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COMPARISON OF SOIL PHOSPHORUS ACCUMULATION IN WASTEWATER-IRRIGATED FORESTS AND CROPLAND

A Thesis in

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ABSTRACT

Land treatment of municipal wastewater effluent avoids direct nutrient discharges to surface waters, but the transport and fate of these nutrients in soil systems needs to be understood. The Pennsylvania State University has applied secondary treated wastewater effluent to forests and agricultural cropland from 1963 – 1976, and continuously since 1983 at the Living Filter (LF) site. The objective of this study was to characterize soil phosphorus (P) accumulation for contiguous wastewater-irrigated forested and grassed areas of the LF. An adjacent unirrigated area served as control. Soil cores were collected from the Hagerstown soil, and divided into five layers by depth (0 – 15, 15 – 30, 30 – 45, 45 – 60, and 60 – 75 cm). The samples were analyzed for Mehlich-3 extractable P, aluminum (M3Al), iron (M3Fe), copper, calcium, as well as pH, total P (TP), and percent organic matter content.

A TP mass balance was performed for the crop field and forest soils for the top 75 cm of soil. Effluent applied P was estimated using historical data and average annual TP loading rates. Biomass removal was subtracted from applied P to determine the net P applied with wastewater irrigation. Control site soil data were used as a baseline to establish the amount of applied TP retained in the top 75 cm of soil since irrigation commenced. The mass balance indicates that 63 and 70% of wastewater-applied TP cannot be accounted for in the top 75 cm of soil in the field and forest, respectively. Because extensive records have been kept of effluent application rates and P concentrations, as well as harvested forage yields and nutrient contents, it is unlikely that imprecision in the values used in the mass balance can explain the magnitude of the unaccounted for effluent-applied P.

Because the samples in the cropped field were taken at summit landscape positions, it is likely that surface runoff and subsurface lateral flow of effluent P, documented by other

researchers, is partially responsible for the deficit of P in the 0-75 cm soil layer. Moreover, changes in the P-retention ability of the soil and the high hydraulic loading rate (irrigation plus natural precipitation of ~300 cm water per year) has probably caused leaching of P below the 75 cm depth.

The capacity of the soil to assimilate and renovate effluent-applied P has been reduced as a result of irrigation with wastewater. M3Al and M3Fe results suggest podsolization may have occurred in both the field and the forest soil profiles, which could explain the lower P-retention properties of the surface soil layers. Since the soils are no longer acidic, the mobilization of Al and Fe is likely less significant than early in the system operation. Copper, which forms strong complexes with soil organic matter, also appears to have leached to a greater extent from the surfaces layers in the wastewater-irrigated forest.

If leaching below 75 cm has occurred, the deep soils (> 200 cm) and distance (> 30 m below surface) to the permanent groundwater table suggest that the penetration of P into the subsoil of the forested area has had little impact thus far on groundwater water quality. Additional research is warranted to understand the long-term impacts of P application on the sustainability of land treatment as a viable means of recycling municipal wastewater effluent.

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Chapter 1

Introduction

The process of effectively treating wastewater is increasingly more important in a world where clean and reliable sources of fresh water are becoming scarce. In developed countries wastewater is typically piped to a treatment facility, treated to fulfill regulatory requirements, and then discharged to surface waters. One important environmental implication to surface water discharge is that effluent nutrients can accelerate eutrophication in receiving waters. Since most freshwater systems are phosphorus (P)-limited, P is particularly a concern in this regard. Land application of effluent avoids this issue, but the fate of nutrients at effluent-irrigated sites must be addressed. This investigation will focus on the fate of P at sites irrigated with wastewater effluent.

1.1 Effect of Excess Nutrients on Natural Freshwater Systems

Plant life in freshwater systems require many nutrients, chief among them are nitrogen (N) and P. In freshwater systems, P is often the most limiting nutrient for plant growth (USEPA, 2007a). Excess nutrient loading in freshwater systems can have a negative impact on aquatic organisms. If excess P is supplied through an external source, such as from a wastewater treatment facility, the stream can exhibit an increase in primary productivity, called accelerated eutrophication (USGS, 2008). Plant life, especially algae, benefit most from an increase in P and can form large blooms. Algal blooms block sunlight to benthic vegetation and can deplete the dissolved oxygen concentration in the water. In the United States, eutrophication has created anoxic zones in the waters of the Chesapeake Bay, Lake Erie and the Gulf of Mexico (Kalff,

2002). Anoxic zones are often called "dead zones" because fish and other aquatic organisms cannot survive in low-oxygen environments. Blooms of dinoflagellates, a type of algae, can also cause fish kills and infect humans with harmful toxins (NMNH, 2002).

According to the USEPA, in 2009 44% of the streams, 64% of the lakes, and 30% of the bays and estuaries surveyed were impaired (USEPA, 2009), with the most prevalent impairment being the inability to sustain healthy populations of aquatic organisms. The wadeable streams assessment section of the National Water Quality Index shows that 41.9% of wadeable streams are in poor biological condition. The assessment claims that 30.9% of poor stream health is caused by excess P (USEPA, 2009).

Accelerated eutrophication is not simply an environmental issue, but also has a significant economic impact. United States commercial fisheries in the Chesapeake Bay, Great Lakes, and Gulf of Mexico contribute $850 million yearly to the U.S. economy and comprise 20.6% of the total U.S. fish catch (Pritchard, 2008).

1.2 Advanced Wastewater Treatment

As a result of the observed water quality problems associated with excess nutrient loading in freshwater systems, there has been an increase in regulation of municipal wastewater treatment plants. As the restrictions for discharge of effluent to surface waters tighten, municipalities will be looking for more efficient and economical methods of achieving higher quality effluent. The most common method for P removal is chemical treatment (Davis and Cornwell, 2008), but biological processes can also be used (Kalff, 2002). Biological nutrient removal (BNR) is a process that is aimed at reducing the N and P loading to streams. Upgrading a sewage treatment facility to perform BNR is costly (USEPA, 2007a,b). The additional treatment process is referred to as tertiary, or advanced wastewater treatment. Wastewater

irrigation is an alternative method for achieving advanced wastewater treatment by allowing the natural soil, plant, and microbial action to attenuate and transform the nutrients. Wastewater can be irrigated on croplands and forests for the beneficial reuse of water and nutrients (Toze, 2006). However, as spray irrigation of wastewater gets more attention, questions arise about the fate and transport of nutrients over the long term.

1.3 Investigation into Penn State Living Filter

The Pennsylvania State University has conducted research on the crop field section of their own wastewater irrigation system since the early 1960s, and much data have been collected (e.g. Hook et al., 1973; Sopper and Kardos, 1973; Kardos and Hook, 1976; Sommers et al., 1979; Walker and Lin, 2008; Jaiswal and Elliott, 2011). The Living Filter system has been studied for over 40 years. Previous research has been conducted on crop uptake of nutrients (Hook et al., 1973; Kardos and Hook, 1976), nutrient behavior in crop soils (Hook et al., 1973; Sommers et al., 1979), forest growth response to irrigation water (Sopper and Kardos, 1973), and N leaching in the forest (Hook and Kardos, 1978). Limited research, however, has been conducted on nutrients in the forest soils at the LF. The forest receives similar irrigation levels (and thus P loading) as the crop fields, so knowledge of the fate of P in forest soils is important. The long-term behavior of P in the wastewater irrigated forest should be studied further. A detailed analysis of P in the forest soils is necessary to understand the effectiveness of the wastewater irrigation system in mitigating negative environmental impacts associated with P. Biomass is not removed in the wastewater-irrigated forest at Penn State and hence the soil accumulation of P is expected to be different than the irrigated cropped fields. This research investigated P dynamics in forest and crop soils related to irrigation of wastewater effluent.

Chapter 2 is a review of literature relating to P dynamics in wastewater-irrigated soils. Phosphorus in municipal wastewater is introduced and followed by background information on land application of wastewaters. A case study approach was used to consider individual wastewater irrigation systems, concluding with the Penn State Living Filter system where the present study was conducted. The goals, objectives, and hypotheses of this research are presented in Chapter 3. In Chapter 4 the materials and methods of the research are described. Detailed descriptions of sample location, collection, and analyses is presented. Information on the statistical methods used is also included.

The study results are presented and discussed in Chapter 5. Statistical comparisons are made between three sampling locations: cropped field, irrigated forest, and an unirrigated control site. Soil depth constituent profiles are evaluated and compared between the three locations. Chapter 6 summarizes the major findings of the research and discusses the implications for long-term sustainability of effluent-irrigated landscapes. Suggestions for future research are included.

Chapter 2

Literature Review

This review focused on P in municipal wastewater treatment, negative effects of wastewater discharge, the benefits of land-application of municipal wastewater, P movement and storage in wastewater-irrigated soils, and P accumulation in wastewater-irrigated forests. A case study approach was used to highlight the results of other studies as they relate to the current research.

