within the contributing watershed in which P transport reduction strategies will be most effective. Sharpley et al. (2007) grouped measures that be taken to reduce P loss into several categories including the management of feed, manure, land, and grazing.

Better feed management aims to reduce the amount of P imported onto poultry farms by decreasing mineral P supplements in feed, including enzymes in feed that enhance nutrient utilization and absorption by poultry and use of crop hybrids that contain lower levels of relatively indigestible phytate-P (Angel et al., 2005; Maguire et al., 2005). Better manure management practices include increasing bulk density and N content while encouraging the transport of manure from manure-rich to manure-deficient areas is desired in order to manage P concentrations in soil. Until practices are improved, manure will continue to be applied through direct land application and direct discharge into water ways (Graham et al., 2010). Manure and litter can be managed to decrease P solubility with chemical amendments and physical treatment, development of alternative uses for manure or litter other than land application, and transport of manure and litter further from where it is produced (Sharpley et al., 2007). Burning litter reduces the volume of manure that needs to be managed and results in products high in P and K. Composing makes manure more physically and chemically uniform which facilitates even spreading at accurate rates (Day and Funk, 1998; Osei et al., 2000), though composting tends to increase the P concentration of manure but the volume is reduced. The physical treatment of manure to improve N:P ratio (Ndegwa et al., 1991), with the desired effect of a higher N:P ratio is desirable because the N:P ratio in unfractionated poultry litter is much lower than that required by plants.

Land Management aims to decrease the potential of P loss in surface and subsurface runoff by use of risk assessment to guild rate, method and timing of poultry manure or litter application, and by targeting critical source areas of P loss for BMP implementations. Generally, the closer a field is from a stream channel, the greater the potential for runoff to contribute P to the stream. The implementation of a riparian/buffer areas to provide physical buffers to sediment bound P, and plant uptake captures P in the runoff resulting in a short-term and long-term accumulation of P in biomass (Groffman et al., 1992; Peterjohn and Correll, 1984; Uusi-Kämppä, 2000). Better grazing management practices include fencing to illuviated the ability of livestock to excrete near waterways can lead to deceased areas of local P accumulation (James et al., 2007). The greater area of nonriparian shade attracted cattle which spent less time in the stream and resulted in a 2-fold reduction in dissolved and 4-fold reduction in total export (Byers et al., 2005). Grazing management and placement of stream bank fencing is important to minimizing watershed export of P. Herd size, pasturing time, and cattle type could all be used to prioritize sites or fence installation (Sharpley et al., 2007).

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CHAPTER III

THE FATE OF AMENDED PHOSPHORUS IN SOILS

ABSTRACT

The continuous and heavy application of manure originating from animal feeding operations has led to phosphorus (P) loading in the environment which can cause eutrophication of nearby water bodies. The objectives were to determine P concentrations in soils following long-term manure and fertilizer application and to evaluate the fate and distribution of the added P in these soils. Soil samples were taken from a century-long continuous winter wheat (*Triticum aestivum* L.) experiment that included four treatments (manure, P and NPK) from five different sampling years. The recovery of added P was calculated based on mass balance of P inputs and outputs. Concentrations of soil P were generally higher in chemical fertilizer- than manure-treated surface soils. However, about 100% of added P was recovered in all evaluated treatments. Aside from the harvested grain-P, most of the added P in fertilizer treatments was found in the top 30 cm of the soil, while about 40% of manure-P was recovered in the 30-90 cm of soil. Following 119 years of manure application, manure-phosphorus did not reach deeper than 90 cm of soil, suggesting that leaching to groundwater is not a concern at this study site.

Keywords:

Animal manure; chemical fertilizer; phosphorus; P leaching; P recovery

Abbreviations:

HABs, harmful algae blooms; P, phosphorus

INTRODUCTION

The overapplication of manure and chemical phosphorus (P) fertilizer has led to the pollution of water bodies due to eutrophication (Daniel et al., 1998). The shift from traditional small livestock operations to large scale feeding operations has resulted in high volumes of concentrated manure accumulation because application to nearby land is the most cost-efficient way of disposal (Long et al., 2018). From 2015-2017, the United States Department of Agriculture (USDA) estimated that livestock production increased from 647 million heads to 677 million (USDA, 2018) and generated over 330 million tons of wet weight manure based on the estimation method by Zhang and Schroder (2014). Manure is sometimes applied to fields based on crop nitrogen (N) demand, with little consideration of the need for P or P concentration in the soil. In animal manure, some N is lost in the form of ammonia, resulting manure to have a narrower N:P ratio (3:1) than what is required for crops (8:1) (Zhang et al., 2004; Bouwman et al., 2017). When manure application is N based, P inputs to the soil exceed crop needs. Accumulation of P in soil following repeated heavy manure application has been observed (Sharpley and Smith, 1995; Jongbloed and Lenis, 1998; Sharpley et al., 2004). Globally, the amount of P that is inputted into soils from manure has increased from 15 Tg yr^{-1} to 24.3 Tg yr^{-1} from 2000 to 2010 (Smil, 2000; Potter et al., 2010). It is estimated that 10% of P inputs from either fertilizer or manure to soils will be lost to the environment (~2-3 Tg P yr^{-1}) (Bouwman et al 2009; Seitzinger et al., 2009). With the increasing concern on harmful algal blooms (HABs) (U.S. EPA, 2015), it is crucial to understand the fate and distribution of manure-P in the environment.

Following century-long cattle manure and chemical phosphorus fertilizer application under continuous wheat production, Parham et al. (2002) found that the recovery of added phosphorus (P) was significantly lower in manure-P compared to fertilizer-P. From a soil depth of 0-30 cm, 32% of P was recovered in manure P, while about 80% was recovered from fertilizer P. The lower recovery of manure P was also reported by van der Bom et al. (2019) who found in a 20-year study that up to 76% of pig manure P was unaccounted for at 0-20 cm soil layer. Whalen and Chang (2001) found that 1.4 Mg P ha^{-1} was not accounted for in irrigated plots receiving 180 Mg cattle manure ha^{-1} yr^{-1}, suggesting that some P was lost through runoff or leached below 150 cm in the soil profile. However, most studies addressing manure P issues were conducted short-term (1-3 years). Studies by Parham et al. (2002) was from a long-term experiment, but only the top 30 cm of soil layer was evaluated. Therefore, the century-old study site was revisited on P recovery in soil depth up to 90 cm. The specific objectives were (1) to determine P concentrations in different soil layers following long-term cattle manure and chemical fertilizer application; and (2) to evaluate the fate and distribution of the added P in soils that were under long-term continuous wheat production.

MATERIALS AND METHODS

Soil samples were obtained from a century-long continuous winter wheat (*Triticum aestivum* L.) experiment located in central Oklahoma, U.S.A. (36°07'03.7"N 97°05'37.0"W). The experiment was initiated on a Kirkland (fine, mixed, thermic Udertic Paleustolls) silt loam. The manure treatment plot was initiated in 1899. The chemical fertilizer treatment plots, P and NPK, were initiated in 1930. Cattle manure from a feedlot was applied every four years at 134.5 kg N ha^{-1} until 1966 and at 269 kg N ha^{-1} since 1967. The manure was incorporated into soil immediately following application to reduce potential surface runoff. The average ratio of N:P of the applied manure was 3.3:1, which suggests that approximately 40.8 kg P ha^{-1} from 1899 to 1966 and 81.5 kg P ha^{-1} from 1967-2018 was applied every four years. Chemical fertilizer plots received an annual application of 67 kg N, 14.6 kg P and 28 kg K ha^{-1} before planting in October.

Composite soil samples were taken prior to planting in five different years, including 1998, 1999, 2000, 2006, and 2018. Samples were taken at depth intervals of 0-15, 15-30, 30-60, and 60-90 cm from the untreated check (CK) and treated with manure (M), phosphorus (P), or nitrogen-phosphorus-potassium (NPK). Long-term experiments could potentially provide insights on the impacts of management practices on soil fertility and health. Unfortunately, application of statistics on agricultural experiments was not yet in place at the time when this study was initiated. To compensate for the no-replication restriction, the underlying changes in these soils were evaluated based on random, individual samples in combination with samples in different years. At each sampling event, each treatment plot was divided into three subplots with composite samples taken from each subplot to account for spatial variation in the field. Soils were ground to pass a 2-mm sieve, air-dried, and kept in sealed containers at 23°C until analysis.

Soil pH values were determined using a combination glass electrode (soil: water ratio = 1:2.5), and those of the organic carbon (C) and total N by dry combustion using a Carlo-Erba NA 1500 Nitrogen/Carbon/Sulphur Analyzer (Schepers et al., 1989). Particle size distribution was determined using the hydrometer method (Gee and Or, 2002). Total P was determined using the wet digestion method referenced by Jones and Case (1990) or EPA 3050B (EPA, 1996). The basic soil properties have been reported before (Parham et al., 2002) and have not changed significantly by 2018. Property of soils sampled in 2018 are shown in Table 1. The recovery of P (%) from the added P was calculated as follows:

% P recovery = ((P removed in grain + P in treated soil – check soil P)/P input)*100

Where P was inputted into the system in the form of manure or chemical fertilizer. Phosphorus might be removed from the system in the harvested grain. Removal P was estimated based on average grain yield and average grain P content. Grain yield was divided into two sections, 1930-1966 and 1967-2018, that corresponds to changes in the different amount of manure input. Average grain P content of 12 years (1980-1986 1991-1995) was used in the calculation. Net P input was calculated based the difference between average grain-P removal of the treatment and CK plot subtracted by the P input (kg P ha^{-1} yr^{-1}). Expected P increase was calculated based on net

P input divided by the number of years from the beginning of the experiment to the sampling year (Table 1). Statistical analysis was performed using SAS 9.4 (SAS, 2014) in which significant treatment differences was conducted using PROC GLM and Tukey's test at an alpha=0.05.

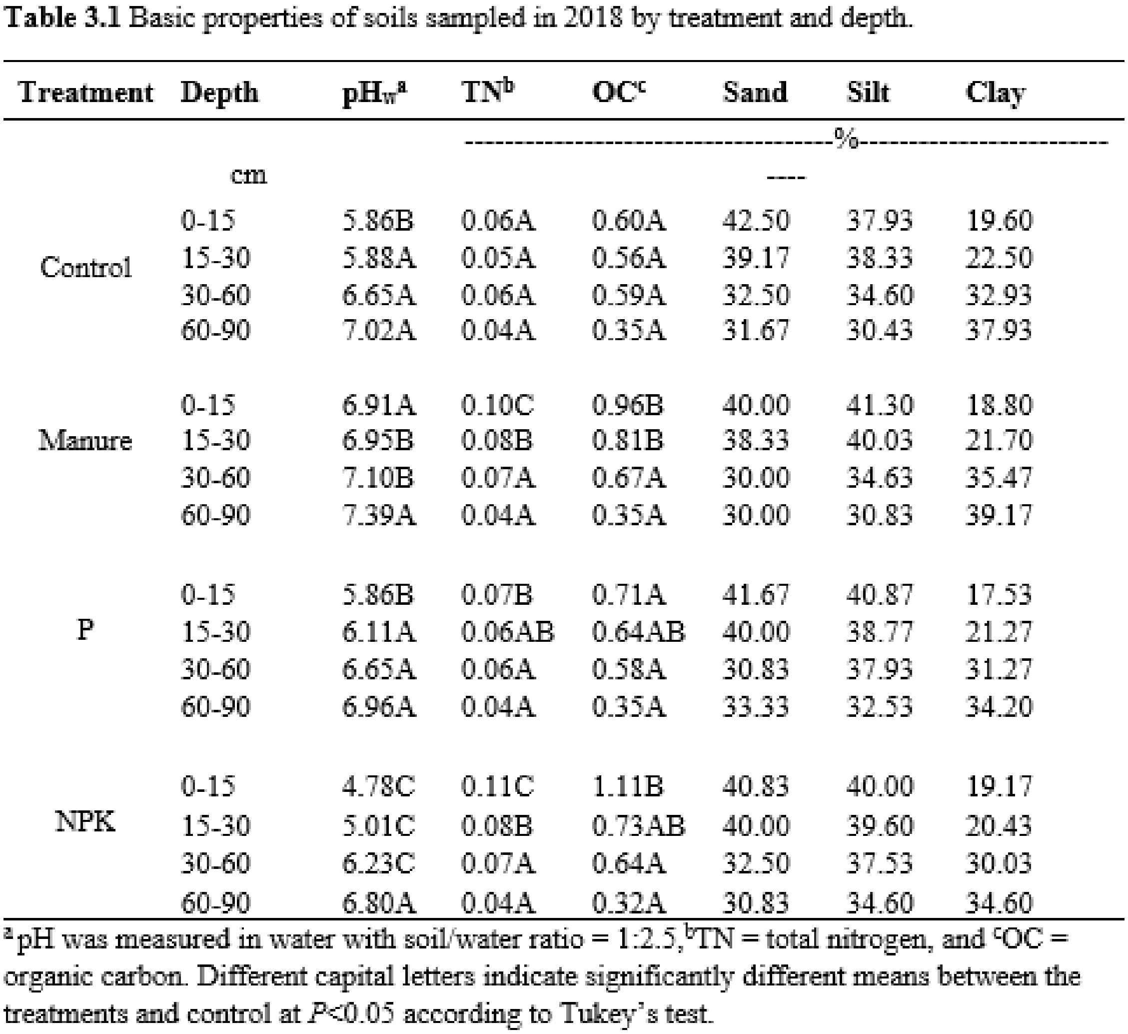

Table 3.1 Basic properties of soils sampled in 2018 by treatment and depth.

