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SOIL PHOSPHORUS LEVELS IN RESIDENTIAL LAWNS AND COMPARISONS AMONG FOUR LAND USES IN SPRINGFIELD, MISSOURI

A Thesis

Presented to

The Graduate College of

Missouri State University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Natural and Applied Science

By

Timothy R. Davis

December 2006

SOIL PHOSPHORUS LEVELS IN RESIDENTIAL LAWNS AND

COMPARISONS AMONG FOUR LAND USES IN SPRINGFIELD, MISSOURI.

Department of Geography, Geology and Planning

Missouri State University

Master of Natural and Applied Science

Timothy R. Davis

ABSTRACT

Eutrophication of surface waters due to high phosphorus (P) concentrations is an important water quality concern in Greene County, Missouri. Phosphorus enrichment has been linked to a variety of non-point sources including runoff from both agricultural and urban land uses. Soil P has been shown to be a source of P in runoff. The differences in soil P among different land uses may provide insight into which land use contributes more P in runoff. This study examines the soil composition, geochemistry and total P concentration of surface soil (0-5cm) in four land uses in Greene County, Missouri. The land uses sampled were residential lawns, city parks, agricultural pastures, and undisturbed forest. The amount of P extracted by de-ionized (DI) water from each land use was also examined. Total P concentrations for all land uses ranged from 250 to 1200 ppm P. Mean P concentrations did not differ significantly (α =0.05) among land uses. Total P was highly correlated with organic matter (OM) for all land uses, indicating that OM is both a significant source of P and a primary sink for P. Organic Matter was used as the primary variable for regression models predicting TP. A mean of 4.05% of the total P in lawns was extractable by de-ionized water. This is significantly higher (α =0.05) than the mean DI water extractable P in the other land uses. This suggests that lawns may contribute more P per unit area to storm runoff than the other land uses examined. The relationship of TP to the % of DI water extractable P was curvilinear for lawns, parks and forested sites indicating a maximum limit of P sorption by runoff water. However, the same relationship was linear for agricultural sites. 75% of sampled lawns had a TP concentration between 300 and 700 ppm. Within this range lawns can contribute a significantly greater percentage of P to runoff water.

KEYWORDS: Phosphorus, soil, water quality, lawns, land use

This abstract is approved as to form and content

Robert T. Pavlowsky, Ph.D. Chairperson, Advisory Committee Missouri State University

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December 2006

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ACKNOWLEDGEMENTS

First and foremost I need to thank Jesus Christ, my savior for bringing me to this point in life and giving me the strength to finish this project. I would especially like to thank Dr. Robert Pavlowsky (chairperson) for his guidance and encouragement throughout my graduate education. Without his generosity it would not have been possible for me to complete my degree. I would also like to thank the other members of my committee Dr. Harry James and Dr. Erwin Mantei for all of their time and constructive criticism. This project was funded by a Thesis Grant from the Missouri State Graduate College and through the Ozarks Environmental Water Resources Institute. I am grateful to Marc Owen for providing me with some of the GIS data for this project and for his helpful writing suggestions. My immense thanks go to all the other graduate students who helped me in the laboratory and working with ArcMap® including Mark Gossard, Derek Martin, Terri Hunsinger, Gopala Borchelt, and Jon Woosley. Finally, I want to thank my wife Laura, for all of her love and encouragement.

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CHAPTER 1

INTRODUCTION

Eutrophication is one of the major consequences of phosphorus (P) enrichment of surface and ground water resulting in the rapid increase of aquatic microorganisms including algae (Brady and Weil, 2002). This leads to adverse effects on water quality such as taste and odor problems for drinking water, reduced water clarity, and reduced dissolved oxygen resulting in fish kills. Within the last few years water quality concerns in the Ozarks have increasingly been focused on the phosphorus concentrations in lakes and streams. In Greene County, Missouri the USEPA has placed the James River on the 303(d) list of impaired waterways partially due to high nutrient levels from multiple point and non-point sources (MoDNR, 2002). A point source is a single, discrete location such as a wastewater treatment outlet that releases pollutants. Most point sources of P can be identified and regulated to reduce P inputs. Non-point source P pollution comes from many diffuse sources throughout the landscape that are not as easy to identify. Due to the large and varied land areas contributing runoff, P from non-point sources can contribute significantly to water quality degradation.

Since about two-thirds of Springfield, Missouri drains to the James River point and non-point P sources within Springfield can contribute to pollution problems in the James River and Table Rock Lake. Much of the P going into the James River can be accounted for from major point sources such as municipal waste water treatment plants (MoDNR, 2001). However, agricultural and urban runoff is also believed to be important non-point source contributors of P to the James River (Kiner et al., 1997; MoDNR, 2001).

Much research has been focused on understanding the loss of P in runoff from agricultural land. There are numerous studies that have examined the correlation of soil P to runoff P concentration (Sharpley, 1995a; Pote et al., 1996; Sharpley at al., 2001; Torbert et al., 2002; Schroeder et al., 2004). These studies have all shown that the amount of P in storm runoff is highly dependent on the amount of P in the soil over which the runoff water flows. The results of these studies have highlighted the importance of conservation measures that reduce runoff from agricultural land and have validated the idea of studying soil P as a way of predicting P in runoff water for grassed land cover.

In the Springfield area, urban runoff has been cited as a significant non-point source of pollution in the James River Basin (Kiner, 1997 and MoDNR, 2001). Unlike agricultural studies, there have been very few studies that look at the relationship of soil P to P in runoff for urban areas. Both Waschbusch et al. (1999) and Garn (2002) found residential lawns to be a significant source of P in urban storm runoff, but neither study examined the relationship of soil P to the concentration of P in runoff water. Therefore it is important to determine if soil P is significantly related to runoff P for residential lawns and other land treatments. The relationship of soil P to runoff P has also not been examined for multiple land use treatments in one geographic region. Therefore there is no information on whether there is a significant difference in what soil conditions and land uses could contribute the most P to runoff water.

Since Urban lawns have been shown to be a significant source of P in runoff then the greater area covered by lawns could mean more P discharged into streams. In the Springfield area residential developments are being built at a very fast pace to

accommodate a rapidly increasing population. These residential areas could potentially be a major source of P either through erosion and soil loss during construction, or increased fertilizer use in lawn maintenance.

This leads to two important research questions. 1) What land uses in Greene County have the highest concentrations of soil P available for transport in runoff and 2) what land uses in this area could potentially be a significant non-point source of P? Answering these questions is important in attempts to focus conservation efforts where they will have the most impact.

Purpose and Objectives

This study will compare P concentrations among residential lawn, agricultural pasture, Springfield City park, and undisturbed forested areas. This study also aims to determine if residential lawns in Springfield have the potential to release significant amounts of P in storm runoff compared to runoff from these other land uses. The specific objectives of this study are:

- 1. To measure soil phosphorus, soil geochemistry and selected physical properties at representative sites from four major land uses in Greene County, Missouri;
- 2. To determine if the phosphorus concentrations of residential lawns are significantly greater than other land uses;
- 3. Quantify the geochemical and soil property relationships of P using Pearson correlations and multiple regression modeling; and
- 4. To measure the concentration of P extractable by water from soil samples as an estimate of potential for runoff to carry dissolved P.

Benefits of the Study

The results of this study will be beneficial to future researchers and to local resource managers. Since soil P is one of the most important sources of P in runoff (Sharpley et al., 2003) knowing the amount of P in the soil surface and how much P can be extracted by water will provide data for future researchers to build upon. Future studies may include storm water sampling of lawn runoff and measurements of runoff volume from various land uses.

Current phosphorus initiatives in the Springfield metro area include the James River Basin Partnership's "Get Tested" program which offers free soil tests and nutrient management plans for home lawns. Results from this initiative have shown that 41% of all lawns tested needed no additional P fertilizer and 22 % needed only a light maintenance application to keep their grass healthy (JRBP, 2006). If further research shows that residential lawns are a significant source of P compared to other land uses then programs such as this could be expanded. However it is not currently known if residential lawns have the potential to contribute more P to runoff than other land uses.

CHAPTER 2

LITERATURE REVIEW

Identifying potential sources of phosphorus (P) from urban areas is critical to understanding how to develop best management practices that protect the waterways around Springfield, Missouri from further degradation. An important step in identifying these sources is to examine the phosphorus content in soils under varying land use conditions and treatments to help determine the potential supply and risk of phosphorus loss to urban waterways. The present study compares acid-extractable phosphorus in Southwest Missouri soil samples among different land-use classes within the Springfield, Missouri metropolitan area to evaluate the total burden of P in the topsoil. It also seeks to determine the relationship, if any, between de-ionized water extractable P and acid extractable P in Southwest Missouri to better understand the potential mobility of Soil P in urban runoff. The land source areas under consideration in this study relate to the land use categories of residential lawns, cattle pastures, park grassland and forest.

The purpose of this chapter is to provide a review of the literature pertaining to soil phosphorus and runoff characteristics of turf grass systems with a focus on residential lawns. Relatively little research has been done specifically on residential lawns in the Springfield, Missouri area and thus literature on agricultural pastures, golf courses and other turf grass systems was examined. Previous research on residential lawn runoff, lawn infiltration and soil phosphorus interactions was used to develop part of the background information. This review of literature includes a discussion of the adverse environmental effects of elevated phosphorus levels, the behavior of phosphorus

within southwest Missouri soils, runoff characteristics of lawns, and the influence of human management decisions.

Water Quality Concern

The main reason for concern about the levels of P found in runoff draining into waterways is that too much P in the water can lead to eutrophication (Waschbusch et al., 1999; Akhtar et al., 2003; Siddique and Robinson, 2004). Eutrophication is the most widespread cause of water quality degradation in U.S. waterways (USEPA, 1996). Phosphorus is not directly toxic to humans or animals when it is present in high levels in bodies of water; problems occur from the excess growth of algae caused by nutrient enrichment (Brady and Weil, 2002). The availability of P is the limiting factor in keeping algal growth under control in most water bodies. Blue green algae are able to utilize N from the atmosphere, but need P to be supplied from the water column (Sharpley et al., 1994; Pote et al., 1996). When P levels increase in the water algae numbers increase rapidly in what is known as an algae bloom (Brady and Weil, 2002). This increases the biological oxygen demand and reduces the amount of dissolved oxygen available for aquatic organisms (Evangelou, 1998). When the algae die the decomposition process by microorganisms further depletes the water of oxygen causing fish kills, limited aquatic vegetation growth, as well as bad smells and tastes in water. The recognition of P in runoff as a significant contributor to eutrophication and increased occurrences of harmful algal blooms have caused increasing concern about P runoff into many urban lakes and streams (Sharpley et al., 2001; Garn, 2002). Thus it is important to understand the sources of P and how the P is held in the soil so that management practices can be developed to prevent excess P from entering urban waterways.

Soil Phosphorus

In order to understand the potential for P to be lost from the soil as runoff, it is important to consider the different forms of P and the chemical behavior of P within the soil. In the soil, P is found 1) as particulate phosphorus (PP) which is attached in various ways to the surface of soil particles; 2) absorbed into the structure of various soil minerals; and 3) dissolved into soil pore water and ground water as dissolved phosphorus (PP). The DP in the soil solution is generally composed of soluble phosphates (dihydrogen phosphate, or $H_2PO_4^-$ and hydrogen phosphate, or HPO_4^{2-}). Particulate P is adsorbed, usually in an insoluble metal-phosphate form, to clays, organic compounds, and to the surfaces of secondary minerals containing Fe^{3+} , Al^{3+} , Ca^{2+} (Brady and Weil, 2002; Dolui and Banjeree, 2001). These minerals can include iazulite (Mg,Fe)Al₂(PO₄)₂(OH)₂ and apatite Ca₅(PO₄)₃(F,Cl,OH) (Wikipedia, 2006). Phosphorus may also be adsorbed in geochemical phases of sedimentary particles such as Fe oxides and hydroxides, Mn oxides and hydroxides, and Al oxides and hydroxides, as well as organic compounds (Mantei, 2006).

Forms of Phosphorus. Phosphorus is found in both the organic and inorganic forms within the soil (Minor et al., 1993). The organic form of P (OP) accounts for greater than 50% of all P found in soil and occurs in humus and plant residues(Evangelou, 1998). Organic forms of P are relatively unavailable to plants and do not easily desorbed until breakdown by microorganisms converts the organic matter into inorganic forms (Minor et al., 1993).