2.1 Phosphorus in Municipal Wastewater Treatment

To investigate the accumulation of P in soils in wastewater irrigation systems the P content of wastewater effluent must be known. Municipal wastewater treatment facilities receive flows from residential and commercial sources. The average total P (TP) concentration in untreated domestic wastewater is approximately 10 mg/L (Davis and Cornwell, 2008). Through the treatment process, biological oxygen demand and suspended solids are reduced. Nutrient loading and other contaminants are also removed, but the process is ineffective at achieving total removal of N and P. Typical TP concentrations in effluent from a secondary treatment system are 3 – 4 mg/L (USEPA, 2007a). Some states have stringent effluent regulations (TP $\leq$ 1 mg/L), which require additional treatment to remove P (Davis and Cornwell, 2008). P removal is most commonly achieved through chemical precipitation with ferric chloride, alum, or lime (USEPA, 2007a, Davis and Cornwell, 2008). Another option for advanced wastewater treatment is biological nutrient removal (BNR) (USEPA, 2007b). Effluent from wastewater treatment facilities that perform chemical/BNR P removal generally contains $\leq$1 mg/L TP (Kalff, 2002; USEPA, 2007b). Retrofitting an existing wastewater treatment system to include BNR can cost

millions of dollars and can be cost prohibitive for municipalities (USEPA, 2007a,b). Wastewater discharge can introduce nutrients, suspended solids, pathogens, and hormones/pharmaceuticals to natural waters. These constituents have the potential to modify or destroy the stream biota and limit the downstream use of water. Nutrients, particularly N and P have received much attention because of the negative effects associated with elevated levels within a water body.

2.3 Introduction to Land-Based Application of Municipal Wastewater

Land-based application of secondary treated wastewater is an alternative to conventional advanced wastewater treatment. The benefits of applying wastewater to the surface of the land include irrigation of crops, reuse of nutrients, reduced pollution to surface waters, and recharge of local groundwater aquifers (Lin et al., 2006; Toze, 2006; Walker and Lin, 2008).

Land-based application of wastewater effluent can benefit production agriculture by providing nutrients, micronutrients, and water for crops. Developing countries can benefit from improved stability in agriculture and water supplies, particularly in semi-arid and arid regions. Groundwater recharge can provide a sustainable source of drinking water for local municipalities or serve as a source for additional irrigation (Hamilton et al., 2007). Land-based application of wastewater reduces the impact on water quality by eliminating the discharge of nutrient-laden wastewater to surface water. Along with nutrients, pathogenic organisms and pharmaceuticals are filtered out by the soil (Lin et al., 2006; Walker and Lin 2008). Wastewater irrigation is particularly prevalent in the Middle East where the demand for freshwater has exceeded supply (Hamilton et al., 2007).

The nutrient content of wastewater can reduce the amount of fertilizer required for optimum crop growth. In fact, the amount of effluent-applied P usually exceeds crop nutrient requirements (USEPA, 2006). In some cases crop production in wastewater-irrigated soils can

exceed the production of crops grown without wastewater irrigation (Parizek et al., 1967; Barton et al., 2005).

There are three main categories of land-based application of wastewater based on the purpose of the system and hydraulic loading rate: Slow Rate, Overland Flow, and Soil Aquifer Treatment. Slow Rate (SR), the most common system in operation, consists of an effluent distribution system that typically applies wastewater with sprinklers to the landscape. An SR system has an effluent application rate ranging from 60 to 610 cm yr^{-1} (USEPA, 1977). These systems are designed to infiltrate all effluent and runoff is prohibited. Vegetation is grown to beneficially use the applied water and nutrients. This review focuses on accumulation and fate of soil P in SR systems.

2.4 Phosphorus in Land Application of Municipal Wastewater

The behavior of ions in the soil is based on adsorption, chemical precipitation, ionic exchange, biochemical transformation, biological adsorption, and physical filtration (Parizek et al., 1967). The behavior of P in cultivated soils depends on a variety of factors including soil type, fertilizer (and in this case wastewater) application rates, annual precipitation, vegetation cover, and land management. Movement of P in soil depends on the physical, chemical, and biological characteristics of the surface and subsurface soils (Barton et al., 2005).

Phosphorus applied to soil quickly reacts with the minerals in the soil, particularly aluminum (Al) and iron (Fe) oxides in the pH range preferred for agricultural crop production. Chemical precipitation with calcium (Ca) occurs more slowly, and Ca bound P becomes immobile and unavailable to vegetation. In acidic soils ($pH < 7.0$) P is typically fixed in the soil by Al and Fe, with greater adsorption occurring in the soil pH range of 3 - 5. At $pH > 7.0$ P binds with Ca and precipitates out of the soil solution (Havlin et al., 2005). In the early stages of the LF

project the soils were acidic (Parizek et al., 1967; Hook et al., 1973), but continual application of treated wastewater effluent has increased the pH (Sopper, 1986), and the surface layers are now pH 7.0 or higher (Walker and Lin, 2008).

2.5 Case Studies in Wastewater Irrigation

Reports on existing wastewater irrigation systems were reviewed to evaluate what is known about the behavior of P in wastewater-irrigated forests and cropland. Each system is unique because of differences in climate, soils, effluent characteristics, and management. This is not an exhaustive review of SR systems; rather it focuses those studies where P accumulation and fate have been investigated.

2.5.1 Muskegon Wastewater Land Treatment System

The Muskegon Wastewater Land Treatment System in Muskegon County, Michigan was started in 1974. Wastewater from a paper mill (50% of effluent), industrial (25% of effluent), and domestic sources (25%) is applied to 53 circular fields consisting of 2104 ha of farmland. The soils are sandy and were acidic (5 - 6 pH) prior to irrigation with wastewater. The site contains three soil types exhibiting similar physical and chemical properties.

After wastewater application the soil pH and exchangeable Ca concentrations increased (to pH 7 in 2003) because of the alkaline nature (pH 8.5) and high salt content of the effluent (Hu et al., 2006). Irrigation has caused leaching and removal of Al in all three soil types (Hu et al., 2005). Hu et al., 2006 concluded that > 70% of absorbed P is bound to Ca and Mg, in contrast with typical agricultural soils where Al and Fe dominate the P sorption.

Total P has increased as a result of irrigation with wastewater effluent, but no increase in available P has been observed (Hu et al., 2006). Isotherm test shows that wastewater effluent can continue to be applied for >50 years on all three soil types (Hu et al., 2006).

2.5.2 Cleveland Waste Water Pollution Control Works, Queensland, Australia

Irrigation with wastewater effluent at the Cleveland Waste Water Pollution Control Works began in 1991. Wastewater effluent is applied to 15 ha of pasture. The sandy A horizon is 30 cm deep underlain by a low permeability clayey B horizon. Vegetation growing in the pasture is cut but not removed. Surface runoff occurs because application rates exceed the infiltration capability of the soil.

The results indicate that P has accumulated significantly in the soil, but only a fraction of the total applied P. The sandy A horizon has little capacity to store P, and low hydraulic conductivity of the underlying clay layer (B horizon) prevents infiltration beyond the A/B interface. The majority of retained P was stored in the organic material on the surface from accumulated vegetation. Adsorption curves overestimated the capacity of the system to store P, and did not take into account accumulation of P in organic matter on the surface (Menzies et al., 1999).

2.5.3 Rotorua Land Treatment System, Whakarewarewa Forest, New Zealand

In 1991 the Rotorua Land Treatment System was constructed to irrigate wastewater effluent in the nearby Whakarewarewa Forest. Activated sludge removes 80% of N and P at the municipal wastewater treatment plant. In addition, the treatment system also includes nitrification and denitrification steps to reduce N in the effluent. The effluent is irrigated on 193

ha of *Pinus radiata* (Monterey pine) grown in 25-30 year cycles. Wastewater is applied at a rate of 71 mm wk^{-1}. Soils are volcanic in origin and have a sandy loam texture, with high infiltration rates (Tomer et al., 2000). After four years of wastewater application 97% of applied P was retained in the top 20 cm. "Concentrations of P in soil solution collected at 0.9 m depth have been consistently non-detectable and thus provide no indication of P movement below the soil root zone (Gielen et al. 2000). Isotherm tests show that the soils can accept effluent applied P for an additional 70 - 80 years (Tomer et al., 2000).

2.5.4 Wagga Effluent Plantation Project, Wagga Wagga, NSW, Australia

The Wagga Effluent Plantation Project was started in 1991. A plantation was established on improved pasture after two fertilizer treatments (superphosphate at 5 kg P ha^{-1}, Calphos™ at 10 kg ha^{-1}). Plots of *Pinus radiata* and *Eucalyptus grandis* were planted and irrigated with wastewater effluent when evapotranspiration exceeded precipitation. After 5 years of irrigation with wastewater effluent, 97% of applied P was retained in the top 0.7 m of soil in the *Pinus radiata* plot (Falkiner and Polglase, 1999).

2.5.5 Apple Valley, Minnesota

Laterell et al. (1982) conducted a 5 year study of wastewater irrigation on corn plots in Minnesota. The study consisted of three treatments: a control treatment that received fertilizer and irrigation with groundwater, a low treatment which received 125 cm yr^{-1} of wastewater effluent, and a high treatment that received 236 cm of wastewater effluent per year. Field drains were installed at 150 cm depth to collect percolating wastewater for analysis. The soil type was

Waukegan silt loam (Typic Hapludoll). Levels of P increased in the soil water at 60 cm in the high treatment plots, showing the possibility of P leaching through the soil profile. The low treatment plots did not have evidence of P leaching (Latterell et al., 1982).

2.5.6 East Lansing Sewage Treatment Plant

Burton and Hook (1979) applied wastewater to forested plots in Michigan for two years. Their system included control, high and low treatments. The high and low treatments received 10 and 5 cm of wastewater effluent per week respectively. The high treatment application rate was greater than the soil infiltration rate, generating surface runoff. The forest soil in the 5 cm per week treatment was able to retain 96.5% of the applied P (Burton and Hook, 1979).