Treatment	Depth	pH_w[a]	TN[b]	OC[c]	Sand	Silt	Clay
			--	-------	----%----	-------	----------------
	cm				----		
Control	0-15	5.86B	0.06A	0.60A	42.50	37.93	19.60
	15-30	5.88A	0.05A	0.56A	39.17	38.33	22.50
	30-60	6.65A	0.06A	0.59A	32.50	34.60	32.93
	60-90	7.02A	0.04A	0.35A	31.67	30.43	37.93
Manure	0-15	6.91A	0.10C	0.96B	40.00	41.30	18.80
	15-30	6.95B	0.08B	0.81B	38.33	40.03	21.70
	30-60	7.10B	0.07A	0.67A	30.00	34.63	35.47
	60-90	7.39A	0.04A	0.35A	30.00	30.83	39.17
P	0-15	5.86B	0.07B	0.71A	41.67	40.87	17.53
	15-30	6.11A	0.06AB	0.64AB	40.00	38.77	21.27
	30-60	6.65A	0.06A	0.58A	30.83	37.93	31.27
	60-90	6.96A	0.04A	0.35A	33.33	32.53	34.20
NPK	0-15	4.78C	0.11C	1.11B	40.83	40.00	19.17
	15-30	5.01C	0.08B	0.73AB	40.00	39.60	20.43
	30-60	6.23C	0.07A	0.64A	32.50	37.53	30.03
	60-90	6.80A	0.04A	0.32A	30.83	34.60	34.60

[a] pH was measured in water with soil/water ratio = 1:2.5, [b] TN = total nitrogen, and [c] OC = organic carbon. Different capital letters indicate significantly different means between the treatments and control at $P<0.05$ according to Tukey's test.

RESULTS

Treatment effect based on soils sampled in 2018 were similar to those reported by Parham et al. (2002). Compared with the Check soil, NPK treatment resulted in significantly lower pH of the top 30 cm soils; but manure application resulted in significant increase in soil pH; and P treatment did not influence soil pH significantly (Table 1). The influence on soil pH due to Manure and NPK treatment was significant down to 60 cm of soil depth. Treatment effect on soil pH in the depth of 60-90 cm was not significant. Organic C and total N levels in manure and NPK treated soils were significantly higher than those of the untreated check soils. Little significant difference was detected in organic C and total N contents between P treated and the Check soils. Soil sand, silt, and clay content was not significantly affected by the tested treatments.

Phosphorus input to soil from manure was lower from 1930 to 1966, but higher from 1967 to 2018 than chemical fertilizer P (Table 2). Analysis of 89 years of yield data suggested that grain yields from Manure and NPK treated plots were not significantly different, while those from the untreated check and P-treated plots were significantly lower (Table 2). Interestingly, the yields in all treatment plots were higher in 1967-2018 than 1930-1966. As a result, net P input were in the two periods were considerably different (Table 2). Some of the treatment effects were reflected in the soil total P concentrations (Table 3). Significant differences in total P concentration were observed in surface 30 cm soils between the check and the treatment plots regardless of year. Total P in the subsurface soils were not significantly different among treatments. In general, all treatment plots had significantly higher total soil P than the Check; chemical fertilizer treated plots had higher total P than the manure plot. Also, worth noting, total P concentration in deep soil layers (30-60 cm and 60-90 cm) was generally higher in Manure than the untreated Check and plots treated with chemical P.

About 100% of added P was recovered in all tested treatments (Table 4). For P and NPK treated soils, the recovery was around 100% in 0-30 cm soil, while for manure treated soil the recovery reached around 100% when soil depth extended to 90 cm. On average, close to 40% manure P was recovered from 30-90 cm soils. However, the majority of the added P was recovered in the top 15 cm of soil (Fig. 1, Table 4). Based on P recovery in the top 15cm soil from 5 years data, NPK recovery was markedly higher than that of manure and P, averaging 67.2% comparing with 38.2% and 51.6% for Manure and P, respectively (Table 4, Fig. 1). Phosphorus recovery (%)

Table 3.2 Input and output of P to the system under the tested treatments.

Treatment	**P input[a]** (kg P ha^{-1} yr^{-1})		**Average yield[b]** (kg ha^{-1} yr^{-1})		**Grain-P[c]** mg P kg^{-1}	**Grain-P removal** kg P ha^{-1} yr^{-1}		**Net P input[d]** (kg P ha^{-1} yr^{-1})	
	1930-1966	1967-2018	1930-1966	1967-2018		1930-1966	1967-2018	1930-1966	1967-2018
Check			864.2A	1002.8A	3860.6	3.3	3.9	-3.34	-3.87
Manure	10.19	20.38	1328.1B	1916.0B	3860.6	5.1	7.4	1.73	9.11
P	14.68	14.68	1157.0A	1104.1A	3860.6	4.5	4.3	6.87	6.54
NPK	14.68	14.68	1342.1B	2073.7B	3860.6	5.2	8.0	6.16	3.33

[a]Cattle manure from feedlot was applied every 4 years at 134.5 kg N ha^{-1} from 1930 to 1966 and at 269 kg N ha^{-1} since 1967. The average ratio of N:P in the applied manure was 3.3:1. Inorganic phosphorus was applied annually in September at 14.68 kg P ha^{-1} yr^{-1}. [b]Yield 1 bu ac^{-1} is equivalent to 67.25 kg/ha. [c]Grain P was average of 12 years (1980-1986 and 1991-1995). [d]Net P input is the difference between p input and grain-P removal. Unit conversions from ha to kg of soil were based on average bulk density of 1.3 g cm^3 for 0-30 cm, 1.25 g cm^3 for 30-60 cm, and 1.2 g cm^3 for 60-90 cm soil layers. For example, 1 ha = $1.95*10^6$ kg for 15 cm of soil when bulk density= 1.3 g cm^3. Capital letters represent significant differences between treatment means at ($P<0.05$) using Tukey's test.

Table 3.3 Total P concentration in soils at depth, treatment, and year specified.

Year	Depth	Total P (mg P kg^{-1} soil) in treatment specified			
		Check	Manure	P	NPK
1998	0-15cm	189.0A	218.6B	310.4C	266.4D
	15-30cm	151.3A	191.7AB	223.7B	202.3B
1999	0-15cm	185.4A	236.0B	307.1C	283.4D
2000	0-15cm	186.3A	254.5B	298.1C	308.6C
2006	0-15cm	208.0A	279.5B	321.8B	332.8B
	15-30cm	186.4A	225.7A	225.3A	210.0A
	30-60cm	152.1A	166.4A	158.3A	154.1A
	60-120cm	105.1A	127.1A	109.9A	104.6A
2018	0-15cm	196.7A	353.3B	396.7BC	406.7C
	15-30cm	180.0A	250.0B	286.7B	283.3B
	30-60cm	166.7A	183.3A	170.0A	180.0A
	60-90cm	126.7A	133.3A	136.7A	126.7A

Different capital letters represent significant differences ($P < 0.05$) between treatments for each row according to Tukey

Table 3.4 Recovery of added P (%) calculated based on input and output by sampling year, soil depth, and treatment. [a]

Year	Depth	% P recovery in treatment specified		
		Manure	P	NPK
1998	0-15cm	17.5	50.5	48.2
1999		27.1	50.5	56.6
2000		44.1	45.8	69.9
2006		45.3	48.1	70.4
2018		56.8	63.4	90.7
Mean ± SE		(38.2 ± 7.0)	(51.6 ± 3.1)	(67.2 ± 7.2)
1998	0-30cm	35.9	79.6	79.9
2006		64.4	66.8	91.0
2018		84.7	97.1	126.3
Mean ± SE		(61.7 ± 14.2)	(81.1 ± 8.8)	(99.1 ± 14.0)
2006	0-90cm	96.0	91.6	105.2
2018		108.2	110.7	129.3
Mean ± SE		(102.1 ± 6.1)	(101.2 ± 9.6)	(117.2 ± 12.0)

[a] % P recovery = ((P removed in grain + P in treated soil – check soil P)/P input)*100; SE indicates standard error.

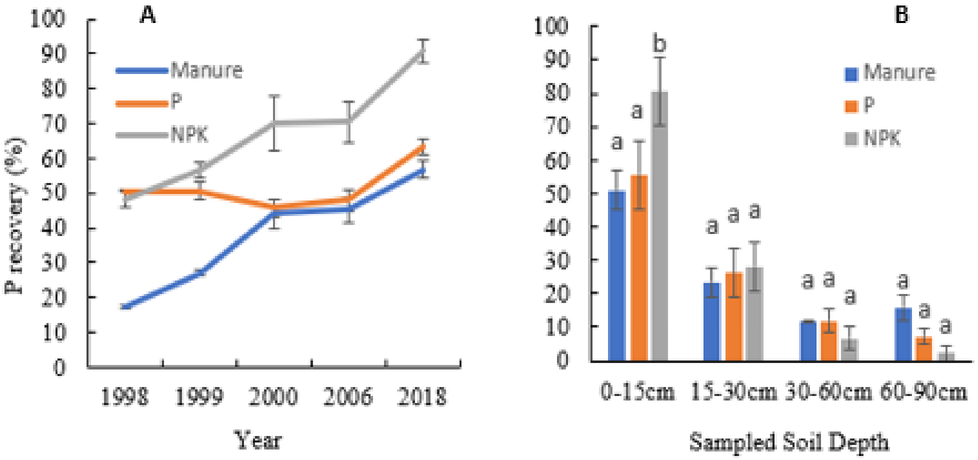

Fig 3.1 A) Average at 0-15 cm for 5 years (1998, 1999, 2000, 2006 and 2018). B) Average at 0-15cm, 15-30cm, 30-60cm, and 60-90cm for 2006 and 2018. Error bars represent standard error and different letter represent significantly different means at ($p<0.05$) determined by Tukey's.

by depth intervals were not significantly different between Manure, P, and NPK in surface soils from 15-30, 30-60, and 60-90cm (Table 4). For each treatment, the P recovery from 0-15 cm was significant from subsurface depths.

DISCUSSION

Accumulation of P in soil following manure application has been widely reported (Reed et al., 1998; Parham et al., 2002). Animal manure application resulted in soil P reaching up to 1121 kg P ha^{-1} in Mehlich-3 extracts (Reed et al., 1998). It is not surprising that accumulation of manure P was found in this study. It is interesting that manure P accumulation in soil was less than the accumulation of fertilizer P following over a century of manure application and 89 years of fertilizer treatment. Yan et al. (2018) reported a similar observation, showing that total soil P concentration in manure and chemical fertilizer treated plots from 0-30 cm were 1008 and 1107 mg P kg^{-1}, respectively. Accumulation of manure P is more a concern than the accumulation of fertilizer P because it has long been recognized that inorganic P is practically immobile in soil (Hannapel et al, 1964; Parham et al., 2002). Leaching of fertilizer P is generally negligible as less than 1% of added fertilizer P is lost through leaching (Smith et al., 1998). Organic P, however, seems more mobile. (Hannapel et al, 1964; Chardon et al., 1997; Parham et al., 2002). The mobility of manure P in subsurface soils has been observed by several studies (Eghball et al., 1996; Eghball, 2003; van Es et al., 2004).

The widespread accumulation of soil P is of environmental rather than agronomic concern (Sharpley et al., 1994). Repeated heavy manure application could saturate the soil's capacity to retain manure-P. Hooda et al. (2001) found that soils in long-term experiment (10-50 years), reached 25% P saturation after 10-30 years. Manure-treated surface soils had essentially no P sorbing capacity (Nair et al., 1998). The concerns are runoff of the excess P could potentially contaminate adjacent water bodies (James et al., 1996) and cause concerns of HABs (U.S. EPA, 2015). Nonpoint sources of P in agricultural runoff now contribute a greater portion of freshwater inputs (Sharpley et al., 1994). However, it remains unclear on the extent of P leaching in transporting P in the environment. Evidence suggested leaching of organic P in soil profiles. About 70 to 90% of total P from leachates of soil columns and lysimeters were in organic form and dissolved organic P (Chardon et al., 1997). Further, the percentage of organic P in total P increased with increasing soil depth (Chardon et al., 1997; Parham et al., 2002). Leaching of P to groundwater would be of environmental concern and was suggested by Whalen and Chang (2001) as a risk of ground water contamination. Leaching and kept to lower soil profile, however, would mean P storage that could enhance P use efficiency in agricultural production.

Based on input and output P balance, 100% of added manure P and fertilizer P were recovered. 100% recovery was also reported by Boitt et al. (2018) who evaluated the top 40 cm of soils that were amended with pig manure for production of various crops for 15 years. They reported a total recovery of 62-94%, of added P, of which 58-83% of added P remained in soil and 7-35% was removed by the harvested grain. Considering the manure treatment in this study has been in place for 119 years, it is not likely that manure P would reach ground water under the evaluated conditions. The obtained results are not consistent with those reported by Whalen and Chang (2001). In irrigated land that was amended with 180 Mg ha^{-1} yr-1 of wet cattle manure, as much as 1.4 Mg P ha^{-1} was not recovered based following 16 years of barley production (Whalen and Chang, 2001). This was equivalent of 7-15% added manure P. Their study evaluated soils up to 150 cm with water table ranging from 50 to 250 cm at the site. The researchers speculated that unaccounted P was lost through leaching, which poses risk to contaminate ground water. Shepherd and Withers (1998) also found close to 100% recovery of added P for manure and chemical fertilizer plots following a 4-year study from 0-35cm. Several other studies have not been able to account for all the added P. In a two-year study, Pheav et al. (2005) found that 25-30% of added P was unaccounted for in the top 20 cm of soil. Lemming et al. (2019) found that up to two-thirds of added manure P from a 12-year experiment was recovered in 0-20 cm soil layer. Both Pheav et al. (2005) and Lemming et al (2019) hypothesized that the uncounted manure P was lost from leaching or erosion.