Inorganic P (IP), also known as orthophosphate is present in soil in two main forms, oxide-phosphate complexes such as a clay edge-phosphate complex, and metal phosphates where the phosphate anion (HPO₄ ²⁻, H₂PO₄¹⁻, or PO₄⁻) is attached to a metal cation such as Al³⁺, Fe^{3+and 2+}, Mg²⁺, Ca²⁺. This process occurs by either surface complexation or diffuse-ion swarm association (Sposito, 1989; Evangelou, 1998). Most of the IP in soils is found as small mineral/colloidal particles. Phosphates that are added to soils are quickly adsorbed on to particle surfaces and then later fixed by chemical precipitation wherein the soluble phosphate is transformed into an insoluble form, usually a metal phosphate (Subbarao, 1977). Soluble P that is not adsorbed onto the mineral surface or otherwise transformed into an immobile form is available for loss.

Phosphorus can be lost from soils in four main ways:

- Leaching of DP lower into the soil profile and into groundwater (Johnson et al., 2004; Akhtar, 2003)
- Erosionby runoff or wind of soil particles with insoluble P adsorbed to the particulate surface as particulate phosphorus, or PP (Brady and Weil, 2002; Sharpley, 1995)
- Dissolved phosphorus (DP) in surface runoff (Brady and Weil, 2002; Sharpley, 1995b)
- 4. Nutrient uptake by plant roots (Brady and Weil, 2002; Sharpley, 1995).

Of particular concern is the DP and PP in runoff water from rainfall events. Particulate P is adsorbed onto the soil particles that are eroded and carried by the water while DP is the soluble phosphate in the soil solution that is carried by runoff water (Sharpley, 1995). Dissolved P is the dominant loss mechanism in grassed areas (Sharpley, 1995) and would therefore be the greatest consideration in Springfield lawns since grass systems are very effective at trapping any mobilized sediment (Gross et al., 1990; Schmitt et al., 1999; Abu-Zreig et al., 2003). These studies found that filter strips planted with grass trapped 70-90% of sediment entrained during artificial rainfall events.

Soil Properties Affecting Phosphorus. There are several important factors in Southwest Missouri soils that influence how tightly P is held in the soil. Among these factors are pH, clay content and organic matter content of the soil.

Acidity-pH. The pH of the soil plays an important part in determining how strongly the phosphate ion is held onto the mineral surface. In acid soils there is usually enough Fe^{3+} , Al^{3+} and Mn^{3+} to precipitate almost all of the soluble phosphate with relatively insoluble Fe^{3+} , Al^{3+} and Mn^{3+} oxides (Brady and Weil, 2002). The maximum availability of P to plants and therefore the most soluble state of phosphate is between a pH of 5.5 and 7.5 because the stability of metal-phosphates is highly pH dependent. At low pH, phosphates are mineralized by precipitation with iron and aluminum. The solubility of Al and Fe increases with decreasing pH. The low pH results in higher concentrations of Al and Fe in the soil solution allowing more HPO₄ to be bound as insoluble aluminum and iron phosphates (Fuqua, 2006). As pH increases these metalphosphate bonds weaken due to competition of $protons(H^{+})$ with metal cations for anion binding sites allowing phosphates to dissociate from metals and form soluble H₂PO₄⁻ and HPO_4^{2-} phosphates (Evangelou, 1998). At high pH levels the soluble phosphate once again decreases due to phosphate precipitation with calcium to form insoluble calcium phosphates (Bohn et al., 1985).

In Greene and Lawrence counties, in Southwest Missouri the soil pH values for surface horizons range from 4.5 to 7.8 (Hughes, 1982). In this range of pH levels the expected predominant phosphate species would primarily be $H_2PO_4^{-1}$ with HPO_4^{2-1}

making up a small portion of the total soluble phosphates in the soil since different phosphate species are more prevalent at different pH ranges (Bohn et al., 1985). Dihydrogen phosphate is is the most prevalent phosphate in soils from a pH of 2 to 7. From a pH of 7 to 13 hydrogen phosphate is the predominant phosphate species in soil (Bohn et al., 1985). This range of pH 4.5 to 7 also encompasses the pH range where the most P is in the mineral forms that are available for plant uptake. The highest P availability for plant uptake is in the pH range of about 5.8 to 7 (Minor et al., 1993). These soluble forms are available to plants and very mobile within the soil profile, but most of the P applied in soluble form is quickly converted to insoluble (and thereby less mobile) forms after application by adsorption onto the surfaces of Fe^{2+ and 3+} and Al³⁺ in acidic (pH <7) soils (Bohn, 1985). This process can occur within a few hours (Brady and Weil, 2002). Soils in the present study had a pH range of 4.8 to 7.8.

Since plants can only absorb P in the soluble phosphate form $(PO_4^{3-}, HPO_4^{2-} or H_2PO_4^{-})$ and most of that is quickly converted to insoluble forms only a very small part of the P that is applied is immediately available for plant uptake or for movement as DP. The rest is held strongly in an insoluble and immobile form as FePO₄, AlPO₄ or on the clay colloid.

<u>Clay.</u> Clay contents in southwest Missouri typically increase in clay percentage with profile depth (Hughes, 1982; NSSC Soil Survey Laboratory Soil Characterization Data High Query Interface, 2006). This is due to the highly weathered nature of Greene county soils which has allowed both mechanical translocation of clay from the in upper horizons into the Bt horizons and neosynthesis of clays in the B horizon from dissolved constituents leached from the A and E horizons. Clay also is also formed directly from the weathering of primary minerals (Buol et al., 2003). For example in the 3Bt1 horizon (at a depth starting at 130 cm) the Bado Series in Greene County has 49.1% clay and the Ap horizon has 11.6% clay (NSSC Soil Survey Laboratory Soil Characterization Data High Query Interface, 2006).

It can be expected that the high clay content in Southwest Missouri soils would provide a lot of surface area and binding sites for any applied P to be adsorbed onto the clay surface or to the Fe³⁺, Al³⁺ and Mn³⁺ ions bound to the clay. This is because surface coatings of Fe³⁺, Al³⁺ on clay surfaces decrease the CEC and increase Anion Exchange Capacity (AEC) allowing phosphate anions (HPO₄ ²⁻, H₂PO₄¹⁻, or PO₄⁻) to form metalphosphates attached to clay surfaces (Bohn et al., 1985; Sposito, 1989). The soils underlying Springfield are characterized by silt loam A horizons and clay rich subsurface horizons. The clays in the Springfield area are predominantly kaolinte from residuum that is usually red in color in subsurface horizons (Hughes, 1982). The structure of kaolinite clays is one Aluminum-Hydroxyl sheet and one Si₄O₁₀ sheet in a repeating pattern (Mason, 1952). This one to one structure means that of the different types of clays kaolinite has the lowest capacity for surface reactions.

Although the subsurface horizons in Missouri soils have properties that should tend to bind and immobilize P such as low pH, and high clay contents; the surface horizons that receive the P inputs have much more varied properties, less clay and less iron than sub-surface horizons (NSSC Soil Survey Laboratory Soil Characterization Data High Query Interface, 2006).

Soil Organic Matter. Soil Organic Matter (SOM) is a highly complex and heterogeneous component of soil. It contributes greatly to the soil's Cation Exchange Capacity (CEC) and forms stable complexes with micronutrients such as iron (Evangelou, 1998). Soil organic matter provides nutrients for plants (such as C, N, and P) and energy for microorganisms (Bohn et al., 1985). It improves soil structure and therefore increases water infiltration and water holding capacity. One of the most important characteristics is that the large surface area exhibited by SOM provides sites for mineral adsorption and chemical reactions (Evangelou, 1998). Soil organic matter is composed primarily of decomposed plant material in the soil. Soil organic matter is formed when plant cellulose is broken into sugars as microorganisms use the carbon and nitrogen present in the plant material. These sugars oxidize and give SOM its characteristic dark color. The final product in the breakdown of plant material is called humus (Evangelou, 1998). As SOM decomposes further one of its products is phosphate, or PO_4^{3-} . Soil organic matter decomposition supplies 50-60% of the phosphates found in unfertilized, temperate soils (Bohn et al., 1985).

Humus makes up 70-80% of SOM by weight. Its prevalence and chemical characteristics make it the most important component of SOM. The colloidal properties of SOM are due to humus since it has a net negative charge due to the dissociation of H^+ ions from the SOM functional groups (Bohn et al., 1985; Evangelou, 1998). This charge, and the fact that the surface area of humus is greater than that of most silicate minerals means that humus contributes a large percentage of the soil's total CEC. Silicate clays usually provide most of the CEC, but in areas with low CEC layer silicates the humus in SOM can provide greater than 45% of the total CEC of the soil (Bohn et al., 1985). Low

CEC silicates would include the kaolins which form most of the clay in Greene county soils (Fuqua, B.D., 2006). Kaolin is formed under conditions of equally concentrated silica and aluminum and the absence of base cations. It has a 1:1 sheet structure and is the most common clay mineral in highly weathered, acid soils (Buol et al., 2003).

The interactions of SOM with clays and metals can best be explained by ion exchange, surface adsorption and chelation reactions (Evangelou, 1998). Soil organic matter is intimately associated with clay sized particles in the soil via bridges of cations (Al³⁺, Fe^{3+and 2+}, Mg²⁺, Ca²⁺) that can bind to negative sites on both the clay surface and the SOM surface (Bohn et al., 1985; Evangelou, 1998). Humic substances form complexes with metals through oxygen containing functional groups such as carboxyl (COOH), hydroxyl (OH) and carbonyl (C=O). These SOM/metal interactions vary with ionic strength, pH, clay mineralogy, type of functional group and type of competing cation (Bohn et al., 1985; Evangelou, 1998). As a direct source of P and a source of binding sites for metal phosphates, SOM is one of the most important elements of the soil to consider in studying how P behaves in Springfield soils.

Relationship of Soil Phosphorus to Runoff Phosphorus

The objective of this study is to gain information on the P content in the surface horizon of Springfield Missouri lawns. Previous research has shown a strong relationship between soil test phosphorus in the upper 0-5 cm of soil and dissolved phosphorus concentrations in runoff. If it can be established that there is a difference in P concentration between urban lawns and other turf grass systems then further research can be done relating soil test P to runoff in Springfield, MO. Phosphorus indices, such as that developed by the USDA-NRCS developed to predict P loss from land try to account for the sources of P and the likely mechanisms of P loss (USDA-NRCS Technical Note, 1994). Soil Test Phosphorus (STP) is the main source component of phosphorus indices and has been shown to be related to DP in a variety of soils with a variety of extraction methods (Pote et al, 1999; Schroeder et al., 2004). It is therefore important to measure STP levels in soil before any runoff data is collected as an indicator of P mobility (Sharpley, 1995b; Pote et al., 1996; Pote et al., 1999; Sharpley at al., 2001; Torbert et al., 2002). Soil test phosphorus is a measure of P present in the soil and refers simply to the amount of P found in the soil as determined by a given extraction method, usually by Melich-3, distilled water, or acid extraction. It is also important that any relationship found between STP and DP in runoff not be generalized beyond the soils within the same geographic area with similar physical and chemical properties in their upper horizons (Sharpley, 1995; Torbert et al., 2002; Schroeder et al., 2004).

Phosphorus Indices. To get a more universal predictor of the loss of DP in runoff water, more factors must be considered than just the STP measures of a given site. To make a more universal predictor of P loss many variations of P indices are in use that include more loss factors than just STP.

The USDA-NRCS developed the first index widely used to assess potential P loss from agricultural fields. It was intended to assess the risk of P leaving an agricultural site and traveling toward any water body (NRCS Technical Note 1901, 1994). This initial index gave rating of site characteristics such as soil erosion, irrigation, soil P-test, and others. These P loss factors were then assigned a Likert scale value ranging from 0 (low

loss risk) to 8 (high loss risk). The individual site characteristics are weighted according to their importance and the total scores are added up to get an overall rating for the specific site (USDA-NRCS, 1994). This index has provided the foundation for numerous states to develop their own phosphorus indices with modifications to the index made to account for local variations in climate, soil and agricultural use (Sharpley et al., 2003). The phosphorus index takes into account P transport factors of rainfall, runoff, erosion and irrigation which influence the movement of P within the landscape (NRCS Technical Note, 1994). It also accounts for the factors that influence the amount and source of P available for transport such as soil P content and the form of P applied (NRCS Technical Note 1901, 1994).