2.5.7 Penn State Living Filter

Researchers at The Pennsylvania State University began the Wastewater Renovation and Conservation Research Project in 1962. Commonly referred to as the "Living Filter" (LF), the wastewater-irrigation system was designed to apply 5 cm wk^{-1} of secondary treated wastewater effluent to crop fields and forestland. Wastewater is irrigated on a *Pinus reisnosa* (red pine) (Morrison soil), agricultural crops (Hublersburg and Hagerstown), and an abandoned field (Hagerstown). The abandoned field area has since developed into a forest (Parizek, et al. 1967, Hook, et al. 1973).

After two years of wastewater application Parizek et al. (1967) determined that 99% of the applied P was retained within the top 20 cm of the Hagerstown silty clay loam soil. Later Kardos and Hook (1976) investigated P in the soil of a *Pinus resinosa* plantation at the LF. Their findings show that 96% of wastewater-applied P was stored in the upper 1.2 m of the sandy loam

(Morrison series) soil. The deeper percolation of wastewater applied P was attributed to the low clay content of the Morrison soil (Kardos and Hook, 1976). Over the life of the system, the literature shows the soils are capable of renovating the wastewater and storing or removing P.

2.6 Summary of Case Studies: Phosphorus in Wastewater-Irrigated Soils

The case studies highlight different management strategies, and results vary depending on multiple factors, chief of which is the biological, chemical, and physical properties of the soils. Sandy soils allow for fast percolation of wastewater and typically contain less organic matter and other P binding media, which allows for vertical migration of P and other nutrients. Sommers et al. (1979) found that in sandy loam soils (Morrison series) P can more-readily migrate downward through the soil profile than in a clay loam (Hublersburg). In a SAT system studied by Lin et al (2006) sandy soils with low clay, aluminum (Al), iron (Fe) and organic matter content were found to have significant P accumulation at a depth of 9.5 meters.

A particularly unique case studied by Menzies et al., (1999), is a wastewater reuse system with sandy surface soil and clayey subsoil. The clay subsoil would not allow deep percolation of irrigation water; and instead generated runoff. The runoff from the site had concentrations of P that exceeded the levels regulated by the Australian government for treated municipal wastewater discharges (Menzies et al., 1999).

Aside from these extreme cases studied by Lin et al. (2006) and Menzies et al. (1999), most of the wastewater applied P appears to be contained within the upper layers of a variety of soil types (Barton et al., 2005) and management strategies (Burton and Hook, 1979, Latterell et al., 1982, Falkiner and Polglase, 1999, Tomer et al., 2000, Hu et al., 2005, Hu et al., 2006). Hook et al. (1973) studied clay loam soils (Hublersburg) at the LF. Their findings showed that after 10

years of wastewater application to crop fields, soil P levels at 1.2 m were consistent with background levels in control soils, and 90% of the applied P was stored within the top 15 cm.

Other studies conducted in the crop soils at the LF have shown that P from wastewater irrigation has not migrated significantly below 1.2 m (Kardos and Hook, 1976; Sommers et al., 1979; Jaiswal and Elliott, 2011). When biomass is harvested, leaching of wastewater-applied P appears to be unimportant in P management at the LF.

Harvested crops remove P from the soil permanently, but on sites where vegetation is not harvested P will eventually cycle back into the soil. In some cases (Hook et al. 1973; Menzies et al., 1999), wastewater applied P accumulation in soils is greater when crops are not harvested. Growing plants accumulate P and other nutrients in living biomass, and return the nutrients to the soil through decomposition of detrital material. In land-based waste disposal systems where vegetation is not harvested, decaying vegetation can retain and slowly release P and other nutrients into the soil. Menzies et al. (1999) found that high concentrations of P (~1500 kg P ha^{-1}) can accumulate in organic material on the soil surface in an unharvested wastewater-irrigated pasture.

2.7 Phosphorus in Wastewater-Irrigated Forest Systems

In the absence of suitable cropland for irrigation, forest soils provide an alternative sink for nutrients found in wastewater. Trees and other forest vegetation benefit from additional nutrients and water (Parizek et al., 1967; Sopper and Kardos, 1973). Vegetation and leaf litter prevent runoff of nutrient-laden irrigation water and allow for slow percolation through the soil profile.

Generally, P uptake by trees can range from 5 – 15 kg ha^{-1} yr^{-1} (Attiwill and Leeper, 1987 as reported by Falkiner and Polglase, 1999), but P retention is lower because fallen leaves and

branches return P to the soil through decomposition. Ducnuigeen et al. (1997) found that P retention of a variety of tree species is less than 5 kg ha^{-1} yr^{-1}. The P applied in wastewater at the LF is approximately 3.4 mg L^{-1} (Salada, 2007), with a 25-year average total P application of approximately 93 kg ha^{-1} yr^{-1} (Jaiswal and Elliott, 2011). Application of more P than required for tree growth makes this a P excess system.

Burton and Hook (1979) applied 5 cm wk^{-1} of secondary treated wastewater to forestland and found that 96.5% of the applied P was stored in the soil after two years. In the same study, wastewater was applied to a different site at 10 cm wk^{-1}, and the amount of stored P was reduced to 66%, because of runoff losses. Falkiner and Polglase (1999) studied P concentrations in the soils of a wastewater-irrigated plantation of *Pinus radiata* (Monterey pine). Labile P was measured in concentrations greater than background levels in the upper 0.5 m of the soil, whereas organic and inorganic P concentrations were significantly greater than control soils down to 1 m depth. The P applied exceeded the requirements for the trees in the plantation, but similar to the findings by Kardos and Hook (1976), 97% of the applied P was contained within the upper 0.7 meters of soil.

The accumulation of P in soil profiles at forested sites used for long-term effluent irrigation has received little attention. This topic, and comparison with an adjacent grassed field, are the basis of this research investigation.

Chapter 3
Goals, Objectives, Hypotheses

3.1 Research Goal

Nutrient management strategies can lead to an improvement of environmental health and more efficient use of nutrients. Movement of P in the soils of a wastewater irrigation system is important to understand because of the potential for harmful effects on water quality. Wastewater-irrigated forests and croplands are managed in different ways, which should influence the behavior of P in these systems. The crops are harvested annually, removing P from the soil, but forest biomass is not routinely harvested. Intuition suggests that the soil P concentrations in the forest should be higher than in the crop fields, but this assumption has not been tested. The goal of this investigation is to determine the vertical distribution of P in the wastewater-irrigated forest and cropland at the Penn State Living Filter system.

3.2 Objectives:

1. Collect soil samples at several depths in irrigated field, irrigated forest, and control forest.
2. Evaluate Mehlich-3, and TP to determine P concentrations of soil samples representing different depths of the soil profile.
3. Compare the M3P and TP concentrations by depth for forest, field, and control soils.
4. Calculate P sorption saturation ratio (Psat) based on Mehlich-3 extractable P, Al, and Fe data to gain insight into vertical movement of P in the soil profiles.

3.3 Hypotheses:

1. The surface soil levels of M3P and TP are higher in the irrigated cropland and forests than the unirrigated forest control.

2. Because of no biomass removal, concentrations of P in surface soils in the irrigated forest will be greater than in the field.

3. Mehlich-3 P has exhibited deeper migration in the wastewater-irrigated forests than the wastewater-irrigated field and control site.

Chapter 4

Materials and Methods

4.1 Site Description

The Penn State "Living Filter" (LF) is located near University Park, Pennsylvania, where secondary treated wastewater is applied via 3,100 sprinklers to approximately 209 ha of agricultural and forest land. The treatment areas in this investigation have received ≤ 5 cm of effluent per week from 1963 to 1976, and from 1983 to present. The treatments under investigation are a wastewater-irrigated field (field) and a wastewater-irrigated forest (forest). Both treatments and an adjacent control forest (control) are on Hagerstown (Typic Hapludalfs) silty clay loam soil (Walker and Lin, 2008). Wastewater is distributed to the field and forest by a series of irrigation lateral piping spaced at 24 m and applied with sprinklers.

The field is approximately 8.5 ha of tall fescue grass, which was previously cropped in reed canarygrass. Multiple cuttings are harvested each growing season according to demand for hay. The forest adjacent to the field is referred to as the "old field" or "abandoned field" in previous literature. The "old field" ceased agriculture production in the 1930s (Hook et al. 1973), and was in the process of succession when irrigation began. Prior to irrigation in 1963 the old field consisted of poverty grass, goldenrod, dewberry, and sparse *Picea glauca* (white pine) (Parizek et al, 1967). After the first few years of irrigation the vegetation in the old field changed to wild aster, goldenrod, wild carrot, and white daisy (Parizek et al. 1967). The vegetation has since grown into a forest ecosystem. Biomass is not removed from the forest, except to maintain access corridors for the irrigation laterals and sprinklers. The control site is a wooded area

adjacent to the field and forest sampling sites. The control consists of mixed hardwoods and has not received fertilizer or wastewater irrigation since the project began.

Figure 4.1- Aerial photo of Astronomy Site, with sampling locations at the Penn State Living Filter, University Park, PA. (a) forest, (b) field, (c) control forest.

4.2 Wastewater Treatment Plant

The wastewater treatment plant (WWTP) at Penn State University uses activated sludge and trickling filters to treat the municipal wastewater generated on the Penn State, University Park campus. The WWTP has the capacity to treat 4 million gallons per day (MGD), but is currently running at 60% of capacity. Characteristics of the treated wastewater effluent are provided in Table 4.1.