In this study, data suggested that a portion of added manure P transported deeper in the soil profile than chemical fertilizer P. Excluding P removed by grain, the added chemical fertilizer P were all still in the top 30 cm of the soil following 89 years of fertilizer application, while by average 40% of added manure P were found in the 30-90 cm of the soil profile. Although 50% of the wheat roots is around 16.8 cm (Fan et al., 2016), the active rooting of winter wheat can reach up to 120 cm (Walsh et al., 2013). Manure P in the deep soil profile could be taken up by plants, thus enhancing P use efficiency. This is consistent with the observation that wheat and maize can use P that has accumulated in soils from long-term fertilizer and manure applications (Khan et al., 2018). Phosphorus is the second most limiting nutrient in agriculture, with a deficiency in nearly 67% of crop-production land in the world (Batjes, 1997). With the worldwide P use efficiency in crop production from 1961 to 2013 of only 16% on average (Dhillon et al., 2017), the potential to enhance P use efficiency is of great significance in promoting crop productivity while preserving environmental health.

Further, P accumulation pattern over soil profile was influenced by crop uptake activities. Phosphorus leached down deeper in the soil profile in the P treated plot than NPK treated plots. Based on evaluation of 89 years of grain yields, the grain yield in the P treated plots was significantly lower than that of NPK treated plot. In fact, the grain yield in the P treat plot was not significantly different from the untreated control, which suggests that P was not a yield limiting factor at this site. It seems that the less active plant P uptake due to slower growth permitted labile P in the system to leach further down in the soil profile. However, the movement is limited since 100% of added fertilizer P was recovered in the top 30 cm of soil.

CONCLUSION

Based on P input and output, 100% of added manure P and fertilizer P were recovered in different depth of soils. Over 50% of added chemical fertilizer P remained in the top 15 cm of soil. Excluding grain P, the added chemical fertilizer P was found in the top 30 cm of the soil, while by average 40% of added manure P were found in the 30-90 cm of the soil profile. Considering the manure treatment has been in place for 119 years, it is not likely that manure P would reach ground water and poses risk to P contamination. Further, leached to lower soil profile could potentially enhance P use efficiency. Data also suggested that P accumulation pattern over soil profile was influenced by crop uptake activities, in that slow uptake may allow labile P more time to leach further down in the soil profile. Such activity is beneficial in preserving P as a crop nutrient, with little potential to contaminate the environment.

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CHAPTER IV

REVIEW OF ANTIBIOTIC LITERATURE

Introduction

The intensive and continuous use of antibiotics to treat infectious diseases in humans and animals, as well as, promote growth and development in the livestock industry has led to an increase in the amount of antibiotics released into the environment (Díaz -Cruz et al., 2003; Batt et al., 2006; Brown et al., 2006; Kümmerer, 2009a,b). Over 269 million antibiotic prescriptions were administered from outpatient sources in the Unites States in 2015 (CDC, 2015). It is estimated that over 80% of the antibiotics (15 million kg) sold in the United States are used in the livestock industry (FDA, 2014, 2015). As much as 90% of orally-administered antibiotic doses may be excreted unmetabolized through waste and eventually be released into the environment through discharge from wastewater treatment plants (WWTPs), rough excrements, sewage irrigation, and composting of sludge (Kumer et al., 2005; Wang and Wang, 2015). Antibiotics are considered emergent pollutants because their release can cause antibiotic-resistant bacteria, which pose long-term threats to human and ecological health (Boxall et al., 2003; Göbel et al., 2005). Concentrations of antibiotics in the natural environment are small (Díaz-Cruz et al., 2003; Golet et al., 2003; Watkinson et al., 2007), though they have been detected at sub-inhibitory concentrations in surface water, groundwater, treated municipal wastewater, municipal biosolids, soil, and sediments (Kolpin et al., 2002; Boxall et al., 2003; Giger et al., 2003; Kümmerer, 2004; Xia et al., 2005). High doses of antibiotic-susceptible or tolerant bacteria can be mixed together during the wastewater treatment process, causing WWTPs to be hot spots for antibiotic resistance spreading into the environment (Alonso et al., 2001; Summer, 2006; Kim and Aga, 2007; Baquero et al., 2008; Kümmerer 2009a,b).

Ciprofloxacin is classified as a fluoroquinolone antibiotic (FQ) and is commonly used as a broad-spectrum agent in both humans and animals (Aristilde and Sposito, 2013; Wang and Wang, 2015). The FDA estimated that 20.3 million prescriptions of ciprofloxacin were administered in the United States in 2015 (FDA, 2015). Ciprofloxacin binds and inhibits bacterial DNA gyrase, type II topoisomerase, and topoisomerase IV, all essential for DNA replication. Therefore, ciprofloxacin is active against both gram-negative and gram-positive bacteria by inhibiting cell division. Ciprofloxacin is frequently detected in the environment and has been proven to be genotoxic (Kümmerer et al., 2000). In soil, ciprofloxacin concentrations range from 0.37 mg kg^{-1} to 0.40 mg kg^{-1} (Golet et al., 2002; Martínez -Carballo et al., 2007), and have been detected at levels of up to 0.036 and 0.45 µg L^{-1} in surface water and wastewater effluent (Batt et al., 2007; Vieno et al., 2007).

The use of FQ antibiotics in poultry production has been banned by both the U.S. Food and Drug Administration (FDA) and the European Union (EU) due to increased resistance found in several bacterial species (FDA, 2005; Cogliani et al., 2011). In much of the world, however, antibiotics are unregulated and used extensively while consumption statistics are rarely collected (Benbrook, 2002; WHO, 2006). One of the challenges that limit the study of the fate of antibiotics is that current available methods for antibiotics quantification may result in significant underestimation of the antibiotic concentrations causing the reproducibility of results to be difficult (Dodgen and Zheng, 2016; Singer et al., 2016). Understanding antibiotic fate and transportation in the natural environment, sorption behavior, and potential microbial resistance can allow for the development of soil-based WWTPs that eliminate the release of antibiotics in the environment during the treatment process.

Sources of Antibiotics in the Soil

Though antibiotics can be synthetic or semi-synthetic, most antibiotics are at least partially formed from microorganisms which inhibit the growth and development of other microbes (Waksman, 1961; Ikehata et al., 2006). In soil, naturally-occurring antibiotics from bacteria and fungi can control the dynamics of bacterial populations (Grenni et al., 2018). Antibiotics enter the environment through sewage, discharges from WWTPs, leaching from landfills, release from pharmaceutical industries, livestock activities, and application of sewage sludge, manure or treated wastewater to agricultural land (Daughton and Ternes, 1999; Boxall et al., 2003; Díaz-Cruz et al., 2003; Thiele-Bruhn, 2003; Kemper, 2008; Topp et al., 2008). Both the physicochemical properties, such as molecular structure, size, shape, solubility, and hydrophobicity of antibiotics and the basic soil properties such as type, texture, pH, and organic matter content of soil strongly affect the behaviors and fate of antibiotics in soil (Kemper, 2008).

Antibiotic Use in Livestock Industry

Land application of manure has been suggested as the main pathway of releasing antibiotics into the environment from the agricultural industry (Baguer et al., 2000). Antimicrobials are delivered to animals for a variety of reasons, including disease treatment, prevention, control and growth promotion, and feed efficiency (Marshall and Levy, 2011). Antimicrobial growth promotions (AGPs) are small, subtherapeutic quantities of antibiotics that are delivered to animals in feed, and shown to enhance the feed-to-weight ratio for poultry, swine, and beef cattle (Summers, 2002). Several studies have researched the effect of using antimicrobial agents in agricultural production and their effect on the health of those who administer the agents. Studies have shown that farms using AGPs developed more resistant bacteria in the intestinal floras of the farm workers and farm animals than in those for similar people and animal on farms not using AGPs (Smith and Crabbe, 1957; Howells and Joynson, 1975; Aarestup et al., 2001; Levy, 2002).

While FQ antibiotics were first introduced in to treat bacterial infections in humans in 1986, the use of them in the agricultural industry, specifically poultry production, began in 1995 (APHA, 2001) Though, the FDA banned the use of FQ antibiotics in poultry production in 2005 and the EU banned the use of antimicrobials as growth promoters in 2006 (Cogliani et al., 2011) due to the rise of resistant *Campylobacter* spp, the use of FQ antibiotics in agriculture is still used in developing counties (Adelowo et al., 2014; Moyane et al., 2014;). Teuber (2001) found two strains of *Campylobacter* (*C. jejuni and C. coli)* in the environment that originated from either animal food sources or feces of boilers, pigs, or human to be 99% resistant to ciprofloxacin. Englen et al. (2005) found that out of 448 *Campylobacter* isolates, ciprofloxacin-resistant *C. jejuni* accounted for 1.8% while *C. coli* accounted for 9% of all resistant strains in a feedlot cattle operation. Agunos et al. (2013) found 4 to 17% resistance of ciprofloxacin isolates from *Campylobacter* spp. that originated from broiler breeder or broiler chicken operations in Canada. Lu et al. (2011) found 59.4% resistance of ciprofloxacin isolates from *Salmonella enteritidis* in chicken operations in China. Numerous studies have found ciprofloxacin-resistant *E. coli* from different agricultural sources including broiler feed in Iceland (Thorsteinsdottir et al., 2010), poultry operation is Nigeria (Ogunleye et al., 2008; Adelowo et al., 2014), and farm animals (broiler chickens, pigs, cattle, and veal) in Belgium (Lambrecht et al., 2018).

Sorption of antibiotics

Understanding the factors that affect antibiotic sorption on soils can lead to the understanding of how antibiotics react in terms of ecotoxicity, degradation, transportation, and bioaccumulation (Wang and Wang, 2015). The sorption behavior of an individual antibiotic can differ from one soil to another due to various basic soil properties such as pH, ionic environment, texture, and organic matter (Tolls, 2001; Jones et al., 2005; Sassman and Lee, 2005; Pils and Laird, 2007). Sorption behavior of antibiotics are measured between the solid and liquid phase of the sorbent and is determined by distribution coefficients (K_d) (Wang and Wang, 2015). K_d values of

FQ antibiotics are generally larger than other antibiotic families, with values of enrofloxacin ranging from 360 to 5610 L kg^{-1} (Nowara et al., 1997), ofloxacin 3554±194 L kg^{-1} (Pico and Andreau, 2007), ciprofloxacin 4844±628 cm^3 kg^{-1}, and norfloxacin 5791±1280 cm^3 kg^{-1} (Conkle et al., 2010).

Ciprofloxacin adsorption is pH dependent, as the molecule can be adsorbed to soil in either a cationic, zwitterionic, or anionic form depending on pH (Gu and Karthikeyan, 2005; Tan et al., 2015). FQ sorption to soil can occur either from the coulombic attraction of the cationic amine moiety on the molecule to negatively charged surface sites (Hari et al., 2005) or cation bridging which involves the interaction of the carboxyl group to exchangeable cations found in soil (Nowera et al., 1997). Tolls (2001) found that hydrophobic partitioning did not appear to drive FQ sorption to soils (Vasudevan et al., 2009). FQ adsorption to soil organic matter is primarily dominated by cation-exchange reactions and occurs via the positively charged amino group of the ciprofloxacin molecule and the negatively charged humic substance groups that contained in organic matter (Carmosini and Lee, 2009) or through hydrogen bonding of the keto functional group of the FQ molecule to the protonated surface hydroxyl in organic matter (Gu and Karthikeyan, 2005).The influence of organic matter on FQ sorption has been inconclusive, with studies showing a positive, negative or no significant relationship (Carrasquillo et al., 2008; Vasudevan et al., 2009; Zhang et al., 2009a; Figueroa-Diva et al., 2010; Pan et al., 2012; Leal et al., 2013; Teixidó et al., 2014).

Wastewater Treatment Plants

As mentioned previously, the presence of antibiotics in WWTPS have led to an increased number of antibiotic resistant microorganisms even at low concentrations (Soge et al., 2009; Araújo et al., 2010). These resistant microorganisms can be transported to surface water and reach groundwater through leaching or by irrigation (Wang and Wang, 2015). It is estimated that 34 million gallons of wastewater is processed in the United States at WWTPs (EPA, 2019), and these nutrient- rich environments offer optimal conditions to promote horizonal gene transfer processes, frequently involving the passage of plasmids and transposons encoding antibiotics resistance to antibiotic-tolerant microorganisms (Alonso et al., 2001; Tran and Jacoby, 2002; Summers, 2006; D'Costa et al., 2006; Kelly et al., 2009). Biological treatment processes at WWTPs can create an environment suitable for resistance development and spread because bacteria are continuously mixed with antibiotics at sub-inhibitory concentrations (Davies et al., 2006; Ferreria da Silva et al., 2006; Auerbach et al., 2007).

According to the EPA (2004), wastewater undergoes two different types of treatment before water is released back into the environment. Primary treatment involves sewage that enters the plant passing through a screen that removes large objects that are present in the waste. The sewage is then processed through a grit chamber where cinders, sand, and small stones are separated from the waste. Solid forms of waste are then removed in a sedimentation tank and suspended solids will sink to bottom and are called raw primary biosolids or sludge. The waste then undergoes secondary treatment that removes around 85% of organic matter present through bacterial processes. This involves either a trickling filter or the activated sludge process. The trickling filter consists of a bed of stones that range from three to six feet deep that microorganisms attach and grow throughout which sewage passes. The treated wastewater then flows to another sedimentation tank to remove excess bacteria and any biosolids remaining before the water is released back into the environment. The activated sludge process allows rapid production of bacteria by bringing air and sludge heavily laden with bacteria into close contact with sewage increasing the efficiency of bacterial processes to break down organic materials. For example, Picó and Andreu (2007) found that 80-90% of ciprofloxacin is removed from wastewater via sorption to sludge. To complete the secondary treatment, effluent from the sedimentation tank is usually disinfected with chlorine. Chlorine kills more than 99% of harmful bacteria in the effluent. (EPA, 1999). Ultraviolet light and ozone can also be used in the disinfection process to kill harmful bacteria. The introduction of lagoons has also been established to be effective as a secondary treatment process. The lagoon allows for sunlight, microorganisms, and oxygen to interact and purify water before water is reintroduced back into the environment.