Since all P indices rely on the inclusion of soil test P as one of the main source factors (Sharpley et al., 2003) and the original NRCS P index gives soil test P one of the highest weighting values the relationship between soil test P and DP in runoff needs to be explored further. The demonstrated relationship between STP and DP concentration is the best method for predicting DP in runoff. More must be known about the state of P in urban lawns in Springfield to be able to assess the potential of lawns to be a source of P in Greene County waterways.

Extraction Method. Strong correlations between STP and DP concentration in runoff were found by Pote et al. (1996). This study examined the relationship between STP and DP concentrations by six different extraction methods (Melich III, Olsen, distilled water, iron oxide paper, Bray-Kurtz, and acidified ammonium oxalate) in 54 grassed plots of fescue on a Captina silt loam all with a 5% slope. The strength of correlation, or r^2 values for all extraction methods ranged from 0.72-0.85 showing a high

correlation between STP and DP with all correlations being statistically significant (p>0.001). This shows that all extraction methods showed similar trends in STP/DP relationships for the tested soils.

Pote et al., (1999) also examined the use of correlations between STP to DP concentration to predict DP in runoff from a variety of soils. The study was conducted in northwest Arkansas and used soils similar to those found in Springfield at the subgroup taxonomic level (eg. Typic Paleudults and Typic Hapludults). The test site was sown in tall fescue. The results of their study showed that STP in surface samples (0-2 cm sampling depth) was strongly correlated with DP concentration for all the tested extraction methods (Melich III, Olsen, Morgan, distilled water, NH4-Oxalate, and Bray-Kurtz P1). The relationship between surface soil STP and DP concentrations in runoff was linear and the correlation coefficient or r-values for all samples were above 0.80 and most were above 0.90 (Pote et al., 1999). Like other studies Pote et al. (1999) found that no single method produced exactly the same regression line for all soils, although they were similar for the tested Ultisols. Therefore the correlation between STP and DP could only be used to predict the DP in runoff from a specific soil, or similar soils in the same geographic location and not as a universally applicable predictor for all soils in all places.

Sampling Depth. A study of the relationship between sampling depth of STP to DRP (Dissolved Reactive Phosphorus measured by the molybdenum-blue method) concentration was conducted by Torbert et al. (2002). They sampled four soils in Bermuda grass pasture at depths of 0-2.5 cm, 0-5 cm, and 0-15 cm. Melich III and distilled water extractions were used to measure STP. Unlike Sharpley (1995) and Pote et al. (1999) Torbert et al. (2002) found high variability affecting the relational

coefficient (r^2) in shallow (0-2.5 cm) surface STP samples. However the 0-5 cm depth samples were the most consistent in accurately predicting the DRP concentration from STP with the least variability $(r^2 = 0.72 \cdot 0.96$ for distilled water and 0.72-0.94 for Melich III). For all the sample plots, DRP concentration increased with increased STP although the proportion of particulate phosphorus (PP) remained the same. The 0-15 cm depth samples showed a steeper curve in the regression line due to dilution of P further down in the profile from non-P enriched soil as P had not leached down very far below the soil surface. It is also important to note that the non-calcareous soils in the study had a 2.5x higher maximum DRP concentration than the calcareous soils (1.5 mg/L and 0.6 mg/L respectively) at the same STP measures. This is important because the non-calcareous nature of soils in the Springfield area may make them more susceptible to P loss.

Sampling Depth and Extraction Method. Schroeder et al. (2004) examined the relationship between STP and DP and between STP and total P in runoff using four different measures of STP and three sampling depths of 0-2 cm, 0-5 cm, and 0-10 cm. These researchers also found strong and significant correlations between the amount of STP and DP as well as between STP and total P in runoff for all extraction methods and all sampling depths. Their data showed, like Torbert et al (2002), that the strongest correlations were at a sampling depth of 5 cm and the P measuring strategies that showed the strongest correlations between STP and total P in runoff was H₂0-extractable (R^2 = 0.68) and Melich III P (R^2 = 0.69).

Similarly, a study by Sharpley (1995a) investigated the relationship between STP and Dissolved P (DP) in soils similar in properties to those in the sampled area. Soil boxes were amended with poultry litter to obtain a wide range of Melich-3 extractable phosphorus soil levels. Soil samples were taken at a depth of 0-1 cm to get the STP from only the soil surface that interacts with runoff. The study found that all forms of DP concentrations in runoff were related ($r^2 0.70-0.80 p>0.05$) to the soil P content in the upper 0-1 cm for all 10 soils tested and for Melich III-extractabel P. This study also found that the concentration of DP in runoff increased as STP increased. The slope of the regression line relating STP and DP was different enough between each soil series that the author concluded that a single model equation could not be used on all soils to predict DP in runoff (Sharpley, 1995a). The P saturation of the individual soil series was also highly correlated with DP in runoff and therefore relating runoff DP to STP must be soil specific (Sharpley, 1995a; Torbert et al., 2002; Schroeder et al., 2004).

Sharpley (1995), Pote et al. (1996), and Pote et al. (1999) also found that the degree of P saturation as well as STP was highly correlated to the DP concentration in runoff. Sharpley (1995a) concluded that P sorption capacity could explain 90% of the variability in DP concentrations and those soils with high sorption capacities will show less potential for P enrichment of runoff water. This may be an important consideration considering that soils in Southwest Missouri are high in Fe and Al oxides and are generally low in pH. All these characteristics increase the P sorption capacity and may act as an attenuating influence on P loss from turf grass areas.

Land Use Management. In a more recent study Sharpley et al. (2001) found a correlation between STP and DP in runoff from farm fields based on landowner supplied

fertilization records and field measured STP and DP values. The DP concentration in runoff was highly correlated with STP only for fields that had not received any fertilizer in the previous six months (R^2 = 0.80). Fields that had been fertilized recently showed no correlation with STP because DP concentration was dominantly controlled by fertilizer on the soil surface (Sharpley et al., 2001). Although this study was conducted on agricultural fields instead of urban areas, and not all of the studied fields were turfgrass, it still highlights the importance of knowing the STP levels in order to understand P in runoff.

Runoff from urban watersheds has been shown to be a significant source of phosphorus (Waschbusch et al, 1999; Garn, 2002). STP has been shown to be strongly correlated to site specific runoff DP concentration and to total P in runoff (Sharpley, 1995; Pote et al., 1996; Pote et al., 1999; Sharpley at al., 2001; Torbert et al., 2002). Given this strong relationship any attempts to understand the P contained in runoff from lawns must first start with the P contained in the soil. Since all P indices rely on the inclusion of soil test P as one of the main source factors and the original NRCS P index gives soil test P one of the highest weighting values the relationship between soil test P and DP in runoff needs to be explored further (Sharpley et al., 2003; USDA Technical Note 1901, 1994). Unless a P index can be developed specifically for Greene County the correlation between STP and DP concentration is the best method for predicting DP in runoff. Therefore much more needs to be known about the amounts of P in urban lawns in Springfield to be able to predict P in runoff.

Effective Depth of Runoff Interaction. Examining the STP content of the surface soil in predicting runoff DP concentration is important because runoff from

rainfall only interacts with a very thin layer of soil at the surface of less that 1cm (Sharpley, 1985). The effective depth of interaction (EDI) was found to have a linear relationship with both rainfall intensity and slope. As rainfall intensity increased so did EDI and as slope increased so did EDI (Sharpley, 1985). These results are reflected in the conclusions of Torbert et al (2002) who found that a sampling depth of 0-15 cm had no relationship to runoff DP concentration because the P was held only in upper 5 cm of soil. Sharpley (1995) and Pote et al. (1999) showed that sampling depth of 0-1 cm showed highly significant relationships between the STP held in surface and runoff DP concentration.

Runoff from Residential Lawns

Urban runoff has been shown to contain high levels of phosphorus (Waschbusch et al., 1999). The environmental effects of storm water runoff from residential lawns have become increasingly important to researchers in recent years. Residential lawns represent a substantial portion of the total land area within urban watersheds. Two urban watersheds studied by Legg et al. (1996) were determined to have up to 65% of their land cover as grassed lawns. Due to the large amount of turfgrass area in urban watersheds the potential exists for these areas to be significant sources of nutrient pollutants although the contributions of turfgrass nutrients to water pollution are not well understood (Gross et al., 1990)

Runoff Volume. Some studies have found the volume of runoff from turfgrass systems to be very low (Morton et al., 1988; Gross, et al., 1990; Harrison et al, 1993). Morton et al. (1988) found that measurable runoff from turfgrass test plots occurred in only two rainfall events over the two years of study. Gross et al. (1990) found that only
seven rainfall events resulted in runoff for a tall-fescue sodded plot during one year of study and that compared to agricultural nutrient losses turfgrass nutrient losses were low. However, it should be pointed out that professionally-controlled test plots do not reflect all lawns in situ and there are many factors that can lead to more runoff from residential lawns than from test plots such as patchy grass, tree shade, and fertilizer frequency (Schueler and Holland: Article 4, 2000; Garn, 2002).

Studies that found little runoff from lawns and other turf grass areas were also conducted on very different soils than are found in the Springfield area. The soils studied were Merrimac sandy loam (Morton et al., 1988), and Westphalia fine sandy loam (Gross, et al, 1990). Both of these soils have > 50% sand in their A horizons (USDA-NRCS OSD, 2005; Shoenberger et al., 2002). However, in the Springfield area finer textural classes are more common and include silt loam, silty clay loam, clay loam and clay (i.e. less than 10% sand fraction in most cases). This difference is important since soils in the Springfield area have virtually no sand in their A horizons and therefore would be expected to have much slower infiltration of rainfall resulting in more runoff than sandy soils. The stormwater regulations manual for Greene County gives residential lawns and pastures a runoff coefficient of 0.10 to 0.30 meaning that 10 to 30% of rainfall is expected to runoff (Greene County, 1999). King and Balogh (2001) found that fine textured soils such as the Mexico series in Columbia, Missouri, with high clay content and low sand contents showed larger volumes of surface runoff and less infiltration as compared to sandier soils.

In addition, other researchers have found that runoff from turfgrass may occur more frequently than previously thought. Garn (2002) concluded that in two urban

Wisconsin watersheds 50% of rainfall events resulted in runoff from residential lawns. Waschbusch et al. (1999) found that lawns in account for 20% of urban runoff volume in Madison, Wisconsin. These runoff events can carry significant concentrations of DP in runoff (Rosenthal, 1990; King et al., 2001; Garn, 2002). Residential lawns comprise such a large area in urban watersheds and there is disagreement among researchers about the volume of runoff from lawns. Therefore the cumulative effect runoff from so many lawns on water quality is not well understood (Garn, 2002). Even if runoff from an individual lawn or test plot is small, in aggregate, many lawns could potentially contribute significant amounts of runoff and DP especially with short runoff distances to impervious surfaces (Schueler and Holland: Article 7, 2000).

The age of the lawn and the construction practices used in building the home can also influence the runoff and infiltration characteristics of residential lawns. Legg et al. (1995) found that lawns in newly developed subdivisions had significantly higher runoff volumes than lawns that had had several years for the soil structure to re-form. He concluded that the compaction during construction reduced the infiltration capacity and hydraulic conductivity of the surface horizons. His conclusions were supported by a study by Partsch et al. (1993) which examined the infiltration rates of lawns receiving three different construction techniques. Homes that had the topsoil stripped and the subsoil compacted before replacing the topsoil and grass establishment had very low infiltration rates compared to non compacted lawns. This was attributed to the destruction of pore space and the development of a limiting layer from compaction that reduced percolation. These lower infiltration rates were still observable in a studied lawn twelve years after construction and compaction (Partsch et al, 1993).

An important aspect of runoff relationship in P-indices is infiltration since rainfall-(infiltration +evapotraspiration) = runoff. Lower infiltration rates equal higher runoff volumes for any given rainfall amount. Studies show that even in coarse material (86-96% sand) compaction by normal construction methods can decrease infiltration by 80-99% from its original capacity (Gregory et al, 2006). This is partly due to the closing of pore space by soil compaction. It can be more than 20 years before the soil is able to regain its original structure and increase infiltration (Partsch et al., 1993). Although livestock compact soil to a certain degree, pastures do not show the same loss of infiltration rates from their original state (Gregory 2006). Therefore lawns tht have been compacted by construction equipment, especially in the clayey soil of the Ozarks may have much lower infiltration rates and much higher runoff rates than previously thought. This may be especially true for the newly built homes that are rapidly springing up due to rapid urban expansion in the Springfield metropolitan area.