Parameter	Concentration
Total alkalinity (mg/L as $CaCo_3$)	179
Biochemical oxygen demand (mg/L)	8
Specific conductance (µmhos/cm)	1109
Total hardness (mg/L as $CaCo_3$)	245
Calcium (mg/L)	47.8
pH	7
Total suspended solids (mg/L)	5
Nitrate (mg/L as N)	12

Table 4.1 Average chemical characteristics of the municipal wastewater used for irrigation from Nov. 2005 until August 2006 (n=21) (Parizek et al., 2006). Calcium data from Kelso and Bowersox, 2004.

4.3 Soil Sampling Procedure

Five soil cores 1 m in length were collected from each of the three treatments in November and December 2009. The samples were collected with a tractor-mounted Giddings soil sampler. The Giddings is a hydraulic powered "direct-push" sampler that extracts an intact soil core from the soil surface to a specified depth. The cores in the irrigated treatments were collected adjacent to sprinkler heads on the local slope summits, 8 m from the lateral, and in the forest sampling locations where effluent was intercepted by vegetation were avoided. The locations were chosen to minimize the effect of topography on the results. The 15 soil samples were cut into subsamples in 15 centimeter increments. Subsamples represent depths of 0 - 15 cm, 15 - 30 cm, 30 - 45 cm, 45 - 60 cm, and 60 - 75 cm.

4.4 Soil Analysis

Each subsample was analyzed for a variety of soil parameters to gain an understanding of the behavior of P in each of the sampling locations. The subsamples were analyzed at the Penn State Agricultural Analytical Services Laboratory (AASL). All samples were air dried and ground to pass through a 2 mm (10 mesh) sieve. Samples were analyzed for Mehlich-3 P, Ca, Al, Fe, Cu; Total P; and percent organic matter.

4.4.1 Mehlich-3 soil extraction

The Mehlich-3 extraction is a soil test intended to replicate the extraction of nutrients from the soil by plants (Mehlich, 1984). Maguire and Sims (2002) determined that the Mehlich-3 test is capable of measuring the agronomic optimum P levels, soil P loss potential, Al, and Fe concentrations in soils. Soil was weighed (2.5g) and placed in a 100 mL bottle with 25 mL of 0.2 *N* CH_3COOH, 0.25 *N* NH_4NO_3, 0.015 *N* NH_4F, 0.013 *N* HNO_3, and 0.001 *M* EDTA. Solution was shaken 200 times per minute for 5 minutes on a reciprocating shaker. Each sample was analyzed for P, Al, Fe, Ca, and Cu using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

4.4.2 Total P Analysis

The soil samples were analyzed for Total P as per EPA method 3051 (USEPA, 1994). Soil (0.5g) was digested with 10 mL concentrated HNO_3 using microwave heating. The solution was then centrifuged and filtered and Total P was measured using ICP-AES.

4.4.3 Other Analyses

Soil pH was determined using a 1:1 mixture of soil and deionized water and measured with a calibrated electronic pH meter.

Percent soil organic matter was measured by loss on ignition. 5 g soil were dried at 105° C for two hours, and weighed. The weighed soil was heated at 360° C for two hours and then weighed again. The percent organic matter was calculated using the equation: ((Weight at 105° C - Weight at 360° C) x (Weight at 105° C $^{-1}$)) x 100

4.4.4 Phosphorus Sorption Saturation

Another method for quantifying the available P storage capacity is P sorption saturation. The P sorption saturation ratio (Psat) is the molar ratio of P and the potential P binding components of the soil, namely Al, and Fe:

$$\boldsymbol{Psat} = \frac{[\boldsymbol{P}]}{\boldsymbol{\alpha}([\boldsymbol{Al}]+[\boldsymbol{Fe}])} \qquad \textbf{Equation 1}$$

The most common method of quantifying the P, Al, and Fe for use in Equation 1 involves soil extraction with a dilute oxalate solution (McKeague, et al., 1971), but Mehlich-3 extractable data can also be used (Kleinman and Sharpley, 2002; Maguire and Sims, 2002). In acidic soils with Mehlich-3 soil test data, Equation 1 is used as shown with $\alpha = 1$. The Mehlich-3 procedure has been used successfully for predicting Psat at the LF site (Jaiswal, 2010).

4.5 Data Evaluation and Statistical Analysis

The data was analyzed statistically based on the advice of the Penn State Statistical Consulting Center. SAS version 9.2 was used to determine the statistical relevance of the data. An Analysis of Covariance was conducted to determine the statistical difference between the three treatments at each depth. Specifically, a generalized linear mixed model (PROC GLIMMIX) was used to analyze the data. The data was "sliced" by depth to compare values within each depth, rather than between depths. See Appendix for an example of the SAS code, as well as the tabular summary of the data.

Chapter 5

Results and Discussion

5.1 Mehlich-3 Phosphorus

The Mehich-3 P (M3P) soil concentrations in the forest, field, and control plots are given in Table 5.1 and shown in Figure 5.1 as a function of soil profile depth. The data show that after long-term application of wastewater, M3P has accumulated in the soil profile, particularly in the 0 – 15 cm and 15 – 30 cm sampling depths. Other studies (Sommers et al., 1979, Burton and Hook, 1979) have also shown an increase in available P as a result of irrigation with wastewater. Typical wastewater loading rates (5 cm wk^{-1}) in conjunction with average secondary effluent P levels (3-4 mg L^{-1}) contribute 93 kg P ha^{-1} yr^{-1}, exceeding the P removal rate of vegetation commonly grown on sites irrigated with wastewater (Elliott and Jaiswal, 2011).

In the surface layer (0-15 cm), the M3P soil concentrations in the field and forest are both significantly higher ($p < 0.05$) than the control forest, but M3P in the field is significantly higher than the forest ($p < 0.05$). At the 15 – 30 cm depth, M3P in the field is significantly higher than the forest ($p < 0.05$) and control ($p < 0.05$), but M3P in the forest is not significantly different from the control ($p > 0.05$). This finding is contrary to the first hypothesis, which states that the M3P soil concentrations in the forest would be higher than the M3P in the field and control soils. In the absence of biomass removal in the forest, M3P would be expected to accumulate at a higher rate than the crop fields, where P is removed annually through crop harvest. This is based on the assumption that the histories of previous P applications are similar for the two areas.

For the 30 – 75 cm interval, the M3P concentrations in the forest and field soil are not significantly different from the control soil, suggesting that M3P is being stored in the top 30 cm. In the early years of the LF system, Hook et al. (1973) also noted that significant accumulation of

Bray extractable P had occurred in the top 30 cm, but accumulation at 60 cm, however, was negligible. The data for this study suggest that available P concentrations at 60 cm remains largely unchanged since the early stages of irrigation at the site.

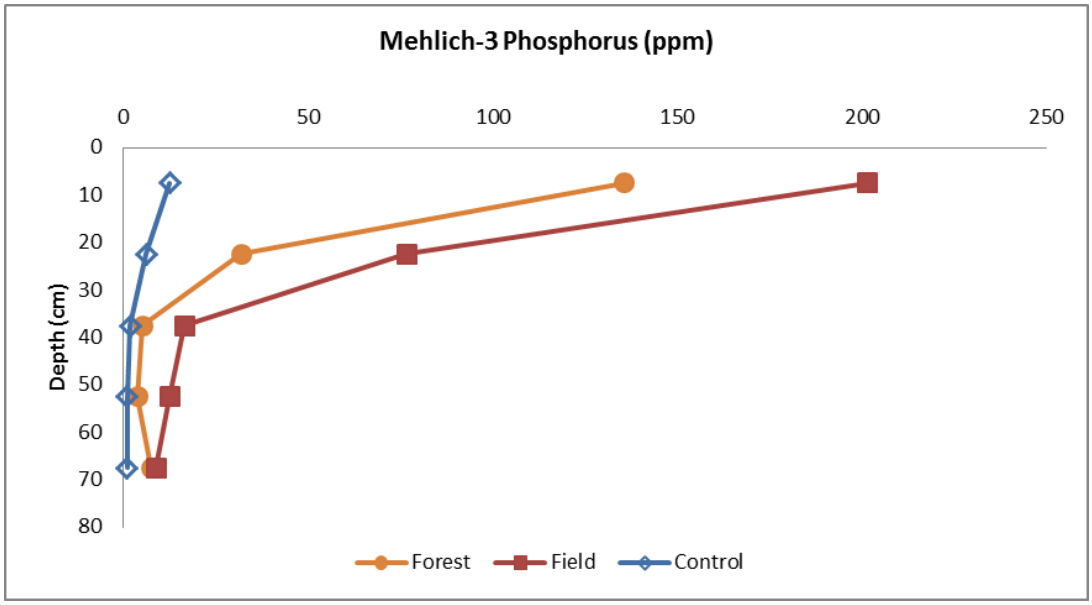

Figure 5.1- Mehlich-3 P concentrations (ppm) verses depth in forest, control forest, and field.

Despite receiving similar loading rates, the calculated total M3P in the top 75 cm of the soil is 368 kg ha^{-1} in the forest, and 632 kg ha^{-1} in the field. Mehlich-3 P has accumulated significantly in the surface soils of both irrigated treatments when compared with the control. The M3P accumulated from irrigation (difference between control and irrigated) in the forest is 323 kg ha^{-1}. Ducnuigeen et al. (1997) report in tabulated data that *Acer rubrum* (red maple) and *Liriodendron tulipifera* (yellow poplar) uptake 5 kg P ha^{-1}, and return 4 kg P ha^{-1} back to the soil on an annual basis, meaning forest biomass retains only 20% of the P taken up on a yearly basis. If forest biomass is not a luxury consumer of P, there must be other processes controlling P removal/transport in irrigated soils in addition to plant uptake.