Due to the increasing concentrations of antibiotics present in wastewater, WWTPs have a difficult time removing certain antibiotics before the release of water back into the environment (Xu et al., 2007; Liu et al., 2014; Rao et al., 2014; Sui et al., 2014; Sun et al., 2014). As conventional water and wastewater treatment processes are inadequately able to remove all recalcitrant pharmaceuticals, it is necessary to introduce additional advance treatment technologies prior to discharge into environment (Tambosi et al., 2010). Various advanced treatment technologies have been evaluated for this purpose, including membrane bioreactors (MRBs) (Kimura et al., 2005; Gebhardt and Schroder, 2007), advanced oxidation processes (Andreozzi et al 2005; Zhang et al., 2008), and adsorption onto activated carbon or other adsorbents (Bajpai et al., 2000; Bekci et al., 2006; Onal et al., 2007).

The residual sludge present in WWTPs can be disposed in several ways in the environment. Most of the sludge remaining is recycled back into the environment through direct application on land as a form of fertilizer. According to the EPA, about 50% of all biosolids produced are recycled and applied to land as fertilizer (EPA, 2004). Only around 1% of the United States agricultural land utilizes biosolids as a form of fertilizer. Incineration is another way to dispose of waste generated in WWTPs, in which the ash created is recycled back into the environment.

An increase in ciprofloxacin-resistant microorganisms originating from WWTPs in the environment at various stages of treatment has been observed (Halling- Sørensen et al., 1998; Daughton and Ternes, 1999; Golet et al., 2003; Wang and Wang, 2015). Manaia et al. (2009) found ciprofloxacin-resistant heterotrophic bacteria and enterobacteria in raw effluent as well as resistant enterobacteria in treated wastewater. Biological treatments that arise in WWTPs have produced resistant microorganisms including ciprofloxacin-resistant *E. coli* in oxidation ponds (Mispagel and Gray, 2005), ciprofloxacin-resistant *A. hydrophilia/caviae and A. veronii/sobria* in biofilms dominated by hospital effluent (Ory et al., 2016), and ciprofloxacin-resistant *E. coli, Shigella* and *Klebsiella* (Ferreira da Silva et al., 2006, 2007; Galvin et al., 2010) and *Acinetobacter* (Zhang et al., 2009b) in activated sludge. One study found that treated wastewater used for irrigation for crop production can contribute $4x10^5$ to $4x10^7$ culturable ciprofloxacin-resistant microorganisms per square meter of soil daily (Negreanu et al., 2012).

Soil-Based Wastewater Treatment Plants and Bioterrorism

Understanding what basic soil properties govern the sorption of antibiotics in the natural soil system can be further applied in order to develop soil-based wastewater treatment plants. These treatment plants can use soil with various basic properties as a treatment buffer to bind with antibiotics and remove them from wastewater before being released back into the environment (Sato et al., 2005). Bioterrorism, by definition, is intentional release of bacterial agents such as bacteria, fungi, and viruses to incite terrorism against a civilian population (CDC, 2018). Antibiotics can be considered ineffective during a widespread bioterrorism events due to antibiotic resistance. The amount of antibiotics needed to combat a bioterrorism event can overwhelm WWTPs and cause the development of resistance bacteria due to the massive influx of antibiotics into the environment. This could leave the population vulnerable to another attack, and increase the risk that antibiotics would not be effective for a second time due to resistance.

Anthrax, caused by *Bacillus anthracis,* can affect both humans and animals and is considered a bioterrorism threat due to the ease of resistance and transportability and the high virulence that the strain contains (Christopher et al., 1997; Cole, 2005; Turnbull and Shadomy, 2011). In 2001, anthrax-contaminated letters delivered to media outlets and Senator’s offices in the United States killed five people and affected 17 others (CDC, 2002) less than one month after the

September 11th terrorist attacks in New York City. Anthrax exposure in 2001 was treated primarily by ciprofloxacin, while doxycycline and amoxicillin were also used (Swartz, 2001). In 2001, only 22 were infected, but another bioterrorism attack in a larger city can be detrimental. In Dallas, Texas where the population is around 1.35 million (Census, 2019), and the local WWTPs treat around 260 million gallons per day (Dallas Water Utilities), a potential anthrax attack can lead to an influx of wastewater released back into the environment with antibiotics still active. If another attack were to occur, the possibility remains that the antibiotic used in the first attack would be ineffective due to resistance, as Choe et al. (2000) found that anthrax resistance was more prevalent in FQ antibiotics compared to doxycycline.

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CHAPTER V

SORPTION OF CIPROFLOXACIN IN SOIL: KINETIC PARAMETERS AND SOIL FACTORS INFLUENCING SORPTION

ABSTRACT

Ciprofloxacin is a broad-spectrum antibiotic of the fluoroquinolone class that is used to treat numerous bacterial infections in both humans and animals. Antibiotics are released into the environment in numerous ways and can lead to the emergence of resistant microorganisms. Although the extent to which ciprofloxacin persists and is transported in the environment remains largely unknown, understanding soil factors that govern its mobility is important to mitigate the potential negative impacts. The determination of ciprofloxacin sorption on 20 different soils with diverse basic properties and vegetation history was studied. Sorption capacity values ranged from 8 to 141 g kg^{-1}; distribution coefficient (K_d) values ranged from 23 to 200 mL kg^{-1} soil; and soil organic carbon-water partitioning coefficient (K_{oc}) values ranged from 54 to 2146 mL g^{-1} organic carbon. Clay content and cation exchange capacity were the most significant factor that influenced sorption capacity and K_d of ciprofloxacin. Soil pH had no significant relationship with ciprofloxacin sorption parameters. Cultivation led to changes in the quality of soil organic matter, resulted in a significant relationship between sorption of ciprofloxacin and soil organic carbon content. Soils are effective in restraining the mobility of ciprofloxacin through adsorption and the effectiveness increases with clay content.

Keywords:

Antibiotic; Clay Content; Ciprofloxacin; Cultivation; Soil Organic Matter; Sorption; pH

Abbreviations

FQ, Fluroquinolone Antibiotic; HPLC, high performance liquid chromatography; OC, organic carbon; PC, principal component; analysis; PCA, principal component analysis; SOC, soil organic carbon; SOM, soil organic matter; WWTPs, wastewater treatment plants

INTRODUCTION

The intensive use of antibiotics to treat numerous bacterial infections in both humans and animals, as well as their use in the livestock industry to promote growth and prevent disease in large-scale feeding operations has led to their continuous release into the environment (Kümmerer, 2004). Fluoroquinolones (FQ) are a class of antibiotics prescribed to treat a broad range of bacterial infections by inhibiting DNA replication (Wolfson and Hooper, 1989). FQ antibiotics can enter the environment through the direct discharge of wastewater from wastewater treatment plants (WWTPs) and aquaculture facilities, animal wastewater, runoff and leaching from agricultural fields and landfills, irrigation practices and leakage of septic tanks (Kümmerer, 2004; Wang and Wang, 2015; Kovalakova et al., 2020). FQ antibiotics have been detected in the aquatic environment ranging from maximum concentrations of 14 to 31 mg L^{-1} in WWTP effluent in India (Larrson et al., 2007; Fick et al., 2009), 2.5 to 6.5 mg L^{-1} in surface waters (Le and Munekage, 2004; Fick et al., 2009), 0.382 to 14 µg L^{-1} in groundwater (Fick et al., 2009; Jiang et al., 2014), and 7.49 µg L^{-1} in animal wastewater (Wei et al., 2012). FQ antibiotics enter into the soil through contact from contaminated water sources or through the application of manure, biosolids, or sludge as a fertilizer source (Van Doorslaer et al., 2014). FQ antibiotics have been detected in soils with a maximum concentration ranging from 1.35 to 9.8 mg kg^{-1} (Morales-Munoz et al., 2004; Li et al., 2011).

Ciprofloxacin is a FQ antibiotic that is used to treat numerous bacterial infections in both humans and animals and was first introduced in 1987. It is estimated that 45-62% of ciprofloxacin is released unmetabolized through urine, while 15-25% is released through feces (Golet et al., 2003). From 2013-2015, the Center for Disease Control and Prevention (CDC) reported that approximately 62 million prescription were obtained from outpatient sources in the Unites States (CDC, 2013, 2014, 2015). The potential long-term exposure to low or sub-toxic concentrations in the environment, as well as the misuse or overuse of antibiotics have increased the emergence of resistant microorganisms (Wang ang Wang, 2015). Ciprofloxacin resistance in the *Campylobacter* species, especially in the strains of *C. jejuni* and *C. coli*, have been observed by calculating resistance based on recovery of manure isolates, with a range of 1.8 to 17% ciprofloxacin-resistance being found (Teuber, 2001; Englen et al., 2005; Agunos et al., 2013). The Food and Drug Administration (FDA) in 2005 and the European Union (EU) in 2006 banned the use of FQ antibiotics in poultry production due to the rise of resistant strains of the *Campylobacter* species (FDA, 2005 Cogliani et al., 2011).

Studies have shown that ciprofloxacin can affect bacterial populations in the aquatic and soil environments. Yi et al. (2017) found that ciprofloxacin concentrations as low as 0.2 mg L^{-1} can inhibit total nitrogen (from 95.8 to 84.9%) and phosphorus removal (from 96.8 to 91.7%) in wastewater processes, while Al-Ahmad et al. (1999) found that *Pseudomonas putida* growth was inhibited by 50% at 80 µg L^{-1}. Bacterial function and processes in soil can be altered by ciprofloxacin as Girardi et al. (2014) found an inhibition rate of 70% in concentrations as low as 0.2 mg ciprofloxacin kg^{-1} and potential nitrification rates inhibited at concentrations as low as 1 mg kg^{-1} (Chu et al., 2014). The bacterial community can also be altered in the presence of ciprofloxacin with Córdova-Kreylos and Scow (2007) concluding that gram negative and sulfate-reducing bacteria favor ciprofloxacin in concentrations as low as 20 ug mL^{-1} in three different salt marsh sediments, while Naslund et al. (2008) found that in concentration as low as 0.2 mg L^{-1} (equivalent to 0.1 ug kg^{-1} dry weight sediment), ciprofloxacin altered bacterial community diversity.

The effect of ciprofloxacin on the microbial community is inversely related to the sorption phenomenon in soils (Córdova-Kreylos and Scow, 2007). Adsorption processes can control the fate of antibiotics in soil (Tolls, 2001; Thiele-Bruhn, 2003; Kümmerer, 2004). Sorption of ciprofloxacin is pH-dependent, as the pH determines the charged species of the ionizable molecule (Carmosini and Lee, 2009;

Vasudevan et al., 2009). Ciprofloxacin in soil can exist in cation, zwitterion, or anion form at environmentally relevant pH (Carrasquillo et al., 2008). Numerous studies have found that cation exchange is the dominant pathway for ciprofloxacin adsorption in soils (Carrasquillo et al., 2008; Vasudevan et al., 2009; Figueroa-Diva et al., 2010; Wu et al., 2010; Leal et al., 2013; Roca Jalil et al., 2015; Kiecak et al., 2019; Zhao et al., 2020), while cation bridging and surface complexation can also influence adsorption (Nowara et al., 1997; Gu and Karthikeyan, 2005). The influence of soil organic carbon (SOC) on sorption of ciprofloxacin has been inconclusive (Carrasquillo et al., 2008; Vasudevan et al., 2009; Zhang et al., 2009; Figueroa-Diva et al., 2010; Pan et al., 2012; Leal et al., 2013; Teixido et al., 2014; Zhou et al., 2014).

Limited studies have been conducted to evaluate the relationship between ciprofloxacin sorption and basic soil properties. Vasudevan et al. (2009) concluded that ciprofloxacin sorption was pH-dependent by studying 30 soils with diverse soil properties. Five buffers (chloroacetate, acetate, MES, PIPES, and MOPS) were used to achieve desired solution pH to determine sorption of ciprofloxacin. However, since ciprofloxacin is not soluble in alkaline conditions, the authors could not obtain sorption capacity and due to the different buffers, the effects of ionic strength is unknown. Carmosini and Lee (2009) observed the pH and ionic strength effect on sorption of ciprofloxacin to four different humic materials and determined that certain humic materials can increase ciprofloxacin mobility. This study did not evaluate the influence that clay minerals have on sorption processes. Therefore, to further the research of ciprofloxacin sorption in the environment, the objectives of this study were: (1) to determine the sorption capacity of ciprofloxacin in soils with diverse properties and vegetation; and (2) to reveal difference in soil properties and the nature of SOC, as well as the ciprofloxacin sorption behavior in soils of different cultivation/vegetation history.

MATERIALS AND METHODS

Soil

A set of 20 surface soils (0-10 cm for croplands and 0-5 cm for pasture and uncultivated soils) of diverse properties and vegetation covers were used in this study (Table 1). These soils included five major soil series in the United States and one soil series from Hungary, which were either cultivated with major crops (soybean, corn, wheat, cotton) and pasture, or uncultivated prairie, woodland, or pine forest. Following the removal of large plant debris and stones, soils were air-dried, ground to pass a 2-mm sieve, and kept in sealed containers at 23ºC until analysis. Soil pH values (soil: 0.01M $CaCl_2$ ratio = 1:2.5) were determined using a Basic® pH meter (Denver Instruments, Denver, CO, USA) equipped with Accumet combination glass electrode (Fisher, Pittsburgh, PA, USA). SOC was determined using a LECO CN 2000 (LECO Corp., St. Joseph, MI, USA) by dry combustion as described by Nelson and Sommers, (1996). Texture was determined using the hydrometer method (Gee and Or, 2002).