Concentrations of DP in Runoff. Even with variable runoff volumes in turf grass plots, Pote et al. (1996) concluded there was still a highly significant concentration of DP in measured runoff and the relationship between STP and DP was also significant (p=0.72-0.85). For the 54 grass plots studied in Arkansas, the de-ionized (DI) water extractable total P ranging from 14 to 110 ppm. Schroeder et al. (2004) found similar ranges of DI extractable total P on pastures in Georgia. There the water extractable P (WEP) ranged from 0.42-1.25 mg/L (10.5 to 31.25 ppm soil P). Likewise, Torbert et al. (2002) found WEP to range from 0.044-1.8 mg/L (1.1 to 45 ppm soil P) in Bermuda grass pastures on Texas. Gross et al (1990), who found little runoff from lawns did

conclude that the runoff that did occur had a significantly higher concentration of DP than unfertilized control plots.

Garn (2002) found that residential lawns were a significant contributor of P by supplying up to 60% of the P flowing into Lauderdale Lakes, WI. He found that lawns receiving regular fertilizer had 1.6 to 1.8 times higher concentrations of P than lawns receiving no fertilizer or unfertilized land, although this difference was only marginally statistically significant (p = .11 and .14 respectively).

A study by Waschbusch et al. (1999) also provides good evidence that runoff from lawns is a significant source of DP in waterways. This Wisconsin study analyzed sediment and runoff from different land covers in urban watersheds. Based on the measured values they found that lawns contributed 21% of the runoff water volume and 71% of the DP to storm water in the Harper drainage basin and 20 % of the runoff water volume and 45% of the DP in the Monroe drainage basin. Put together, the runoff from lawns and sediment within streets accounted for 80 % of the total P in urban runoff. Runoff from lawns had the highest total phosphorus (TP) and dissolved phosphorus (DP) concentrations of any sources areas tested in both study drainage basins including streets, woodlots, and parks (Waschbusch et al., 1999). However, since the study did not report the soil types it is unknown how the runoff volumes would be affected by infiltration rates or interaction depths. It also means no direct comparisons can be made to Springfield area soils.

Connectivity of Lawns to Streams. An important consideration in evaluating the potential of lawns to be a significant contributor of P is the distance from the lawn to any impervious surface downhill from the lawn. Phosphorus indices are used to measure

the potential of a particular site to lose significant phosphorus in runoff. Although P indices were developed to predict the potential loss of P from agricultural areas they do have many components that are applicable in the study of lawns.

One of the main predictor variables they use is soil P which has been shown to have a relationship with DP in many settings. These indices also consider other variables such as the distance overland flow must travel before it reached a drainage way or watercourse. A modification to the original USDA-NRCS P-index adopted by the state of Pennsylvania has important implications for the development and application of a P index for urban areas (USDA-NRCS Technical Note, 1994; Sharpley et al, 2003). Pennsylvania considers the distance to a watercourse as a very important transport factor in the P index. It is well documented that the increased impervious area in urban areas conducts runoff and through storm drains increases the connectivity between urban areas and streams. Waschbusch et al. (1999) found that street sediment was the second biggest contributor of P to runoff water (although they did not study whether this sediment was from lawns or other sources). Shueler and Holland (2000, article 4) state that short transport distance from lawns to impervious area can influence P loss. It's not implausible that the proximity of many lawns to an impervious surface such as a driveway or street can magnify the effect of lawns on runoff quality by allowing runoff water from lawns to be quickly and directly transported into our streams via storm water drains.

Home Lawn Management. The management of residential lawns by the homeowner is an important influencing factor on both how much P is in the surface soil horizons and how much could be lost in storm runoff. Sharpley et al. (2001) found that if

fertilizer had been applied recently there was a significant increase in both STP and DP, but STP was not correlated to DP concentrations in runoff. The application of fertilizer had overwhelmed the natural relationships found between soil properties and P. This would seem to imply that the timing and application rate of fertilizer by the homeowner can affect how much P is lost in runoff. In a survey of Georgia homeowners Varlamoff et al. (2001) found that 50% of homeowners applied fertilizer to their lawns. Fewer than 6% of the homeowners knew the correct amount of fertilizer is good, more is better. For homeowners who fertilized their lawns, most applied the fertilizer in the spring. This seasonal period usually coincides with the highest amounts of rainfall during the year (Varlamoff et al., 2001) and therefore can lead to both high concentrations and yeilds of DP in runoff from lawns.

The granular forms of fertilizers used by many homeowners can also be suspended in the thatch layer of grass clippings above the soil surface. Application technique also has an impact on P mobilization. The lack of incorporation into the soil in a lawn setting can result in greater loss of nutrients in runoff. King et al. (2001) said that some of the higher than expected nutrient losses from a golf course were due to the suspension of granular fertilizers in the thatch layer making them more readily available for transport in runoff water. Fertilization amount, timing both by season and in relation to rainfall events as well as application technique can all influence the potential for nutrient pollution in runoff.

Summary

Eutrophication of surface waters is a growing concern that has been linked to inputs of P from different sources. A possible source of P is storm runoff water that flows over agricultural fields and over residential lawns into streams. Research has shown a strong correlation between the concentrations of P in runoff and the P found in the upper few centimeters of soil over which the water flows. It has also been shown that runoff from residential lawns can be a significant contributor of both water volume and the amount of DP delivered to nearby streams relative to other land use areas. Therefore to adequately study the amount of P in runoff from lawns, a general idea of P levels in Springfield soils must be established for several land uses.

There are many properties of soil that can affect the availability of P for loss in runoff. The amount of clay in the soil surface and its mineralogy affect the number of binding sites for aluminum and iron cations that are crucial to the immobilization of phosphates. These reactions are controlled by soil pH. The presence of organic matter provides a large sink/source of P in soil and dominates many of the chemical interactions.

The interactions of these variables in Springfield, Missouri soils are not well understood in terms of their effect on soil P levels or on the mechanisms by which P is transported from the soil into waterways. The research that has been reported on relating soil P to runoff has all been conducted on different soils and in different climatic and hydrologic regimes. It is therefore important that similar research designs to study soil P be used in Springfield, Missouri to understand this possible source of P pollution.

CHAPTER 3

STUDY AREA

All of the City of Springfield and most of Greene County, Missouri is located within the Springfield Plateau of the Ozarks Physiographic Region, an area of approximately 10,000 square miles (Adamski, 1995) (Figure 3.1). It is characterized as a gently rolling plain from 900-1500 feet above sea level, but local relief rarely exceeds 300 feet (Hughes, 1982; Adamski, 1995). The plateau is underlain predominantly by Mississippian limestone and as a result sinkholes and springs are prominent topographic features (Emmett et al., 1978). The Springfield Plateau is considered to be in a temperate climate with an average daily temperature of 56.2°F and an average annual rainfall of 39.7 inches, most of which falls in the spring and summer (Emmett et al., 1978; Hughes, 1982).

Greene County Geology

The bedrock of Greene County is composed of several different types of sedimentary rocks of different ages (Table 3.1). Limestone is the dominant lithology, but dolomite is also somewhat common. Thin beds of sandstone and shale outcrop locally. By far the most extensive surface bedrock in Greene County is Mississipian limestone of the Burlington-Keokuk formation (Figure 3.2). This formation is 150 feet thick and is composed of 97-99% calcium carbonate (Hughes, 1982). Ground-water activity in the Burlington-Keokuk formation results in a large number of sinkholes, caves and springs in Greene County.



Figure 3.1. The Ozarks Physiographic Region and Springfield Plateau

Greene County has more known caves than any other county in Missouri (Hughes, 1982). Specifically, these caves form when CO₂ from the atmosphere, produced by the oxidation of OM in soil mixes with rainwater to form carbonic acid. This acid reacts with the calcium carbonate in the limestone and breaks it down into Ca²⁺ and bicarbonate ions which are then carried off by the water leaving a void (Adamski, 1995). The karst nature of Greene County allows an extensive connection of ground and surface waters with sinkholes and caves allowing for very rapid transport of surface waters into ground water systems (Petersen, et al, 1998). This direct connection of the surface waters to ground waters by-passes the natural filtering role of the soil and so in many places there is little chance to remove nutrient contaminants such as P from surface water before it enters ground water (Adamski, 1995).

The limestone underlying Greene County also contains large amounts of chert (Hughes, 1982). As the limestone weathers into the residuum that forms the parent material of the soils the chert is left behind. This causes the soils in Green county to be very gravelly with many soil series having >15% gravel in their A-horizons and nearly all having >15% in the B-horizons (Hughes, 1982). This emphasizes the fact that soil characteristics are a function of the characteristics of the underlying bedrock (Table 3.2).



Figure 3.2. Geologic map of Greene County, Missouri.

System	Series	Formation	Rock Type
Pennsylvanian	Desmoinesian	Warner	Sandstone and Shale
	Osagean	Burlington/Keokuk	Limestone
		Elsey	Very Cherty Limestone
Mississippian		Reeds Springs	Limestone
		Pierson	Limestone
	Kinderhookian	Northview	Shale
		Compton	Limestone
Ordovician	Ibexian	Cotter	Cherty Dolomite with Sandstone Lenses
		Jefferson City	Cherty Dolomite
		Roubidoux	Sandstone, Dolomitic Sandstone and
			Cherty Dolomite
Cambrian	Croxian	Emminence	Dolomite
	Croxian	Potosi	Dolomite

(From Hughes, 1982; Thompson, 1995; and Middendorf, 2003)

 Table 3.2. Function of bedrock in soil formation.

Bedrock	Parent Material	Landform	Soil Series	Great Group
	Cherty		Eldon	Paleudalf
	Limestone	Slopes	Keeno	Fragiudalf
	Residuum		Wilderness	Fragiudalf
	Loess		Creldon	Fragiudalf
	Over		Hoberg	Fragiudalf
		Uplands	Viraton	Fragiudalf
Cherty	Cherty Limestone		Needleye	Fragiudult
	Residuum		Pembroke	Paleudalf
Limestone		Upland Plateaus	Newtonia	Paleudoll
	Alluvium over	Floodplains	Lanton	Haplaquoll
	Cherty Limestone	and	Hepler	Ochraqualf
	Residuum	Terraces	Huntington	Hapludol
	Loess over			
	Shale Residuum over	Uplands	Sampsel	Argiaquoll
	Cherty Limestone Residuum			
	Cherty Limestone Residuum			
	And	Slopes	Goss	Paleudalf
Cherty Limestone	Dolomitic Limestone Residduum			
and	Loess or Alluvium over	Floodplains		
Cherty Dolomite	Cherty Limestone Residuum	or	Doridao	Deloudolf
	And		rendge	Faleuuali
	Dolomitic LimestoneResiduum	Uplands		

(from Hughes, 1982)

Greene County Soils

Prior to European settlement in the Springfield Plateau the land was covered with both forests and tall grass prairies (Sauer, 1920; Rafferty, 2001). Thus the soil orders present in Greene County are determined in part by this historic vegetation cover. Alfisols form primarily under forest vegetation and Mollisols form under prairie grass vegetation. Both of these soil orders dominate Greene County. Of the 33 named soil series in Greene County 20 are in the Alfisol order and 8 are Mollisols (Hughes, 1982). The remaining Greene County soils are in the Ultisol, Entisol and Inceptisol orders. All sample sites for this study were on Alfisols or Mollisols. Table 3.3 shows the parent material from which each sampled soil series in Greene County is derived. Table 3.4 shows the physical and chemical properties typical of the A horizon for sampled soil series the Appendix H shows the soil series and subgroup name for each sampled site.

Alfisols. Alfisols cover 78% of the land surface in Greene County (Hughes, 1982). They are distinguished by an accumulation of layer-lattice clay in the subsurface horizons which usually forms an argillic horizon and a base saturation greater than 35%, but less than 50% in the control section (Buol et al., 2003). In Southwest Missouri it is nearly always an argillic diagnostic horizon that is formed (Hughes, 1982). The organic matter of Alfisols is usually concentrated in the O-horizon under a forest canopy cover. In areas without forest cover the O-horizon of most Alfisols has been eroded away and most OM is concentrated in the mineral A-horizons. As such it would be expected that forested soils would contain a higher OM content due to the presence of an O-horizon. Alfisols formed in forest vegetation on stable landscapes of early Holocene age or older (Buol et al., 2003). Since they are from older deposits they have undergone a long

weathering process which has leached out most of the weatherable cations. The result is a base saturation of greater than 35% and less than 50% in the control section. The base saturation usually remains constant or increases with depth. Alfisols usually have an ochric epipedon and neutral (6.5-7 pH) A-horizons and acidic (4.8-5.8 pH) sub-surface horizons. Fragipans are also commonly formed in temperate regions (Buol et al., 2003). This is typical of the neutral A-horizons and acidic B-horizons of Greene County as well as the high occurrence of fragipans (Hughes et al., 1982).