	Depth (cm)	Field			Forest			Control		
		ppm		stdev	ppm		stdev	ppm		stdev
Mehlich-3 P	0-15	201.4	a	62.81	135.6	b	69.32	12.6	c	5.59
	15-30	76.8	a	46.79	32	b	22.83	6.2	b	4.76
	30-45	16.6	a	10.36	5.2	a	5.71	1.8	a	1.30
	45-60	12.6	a	15.16	3.8	a	5.96	1	a	0.00
	60-75	8.8	a	14.13	7.6	a	3.48	1	a	0.00
Total P	0-15	1089.1	a	86.74	754.7	b	150.65	329.6	c	41.30
	15-30	615.5	a	103.38	428.9	b	136.10	264.9	c	32.17
	30-45	398.9	a	51.00	287.1	ab	90.86	254.6	bc	15.45
	45-60	297.0	a	68.72	274.1	a	104.60	212.4	a	31.73
	60-75	270.2	a	78.34	305.1	a	127.28	217.8	a	29.66
Sum: Total P (kg ha^{-1})		5341			4100			2559		

Table 5.1 – Mean Mehlich-3 P and Total P and the standard deviations in the Field, Forest, and Control plots. Sum of Total P are calcualted values. Values followed by the same symbol are not statistically different (p = 0.05) for a given soil depth.

5.2 Total Phosphorus

The total P (TP) concentrations in the soils of the forest, field, and control are given in Table 5.1 and shown in Figure 5.2. The data show that the TP concentrations in the surface soils (0 – 15 cm) of the field were significantly higher than the forest and the control ($p < 0.05$). The TP concentrations at the 0 – 15 cm depth in the forest soil were also significantly higher than the control ($p < 0.05$). At the lower depths (below 45 cm) the TP concentrations in both treatments were not significantly different ($p > 0.05$) from the control forest, suggesting that P has accumulated within the top 30 cm of soil. Hu et al. (2005, 2006) also observed an increase in TP in the surface soils of the Muskegon system after more than 30 years of irrigation with wastewater.

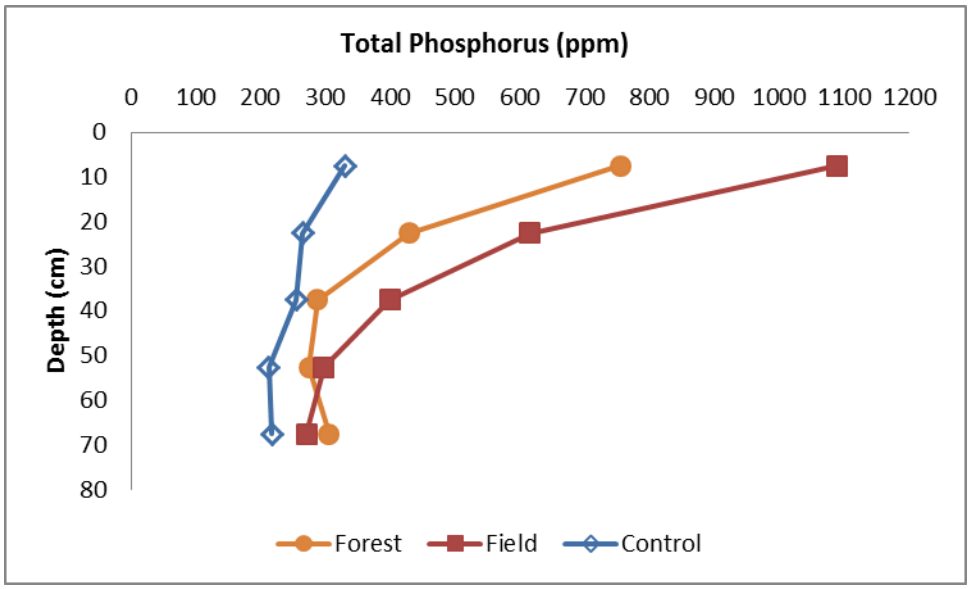

Figure 5.2 – Mean Total P concentrations (ppm) verses depth for the forest, field, and control plots.

The TP concentrations in the surface soils have changed little in the past ~40 years (Figure 5.3). Sommers et al. (1979) reported an increase in TP in the surface soils of the field and forest after ~10 years of irrigation at the LF site. The TP concentrations they found in the top 15 cm (854 kg ha^{-1} in the forest, and 898 kg ha^{-1} in the field) are comparable to the current TP concentrations in both the field and forest (Table 5.1). For the concentrations to be similar despite significant P loadings, leaching or runoff must have occurred. Hook et al. (1973) observed leaching of solution P at the 120 cm depth in the forest of the LF. They concluded that P was leaching because of the absence of biomass removal. Later Sommers et al. (1979) theorized that a faulty suction lysimeter may have been "short circuited" and concluded Hook et al. (1973) must have overstated the extent of P leaching.

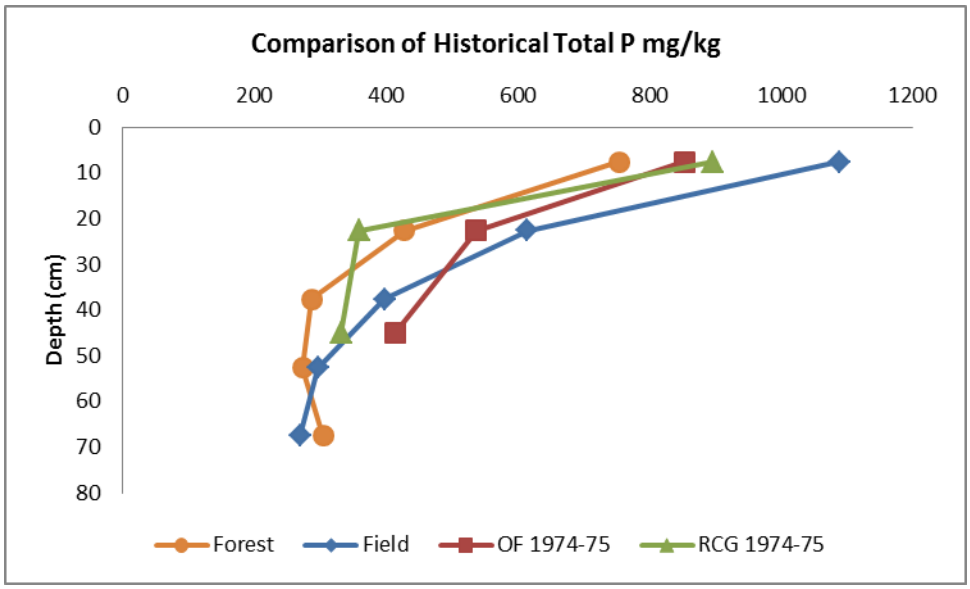

Figure 5.3 - Comparison of Total P from 1974-75 (Sommers et al., 1979) with data collected in this investigation in 2009. OF stands for Old Field, which is now the Forest, and RCG stands for reed canarygrass, which is now the Field.

5.2.1 Total Phosphorus Mass Balance

A TP mass balance was performed for the cropped field and forest soils for the top 75 cm of soil (Table 5.2). The soils were described by Walker and Lin (2008), and were found to have similar bulk densities across each depth, avoiding the need to account for different soil masses between sampling depths. The TP applied was calculated based on data from the first 12 years of system operation provided by Sommers et al. (1979), and the accumulated average annual TP application (93 kg ha^{-1}) over the last 26 years. Biomass removal in the field was calculated based on annual removal of P in tall fescue grass (Salada, 2007) only for the final 26 years, because control plot P data for the field in 1975 included biomass removal spanning the first 12 years of the system (Sommers, et al. 1979). Biomass removal in the forest was calculated based on average annual TP retained in the forest biomass (Ducnuigeen et al., 1997), assuming that trees are not luxury consumers of P. The organic horizon in the forest was possibly a potential source of P storage not included in the soil sampling, but Talkner et al. (2009) concluded < 22 kg TP ha^{-1}

is tied up in the organic horizon on the soil surface in a variety of forest types. This is an insignificant amount when considering the total amount of P applied. P retained in soil was calculated based on the difference between net P applied and control data provided by Sommers et al. (1979). Where historical control TP data was lacking (60 – 75 cm), the 2009 TP data for the control forest was used. The tabulated data show that nearly 63% and 70% of P applied cannot be accounted for in the top 75 cm of the soil of the field and forest, respectively.

Total P mass balance (kg ha^{-1})		
	Field	Forest
P applied[c]	5215	3532
biomass removal	838	40[a]
net P applied	4377	3492
P retained in soil[b] (0 - 75 cm)	1107	1024
Difference	3270	2468

Table 5.2 – P mass balance for cropped and forested sites. (a) Estimated from 5 kg ha^{-1} yr^{-1} forest uptake – 4 kg ha^{-1} yr^{-1} returned to soil. (b) 2009 TP values – control TP values (Sommers et al., 1979). (c) Using 3.5 mg TP L^{-1} and 3 cm wk^{-1} year-round application since 1983, and application data supplied by Sommers et al. (1979). Notes: Earlier in system operation P content of effluent was higher (7.7 mg L^{-1} (USEPA, 1981)) and more wastewater was applied per week. The history of fertilizer and manure application are unknown at both sites.

One possible reason for the discrepancy between forest and field "difference" could be underestimation of P removed by crop harvesting. Reed canarygrass was grown in the field in the early years of the system, and likely had a higher than estimated yield as a result of irrigation. Greater crop yield in the irrigated field would increase P removed and reduce the amount of P not accounted for in the mass balance ("difference" in Table 5.2).