Reagents and Standards

Ciprofloxacin (1-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1-ylquinoline-3-carboxylic acid, $C_{17}H_{18}FN_3O_3$) was purchased from Sigma-Aldrich (catalog # 17850, HPLC grade; St. Louis, MO, USA). Acetonitrile, hydrochloric acid and other solvents were purchased from Pharmco-Aaper (Brookfield, CT, USA). Water and all solvents were HPLC grade. Other chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) or Fisher (Pittsburgh, PA, USA) and were at least of analytical grade. The ciprofloxacin had the following physical-chemical properties: molecular weight = 331.34, log K_{ow} = 0.28, water solubility = 0.09 M, pKa_1 = 6.09, and pKa_2 = 8.74. The ciprofloxacin stock solution (1.0 mg mL^{-1}) was prepared by dissolving 0.5 g of ciprofloxacin into 500 mL of 0.1 N HCl in a volumetric flask. The phosphate buffer (0.02 M) was prepared by dissolving 2.84 g of Na_2HPO_4 in about 700 mL of deionized water and adjusted to pH 2.7 with phosphoric acid (H_3PO_4).

High Performance Liquid Chromatography Analysis

All solutions were filtered through a 0.22 µm filter prior to be used in the HPLC analysis. For the determination of ciprofloxacin concentrations in aqueous solutions, HPLC analysis was performed using a modified method described by Vella et al. (2015), employing a Waters HPLC Breeze system equipped with 1500 Series HPLC pump, 2487 dual wavelength absorbance detector and 717 plus autosampler (Waters, Milford, MA, USA). Separations were carried out using an Xterra Shield RP18 reverse phase 5 µm 4.6 × 150 mm column (Waters, Milford, MA, USA) under isocratic elution with a flow rate of 1 mL min^{-1}. The mobile phase consists of 80% phosphate buffer (pH 2.7) and 20% acetonitrile. The 0.02 M phosphate buffer was made with Na_2HPO_4 and H_3PO_4 and titrated with HCl. The analysis was conducted by the injection of 50 µL of sample solution and recording UV signals at 244 nm (8 min run time and approximately 4.35 min retention time for ciprofloxacin). Ciprofloxacin concentration in the solution was calculated based on peak area in reference to a calibration curve that was constructed using standard ciprofloxacin solutions in the range of 0.0 to 10.0 µg ciprofloxacin mL^{-1} and prepared in 0.1 N HCl.

Determination of ciprofloxacin sorption and isotherms

Sorption of the ciprofloxacin to the soil was determined by batch sorption. Sorption equilibrium of ciprofloxacin between aqueous phase and soil was evaluated by shaking 0.5 g of soil with 100 mL ciprofloxacin solution in 250 mL Nalgene bottles. Ciprofloxacin concentrations tested included 0, 20, 40, 80, 120, 160, 200, 300, 400, and 500 µg ciprofloxacin mL^{-1}. A preliminary experiment indicated that ciprofloxacin adsorption by soils was not significantly different when shaken for 30 min or 24 hrs. Since ciprofloxacin is only soluble in acidic solution and all ciprofloxacin solutions were made with 0.1 N HCl, the batch sorption reaction mixtures were adjusted to contain a final concentration of 0.05 N HCl to limit the effect of varying ionic strength on sorption. Samples were shaken for 30 minutes on an orbital shaker at 200 rpm, and then filtered through a Whatman 42 ashless filter to quickly separate the ciprofloxacin solution from soil. A portion of the ciprofloxacin solution was further filtered through a 0.22 µm membrane using a 25 mm corning sterile syringe filtration setup for HPLC analysis. Dilutions were

Table 5.1 Properties of 20 soils used in this study.

Soil				Vegetation	pH[a]	CEC[b]	Clay[c]	Silt[d]	Sand[e]	OC[f]
#	Series	Subgroup	(City, State)							
						cmole kg^{-1}	------------------%-------------------			
1	Cordell	Thermic Lithic Haplustepts	Bessie, OK	Pasture	7.3	3.05	19.0	49.0	32.0	1.9
2	Dill	Thermic Typic Haplustepts	Washita OK	Cotton	6.3	0.87	19.0	26.0	55.0	0.4
3	Easpur	Thermic Fluventic Haplustolls	Stillwater, OK	Bermuda grass	5.5	1.01	20.0	33.0	47.0	0.9
4	Easpur	Thermic Fluventic Haplustolls	Stillwater, OK	Wheat	5.1	0.96	15.8	35.8	48.5	0.5
5	Easpur	Thermic Fluventic Haplustolls	Stillwater, OK	Switchgrass	5.4	1.20	18.3	37.3	44.5	0.7
6	Kirkland	Thermic Udertic Paleustolls	Medford, OK	Native prairie	6.1	1.78	30.0	62.5	7.5	4.4
7	Kirkland	Thermic Udertic Paleustolls	Medford, OK	Prairie under CRP	4.7	1.62	32.5	55.0	12.5	2.8
8	Kullit	Thermic Aquic Paleudults	McCurtain, OK	Pine forest	3.9	1.58	27.5	52.5	20.0	1.4
9	Norge	Thermic Udic Paleustolls	Pawnee, OK	Wheat	4.8	1.48	17.5	40.0	42.5	1.5
10	Richfield	Mesic Aridic Argiustolls	Panhandle, OK	Corn	7.7	0.76	27.5	42.5	30.0	1.1
11	Teller	Thermic Udic Argiustolls	Perkins, OK	Wheat	4.6	0.75	12.5	69.4	18.3	0.8
12	Canisteo	Mesic Typic Endoaquolls	Clay, IA	Native tall prairie	7.5	7.82	37.5	35.0	27.5	4.8
13	Dickinson	Mesic Typic Hapludolls	Dickinson, IA	Soybean	6.6	1.58	17.5	15.0	67.5	1.0
14	Hanlon	Mesic Cumulic Hapludolls	Hanlon, IA	Corn	7.0	2.24	22.5	17.5	60.0	2.1
15	Hayden	Mesic Glossic Hapludalfs	Des Moines, IA	Woodland	6.7	2.47	20.0	35.0	45.0	4.7
16	Sumter	Thermic Rendollic Eutrudepts	Dallas, AL	Soybean	7.0	21.5	52.5	40.0	7.5	5.6
17	Vaiden	Thermic Aquic Dystruderts	Dallas AL	Woodland	5.3	3.52	60.0	30.0	10.0	2.3
18	Manor	Mesic Typic Dystrudepts	Paoli, PA	Native forest	5.7	3.70	25.0	35.0	40.0	12.6
19	Swartswood	Mesic Typic Fragiudepts	Blairstown, NJ	Native forest	3.8	1.37	17.5	35.0	47.5	4.2
20	Chernozem	Mesic Udic Boroll	Hungary	Native riverside	7.5	4.78	24.4	61.8	13.7	0.8

[a] pH, soil/0.01 M $CaCl_2$ ratio = 1:2.5;[b] cation exchange capacity; [c] sand, 0.05 to 2.0 mm; [d] silt, 0.002 to 0.005 mm; and [e] clay, < 0.002 mm. [f] OC, organic carbon

performed when ciprofloxacin concentrations exceeded the range of the calibration curve. For quality control, ciprofloxacin standards were analyzed at the beginning and ending of each batch analysis, with insertion of standards following analysis of every 10 samples. Limited variations on the standards were observed and the calibration curve was developed with mean values of all data obtained.

Ciprofloxacin adsorption isotherms were generated to estimate how much ciprofloxacin was adsorbed by soil (g kg^{-1}) and how much remain in the solution (mg L^{-1}). The obtained adsorption data were fitted to two isotherm equations, the Langmuir and Freundlich, to determine the best fit given by *r* values. The Langmuir (Langmuir, 1918) isotherm is a theoretical model that assumes that adsorption only occurs at a monolayer surface and that no interaction exists between adsorbed molecules and the surface. The Freundlich isotherm (Freundlich, 1909) is an empirical model of multilayer adsorption and for the adsorption on heterogeneous surfaces.

The Langmuir equation is expressed as follows:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$$

where q_e is the amount of ciprofloxacin adsorbed (g kg^{-1} soil), Q_0 is the sorption capacity of the soil (g kg^{-1} soil), K_L is the distribution coefficient (mL kg^{-1}) and C_e is the concentration of ciprofloxacin in the solution (mg L^{-1}). The Langmuir equation was transformed into three linearized forms; Eadie-Hofstee, Lineweaver-Burk, and Hanes-Woolf all as follows (Saha and Inoue, 1997):

Eadie-Hofstee: $q_e = \frac{q_e}{K_L C_e} + Q_0$

Lineweaver-Burk: $\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e}$

Hanes-Woolf: $\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 K_L}$

The Freundlich isotherm is as follows:

$$q_e = K_f {C_e}^{1/n}$$

where K_f and n are empirical constants derived from the intercept and slope, respectively. K_f is a measure of quantity of adsorbate on the absorbent, while $1/n$ measures the intensity of sorption (Elhussien et al., 2017). $1/n$ value above 1 indicates corporative adsorption while $1/n$ values below 1 indicate normal adsorption (Mohan and Karthikeyan 1997; Dada et al., 2012). The Freundlich isotherm can be linearized to the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n} lnC_e$$

To determine which transformation of the isotherms was the best fit, r values were calculated based on a q_e vs. q_e/C_e plot for Eadie-Hofstee, $1/ q_e$ vs. $1/ C_e$ plot for Lineweaver-Burk, C_e/q_e vs. C_e plot for Hanes-Woolf and ln q_e vs. ln C_e for linearized Freundlich isotherm.

Since the Freundlich isotherm does not estimate sorption capacity of a soil, sorption capacity for each soil tested was calculated by the average of all three sorption capacities determined from the three linear transformation of the Langmuir isotherms. Ciprofloxacin sorption distribution coefficient (K_d) was determined based on sorption of ciprofloxacin concentration up to 80 µg mL^{-1}. The linear correlation coefficient, r values, between ciprofloxacin adsorbed to soil and those remained in the solution in this concentration range were 0.82*** to 1.00*** for the 20 soils tested. The K_d value is the slope of the linear regressions expressed as:

$$K_d = \frac{\text{Ciprofloxacin sorbed (g kg\_1 soil)}}{\text{Ciprofloxacin in solution (mg L\_1)}}$$

The soil organic matter partition coefficient (K_{oc}) was calculated to normalize K_d values by the amount of organic carbon (OC) in the soil. This was done to reduce the variability of data due to the variability of OC found within the tested soils. K_{oc} was calculated by dividing a K_d by the OC fraction, f_{OC}, of a specific soil:

$$K_{oc} = \frac{K_d}{foc}$$

Data and Statistical Analysis

Statistical analysis was performed using SAS 9.4 (SAS, 2014), utilizing PROC REG and PROC PRINCOMP. All results reported are averages of duplicate analyses, unless otherwise indicated. All results were expressed on soil dry weight basis. Soil moisture content was determined based on weight loss after drying the soils at 105°C for 48 h.

RESULTS

Soil pH ranged from 3.8 to 7.7 (avg. 6.0), OC from 0.4 to 12.6 (avg. 2.7) %, cation exchange capacity (CEC) from 0.75 to 21.5 (avg. 3.2) cmol kg^{-1} , clay from 12.5 to 60.0 (avg. 26.0) %, fit both the Langmuir and Freundlich isotherms (Fig. 1) and the linearized transformations (Fig. 2), with correlation coefficients (*r* values) of respective silt 15.0-62.5 (avg. 40.4)% and sand from 7.5 to 67.5 (avg. 33.8)% (Table 1).

Data on adsorption parameters ranging from 0.61 to 1.00 and in the following orders: Lineweaver-Burk (*r:* 0.92-1.00) > Hanes-Woolf (*r:* 0.91-1.00) >Freundlich (*r:* 0.85-1.00) >Eadie-Hofstee (*r:* 0.61-0.97). K_f values ranged from 0.40 to 1.94 g kg^{-1}; and *n* values ranged from 1.22 to 2.94 mL kg^{-1} for the Freundlich isotherm. The observed <1 1/*n* values in the Freundlich isotherms of the 20 tested soils suggested that the adsorption follows an L-shaped curve (data not shown), which indicated that sorption of ciprofloxacin to these soils were strongly favored at lower concentrations and decreased with increasing concentration (Sposito, 1989). Sorption

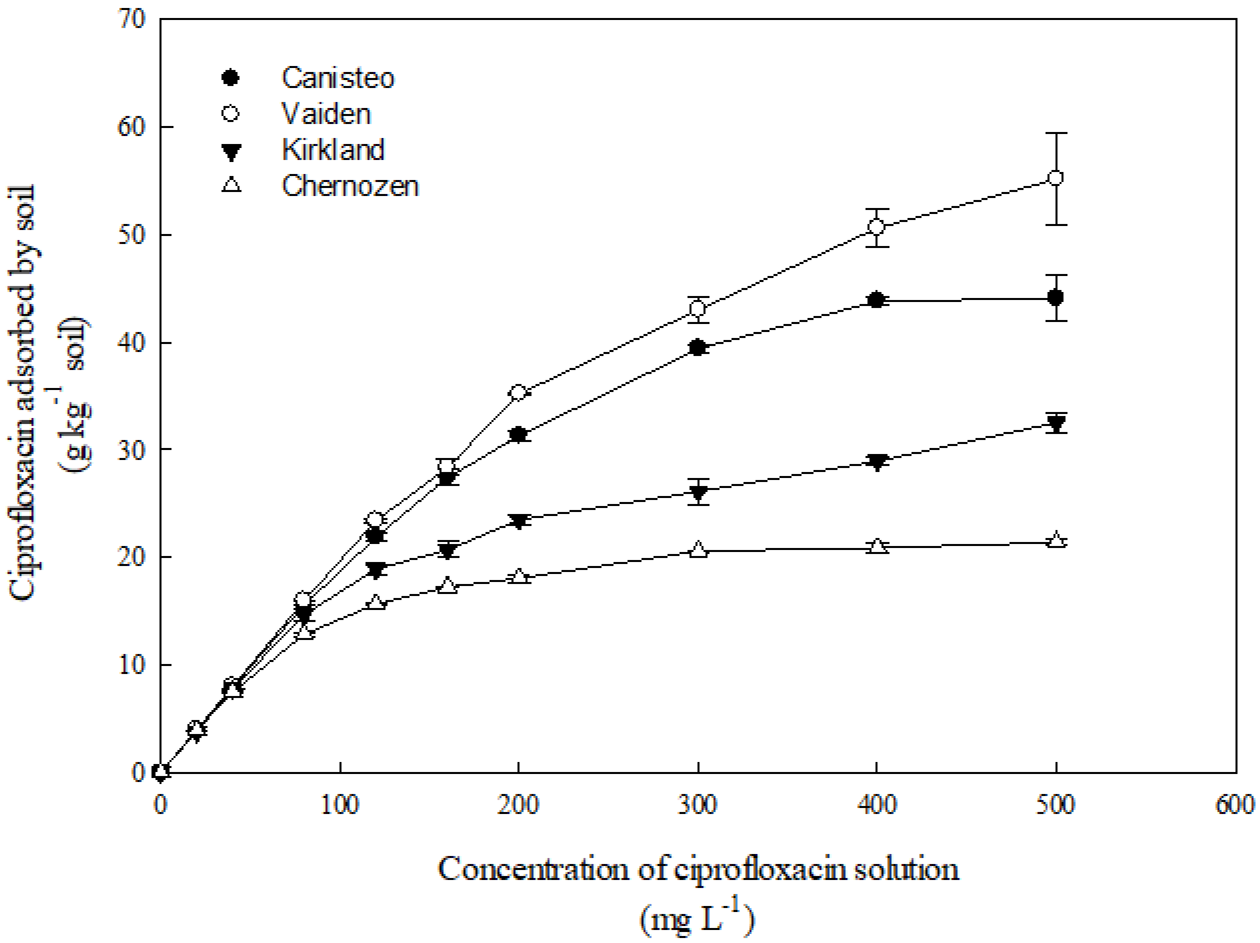

Fig. 5.1 Sorption isotherms for soil 6, 12, 17, and 20 of the 20 soils tested. All 20 soils followed both the Freundlich and Langmuir isothermal shape as determined by correlation (*r*) values.