Mollisols. Mollisols are formed on late Pleistocene and early Holocene deposits under prairie grass vegetation such as the big-bluestem prairies that once covered part of Greene County. Mollisols cover approximately 13.5% of Greene County's area (Hughes, 1982). They are typified by deep (>10 in), dark (10 YR 3/3) friable surface horizons that form a mollic epipedon and high base saturation of >50% (Soil Survey Staff, 2003). Mollisols usually have a cambic or argillic horizon, but the argillic horizons are not as strongly expressed as in Alfisols because of the slowing of clay translocation by organoclay complexation. They exhibit fairly high organic matter contents due to the in situ death of grass roots (Buol et al., 2003). Mollisols are commonly used for both crop and hay production.

Series Name	Sub-Group	Landscape	Parent
		Position	Material
Cedargap	Cumulic Hapludoll	Floodplains	Cherty Alluvium
Creldon	Mollic Fragiudalf	Uplands	Loess, Colluvium, and Cherty LimestoneResiduum
Eldon	Mollic Paleudalf	Uplands	Cherty Interbedded Limestone Residuum
Goss	Typic Paleudalf	Uplands	Cherty Limestone Residuum and Colluvium
Huntington	Fluventic Hapludoll	Floodplains	Alluvium
Keeno	Mollic Fragiudalf	Uplands	Cherty Limestone Residuum
Needleye	Aquic Fragiudult	Uplands	Loess and Limestone Residuum
Newtonia	Typic Paleudoll	Upland Plateaus	Loess and Limestone Residuum
Pembroke	Mollic Paleudalf	Karst Uplands	Loess, Limestone Residuum, and Alluvium
Peridge	Typic Paleudalf	Uplands and Stream Terraces	Limestone, Sandstone, Shale Alluvium and Colluvium and Residuum sometimes overlain by loess
Sampsel	Typic Argiaquoll	Upland Slopes	Shale Alluvium and Colluvium
Secesh	Ultic Hapludalf	Floodplains	Limestone and Sandstone Alluvium and Residuum
Wildernes	Typic Fragiudalf	Hillslopes	Cherty Limestone Residuum

 Table 3.3. Characteristics of sampled soil series.

(From Hughes, 1982; USDA NRCS OSD 2006)

	Typical A - Horizon						
Series	Depth	Toxturo	Clay	лЦ	Permeability		Color
Name	(inches)	Texture	(%)	рп	(in./hr)	Class	COIOI
Cedargap	0-6	sil	15- 27	5.6- 7.3	0.6-2.0	Moderate	10YR 2/2
Creldon	0-9	sil	15- 25	4.5- 7.3	0.6-2.0	Moderate	10YR 3/2
Eldon	0-10	cherty sil	7-27	5.1- 6.0	2.0-6.0	Moderately Rapid	7.5YR 3/2
Goss	0-8	cherty sil	7-27	4.5- 7.3	2.0-6.0	Moderately Rapid	10YR 4/2
Huntington	0-12	sil & sicl	18- 30	5.6- 7.8	0.6-2.0	Moderate	10YR 3/2
Keeno	0-17	cherty sil	15- 25	4.5- 7.3	2.0-6.0	Moderately Rapid	10YR/3/3
Needleye	0-7	sicl	15- 25	4.5- 7.3	0.6-2.0	Moderate	10YR 4/2
Newtonia	0-10	sil	10- 24	5.6- 6.5	0.6-2.0	Moderate	7.5YR 3/2
Pembroke	0-8	sil	12- 27	4.5- 6.0	0.6-2.0	Moderate	10YR 3/3
Peridge	0-9	sil	10- 20	4.5- 6.5	0.6-2.0	Moderate	7.5YR 4/4
Sampsel	0-8	sil & sicl	25- 35	5.6- 7.3	0.2-0.6	Moderately Slow	10YR 3/1
Secesh	0-8	sil	15- 25	5.6- 6.5	0.6-2.0	Moderate	10YR 3/3
Wildernes	0-10	cherty sil	18- 27	4.5- 7.3	2.0-6.0	Moderately Rapid	10YR 4/2

Table 3.4. A-horizon characteristics of sampled soil series.

(From Hughes, 1982; Shoenberger et al., 2002)

Greene County Land Use

Prior to European settlement the Springfield Plateau, including Greene County was evenly divided between forests and prairie lands of big-bluestem grass with the prairies mainly on the uplands and forests growing in valleys and on slopes (Sauer, 1920; Rafferty, 2001). Upon the arrival of European settlers the area underwent many successive changes in land use. The Ozarks timber boom which started with the arrival of the railroads and continued from approximately 1880-1920 saw the clearing of many forested areas and the plowing of the prairies (Rafferty, 2001). After the forests had been cut the primary economic emphasis of the area turned to agriculture.

Agriculture. The first settlers in the Springfield area relied on general agriculture to grow all varieties of crops they needed with emphasis on row crops such as wheat and corn. By 1900 nearly one-third of Greene County was planted in corn or wheat (Hughes 1982). After the timber boom ended in the early 1920's an attempt was made to increase the row crop production by planting on the cut-over ridge-tops in the Ozarks, but was unsuccessful due to the fragic nature of most upland soils (Rafferty, 2001). Cultivation of row crops on marginal areas such as uplands and slopes caused a considerable increase in runoff and soil erosion (Jacobson and Primm, 1997). By the 1930's row crops gave way to beef and dairy production in the Springfield area.

Steady growth of livestock agriculture and the de-emphasis on row crops has resulted in the primarily beef cattle based agriculture in Greene County today. By 1990 nearly all corn and wheat had disappeared from Greene County with only insignificant amounts being grown in river bottoms. Nearly 70% of the agricultural land in Greene County is now grown in tall fescue either as pasture for cattle or to be cut as hay (Rafferty, 2001). The beef industry in the Springfield area is pasture based with very few confined animal feeding operations (CAFO). In addition to beef, poultry production is a growing trend in the region's agriculture while the number of dairies has been declining (Hughes, 1982; Rafferty, 2001).

Urban Growth. Springfield, the largest city in the Missouri Ozarks, was founded in 1830, but growth was slow for the city and surrounding areas until the introduction of the railroads in the post-civil war era (Rafferty, 2001). The construction of large man-

made reservoirs and lakes beginning in the 1960's created many opportunities for tourism and initiated the rapid growth of the area's population (Rafferty, 2001). The area around Springfield Missouri has experienced extremely rapid urban growth in the last 15 years (Figure 3.3).

Greene County Missouri is the fifth most populous, and one of the fastest growing counties in the state. Located within Greene County, Springfield is the state's third largest city. Christian County, just to the south of Greene County contains the cities of Ozark, Nixa and Republic which are counted in the Springfield metropolitan statistical area (MSA). These communities have grown extremely rapidly in recent years and are connecting with the City of Springfield as they grow northwards. As these communities grow to the north they are beginning to connect with the City of Springfield to form a single, very fast growing urbanized area.

The data on the population of Springfield does not show the same kind of growth as the surrounding communities. During the years 2000-2004 Springfield's population has actually decreased from 151,580 to 150,704 (U.S. Census Bureau, 2006). However, just taking into account the population growth within the city limits can be misleading. Within the same years 2000-2004 the population of Greene County has grown from 240,391 to 247,992 and from 1990 to 2000 the Springfield MSA has grown immensely from 264,346 to 325,721 (U.S. Census Bureau, 2006). The city boundaries are not being expanded to keep up with population growth. As a result the population of the city appears to be staying steady, while in reality the city is expanding rapidly into the surrounding countryside (Figure 3.4).

As a result of the rapid expansion of Greene County's population, the land use changes that have occurred in the last 40 years have been tremendous. In 1972, the Springfield Area was composed of 36,996 acres of urbanized land, 58,877 acres of forest and 118,064 acres of grassland (MoRAP, 2003). By the year 2000, the urban area had grown by 66,571 acres to 103,567 acres, a 179% increase (Figure 3.5). During that same period, forests and grasslands both decreased by 36% (MoRAP, 2003).





Figure 3.3. Landsat TM images of urban growth from 1972-2000. Urban areas are colored yellow. (Mo-RAP, 2003)

Current Land Use. The land cover of Greene County is predominantly grasslands used for livestock agriculture. There are also significant areas of cedar dominated forests. Springfield and the smaller town of Republic constitute the county's urban centers which make up a substantial and growing percentage of urban land cover in Greene County (Table 3.5). These urban areas constitute a growing residential area with its corresponding increase in area covered by lawns. Figure 3.6 is a map showing the current (as of 2004) land uses in Greene County, Missouri.



Figure 3.4. Population growth of Greene County and the City of Springfield, Missouri (U.S. Census Bureau, 2006)



Figure 3.5. Land use trends for Springfield, Missouri (data from MoRAP, 2003).

Table 3.5. Study area land use classes as a percent of total area.

	% Ground Cover		
Land Cover Class	Springfield	Greene Co	
Urban/Impervious	32.33	5.71	
Residential	42.42	7.81	
Bare Ground/Transitional	0.15	0.61	
Crops	0	5.34	
Grass/Pasture/Hay	17.31	54.44	
Evergreen Forest	4.65	20.63	
DeciduousForest/Shrubs	1.99	4.6	
Water	1.15	0.86	
Total	100	100	
Total Area (Km ²)	961.74	961.74	
E EGDI INCOND	````````````````````````````````````		

Study Area Land Use/Land Cover

(From ESRI and MoRAP)



Figure 3.6. 2004 land use map of Greene County.

CHAPTER 4

METHODOLOGY

Methods for this study include field methods, laboratory methods and statistical analysis methods. Field methods include soil sampling and collection of data on site characteristics, including location using a Global Positioning System (GPS). Laboratory Methods include soil sample preparation, chemical analysis, water extraction analysis, grain size analysis, and organic matter content analysis. Statistical methods include descriptive statistics, comparative statistics using scatter plots and production of multivariate models using stepwise regression.

Field Methods

Site Selection. Lawns sample sites were selected based on availability and permission of the owner. Friends and acquaintances of the experimenter and advisor were asked if samples could be taken from their lawns. This non-random selection may have introduced some error since the owners of sampled lawns may tend to be similar in age, education, and socioeconomic status. Lawns were also selected by location within Springfield to give a spatial distribution that was as uniform as possible. An attempt was made to select lawns from different ages of neighborhoods in the city.

Agricultural sites were selected by cooperation with the USDA-Natural Resource Conservation Service. Landowners who had not previously used organic fertilizers such as poultry litter, manure or sewage sludge were contacted for permission to sample their property. Only land used for cattle pasture, or hay harvest was sampled. **Soil Sampling.** Soil samples were collected from each of four land use classes using a ³/₄ inch hand-held tube-style soil probe. The four land-uses sampled were residential lawns, agricultural pastures and hayfields, city parks, and forested areas (Table 4.1) for a total n of 92. Figure 4.1 shows the location of each sample site for all land uses. Samples were taken from the soil surface to a depth of 5 cm. This is the depth found to most closely relate soil P to runoff P (Sharpley et al., 2001; Torbert et al., 2002; Schroeder et al., 2004). Due to the natural variability in soil nutrients, a grid based sampling scheme adapted from Donohue (2002) and Sharpley et al. (2001) was used to obtain a representative sample. A 1m x 1m square was constructed of 1 inch PVC pipe. This was then divided into a grid consisting of nine cells, each 0.11m x 0.11m.

At each sampling site the grid was placed on the ground and one soil core was taken from the center of each of the nine cells in the grid. All nine cores were placed into the same zip-lock bag labeled with the site location, sample number and collection date. This was considered one composite sample. The grid was then moved 1 meter along the slope and a second composite sample was taken. This gave two samples per site location for lawns, parks and forested areas. Due to the larger area of most pastures and hayfields, samples were collected at three sampling sites per farm where possible. Sample locations were selected by landscape position with one sample site on the summit, one on the shoulder, and one on the toe or floodplain position. As before, two separate composite samples were collected at each of these landscape positions.