What the field and forest mass balances do have in common is the substantial amount of TP that could not be accounted for by biomass removal and accumulation in the soil. Reasons for this phenomenon are discussed in Section 5.8.

5.3 Phosphorus Binding Soil Components

Al and Fe are two important elements influencing storage and mobility of P in acidic soils, and Ca is an important P binding constituent in alkaline soils (Kleinman and Sharpley, 2002). Behavior of P binding soil components is highly dependent on pH (Havlin, et al., 2005). In the early years of the LF system, the pH of the surface soils in both the forest and the field was approximately 5.2 (Hook et al. 1973). At this pH, P is typically bound in the form of $AlPO_4$ and $FePO_4$ minerals (Havlin et al. 2005). Since at least 1997 the pH of the surface soils has been > 7.0 (Kelso and Bowersox, 2004), and currently the top 45 cm of soil in the forest have a pH > 7.2, and the top 60 cm of soil in the field has a pH > 7.4 (Table 5.4). The addition of alkalinity in the wastewater (Table 4.1) is likely the cause of the steady increase in soil pH. At the current soil pH, Al- and Fe- phases are less important in P fixation; the majority of P should be bound by Ca minerals causing P to be less available for plant uptake (Havlin et al. 2005) as measured by the Mehlich-3 extraction. The surface soils in the control forest, which have received no lime or wastewater, have a pH ≈ 5.

5.3.1 Mehlich-3 Aluminum

A review was conducted by Beauchemin et al. (2000) and cited by Kleinman and Sharpley (2002) concluded that Al is potentially the most important P binding element in acidic soils. The M3Al data are shown in Figure 5.4, and provided in Table 5.3. Irrigation on the site has caused M3Al to leach or possibly Al has been converted to forms less readily extractable by the Mehlich-3 reagents. Hu et al. (2005) noted complete removal of extractable Al from the top 15 cm of three sandy soils after long-term effluent application. At the LF the M3Al concentrations at 0 - 15 cm are not significantly different between the irrigated treatments, but

both are significantly lower than the M3Al level in the control. M3Al appears to be accumulating in the forest soil in the deeper B horizon (45 – 75 cm). The mass of M3Al in the top 75 cm is 8.63 tonnes ha^{-1}, and 9.4 tonnes ha^{-1} in the forest and field, respectively. Comparing the forest and the control, 3.3 tonnes M3Al ha^{-1} have either leached from the forest soil or become unavailable to the Mehlich-3 reagent. Leaching of Al in soil can reduce the potential P storage capacity, and this will be further discussed in section 5.7. This data suggests that the storage capacity for P in both irrigated treatments has been reduced as a result of effluent application.

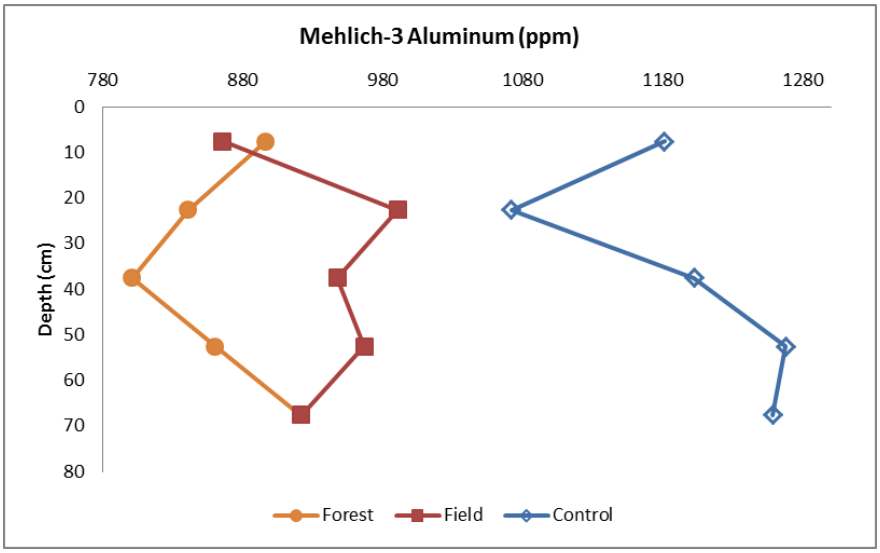

Figure 5.4 - Mehlich-3 Al concentrations (ppm) verses depth in the forest, field, and control.

	Depth (cm)	Field		Forest		Control	
Mehlich-3 Al	0-15	865.7	a	896.2	a	1181.0	b
	15-30	990.5	ab	841.1	b	1071.8	a
	30-45	947.4	a	801.0	a	1202.0	b
	45-60	966.7	a	860.1	a	1267.4	b
	60-75	921.9	a	921.1	a	1258.4	b
Mehlich-3 Fe	0-15	276.5	a	142.3	b	267.6	a
	15-30	169.3	a	88.4	b	107.2	ab
	30-45	79.9	a	69.5	a	44.0	a
	45-60	74.8	a	66.1	a	36.5	a
	60-75	63.6	a	103.9	a	40.0	a
Mehlich-3 Cu	0-15	10.2	a	3.4	b	1.6	c
	15-30	3.5	a	1.5	b	1.2	b
	30-45	1.5	a	1.1	a	1.0	a
	45-60	1.5	a	1.3	a	1.0	a
	60-75	1.0	a	1.0	a	0.8	a
Mehlich-3 Ca	0-15	1956.3	a	2042.8	a	204.18	b
	15-30	1175.08	a	834.9	b	116.24	c
	30-45	1047.36	a	618.72	a	378.62	b
	45-60	1029.12	a	566.7	b	498.96	b
	60-75	1056.58	a	551.26	b	384.32	b

Table 5.3 - Mehlich3-Al, Fe, Cu, and Ca concentrations with respect to depth in the field, forest, and control plots. Values followed by the same symbol are not statistically different (p = 0.05) for a given soil depth.

5.3.2 Mehlich-3 Iron

M3Fe concentrations are reported in Figure 5.5 and Table 5.3. In the top 15 cm, the M3Fe concentrations in the field and control soils are significantly higher ($p < 0.05$) than the M3Fe concentrations in the forest soil. In the next layer (15 – 30 cm), M3Fe in the field is significantly greater than the forest and control. At the lower depths (45 - 75 cm) the concentrations of Mehlich-3 Fe are not significantly different between the treatments. The concentration of M3Fe in the surface soil of the forest is nearly half the concentration of M3Fe in the field soil, which

suggests that M3Fe may be moving down through the soil profile in the forest. Kleinman and Sharpley (2002), however, suggested that Fe plays a minor role in P sorption compared to Al.

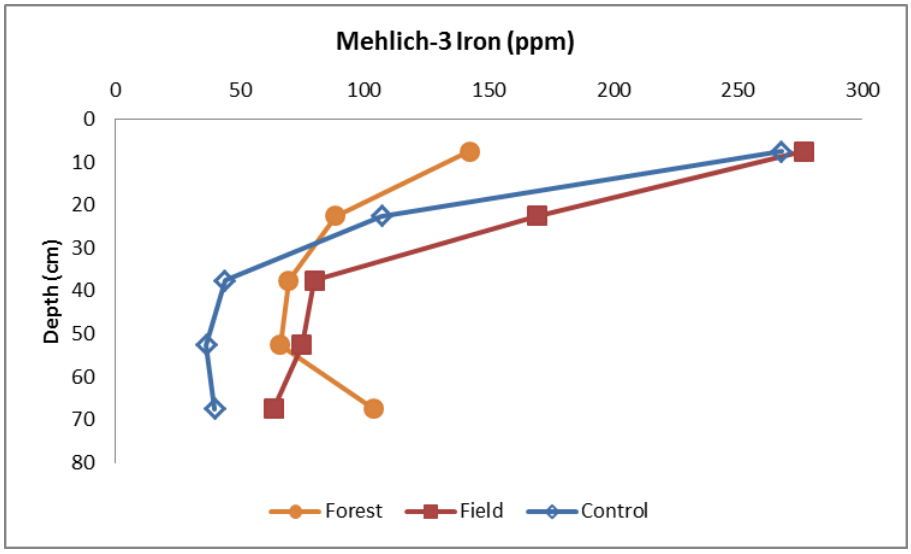

Figure 5.5 - Mehlich-3 Fe concentrations (ppm) verses depth in the forest, control, and field.

5.3.3 Mehlich-3 Calcium

M3Ca data are given in Table 5.3, and shown in Figure 5.6. The data show that M3Ca has increased significantly ($p < 0.05$) in the surface layers (0 – 45 cm) as a result of irrigation with wastewater. M3Ca in the field is significantly greater ($p < 0.05$) than the forest at 15 – 30, and 45 – 75 cm. The field may have been limed in the past, which would explain the increase in available Ca. The increase in Ca in both irrigated soils suggests that Ca has become increasingly important in P binding as a result of effluent irrigation. Hu et al. (2005) reported that Ca-bound P accounted for more than 70% of the total soil-bound P after 30 years of effluent irrigation in Michigan at the Muskegon system. These researchers propose soil retention of effluent Ca could extend the useful life of the site.