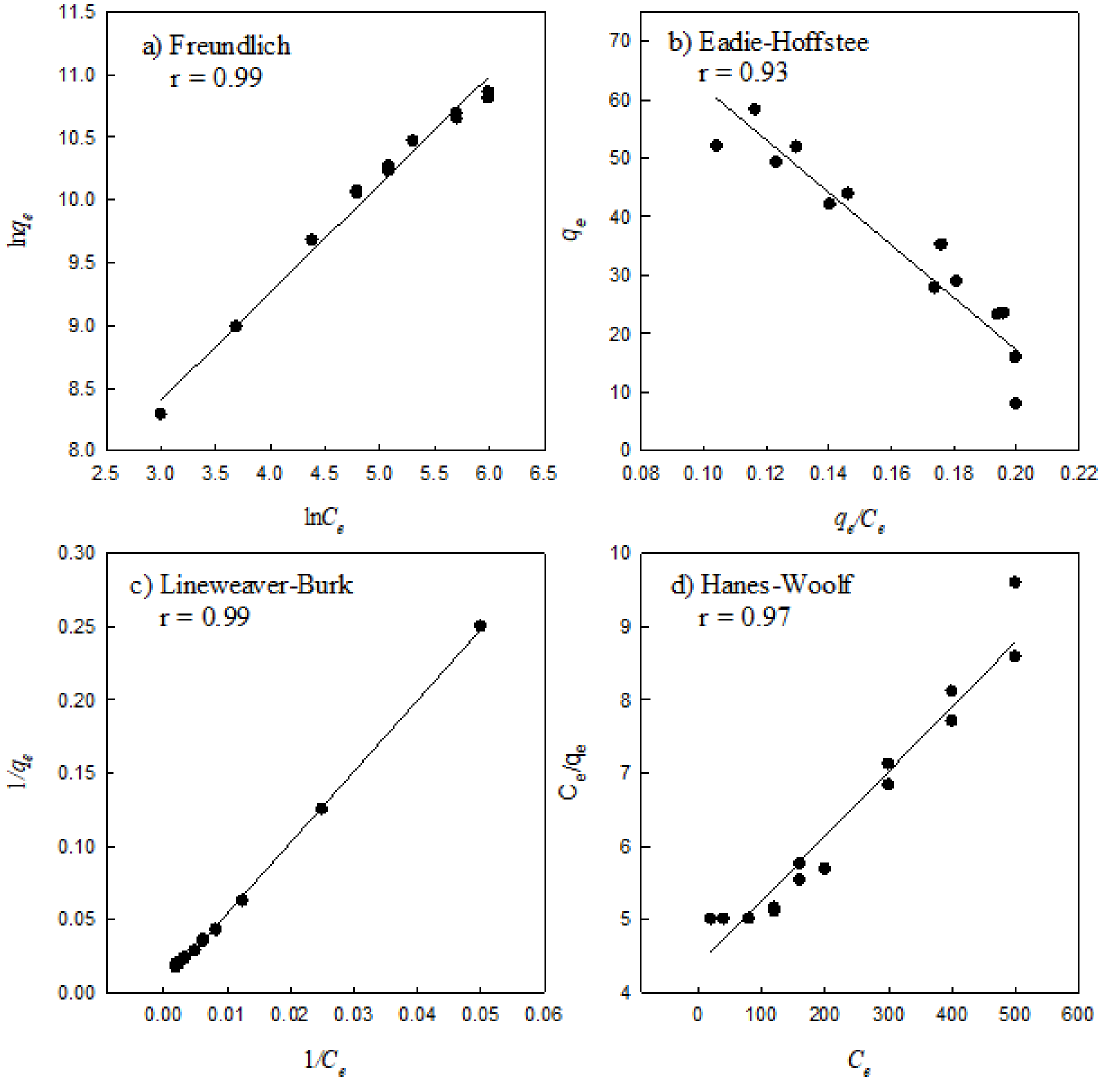

Fig. 5.2 Linear transformations of both Freundlich and Langmuir isotherms for soil 17 in Table 1. Each individual soil tested were linearly transformed by a) Freundlich and the Langmuir linear transformations b) Eadie-Hoffstee c) Lineweaver-Burk and d) Hanes-Woolf with the linear equation and correlation coefficients calculated for each. Where q_e is the concentration of ciprofloxacin adsorbed in the soil (in g kg^{-1}) and C_e is the concentration of ciprofloxacin in the solution (mg L^{-1}).

capacity varied considerably among soils, ranging from 8 to 141 g ciprofloxacin kg^{-1} soil (Table 3). K_d values among soils ranged from 23 to 200 mL ciprofloxacin kg^{-1} soil K_{oc} values ranged from 54 to 2146 mL g^{-1} OC (Table 3).

A significant relationship was found between sorption capacity and OC (r =0.46**, Fig 3a). Clay content was the most significant factor influencing sorption capacity as indicated by *r* value of 0.92*** (Fig. 3b). Little significant relationship was found between sorption capacity and pH (Fig. 3c). CEC had a significant relationship with sorption capacity with a *r* value of 0.64***(Fig. 3d). Relationships between K_d and the tested soil properties were similar to those observed for sorption capacity. The relationship between K_d and OC was not statically significant (r = 0.35, Fig. 3e). Soil clay content was the most significant factor influencing K_d values with a *r* value of 0.64***(Fig. 3f). Little relationship was observed between K_d and pH (Fig. 3g). CEC had a significant relationship with K_d with an *r* value of 0.53** (Fig. 3h). When the K_d values were expressed based on OC content as the K_{oc} values, there were little relationships observed between K_{oc} and basic soil properties (Fig. 3i-l). Although the correlation coefficient between K_{oc} and OC was significant (r = 0.60***), this is, in part, due to self-correlation (Fig 3i). For the determination of the effect of SOC on sorption parameters, soil 18 was excluded from the data set because it was determined to be an outlier due to a 12.6% OC, since the OC of most agricultural soils found in the United States is less than 5% (Lehmann and Kleber 2015). For the determination of the effect of CEC on sorption parameters, soil 16 was excluded from the data due to its high CEC value.

Cultivation influenced the relationships between sorption parameters and OC (Table 4). Sorption capacity was not significantly correlated with OC in uncultivated soil (*r* = 0.16, n = 9), but strongly significant in cultivated soils (*r* = 0.96***, n = 10). Sorption capacity was significantly correlated with clay content regardless of cultivation history (cultivated, *r* = 0.90***) and uncultivated soils: (*r* = 0.94***). Little statistical relationship was found between pH and clay content when grouped by cultivated or uncultivated practices. CEC was also significantly correlated with sorption capacity regardless of cultivation history (cultivated, r = 0.82***, n = 9) and uncultivated soils (r = 0.60*, n = 10). The relationships between K_d and soil properties were similar to those shown for sorption capacity. Although uncultivated soils still showed no significant relationship between K_d and OC (r = 0.03, n = 9), cultivated soils now show a significant relationship (r = 0.72**, n = 10). Soil clay content was significantly correlated with K_d, regardless of cultivation history with r of 0.56* in cultivated and 0.69** in uncultivated soils. Little statistical relationship was found between pH and OC when grouped by either cultivated or uncultivated practices (r = 0.28 and 0.31) respectively. K_d was not significantly correlated with CEC in uncultivated soil (r = 0.41, n = 10), but strongly significant in cultivated soils (r = 0.83***, n = 9). No statistical relationship was found between K_{oc} and basic soil properties.

The relationships between sorption parameters and soil properties were further evaluated based on principle component analysis (PCA). In PCA, the multidimensional data set was reduced into three principle components (PCs), which accounted for 77.0% of the total variance (Table 5). Principle component 1 (PC1) accounted for 40.1% of the total variance and was loaded positively by sorption capacity, CEC, clay content, and K_d, and negatively by sand content. Principle component 2 (PC2) accounted for 19.1% of the total variance and was loaded positively by OC and negatively by silt and $K_{oc.}$ Principle component 3 (PC3) accounted for 17.8% of the total variance and was loaded positively by $K_{oc.}$ And pH and negatively by silt content. Clay content, CEC, $K_{d\,,}$ sorption capacity, and K_{oc} values were each grouped into three ranges that included low, medium, and high values, to see if separation or clustering occurred in regards to PC1 and PC2.

Table 5.2 Best fit data for Langmuir and Freundlich Isotherms for all 20 soils.

	Freundlich			Langmuir								
				Eadie-Hofstee			Lineweaver-Burk			Hanes-Woolf		
Soil #	K_f[a]	n[b]	r	Sorption[c] Capacity	K_L[d]	*r*	Sorption Capacity	K_L	*r*	Sorption Capacity	K_L	*r*
	g kg^{-1}	mL kg^{-1}		g kg^{-1}	mg L^{-1}		g kg^{-1}	kg L^{-1}		g kg^{-1}	kg mg^{-1}	
1	1.34	2.08	0.92	25.0	83	0.89	33.3	140	0.99	25.0	70	0.99
2	1.74	2.85	0.91	14.7	50	0.88	14.3	53	0.98	14.3	37	0.96
3	1.94	2.94	0.91	14.9	47	0.85	16.7	60	0.97	16.7	65	0.96
4	1.37	2.50	0.98	16.1	63	0.95	16.7	65	0.99	16.7	83	0.98
5	1.67	2.50	0.85	18.2	47	0.61	25.0	100	0.98	16.7	38	0.98
6	0.74	1.59	0.97	38.0	134	0.87	50.0	230	0.99	33.3	107	0.97
7	1.14	2.00	0.96	26.6	102	0.97	33.3	143	0.99	25.0	93	1.00
8	0.93	1.69	0.95	37.3	135	0.92	50.0	225	1.00	33.3	117	0.99
9	1.54	2.44	0.92	18.9	66	0.93	20.0	80	0.99	16.7	45	0.99
10	1.10	2.50	0.95	12.6	54	0.73	11.1	43	0.94	16.7	142	0.91
11	0.85	2.44	0.96	9.6	50	0.71	10.0	45	0.92	14.3	161	0.92
12	0.49	1.32	0.98	80.6	342	0.94	125.0	550	1.00	100.0	420	0.97
13	1.56	2.94	0.95	12.3	45	0.87	12.5	44	0.97	14.3	67	0.97
14	1.24	2.04	0.93	26.8	89	0.89	33.3	140	0.99	25.0	85	0.98
15	1.39	2.33	0.92	19.7	71	0.92	20.0	86	0.99	16.7	48	0.99
16	0.49	1.33	0.99	75.0	341	0.97	100.0	480	1.00	100.0	450	0.99
17	0.40	1.22	0.99	112.5	490	0.93	200.0	980	1.00	111.1	489	0.97
18	0.48	1.67	1.00	21.4	151	0.89	20.0	128	0.99	25.0	223	0.96
19	0.27	1.82	0.97	7.7	92	0.70	5.0	57	0.96	12.5	24	0.87
20	1.12	1.96	0.95	27.3	104	0.96	33.3	147	1.00	25.0	85	1.00

[a] K_f was determined from the intercept of the Freundlich isotherm plots; [b] *n* was determined from the slope of the Freundlich isotherm plots; [c] Sorption Capacity was determined from each of the three Langmuir isotherms plots; [d] K_L was determined from each of the three Langmuir isotherms plots.