Site Characteristics. In addition to soil samples, data was gathered on several other site characteristics that can influence runoff or P sources (Table 4.2). Many of these characteristics are important in a P-index as either transport or source parameters.

The data collected included slope, which was measured with a Macklanburg-Duncan Smart-Tool. Aspect (azimuth direction of slope) was determined using a Brunton, handheld compass. Distance of the sampling location from both the house and any impervious area down the slope was measured with a 30 meter surveyor's tape. Each homeowner was also asked about the fertilization history of his/her lawn such as what kind of fertilizer is used and how often it is applied if at all, as well as how long it has been since the home was constructed. A likert-scale estimate of tree canopy density (none, little, moderate, heavy) was made and grass species was also identified for each lawn. Appendix A shows the location and selected physical attributes for each sample site.

 Table 4.1.
 Sample size by land use class.

Land Use Classification	Number of Sample Sites	n
Residential Lawns	20	40
Pastures and Hayfields	13	26
City Parks	6	12
Undisturbed Forested	7	14



Figure 4.1. Study area sampling locations by land use.



Figure 4.2. Location map showing site numbers.

Site Characteristic	Importance	Source
Slope	Determinant of soil runoff class and affects rate of infiltration and runoff	USDA-Technical Note, 1994; Sharpley et al, 2003
Aspect	Influences soil temperature and soil moisture conditions; temperature affects rate of P mineralization.	Buol, et al., 2003; Minor et al., 1993
Distance from sample site to the house	Soil samples taken near buildings can be non-representative due to fertilizer or insecticides applied to landscaping	Donohue, 2002
Distance to down-slope impervious area	Short distances can limit water infiltration and increase the direct connection of runoff to streams.	Sharpley et al., 2003
Fertilization	Serves as a direct source of P.	Sharpley et al., 2001
Irrigation	Can quickly induce saturation overland flow by increasing antecedent soil moisture	Knighton, 1998
Age of home	Recent construction (up to 20 years) compacts the soil, reducing infiltration and increasing runoff	Partsch et al., 1993
Tree cover	Leaves can be a source of P	Waschbusch et al., 1999

Table 4.2. Importance of sample site physical characteristics.

Laboratory Methods

Sample Prep and Chemical Analysis. Soil Samples were dried in an oven at 65 °C for 2-4 days until all pore water had been removed. After drying, all samples were disaggregated using a mortar and pestle. Samples were then passed through a 2 mm sieve. All particles larger than 2 mm were discarded. Soil samples were then sent to

Chemex Labs for chemical analysis using Inductively Coupled Plasma-Atomic Emissions Spectroscopy (ICP-AES). Total P concentration (ppm) in soil samples was determined by hot, strong acid extraction with 3:1 HCl: HNO₃, or Aqua-Regia. An additional 33 elements were also analyzed including Al, Fe, Mg, Ca, and Zn. Appendix B shows the concentrations of elements discussed in the current study for each sample. Appendix I shows the concentrations of elements that were analyzed, but not discussed in the current study. Triplicate samples from several sites were analyzed to test for variability within each sample and check the precision of the chemical analysis. Appendix C shows the triplicate analysis data.

Grain Size Analysis. Soil textural analysis was conducted in the Geomorphology Laboratory at Missouri State University using the standard hydrometer method to measure the relative percentages of sand, silt and clay (Gee and Bauder, 1986; Pavlowsky, 1995). Approximately 40 grams of soil was weighed into each 250ml beaker with 50 ml of de-ionized water for analysis. Soil samples were then digested in 10 ml of a 1% Glacial Acetic acid solution and 5-10ml of 30% H₂O₂ for at least 10 hours to digest any organic matter. The samples were heated to 90 °C for one hour to complete the digestion. Once the liquid was clear the supernatant liquid was decanted with a vacuum pump and the samples placed in a 110 °C oven to dry thoroughly. The dry post-digested samples were then weighed.

The dried samples were then mixed with 125 ml of a 4.6% (by mass) sodiumhexametaphosphate solution in a blender for 15 minutes to disperse clay particles. Samples were then poured into a standard 1-liter hydrometer and de-ionized water was added to get a total water and sediment volume of one liter. The solution was then

allowed to sit overnight for the water temperature to reach equilibrium with the ambient temperature in the lab.

Samples were then re-suspended in the cylinders using a plunger and a standard hydrometer was used to measure the specific gravity (density) of the water column for the $63\mu m$ and $2\mu m$ size fractions. Prior to each set of readings the temperature and a "blank" hydrometer reading were taken from a cylinder containing only water and the dispersant solution. This took into account any changes in temperature between reading times. After the $2\mu m$ reading was taken the samples were then wet-sieved through a $63\mu m$ filter to separate and keep the sand fraction. The sand was then dried and weighed to validate the $63\mu m$ reading. Appendix B shows the data from the hydrometer analysis. The coefficient of variance from a triplicate analysis of clay ranged from 0.18% to 9.51% with a mean of 5.23%. Appendix D contains the results of the triplicate analysis for clay.

Organic Matter Analysis. Organic matter content of samples was analyzed in the Geomorphology Laboratory at Missouri State University using standard methods (Dean, 1974; Pavlowsky, 1995). The loss in ignition (LOI) technique was utilized to measure soil organic matter content. A 5-gram sample was placed into a ceramic crucible and then dried in an oven at 105 °C for two hours to remove any soil moisture. The pre-burn weight of the crucible and dried sample was recorded. The samples were then placed in a muffle furnace and heated to 600 °C for six hours to burn off all organic matter in the soil. After cooling, the post-burn weight was recorded and subtracted from the pre-burn weight. The difference was divided by the pre-burn weight to obtain the organic matter content as a percent by weight. Appendix B displays the OM content of

all soil samples. The coefficient of variance from a triplicate analysis of OM ranged from 3.68% to 11.70% with a mean of 6.51%. Appendix E contains the results of the triplicate analysis for OM.

Acidity-pH. The pH of soil samples was analyzed in the Geomorphology Laboratory at Missouri State University using standard methods (Janitzky, 1986; Pavlowsky, 1995). Soil pH was measured using a 1:2 soil to water mixture. Approximately 10 grams of each sample was placed in a 50 ml beaker and 20 ml of deionized water added. The mixture was stirred for 5 seconds to ensure thorough mixing. Samples were then allowed to stand for one hour. After one hour the samples were again stirred for 5 seconds then allowed to settle for ten minutes. A Hanna Instruments pHep hand-held pH meter was then inserted into the sediment and allowed to stabilize for approximately 20 seconds. The pH was then read and recorded. Appendix B shows the pH data for each sample. The coefficient of variance from a duplicate analysis of aciditypH ranged from 0.00% to 5.94% with a mean of 1.13%. Appendix F contains the results of the triplicate analysis for OM.

De-Ionized Water Extractable Phosphorus. A subset of lawn soil samples was selected to analyze for P using the de-ionized water extraction method (Pote et al, 1996). This is a pilot experiment to predict water soluble contribution. Therefore, effort was made to select typical samples in terms of geochemical properties for analysis. Samples to be analyzed by this method were selected by a two step process. First a plot of pH over OM was examined to determine if any soil samples were outside the normal range of pH for a given OM %. All sites within this pH range were then selected based on a graph of P over OM for each land use class (Figure 6.5-6.8). Any samples that fell within

two standard errors (95% confidence interval) of the regression line of P v. OM were considered. Fourteen soil samples were selected based on fit to the regression line and a range of P within the standard errors for a given OM%.

Once the samples were selected one gram of soil was weighed out to within 0.0005g using a Sartorius tare scale. Three sub-samples were taken from each of the 14 selected samples sites to examine variability of distilled water extraction within each sample. Forty-Two sub-samples from the original samples were used in this analysis. Each sub-sample was placed in a labeled 50 ml centrifuge tube with 25 ml of de-ionized water for a soil to water ratio of 1:25. Samples were then placed on a New Brunswick Scientific C2 platform shaker for one hour. The sub-sample tubes were then placed in a centrifuge at 2,600rpm for five minutes. The water was them filtered through a $0.45\mu m$ filter into a sterile labeled centrifuge tube.

The filtrate was analyzed for total phosphorus in the Chemistry Research Laboratory at Missouri State University using standard methods (Murphy and Riley, 1962). Phosphorus analysis was performed using spectrophotometry. This is a common method of measuring phosphorus in water samples. Ten ml of each sub-sample was transferred into glass test tubes using a pipette. Sixteen grams of Ammonium Persulphate was mixed with 50 ml of de-ionized water and 0.25 ml of this solution was added to each test tube along with 0.2 ml of 5.4 M H₂SO₄. This was to convert any organic P into inorganic orthophosphate. Each sample tube was then placed on a Vortex Genie mixer to thoroughly mix the digestion reagent. All sample tubes were then cooked in an autoclave for 50 minutes.

Upon cooling, 0.5 ml of 6M NaOH and 1 drop of phenothaline were added to each sample tube. An amount of 0.2 ml of 5.4M H₂SO₄ was then added to neutralize the samples. A combined reagent was mixed using 23 ml of 5.4M H2SO4, 0.53 g of solid ascorbic acid, 5 ml of antimony potassium and 15 ml of ammonium molybdate (reacts with phosphate to form a blue color). This reagent was diluted with de-ionized water to a volume of 100 ml and 1.5 ml of the reagent solution was added to each test tube. A Spectronic 20 Genesys spectrophotometer was set to a wavelength of 880 nm and calibrated using seven standards of known phosphorus concentration. All samples were then run on the spectrophotometer. Appendix G shows results of the de-ionized water triplicate analysis. Appendix H shows the standard calibration curve, laboratory standard and blank results used in the phosphorus analysis.

Measurements from the spectrophotometer were converted from mg/L to ppm by multiplying by the dilution factor of the soil samples (25 ml). Since the soil ratio was 1:25 for the water analysis multiplying by 25 give the water extractable TDP in the soil. *DI Water extractable soil P (ppm) = TDP (mg/L) x 25*

Once the water extractable TDP was calculated this umber was then divided by the TP extracted by aqua regia for that sample to obtain the % of the total as DP.

Total Dissolved P % = $\underline{DI \ extractable \ soil P \ (ppm)} x \ 100}{TP \ (ppm)}$

Statistical Analysis Techniques

Statistical analysis for this study involves descriptive statistics, comparative statistics and some multivariate regression modeling. Descriptive statistics for geochemical data is displayed using grid charts and box plots. These were created in

Microsoft Excel, 2003 and SPSS 11.0. Comparative statistics use Pearson Correlation matrices and two sided t-tests to identify correlated variables to understand the relationships between geochemical and site variables. Two-tailed t-tests were used to compare the difference in means between land uses for TP and for water extractable P. These t-tests were done using the data analysis tool in Microsoft Excel, 2003. Scatter plots of the relationship between predictor variables and TP were created in Microsoft Excel, 2003. For organic matter the 95% confidence intervals were estimated using the Y-value from the regression equation +/- two times the standard error (SE) for all x-values in each land use class. Thus the 95% CI is $Y = \beta_1 x + \beta_0 + 2(SE)$ (Kutner et al., 2004).

Pearson Correlation matrices were also produced using Microsoft Excel, 2003. Stepwise regression analysis was performed using S-Plus 7.0 and SPSS 11.0 statistical software. Stepwise linear regression modeling was used to selectively choose geochemical and site characteristics that best explained the variance in P values for the soil samples.

Confidence Intervals were used to gauge the accuracy of a single variable predictor. The confidence interval (CI) is based on the same 0.05 alpha as the p-value. The 95% CI is a measure based on the linear regression equation of the values of Y (TP) for a given x-value (OM). This means that for any given x-value, the predicted Y-value from the regression equation would be expected to fall within the CI for 95 out of 100 iterations if the alpha level is 0.05 (Kutner et al, 2004).

CHAPTER 5

RESULTS AND DISCUSSION:

SOIL PROPERTIES AND PHOSPHORUS CONCENTRATIONS

This chapter evaluates the relationships between TP and soil properties, geochemistry, and location/land use and is presented in five sections. The first section addresses characteristics of soil composition that can influence TP. Descriptive statistics and box plots are used to describe the distribution of sand, silt and clay fractions that make up soil texture, as well as OM and soil acidity-pH. The second section likewise uses descriptive statistics and box plots to examine the distribution of geochemical elements that influence TP sorption and behavior in the soil such as aluminum (Al), iron (Fe), and calcium (Ca). The micronutrients copper (Cu) and zinc (Zn) are also discussed. In addition two metals normally attributed to pollution sources, lead (Pb) and mercury (Hg), are also examined. The third section uses the same statistical methods and focuses specifically on the distribution of TP within the study area to be able to answer the main research question of what land uses have the most soil P available for transport. The fourth section examines soil color and the effects of soil formation, or parent material on TP. The final section extends the soil formation analysis by examining the differences in TP among soil orders and the effect that OM has on TP for all soil orders.