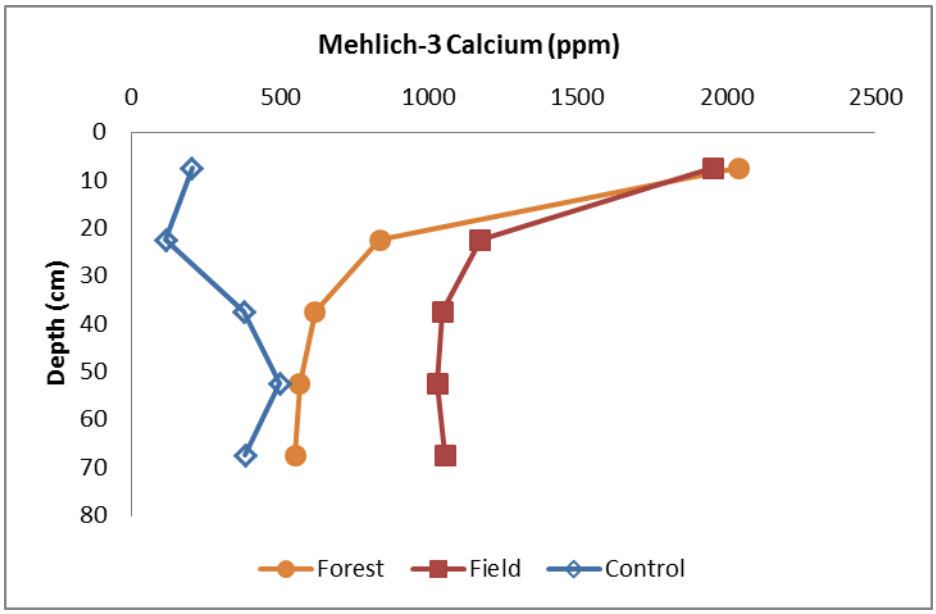

Figure 5.6 - Mehlich-3 Ca concentrations verses depth in the forest, field, and control plots.

5.5 Organic Matter

Many studies have been conducted on the dynamics of Al and Fe in both acidic and calcareous soils, and the relationship of OM on their mobility (van Hees, et al. 2000, Jansen, et al. 2003, Jansen, et al. 2005, Wandruszka, 2006;). In forests with acidic soil conditions, OM bonds with Al and Fe in the soil. These organo-metal complexes can be readily leachable in the soil column. Chantigny (2003) cited several studies (Hughes et al., 1990, Strobel et al., 1999, Delprat et al., 1997, and Leinweber et al., 2001) to conclude that large molecules of OM in forest soils are more suitable for complexation than smaller OM molecules found in agricultural soils. The larger molecules of dissolved OM (DOM) in the forest can complex the Al and Fe ions. Chantigny (2003) suggests that the greater prevalence of organo-metal complexes in forest soil is because forest OM is more persistent in the environment. The organo-metal complexes leach through the soil profile and can accumulate in the B horizon. Jansen et al. (2003) report accumulation of M3Al in the B horizon because DOM is absorbed directly by sesquioxides and

clays. Leaching of metals from the A horizon to the B horizon is often referred to as podzolization, and most commonly occurs in acidic forest soils in humid climates (Buckman and Brady, 1969). The soils at the LF were acidic at the outset of irrigation (Hook et al., 1973) and the pH has gradually increased over time, and irrigation has resulted in hydraulic loadings comparable to precipitation levels in the tropcis.

The soil OM as a function of soil depth is reported in Figure 5.7. Percent OM in the surface soils (0 – 15 cm) of the cropped field was significantly greater than the control ($p < 0.05$), but not different from the forest. The % OM did not differ in the forest and control locations, but during sampling the surface debris was removed to provide a clean sampling surface, possibly leading to the lack of significance between the forest and field.

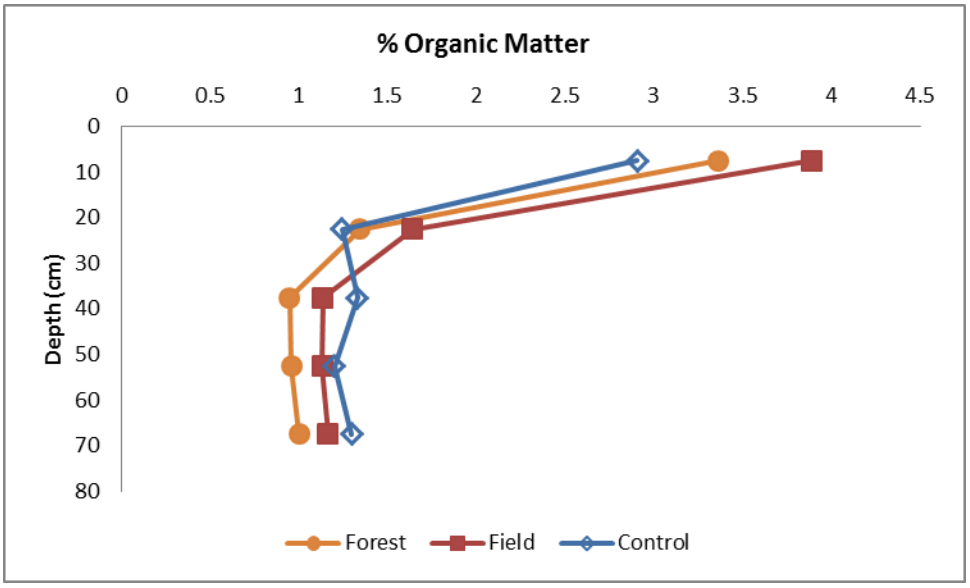

Figure 5.7 - Mean soil percent organic matter with respect to depth in the field, forest, and control plots.

The competition between OM and P for binding Al/Fe can lead to leaching of P in soils high in OM content or forest soils with more persistent OM. In the early years of the LF system the low pH, DOM in the forest, and application of effluent appear to have caused leaching of Al and Fe from the surface soils. Without considering the impact of other components potentially

influencing P fixation, the data suggests the ability of the forest and field soils to assimilate P and renovate wastewater has been reduced.

5.6 Mehlich-3 Copper

Mehlich-3 copper (M3Cu) data are shown graphically in Figure 5.8. M3Cu has accumulated significantly ($p < 0.05$) in the surface soils of the irrigated treatments compared with the control site. Accumulation of M3Cu must be due to Cu added via the irrigated effluent. Copper is known to complex with solid soil OM which reduces the soil solution concentration (Bohn et al, 1979).

In the surface layers the concentration of M3Cu in the field is significantly greater ($p < 0.05$) than the M3Cu concentration in the forest. This data appears to support the previous assertion that forest organic matter is more likely to complex metals in a manner that preferentially causes them to leach deeper in the soil profile. This reasoning is based on the assumption that the total amount of Cu added to the two areas is comparable. Differences in management intensity and the source of soil organic matter (i.e. grass versus detrital material from tree canopy) apparently influence the complexing ability of the dissolved organic matter in soils (Chantigny, 2003).

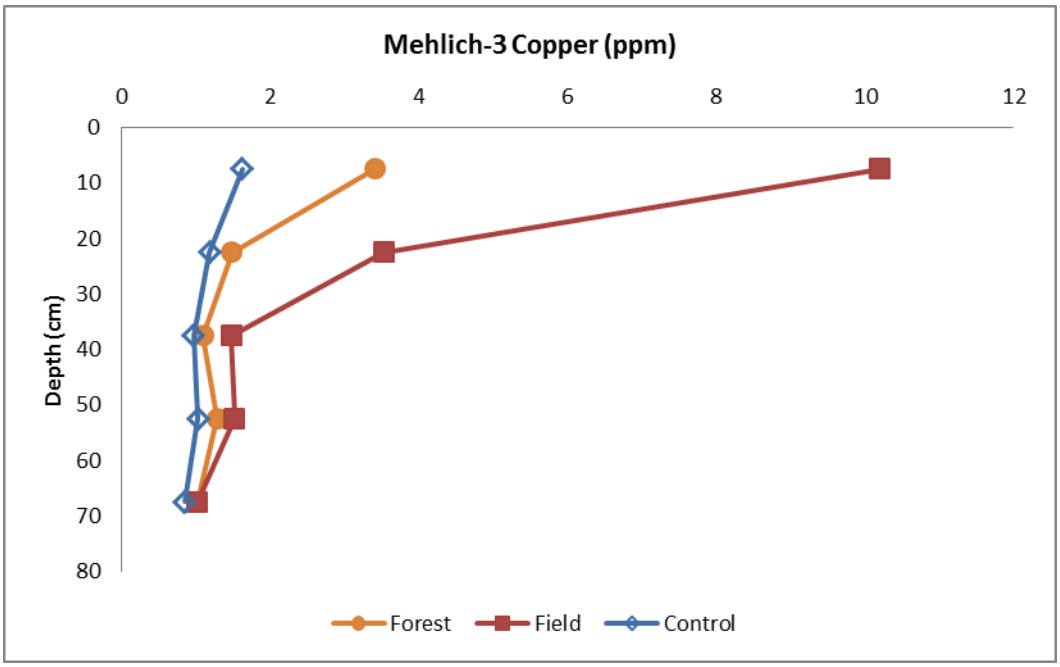

Figure 5.8 – Mean Mehlich-3 Cu concentrations (ppm) verses depth in the forest, control, and field.

5.7 Phosphorus Saturation

The P sorption saturation ratio (Psat) (Figure 5.9 and Table 5.4) was calculated for each subsample with respect to depth using mean M3P, M3Al, and M3Fe data (see Chapter 4). Breeuwsma et al. (1995) established 25% as the maximum Psat percent before leaching occurs using oxalate extractable data for sandy soils in the Netherlands. Their 25% threshold Psat value was based on using $\alpha = 0.5$ in the Psat equation (see Section 4.4.4). Maguire and Sims (2002) adjusted the 25% threshold Breeuwsma et al. (1995) established with oxalate extractable data to 6.2% when using Mehlich-3 extraction data and $\alpha = 1$. Jaiswal (2010) calculated that P leaching occurs in the agricultural soils at the LF site when Psat ≈ 6.5%. For this investigation the threshold value proposed by Jaiswal (2010) was used.