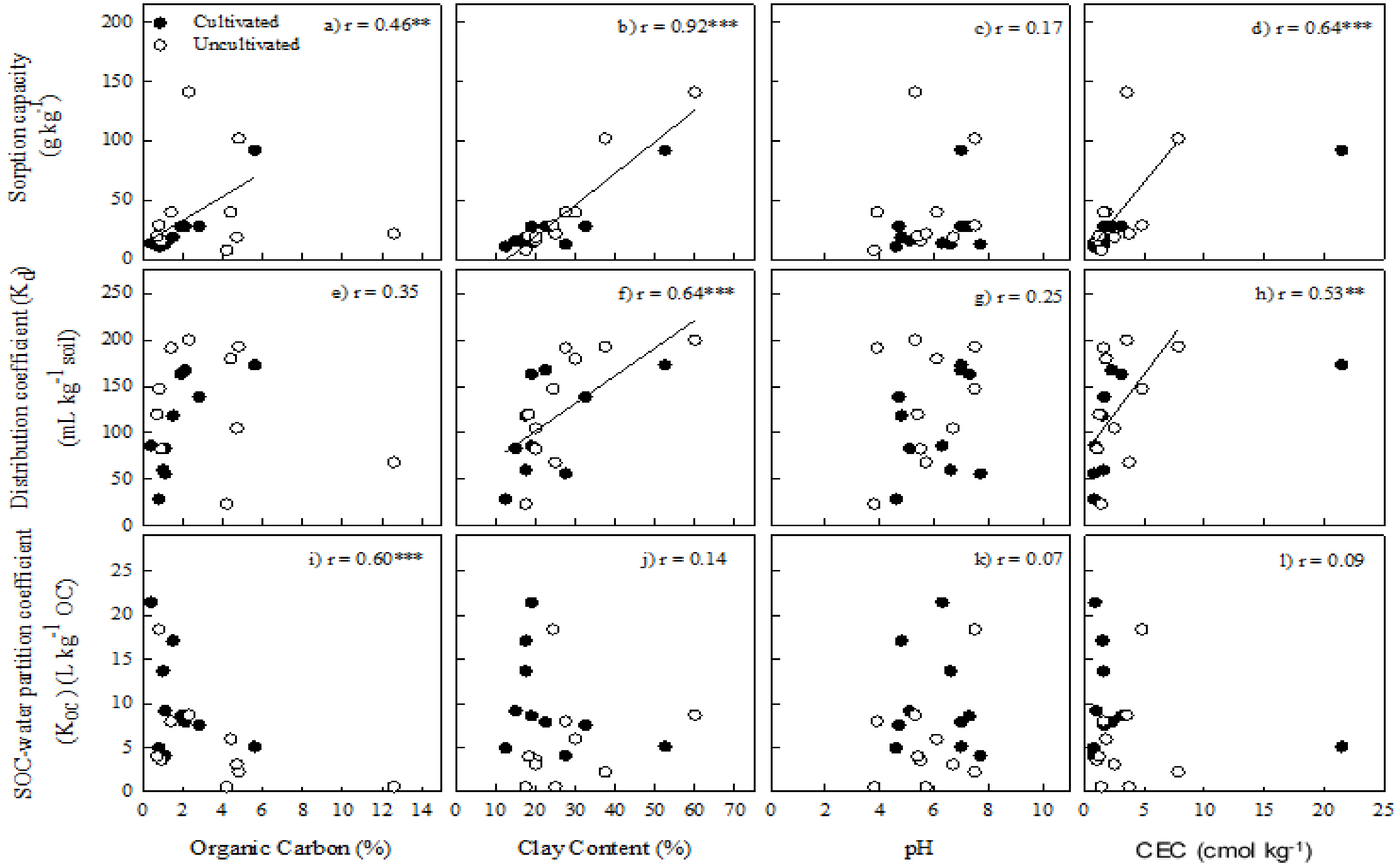

Fig. 5.3 Relationships between a) organic carbon and sorption capacity b) clay content and sorption capacity c) pH and sorption capacity d) CEC and sorption capacity e) organic carbon and distribution coefficient f) clay content and distribution coefficient g) pH and sorption coefficient h) CEC and distribution coefficient i) organic carbon and SOC-water partition coefficient j) clay content and SOC-water partition coefficient k) pH and SOC-water partition coefficient l) CEC and SOC-water partition coefficient separated by cultivated and uncultivated management practices. Soil 18 from Table 1 was excluded from organic carbon content calculations due to the high organic carbon content of 12.6% for a) e) and i). Soil 16 from Table 1 was excluded from CEC calculations due the 21.50 cmol kg^{-1}. Correlation coefficients (*r*) for all 20 soils, regardless of management history are listed. Linear regression is shown only with significant results ($p<0.01$) for b) and e) and ($p<0.05$) for a).

Table 5.3 Sorption Capacity and sorption coefficients K_d and K_{oc} of ciprofloxacin in soils used in this study

Soil #	Sorption[a] Capacity	K_d[b]	K_{oc}[c]
	g kg^{-1}	mL kg^{-1} soil	L kg^{-1} OC
1	28	163	8.58
2	14	86	21.46
3	16	82	9.15
4	16	83	7.54
5	20	120	17.10
6	40	180	4.08
7	28	139	4.95
8	40	191	13.66
9	19	118	7.89
10	13	56	5.09
11	11	29	3.57
12	102	193	4.01
13	13	60	5.97
14	28	168	7.98
15	19	105	2.23
16	92	173	3.09
17	141	200	8.68
18	22	68	0.54
19	8	23	0.55
20	29	147	18.40
AVG	35	119	7.73

[a] Sorption capacity (determined based on transformation equations), [b] K_d: Distribution coefficient (determined based on slope of transformation equations), [c] K_{oc}: SOC-water partition coefficient (=K_d/OC fraction).

Table 5.4 Relationship between soil properties (x) and sorption parameters (y) defined by best fit equations and coefficient of variance (*r*) when grouped by cultivation.

Parameter	Management[a]	Organic Carbon (%)		Clay Content (%)		pH		CEC (cmole kg^{-1})	
		y=mx+b	*r* value	y=mx+b	*r* value	y=mx+b	*r value*	y=mx+b	*r value*
Sorption Capacity[b]	Cultivated	15.42x-2	0.97***	1.83x-17	0.90***	5.66x-8	0.28	7.67x+8	0.82***
	Uncultivated	4.03x+35	0.16	3.26x-48	0.94***	6.65x+6	0.21	11.52x+10	0.60*
K_d[c]	Cultivated	24.80x+62	0.72**	3.15x+49	0.56*	12.05x+34	0.28	53.25x+21	0.83***
	Uncultivated	-1.05x+141	0.03	2.46x+39	0.69**	14.41x+47	0.31	11.80x+94	0.41
K_{oc}[d]	Cultivated	-158.12x+1051	0.45	-14.38x+1100	0.32	37.78x+530	0.09	-0.49x+9	0.07
	Uncultivated	-325.07x+1439	0.90	-1.01x+812	0.02	33.83x+590	0.06	-0.31x+9	0.10

[a] Soil grouped by cultivated and uncultivated practices, [b] Sorption capacity was determined based on transformation equations, [c] K_d: Distribution coefficient (determined based on slope of transformation equations), [d] K_{oc}: SOC-water partition coefficient (=K_d/OC fraction

Table 5.5 Principal component loadings between selected variables and the first three PCs.

Parameter	PC1	PC2	PC3
Eigenvalues	3.61	1.72	1.60
Total variance (%)	40.1	19.1	17.8
Cumulative variance (%)	40.1	59.2	77.0
pH	0.15	0.15	0.41
Clay	0.49	0.04	0.08
Silt	0.09	-0.48	-0.54
Sand	-0.39	0.34	0.36
OC	0.19	0.52	-0.32
[a]CEC	0.40	0.21	0.06
Sorption Capacity	0.47	0.01	0.16
[b]K_d	0.40	-0.24	0.24
[c]K_{oc}	-0.09	-0.51	0.46

[a]Cation exchange capacity (cmol kg^{-1}), [b]K_d: Distribution coefficient (determined based on slope of transformation equations), [c]K_{oc}: SOC-water partition coefficient (=K_d/OC fraction).

Grouping was evident between clay content, sorption capacity and K_d values on the PC1 axis. Soils grouped by clay content (Fig 4a), sorption capacity and K_d (data not shown) values showed similar results, in that the lower group was negatively loaded by PC1 and the high value group was loaded centrally along the PC2 axis. Soil OC values were grouped and showed separation between the groups along the PC2 axis (Fig 4b). The lower group was negatively loaded by PC2 while the higher group was positively loaded on the PC2 axis.

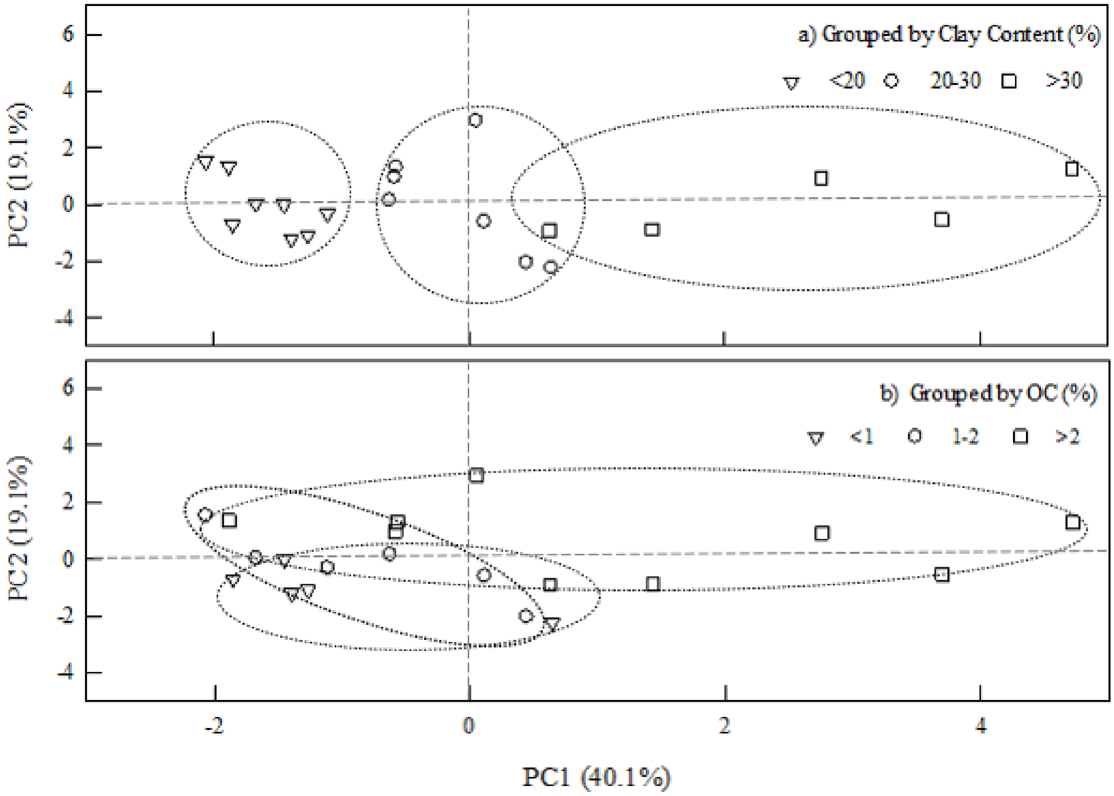

Fig. 5.4 Principal component score plot of certain basic soil properties and sorption parameters against the first two principle components. A. clustering of clay content based on low, medium, and high values plotted against the first two PCs, similar trends were observed for sorption capacity and distribution coefficient (K_d). B. clustering of OC% based on low, medium, and high values plotted against the first two PCs.

DISCUSSION

Ciprofloxacin adsorption is closely associated with surface functional groups and their charges. Charges of molecules are pH dependent, as the molecule can be adsorbed to soil in either a cationic, zwitterionic, or anionic form depending on pH (Gu and Karthikeyan 2005; Tan et al., 2015). Clays in soil have two sources of charges, isomorphous substitution and broken edges. The charges from isomorphous substation are considered permanent charges and are not affected by soil pH, while charges from broken edges are pH dependent. The coulombic attraction of the cationic amine group of the ciprofloxacin molecule to negatively-charged soil sites facilitates cation exchange (Carrasquillo et al., 2008; Vasudevan et al., 2009), while cation bridging occurs via a bond bridge between carboxyl group of the ciprofloxacin molecule and the cations on the soil surface (Nowara et al., 1997). Surface complexation via the carboxylic acid group on the ciprofloxacin molecule with other metal cations and hydrogen bonding through the weak association of the keto functional group of the ciprofloxacin molecule and the protonated surface hydroxyl also can facilitate ciprofloxacin adsorption to soil (Gu and Karthikeyan, 2005). The adsorption of ciprofloxacin to soil organic matter (SOM) is primarily dominated by cation exchange reactions and occurs via the positively charged amino group of the ciprofloxacin molecule and the negatively charged humic substance groups that SOM is composed of (Carmosini and Lee, 2009). Adsorption mechanisms of fluoroquinolone antibiotics to soil is dependent on basic soil properties including SOC, clay content, CEC, soil pH, and metal ions present in soil (Picó and Andreu, 2007).

Effect of clay content: The influence of clay content on the adsorption of ciprofloxacin in soils can be attributed to the high specific surface area and high quantities of cation exchange sites usually found on clays (Carretero and Pozo, 2009). Numerous studies have found that cation exchange is the dominant pathway for ciprofloxacin adsorption in soils (Carrasquillo et al., 2008; Vasudevan et al., 2009; Figueroa-Diva et al., 2010; Wu et al., 2010; Leal et al., 2013; Roca Jalil et al., 2015; Kiecak et al., 2019; Zhao et al., 2020). In the present study, the significant relationship found between sorption capacity and K_d values in regards to clay content and CEC also suggest that cation exchange is dominant.

In addition to cation exchange on the soil surface, the type of clay mineral can influence adsorption of ciprofloxacin. The differences between 1:1 and 2:1 clays can affect the amount of cation exchange sites, specific surface area, and the presence of an expandable interlayer that can increase adsorption potential (Essington, 2015; Awad et al., 2019; Kiecak et al., 2019). Chen et al.