Physical and Chemical Properties

This section utilizes descriptive statistics to generally describe the distribution of soil and geochemical properties as well as the concentration of P in soil for all land uses.
Texture. The relative percentages of sand, silt and clay determines soil texture. In the present study 71% of the collected samples were classified as silt loam and 21% were classified as silty clay Table 5.1 shows the soil texture by land use based on mean values of sand, silt, and clay. The surface soil of most sample sites was classified as silt loam with the remainder being silty clay loam (Table 5.2)

Sand Fraction. Although the sand fraction in this study varied a lot among sample sites, the means for each land use class were very similar. The fraction of sand ranged from 1.1% to 24.4% across all sample sites with a relatively high coefficient of variation for each land use class (Table 5.3). The mean sand fraction for forests was slightly higher than that of lawns, parks, or agricultural sites. However, there were no statistically significant differences in the percentage of sand for any of the land uses (Table 5.4). The distribution of percent sand to land use is shown in Figure 5.1. The distribution of sand is very similar for all land uses with very few differences. In lawns the three outlying values are most likely due to differing fill material. The outlying value with high sand content for forest was taken in the floodplain of Wilson's Creek very close to the stream where sand contents would be expected to be higher. With no significant differences in the distribution of sand any differences in textural relationships to TP must be a result of either silt or clay content.

Table 5.1. Average soil texture by land u
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Land Use	Sand (%)	Silt (%)	Clay (%)	Textural Class
Lawns	6.92	68.96	24.12	Silt Loam
Parks	6.52	69.30	24.17	Silt Loam
Agriculture	6.96	73.71	19.33	Silt Loam
Forest	7.57	67.09	25.34	Silt Loam

Land use	Silt Loam (%)	Silty Clay Loam (%)
Lawns	78	22
Parks	46	54
Agriculture	71	29
Forest	100	0

 Table 5.2.
 Textural class of samples by land use.

 Table 5.3.
 Descriptive statistics for sand (%) by land use.

Land Use	Mean	median	min	max	sd	cv%
Lawns	6.92	5.70	2.93	24.36	4.13	59.68
Parks	6.52	6.57	3.37	12.12	2.47	37.89
Agriculture	6.96	7.33	1.15	11.12	2.82	40.55
Forest	7.57	6.36	3.40	18.50	4.30	56.82

 Table 5.4.
 Comparison of sand % among land uses using a Two-Tailed t-Test.

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	-0.05	2.00	0.96
Lawns v. Parks	0.41	2.04	0.69
Lawns v. Forest	-0.49	2.07	0.63
Parks v. Forest	-0.77	2.08	0.45
Agriculture v. Parks	-0.48	2.06	0.63
Agriculture v. Forest	-0.48	2.09	0.64



Figure 5.1. Distribution of sand by land use. Note: bolded line is median value, O = outlier value, * = extreme value.

Silt Fraction. The percentage of silt in soil samples was much less variable than the sand fraction. Although the silt fraction ranged from 52% to 79% the coefficient of variance was much smaller for all land uses with only forested sites having a cv% above 10% (Table 5.5). The mean silt fraction of agricultural sites was significantly higher than the mean of lawn, park, and forest sample sites (Table 5.6). Figure 5.2 shows the distribution of percent silt by land use type. Agricultural sites clearly have a greater proportion of silt. This is unexpected considering that higher erosion rates in the past when the area was dominated by row crops should have carried silt down slope to the toe and floodplains leaving less on the hill sides. However there was no difference in soil texture by landscape position.

Land Use	Mean	median	min	max	sd	cv%
Lawns	68.96	69.52	51.98	79.25	4.72	6.85
Parks	69.30	67.06	61.14	77.35	5.91	8.53
Agriculture	73.71	73.88	67.14	79.10	3.23	4.38
Forest	67.09	69.97	55.45	78.27	8.24	12.29

 Table 5.5.
 Descriptive statistics for silt by land use.

 Table 5.6. Comparison of silt % among land uses using a Two-Tailed t-Test.

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	-4.85	2.00	<0.01*
Lawns v. Parks	-0.18	2.13	0.86
Lawns v. Forest	0.80	2.12	0.43
Parks v. Forest	0.79	2.07	0.44
Agriculture v. Parks	-2.42	2.14	0.03*
Agriculture v. Forest	2.89	2.13	0.01*



Figure 5.2. Distribution of silt by land use. Note: bolded line is median value, O = outlier value, * = extreme value

Clay Fraction. Since each land use has nearly identical sand distribution any relationships between geochemistry and texture must be dominated by either silt or clay. If sand is approximately equal for all land uses then surface soil texture is a function of clay only. Clay in the study area ranges from 11% to 39% (Table 5.7). The clay fraction is significantly lower for agricultural sites than for the other land uses (Table 5.8). Since sampling of agricultural sites was done at summits, shoulder slopes and toe/floodplain areas the clay results were stratified by these landscape positions to determine if the difference in clay for agricultural sites was due to particularly low clay contents on one or more landscape positions. Sample sites on summits had a mean of 17.96%, shoulder sites had a mean clay content of 19.08% and floodplain/toe slope sites had a mean of 21.01%. The differences between summits and shoulders was not significant (p=0.43) while the difference between summit sites and floodplain/toe slopes was not quite significant (p=0.058, α =0.05). The difference in clay contents between land use samples therefore cannot be explained by landscape position. It may be a function of natural variability in different soil series, however the data provided by Hughes (1982) on the clay ranges for particular soil series is too wide to allow a comparison of soil series between sites.

 Table 5.7. Descriptive statistics for clay (%) by land use.

Land Use	Mean	median	min	max	sd	cv%
Lawns	24.12	23.43	17.82	32.03	3.07	12.72
Parks	24.17	26.43	11.48	34.31	7.45	30.81
Agriculture	19.33	18.84	13.92	25.86	3.12	16.14
Forest	25.34	25.06	15.70	39.32	7.73	30.50

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	6.14	2.01	<0.01*
Lawns v. Parks	-0.02	2.18	0.98
Lawns v. Forest	-0.58	2.14	0.57
Parks v. Forest	-0.39	2.06	0.70
Agriculture v. Parks	-2.17	2.16	0.05*
Agriculture v. Forest	-2.79	2.13	0.01*

 Table 5.8.
 Comparison of clay % among land uses using a Two-Tailed t-Test.



Figure 5.3. Distribution of clay by land use. Note: bolded line is median value, O = outlier value, * = extreme value

Organic Matter. Organic Mater (OM) is the soil property with the strongest relationship to TP for the sites sampled in this study. For all sampled sites combined the coefficient of determination (R^2) is 0.508 and the p value is <0.01 meaning that OM alone can explain 51% of the variance between P levels among land uses. The OM

content of all land uses ranges from 1.42% to 7.37% and a fairly high coefficient of variance ranging from 21.86% to 41.55% (Table 5.9).

The OM content of agricultural soils was significantly lower than that of parks or forested sites. There were no other significant differences at the α =0.05 level (Table 5.10). The mean OM content of agricultural sites was lower than that of lawns, however the difference was not quite significant (p=0.06). Utilization of organic carbon (OC) by forage crops is one possible explanation for this difference.

The distribution of OM among land uses is similar to most other elements with parks and forested sites having the widest distribution and agricultural sites having the narrowest (Figure 5.4). Once again, the narrow distribution and lower mean values of agricultural areas may reflect the uptake of OC by plants and its permanent removal in hay or conversion into livestock biomass which would lower the OM content of the soil. The higher OM levels in forested areas may be attributable to the yearly deposition of leaves on the soil surface. This leaf deposition develops into an OM-rich O-horizon in forested soils (Buol et al, 2003).

Land Use	Mean	median	min	max	sd	cv%
Lawns	3.08	2.86	1.42	6.91	1.03	33.60
Parks	3.87	3.40	2.39	7.09	1.61	41.55
Agriculture	2.69	2.67	1.83	4.62	0.59	21.86
Forest	3.70	3.18	1.99	7.37	1.52	41.10

Table 5.9. Descriptive statistics for OM (%) by land use.

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	1.91	2.00	0.06
Lawns v. Parks	-1.61	2.14	0.13
Lawns v. Forest	-1.42	2.11	0.17
Parks v. Forest	0.27	2.07	0.79
Agriculture v. Parks	-2.45	2.18	0.03*
Agriculture v. Forest	-2.38	2.13	0.03*

Table 5.10. Comparison of OM % among land uses using a Two-Tailed t-Test.



Figure 5.4. Distribution of OM by land use. Note: bolded line is median value, O = outlier value, * = extreme value

Acidity-pH. The relative acidity and alkalinity (pH) of the soil plays a large role in determining the fates and forms of many nutrients as well as determining what types of chemical reactions can take place and how tightly some elements are held in the soil either through precipitation (forming a solid), absorption (being incorporated into chemical structures), or adsorption (being bound to the soil particle surface by ionic charge). There was a wide range of pH levels from 4.8 to 7.8 (Table 5.11). The mean pH of agricultural sites, parks and forested sites was slightly below the neutral value of seven. These three land uses did not differ significantly from each other (Table 5.12). Lawns samples however, had a mean pH of 6.19 which was significantly lower (p<0.01) than all three of the other land uses. The box plots of pH distribution (Figure 5.5) also show that lawns have a much wider range of values than agriculture, parks or forest.

The disturbance or removal of the A-horizon and subsequent mixing of subsoil into surface locations during construction may influence the pH of the present soil surface. Mixing with subsoil may lower the overall pH of the surface soil since Bhorizons in Greene County are generally lower in pH than the A-horizons by 1 to 3 orders of magnitude (Hughes, 1982). Another likely possibility is that excess nitrogen (N) in lawns may be lowering the pH. Urea CO(NH₂)₂ is the form of N most common in fertilizers applied to lawns, whereas ammonium nitrate (NH₄NO₃) is most commonly applied to pastures and hayfields (Hansen, 2006). As NH₄⁺ is converted to nitrate H⁺ ions are released, lowering the pH. Urea is much more acid than ammonium nitrate, requiring 73% more CaCO₃ to neutralize than does the ammonium nitrate (Hansen, 2006). Thus the type of N applied to lawns could cause them to be more acidic. Nitrogen forms and concentrations were not analyzed in the present study so this possibility could not be tested.

Land Use	Mean	median	min	max	sd	cv%
Lawns	6.19	6.20	4.80	7.60	0.78	12.66
Parks	6.83	6.95	5.50	7.50	0.63	9.16
Agriculture	6.82	6.90	5.40	7.80	0.65	9.56
Forest	6.89	6.90	5.90	7.50	0.42	6.03

Table 5.11. Descriptive statistics for pH by land use.

 Table 5.12.
 Comparison of pH among land uses using a Two-Tailed t-Test.

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	-3.59	2.00	<0.01*
Lawns v. Parks	-2.86	2.08	<0.01*
Lawns v. Forest	-4.22	2.02	<0.01*
Parks v. Forest	-0.27	2.10	0.79
Agriculture v. Parks	-0.08	2.08	0.94
Agriculture v. Forest	-0.47	2.03	0.64



Figure 5.5. Distribution of pH by land use. Note: bolded line is median value, O = outlier value, * = extreme value

Geochemistry

The following section uses descriptive statistics to examine the distribution of elements that are important in the chemical reactions of P in the soil. Box plots are used to show the sample distribution of each element. Aluminum, iron, and calcium are discussed first since they are the most predominant and important minerals in determining the fate of P in Southwest Missouri Soils. The trace metals zinc and copper are micronutrients and sometimes considered a pollutant. These are discussed because of their strong correlation to TP in most land uses discussed in the next chapter. Finally, the distribution of mercury and lead are briefly discussed as a measure of anthropogenic pollution.