As shown in Figure 5.9, both the field and forest are above the leaching threshold in the top 15 cm. From 15 – 30 cm the field is close to the leaching threshold value, while the forest is not. The Psat in the control plot does not approach the leaching threshold value at any depth.

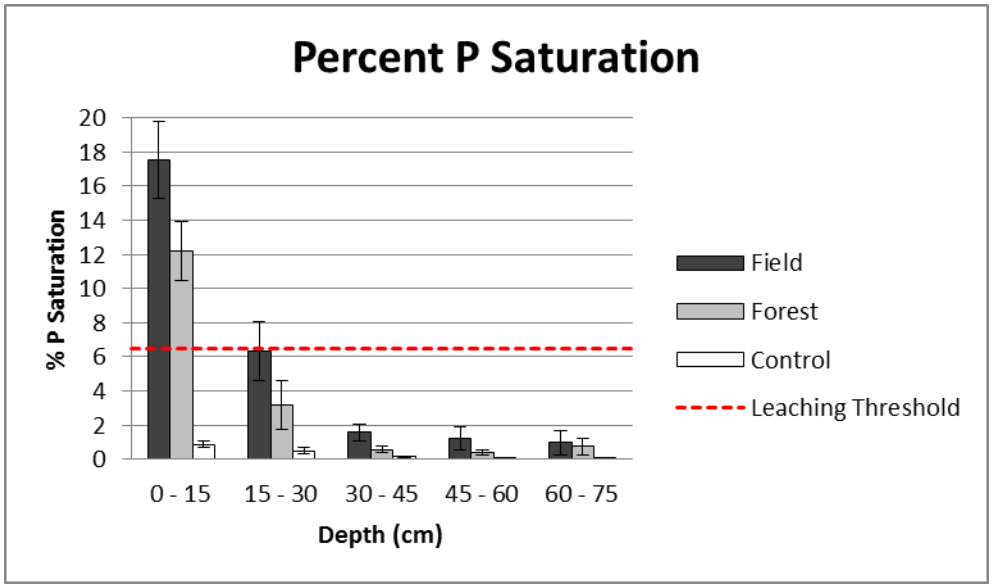

Figure 5.9 – Mean Mehlich-3 P Saturation percent at each depth in the field, forest, and control plots. Error bars represent the standard error of the Psat values for each depth (see Table 5.4).

	Depth (cm)	Calculated % Psat by Sample Number					Mean % Psat	Standard dev	Standard error	Mean pH
		1	2	3	4	5				
Field	0-15	16.71	11.64	19.98	14.50	24.79	17.52	5.081	2.272	7.36
	15-30	8.32	0.97	8.86	3.65	9.82	6.32	3.822	1.709	7.39
	30-45	2.08	0.23	1.66	0.87	2.95	1.55	1.056	0.472	7.45
	45-60	0.51	0.14	3.68	0.18	1.46	1.19	1.489	0.666	7.42
	60-75	0.26	0.08	3.87	0.18	0.38	0.95	1.635	0.731	6.81
Forest	0-15	16.18	12.59	8.23	15.68	8.18	12.17	3.875	1.733	7.37
	15-30	0.75	8.26	0.55	3.62	2.65	3.16	3.124	1.397	7.406
	30-45	0.21	0.77	0.45	1.15	0.18	0.55	0.411	0.184	7.286
	45-60	0.35	0.23	0.29	1.05	0.07	0.40	0.381	0.170	6.354
	60-75	0.17	0.41	2.77	0.21	0.07	0.73	1.152	0.515	5.736
Control	0-15	0.798	0.459	1.417	0.510	1.054	0.85	0.398	0.178	5.38
	15-30	1.183	0.159	0.212	0.396	0.525	0.50	0.412	0.184	4.97
	30-45	0.265	0.078	0.064	0.075	0.150	0.13	0.085	0.038	5.05
	45-60	0.066	0.077	0.058	0.075	0.066	0.07	0.008	0.003	5.22
	60-75	0.068	0.073	0.060	0.074	0.067	0.07	0.005	0.002	5.08

Table 5.4 - Mehlich-3 P sorption saturation data and error analysis.

The likelihood of P leaching in the soil increases as the Psat approaches the leaching threshold value. The data suggest that leaching of P has occurred in soils at the LF, and is still occurring in both the forest and the field. P in the field is likely leaching from the top 30 cm to the soil below. P in the forest is likely leaching from the top 15 cm to the next layer below.

The relationship between P and P binding soil components is largely understood under static soil conditions, but irrigation with wastewater causes incremental changes in soil chemistry that confound the understanding of P dynamics. The gradual increase in soil pH and the addition of Ca has possibly led to changes in how P is absorbed by soil OM and minerals. The equations used for calculating Psat are limited by including only Al and Fe, or only Ca (Kleinman and Sharpley, 2002). For systems like the LF where significant pH changes have occurred over time, a Psat expression including Al, Fe, and Ca would be useful in understanding the changing P-leaching potential over the site life.

5.8 Potential Phosphorus Transport Mechanisms

There are several potential transport pathways that may explain the inability to account for P in the mass balance (Table 5.2). The first and most likely transport process is leaching of P through the soil profile. The data show that M3P, TP, M3Al, M3Fe, and M3Cu are reduced in the surface soils of the forest compared with the field. Podzolization is an important process in leaching of metals through the soil profile, and is possibly occurring in the forest. The data, however, does not show evidence of active movement of these elements through the soil profile. The absence of elevated concentrations of each of the elements in the sampled soil layers compared with the control indicates that leaching may have occurred to depths greater than 75 cm, or other transport processes have had a significant impact on fate of P.

Another important P transport process is movement of P through runoff or interflow. The soil samples in the field were collected on the local summits, to minimize the effect of topography on the results. The unintended consequence of the sampling regimen may be that irrigation water has carried P from the summits to the sideslopes and depressional areas during irrigation as surface runoff or through subsurface lateral flow following irrigation. This assumption is corroborated by Hook et al. (1973) who cited Myers (1967) and Rebuck (1967) and concluded that interflow affects the fate of P at the LF site. Walker and Lin (2008) also observed subsurface flow at the LF site. Jaiswal (2010) observed an increase in M3P in depressions compared to summits and sideslopes, suggesting movement of available P in surface runoff and subsurface lateral flow. While runoff from the LF site has been minimal (O'Driscoll and Parizek, 2003), localized runoff of effluent within the site has likely occurred.

The third potential P transport mechanism is biomass uptake and removal. The forest biomass may be a luxury consumer of P, understating the P retained in the forest biomass. The P removed in harvested grasses in the field may also be understated. The irrigation water may have caused higher than typical yields of grasses, removing more P than was estimated in the P mass balance calculation.

Chapter 6

Concluding Remarks

Long-term application of wastewater has caused significant changes in soil chemistry that affect the dynamics of effluent applied P. Soil pH has increased from 5.2 before wastewater application to 7.3 in 2009. In addition to pH change, available Al and Fe have either leached through the soil profile, or formed compounds not readily extractable by the Mehlich-3 reagent. Organic matter is another important factor influencing behavior of Al and Fe in soil. Although percent OM did not differ between irrigated treatments, the nature of the OM is different. According to Chantigny (2003), larger molecules of OM in forest soils are more likely to form organo-metal complexes with the Al and Fe. The presence of organo-metal complexes combined with historically low soil pH suggests that podzolization is driving leaching of M3Al and M3Fe in the soil profile. Loss of Fe, and particularly Al, in soil reduces the P storage capacity.

P has accumulated significantly in the surface soils of the LF in both the forest and field. In the irrigated forest M3P and TP have increased compared with background soil conditions in the control forest. Calculated Psat values indicate that leaching is occurring in the surface layers of both the field (0 – 30 cm) and the forest (0 – 15 cm) soils. The extent of downward P migration is unknown because recent soil sampling has only focused on shallow soils (Walker and Lin, 2008; Jaiswal, 2010, Jaiswal and Elliott, 2011), but with a depth to groundwater greater than 30 m (O'Driscoll and Parizek, 2003), the short-term threat of P leaching to groundwater appears to be minimal. Other P transport mechanisms including surface runoff and subsurface lateral flow have likely contributed to the loss of effluent-applied P from the surface soils.

As a result of this study, new questions have arisen about the long-term fate of P in wastewater-irrigated forests. The reported results indicate movement of P, Al and Fe from the surface soils has occurred. Future studies should include sampling deeper in the soil profile to

determine the downward extent of P migration. Additionally, more samples should be collected from each of the treatments to limit the influence of outliers on the data. Sampling should also be conducted in a variety of soil types and landscape positions to gain a broader understanding of P dynamics in effluent irrigated soils. For example, much of the forested area of the LF site is on Morrison sandy loam soil. Given its coarser texture compared to the Hagerstown silt loam, leaching of P might be expected to have occurred to a greater extent where Morrison soil exists (Sommers et al., 1979). Answering these questions is important to sustaining land treatment as a viable means of recycling municipal wastewater effluent.

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Appendix

Example of SAS Code

```
proc glimmix data=mehlichp;
class envtype sampleid depth;
model mehlichp=envtype depth envtype*depth;
random _residual_ / subject=sampleid(envtype) type=ar(1);
lsmeans envtype*depth / slicediff=depth adjust=tukey;
run;
```