(2015) found that the maximum adsorption of ciprofloxacin for kaolinite (1:1 clay) was 26 mg kg^{-1}, while montmorillonite (2:1 clay) was 23 g kg^{-1}. Tolls (2001) found that another member of the FQ class, enrofloxacin, had sorption coefficients on different clay minerals increase following the order of kaolinite < illite < vermiculite ≈ montmorillonite. Sorption of ciprofloxacin to illite was found to be restricted to the external surface and dominated by cation exchange, due to the decrease of surface area and cation exchange sites on the 2:1 nonexpanding clay (Wang et al., 2011; Awad et al., 2019). Due to isomorphic substitution, FQ antibiotics can be exchanged with cations found in the interlayer of expandable clays by the same process as surface cation exchange (Sposito et al., 1999; Okaikue-Woodi et al., 2018) Evidence of interlayer adsorption of ciprofloxacin has been observed in montmorillonite (Wang et al., 2010; Wu et al., 2010; Roca Jalil et al., 2015), rectorite (Wang et al., 2011; Jiang et al., 2013), and fluorohectorite (dos Santos et al., 2018).

Effect of OC: The influence of OC content on ciprofloxacin adsorption in soils has been inconclusive based on several studies. Teixido et al. (2014) found a significant correlation between the K_d values and OC by comparing two different loamy soils from Spain and amending them with different concentrations of humic acids (0,1,3,5 wt %). Zhang et al. (2009) found that sorption of norfloxacin in three soils with SOM removed was higher than that of three bulk soils where SOM was retained, indicating a negative relationship between sorption and SOM. The authors concluded that this can be possibly explained by either more sorption sites in clay minerals were available for norfloxacin because of SOM removal or that negative charges on the SOM of the bulk soil could partially block the sorption of norfloxacin. Zhou et al. (2014) suggested that ofloxacin sorption decreased with increasing OC in soils in the same geographic location, but comparing all 11 soils regardless of geographic location, the authors did not find a significant relationship between sorption and OC. Pan et al. (2012) found that sorption of ofloxacin significantly decreased when OC increased. However, several other studies found little to no relationship between sorption of ciprofloxacin and SOC. Carrasquillo et al. (2008) and Vasudevan et al. (2009) both found that PCA results did not show a significant correlation between K_d values and OC. In these studies, the same 30 soils were used (Jones et al., 2005) in which ranged from 0.05-8.93% OC from five different soil series (Alfisols, Inceptsols. Spodosols, Ultisols, and Vertisols). Figueroa-Diva et al. (2010) also found no significant correlation between K_d and OC using 7 of the soils from the study of Jones et al. (2005). Leal et al. (2013) found no significant correlation between K_d and OC using 13 soils from 6 soil orders (oxisols, ultisols, entisols, inceptisols, alfisols, mollisols) with OC range of 6.7-213.4 g kg^{-1}. It is important to note that 12 of the 20 soils used in the present study were from the Mollisol soil order and had various OC compared to only one soil from the above studies, suggesting that soil order can influence ciprofloxacin sorption. The results of the present study suggest that organic matter could have increased the number of cation exchange sites available for ciprofloxacin sorption.

The influence of OC on other antibiotic families has been widely reported and is widely variable in comparison between families. A direct relationship between OC and sorption has be suggested for the sulfonamide antibiotic class with Srinivasan et al. (2014) concluding that hydrophobic partitioning onto soil organic matter was a dominant sorption pathway for sulfonamide antibiotics. Higher K_d values were observed in soils with high OC for both Sulfamethoxazole (Drilla et al., 2005; Srinivasan et al., 2013) and Sulfamethazine (Lertpaitoopan et al., 2009). In comparison, no significant relationship was found between OC and sorption of antibiotics from both the tetracycline and macrolide families (Jones et al 2005; Srinivasan et al., 2014).

Effect of pH: The determination of little significance between the relationship of sorption of ciprofloxacin and pH in the present study was concluded based on the natural soil pH. For other studies that determined that ciprofloxacin sorption was pH-dependent, the pH effect was measured by adjusting soil pH to desired target pHs through the addition of acid or base, and then observing the trend between each individual soil (Vasudevan et al 2009; Wu et al., 2012). Vasudevan et al.

(2009) concluded that ciprofloxacin sorption was pH-dependent due to the form of positively charged ciprofloxacin ion that dominated adsorption at a lower pH, while adsorption decreased as pH increased. The authors found that ciprofloxacin adsorption followed either two trends: a decrease in sorption with an increase in pH, with the greatest sorption found in pH range of 3-5.5 or an initial increase in sorption, a peak at pH of 5.5 and a decrease in sorption at pH range of 7-8.

Similar results of ciprofloxacin adsorption were observed by Wu et al. (2012) on either sodium (Na), calcium (Ca), or aluminum (Al) montmorillonite, by Córdova-Kreylos and Scow (2007) on three California salt marches, and by Zhang and Huang (2006) on goethite. However, other studies have concluded an inconclusive relationship between sorption and pH. Wu et al. (2010) found that at an initial concentration of 1500 mg L^{-1}, the amounts of ciprofloxacin adsorption were relatively constant at 209 to 300 mg g^{-1} in the pH range of 3 to 8, potentially indicating that the ammonium group in the zwitterionic form could contribute to cation exchange. Because none of our soils tested had a pH value that was above the pKa_2 value of 8.74, we assume that the dominant form of ciprofloxacin adsorbed was in the cationic or zwitterionic form, with little interaction of the anionic form.

Other fluoroquinolones antibiotics are also known to have pH-dependent sorption. Qin et al. (2013) investigated the effect of pH on sorption of levofloxacin onto goethite and found that an increase in electrostatic repulsion when the pH is raised contributes to a decrease in adsorption of levofloxacin and that the maximum adsorption occurred at pH of 6, which is near the pKa1 value of 5.45. At a pH above 7, most of the carboxyl groups of levofloxacin were deprotonated leading to a decrease in sorption. Li et al. (2017) found that ofloxacin sorption onto kaolinite was pH dependent with a pH range of 3 to 10. The authors found a decrease in the positively charged ofloxacin ion when the pH was greater than 7. Zhang et al. (2009) found that norfloxacin in solution changed as a result of shifted solution pH and that in a pH range of 3.4 to 7.5, basic groups of the norfloxacin ion are protonated leading to an increase in positively charged ions that can bind with CEC sites.

This trend in pH-depended sorption was also observed in other antibiotic classes. It was observed that the maximum sorption capacity for tetracycline to montmorillonite and kaolinite decreased with when the pH was raised from 1.5 to 11 (Porubcan et al., 1978), while the adsorption decreased when the pH was raised from 4 to 9 (Figueroa et al., 2004; Wang and Wang 2015). It was also found that when the surface of clays contains large amount of exchangeable cation, pH can alter the number of positively charged oxytetracycline ions in soils (Wang and Wang 2015). Lertpaitoonpan et al. (2009) found that K_d values of sulfamethazine decreased as the pH increased from 5.5 to 9 for each of the soils tested. This could be because as the pH increases, the anionic form of sulfamethazine becomes dominant over the positively charge form (Wegst-Uhrich et al., 2014). Similar trends of increasing K_d values with decreasing pH was observed with tylosin, sulfachloropyridazine, and oxytetracycline adsorption (ter Laak et al., 2006).

Effect of soil management practices on ciprofloxacin adsorption: Soil organic matter is composed of plant, animal, and microbial residues at various stages of decomposition, which can influence biological, chemical, and physical properties of the soil (Sylvia et al., 1998). Eighty percent to 100% of organic matter is humic material, which arises from chemical and biological degradation of plant and animal residues and from synthetic activities of microorganisms (Schnitzer and Khan, 1975; Sylvia et al., 1998). The CEC for soil organic matter can range from 250 to 400 meq $100g^{-1}$ (Moore, 1998), and can contribute 20-80% of CEC sites in mineral soils (Sylvia et al., 1998). Soil organic matter contains large numbers of the carboxylic functional groups that promotes antibiotic adsorption through hydrogen-bonding, ion-dipole, and aromatic electron donor-acceptor processes (Sibley and Pedersen, 2007; Conkle et al., 2010; Riaz et al., 2018). However, organic matter can shield cation exchange sites and cause a decrease in adsorption (Wang and Wang, 2015).

The significant influence of cultivation on ciprofloxacin adsorption can possibly be attributed to the type and chemistry of SOC found in plant litter for natural systems and agricultural practices that build up organic matter in cropping systems. Other factors, such as climate conditions, types of vegetation, and basic soil properties can influence SOC (Alvarez and Lavado, 1998; Dawson and Smith, 2007). Cultivation depletes SOC through tillage practices, which degrades the soil structure by the destruction of soil aggregates, causing organic matter to be transformed by microorganisms (Poeplau and Don, 2015) and through the removal of crop biomass during harvest (Burke et al., 1989; Drewniak et al., 2015).

Grasslands, pastures, and forests generally have higher SOC than cultivated counterparts due to the depletion of soil organic matter during cultivation (Greacen, 1958). Guo and Gifford (2002) found that 42% of SOC was lost through cultivation of forest land, and 59% was lost through cultivation of pastureland. Root distributions can affect the placement of carbon in soils, as root allocation can affect the relative amount of carbon that can reach the soil surface. Jackson et al. (1996) reviewed root distributions between grasses, trees and shrubs and found that grasses had the shallowest root profiles while shrubs had the deepest root profiles (Jobbagy and Jackson, 2000). Fresh root inputs may prime microbial activity, leading to faster decomposition of older organic matter (Fontaine et al., 2007; Kuzyakov and Gavrichkova, 2010; Schmidt et al., 2011). Grazing management of grasslands and pastures can also affect SOC, with higher levels of SOC reported on grasslands that contain C4 or C3-C4 mixed species (McSherry and Ritchie, 2013). Grasslands tend to have less recalcitrant organic material compared to forest litter, which is easier to decompose by microorganisms (Smith, 2008). Lignin content is another important control of decomposition rates in soils (Menteemeyer 1978, Melillo et al., 1982, Austin and Vitousek 1998), and may contribute to differences of SOC found in forests and grasslands, as woody inputs generally have lower decomposition rates which can increase SOC storage in surface soils compared to grasslands (Jobbagy and Jackson, 2000).

In order to replenish SOC in cropping systems, the use of fertilizers and the incorporation of crop residues can increase SOC (Ren, 2020). The incorporation of crop residues to soil has been shown to increase the SOM of topsoil in many long-term field experiments (Salines-Garcia et al., 2001; Chan et al., 2003; Heenan et al., 2004; Wang et al., 2004; Alvarez, 2005). When crop residues are incorporated into soils, they can undergo decomposition and mineralization by microorganism and eventually become soil organic matter (Singh and Rengel, 2007). The addition of crop residues to soils can enhance numerous soil properties such as ion exchange capacity, soil structure, and water holding capacity (Dhaliwal et al., 2019). The use of certain crops can also improve SOC, with perennial crops/forages and cover crops shown to have higher SOC stocks (Jarecki and Lal, 2003). Crops with extensive root systems can also promote SOC storage (Kätterer et al., 2011). The use of fertilizers in cropping systems has also been known to promote SOC when crop residues are utilized (Halvorson and Reule, 1999; Alvarez, 2005).

CONCLUSION

The sorption capacity of ciprofloxacin in the tested 20 diverse soils ranged from 8 to 141 g kg^{-1}; K_d values ranged from 23 to 200 mL kg^{-1} soil; and K_{oc} values ranged from 54 to 2146 mL g^{-1} OC. Clay content was the most significant factor that influenced sorption capacity and the K_d of ciprofloxacin, as demonstrated by their significant correlation coefficients and by principal component analysis. The correlation coefficients *(r)* between clay content and sorption parameter were 0.92*** and 0.64*** for sorption capacity and K_d, respectively. CEC also had a significant relationship with sorption capacity and K_d values while SOC had a significant relationship with sorption capacity. The influence of pH and K_{oc} on sorption of ciprofloxacin was not significant. In soils originated from cultivated cropland, there was a strongly significant relationship between SOC and sorption capacity or K_d values, while those relationships were not observed in the uncultivated soils. Soils are effective in restraining the mobility of ciprofloxacin through adsorption and the effectiveness increases with clay content.

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CHAPTER VI

CONCLUSION

Based on P input and output, 100% of added manure P and fertilizer P were recovered. Following 89 years of chemical fertilizer application under continuous winter wheat cultivation, over 50% of added chemical fertilizer P remained in the top 15 cm of soil. Excluding grain P, all added chemical fertilizer P was found in the top 30 cm of the soil, while by average 40% of added manure P were found in the 30-90 cm of the soil profile. Considering the manure treatment has been in place for 119 years, it is not likely that manure P would reach ground water and poses risk to P contamination. Further, manure P leaching to lower soil profile but still stay within the plant root zone could potentially enhance P use efficiency. Data also suggested that P accumulation pattern over soil profile was influenced by crop uptake activities, suggesting that slow P uptake may allow labile P more time to leach further down in the soil profile. However, the transported distance was limited, which resulted in P being relocated to the most active nutrient uptake zone by wheat plants. Further, reasonable amount of P application has low potential for P loss to the environment.

Sorption capacity of ciprofloxacin in the tested 20 diverse soils ranged from 8 to 141 g kg^{-1}; distribution coefficient (K_d) values ranged from 23 to 200 mL kg^{-1} soil; and soil organic carbon-water partition coefficient (K_{oc}) values ranged from 54 to 2146 mL g^{-1} organic carbon.

Clay content was the most significant factor that influenced sorption capacity and the K_d of ciprofloxacin, as demonstrated by their significant correlation coefficients and by principal component analysis. The correlation coefficients (r) between clay content and sorption parameter were 0.92*** and 0.64*** for sorption capacity and distribution coefficient, respectively. CEC also had a significant relationship with sorption capacity and K_d values while SOC had a significant relationship with sorption capacity. The influence of pH and K_{oc} on sorption of ciprofloxacin was not significant. In soils originated from cultivated cropland, there was a strongly significant relationship between organic carbon and sorption capacity or K_d values, while those relationships were not observed in the uncultivated soils. Soils are effective in restraining the mobility of ciprofloxacin through adsorption and the effectiveness increases with clay content.

The findings of this study concluded that both natural and anthropologic sources contribute to environmental contamination. Understanding the mobility and fate of contaminants in the soil environment could facilitate developing management strategies to limit their negative impact while preserving the quality of life.

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