Aluminum. The aluminum (Al) fraction of sampled soil ranges from 0.78% to 1.93% throughout the study area (Table 5.13). Agricultural sites showed significantly lower levels of aluminum than lawns, parks or forested sites while these three land uses did not differ significantly from each other (Table 5.14). The mean (0.86%) and coefficient of variation (10.58%) for aluminum was lowest for agricultural areas (Table 5.13). This could be due to aluminum uptake and removal in plant tissues by haying or digestion by livestock. However, since aluminum and clay are highly correlated (R^2 =0.78, p<0.01 for all sample sites) and clay % also shows a significant decrease in agricultural sites, this decrease in aluminum is probably controlled to a greater extent by pedogenetic geomorphic processes which control grain size such as having a greater amount of loess parent material instead of more residuum found in other sites. The decrease in aluminum may also be due to sampling effects as well. It is possible that the

non-random selection of sample sites resulted in a skewed data set that included sites that happened to have lower clay fractions in the upper five centimeters.

The distribution of aluminum mirrors that of clay (Figure 5.6). This is to be expected partly due to the high correlation between clay and aluminum in this study and others (Shade, 2003; Rodgers, 2005). This similarity is also partly explained by the predominance of kaolinitic clay in the soils of Greene County. Kaolinite $[Al_2Si_2O_5(OH)_4]$ is a secondary mineral derived from alumino-silicate minerals (Al-Kanani, 1991). Its structure is of one Aluminum-Hydroxyl sheet and one Si₄O₁₀ sheet (Mason, 1952). As such aluminum is one of the main components of the parent material which forms the clay in this area and the predominance of kaolinite means that aluminum will be highly correlated with clay.

Land Use	Mean	median	min	max	sd	cv%
Lawns	1.06	1.03	0.78	1.67	0.22	20.75
Parks	1.17	1.23	0.63	1.78	0.41	34.97
Agriculture	0.86	0.84	0.74	1.05	0.09	10.58
Forest	1.16	1.13	0.58	1.93	0.43	36.73

Table 5.13. Descriptive statistics for Al (%) by land use.

 Table 5.14.
 Comparison of Al concentration among land uses using a Two-Tailed t-Test.

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	5.16	2.00	<0.01*
Lawns v. Parks	-0.87	2.16	0.40
Lawns v. Forest	-0.82	2.12	0.42
Parks v. Forest	0.06	2.06	0.96
Agriculture v. Parks	-2.59	2.18	0.02*
Agriculture v. Forest	-2.60	2.14	0.02*



Figure 5.6. Distribution of Al by land use. Note: bolded line is median value, O = outlier value, * = extreme value

Iron. In this study the Fe concentrations at all sample sites ranged from 0.92% to 2.47% (Table 5.15). When compared among land uses, the mean concentration of iron was significantly higher in lawns only when compared to agricultural sites (Table 5.16). The mean Fe concentration did not differ significantly between lawns, parks or forest land uses. This indicates a mixing of the subsoil with the topsoil, most likely attributable to soil management during construction of the home. During construction topsoil is scraped off the building site and stockpiled nearby. During this process some of the underlying B-horizons is inevitably scraped up and mixed with the soil that was in the A-horizon. The subsoil typically has higher clay content than the A-horizons and the redder color indicates an accumulation of iron due to the weathering of more soluble minerals

out of the soil profile (Hughes, 1982; Buol et al, 2003). When the topsoil is spread back onto the construction site (if at all) the topsoil would be expected to have a higher iron concentration due to the addition of soil from subsoil horizons. However this can only partially explain the distribution of Fe since there was no significant difference in clay contents between lawn samples with a hue of 7.5 YR and those with a hue of 10 YR (p=0.12). The distribution of Fe is similar to that of both Al and Cu in that agricultural sites have both the lowest concentration of Fe and show a lower coefficient of variance (Figure 5.7).

Land Use	Mean	median	Min	max	sd	cv%
Lawns	1.65	1.56	1.14	2.40	0.33	19.82
Parks	1.70	1.73	0.92	2.47	0.51	29.99
Agriculture	1.47	1.41	1.12	2.28	0.27	18.19
Forest	1.58	1.70	0.94	2.11	0.33	20.68

Table 5.15. Descriptive statistics for Fe (%) by land use.

Table 5.16. Comparison of Fe concentration among land uses using a Two-Tailed t-Test.

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	2.47	2.00	0.02
Lawns v. Parks	-0.28	2.14	0.79
Lawns v. Forest	0.69	2.07	0.50
Parks v. Forest	0.66	2.10	0.52
Agriculture v. Parks	-1.44	2.14	0.17
Agriculture v. Forest	-1.09	2.07	0.28



Figure 5.7. Distribution of Fe by land use. Note: bolded line is median value, O = outlier value, * = extreme value

Calcium. Calcium (Ca) concentration ranged from 0.13% to 4.36% for all sampled sites (Table 5.17). Parks and forested areas both had a higher mean Ca value than either lawns or agricultural sites. This difference was significant, however the difference in means between lawns and agriculture was not, nor was the difference between parks and forested sites (Table 5.18).

The distribution of calcium among land use classes is different for both aluminum and clay with parks showing a very wide range of values (Figure 5.8). This may not be explained fully by natural variability in the soil since both the parks and forested sites are un-amended, yet have a higher level of Ca and greater variability. However, the relationship of Ca to P is strongest for the un-amended parks (R^2 =0.49, p=0.01) and forested sites (R^2 =0.61, p<0.01), both of which have significantly higher Ca

concentrations than lawns or agricultural sites. This may suggest that the sources of Ca in parks and forest samples are naturally occurring minerals such as apatite [Ca₅(PO₄)₃(OH,F,Cl)] inherited from limestone weathering. The significantly higher concentration and wider distribution of Ca for parks seen in Figure 5.8 is not readily explainable since parks are not limed at all. If lime application were the source of extra Ca the pH should be higher in agricultural sites, but that was not the case. The lower aluminum and clay concentrations point to the possibility that agricultural sites have greater amounts of loess parent material in their A-horizons. If this is the case, then the additional Ca may be the result of a higher residual Ca level due to less weathering of the Pleistocene loess. However, the age of Ozark soils would mean that this Ca should have long ago been weathered out of the upper horizons since Ca very easily leached out of the soil profile by rainwater percolation. The non-random selection of sample sites could also explain this greater variation among the un-amended sites, or other untested factors could influence Ca levels since no strong trend is apparent between Ca and pH ($R^2=0.19$ p < 0.01), Ca and OM ($R^2 = 0.289 p < 0.01$), or Ca and clay % ($R^2 = 0.006 p = 0.45$).

Land Use	Mean	Median	min	max	sd	cv%
Lawns	0.41	0.33	0.13	1.21	0.24	57.91
Parks	1.42	0.60	0.33	4.63	1.46	103.07
Agriculture	0.46	0.43	0.17	1.20	0.24	52.68
Forest	0.89	0.74	0.22	1.96	0.57	63.54

Table 5.17. Descriptive statistics for Ca (%) by land use.

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	-0.82	2.01	0.42
Lawns v. Parks	-2.37	2.20	0.04*
Lawns v. Forest	-3.06	2.13	<0.01*
Parks v. Forest	1.17	2.14	0.26
Agriculture v. Parks	-2.25	2.20	0.05*
Agriculture v. Forest	-2.69	2.12	0.02*

Table 5.18. Comparison of Ca concentration among land uses using a Two-Tailed t-Test.



Figure 5.8. Distribution of Ca by land use Note: Bolded line is median value, O = outlier value, * = extreme value

Trace Metals

Copper. Copper (Cu) ranged from 7 ppm to 31 ppm in all sampled sites (Table 5.19). Although the range of Cu values overlaps for all land uses the mean values for lawns, parks and forested sites did not differ significantly from each other, yet all were

significantly higher in Cu concentration than the agricultural sites (Table 5.20). This was in spite of high coefficients of variability for all four land classes (Table 5.19). The distribution of Cu shows similar trends to Al and clay and Ca (Figure 5.9). Although there is some variation in Cu concentration among the four land areas studied, they are all very close to the background concentrations of 12-17 ppm and 15 ppm found by Rodgers (2005) and Shade (2003) respectively.

The differences in Cu concentration among land uses could be a direct result of plant uptake and grass management. The agricultural sites were all used either for grazing of cattle or for hay production. When plant biomass is removed, all the micronutrients such as Cu are removed as well, either absorbed by animal tissue or

Land Use	Mean	median	min	max	sd	cv%
Lawns	13.58	12.00	8.00	26.00	4.63	34.10
Parks	15.83	16.00	11.00	22.00	3.10	19.57
Agriculture	10.62	10.00	7.00	19.00	3.43	32.31
Forest	16.71	16.00	7.00	31.00	7.49	44.80

Table 5.19. Descriptive statistics for Cu (ppm) by land use.

Table 5.20. Comparison of Cu concentration among land uses using a Two-Tailed t-Test.

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	2.98	2.00	<0.01*
Lawns v. Parks	-1.95	2.05	0.06
Lawns v. Forest	-1.47	2.11	0.16
Parks v. Forest	-0.40	2.10	0.69
Agriculture v. Parks	-4.66	2.06	<0.01*
Agriculture v. Forest	-2.89	2.12	0.01*



Figure 5.9. Distribution of Cu by land use Note: Bolded line is median value, O = outlier value, * = extreme value

moved to a different location in hay. Although grasses have a lower concentration of Cu in their tissues than legumes, the greater mass of dry matter means that grasses can remove a significant amount of Cu from the soil (Pederson et al, 2002). In lawn and park settings this plant matter remains in place when grass clippings are left on the yard. The grass in forested areas also decays in situ and re-deposits any Cu that has been taken up. Agricultural sites permanently remove the grass plant along with any Cu taken up by the grass.

Zinc. The concentrations of zinc (Zn) for this study varied widely among all sample sites with a minimum of 17 ppm at an agricultural site and a maximum of 341

ppm at a forested site (Table 5.21). Agricultural sites had the lowest mean Zn concentration (31.3 ppm) with all other land uses being significantly higher (Table 5.22). The distribution of Zn again is similar to other elements such as Al, Cu, and Fe in that forested sites have the widest distribution with agricultural areas having the lowest concentrations on average and narrowest range (Figure 5.10). Background levels of Zn in the study area are about 45-70 ppm (Rodgers, 2003). In the present study only forested sites were outside of this range (possibly due to contamination of sites 31 and 32).

Agricultural sites have a significantly lower concentration of Zn most likely from nutrient uptake in forages and removal as forage or hay. Pederson et al. (2002) found that grass species all have similar concentrations of Zn in the plant tissue meaning that no matter what type of grass is being produced by the farmers in Greene County, the uptake of Zn will be similar. Pederson et al (2002) also found that Zn removal was closely related to dry matter weight with stems (12 mg Zn /m²) and leaves (7.0 mg Zn/m²) containing the most Zn per hay cutting. Stems and leaves are the plant parts eaten by cattle and removed in hay. This results in a greater loss of Zn from agricultural areas than lawns, parks or forested sites. In addition, like Cu, any Zn taken up by turf grass in lawns and parks would be re-deposited in grass clippings when the grass is cut.

The high coefficient of variation % for forested areas may be the result of sampling bias resulting from the limited areas of mature forest, or it may reflect a difference in tree species zinc concentrations in fallen leaves. Two of the forested sites (sites 31 and 32) showed very high concentrations of Zn. Site 32 was located in the Wilson's Creek floodplain and site 31 was located just above it on a hill slope out of the floodplain. These sites were located downstream of the Springfield wastewater treatment

plant. During flooding this area may have been contaminated by excess amounts of Zn and other heavy metals. However, when site 32 was removed from consideration, forested sites are still significantly higher in Zn concentrations than lawns (p=0.02) with agricultural areas being significantly lower in Zn concentration. Although site 32 also shows elevated Cu levels, site 31 does not. It is not entirely clear why forested sites other than sites 31 and 32 would have elevated levels of Zn (Appendix B). It's doubtful that these metals were from the nearby southwest power plant because sites 30, 36, 37, and 38 were very close to sites 31 and 32 (Figure 4.2), yet show no elevated Zn concentrations. While sites 9, 18, 19, and 22 are in the middle of the city of Springfield away from the power plant and have elevated Zn concentrations (Appendix B).

Land Use	Mean	median	min	max	sd	cv%
Lawns	60.23	44	23	207	45.59	75.70
Parks	70	74.50	34	101	21.45	30.65
Agriculture	31.27	28	17	58	10.95	35.02
Forest	103	77	24	341	91.96	89.28

Table 5.21. Descriptive statistics for Zn (ppm) by land use.

Table 5.22. Comparison of Zn Concentration Among land uses using a Two-Tailed t-Test.

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	3.85	2.01	<0.01*
Lawns v. Parks	-1.03	2.02	0.31
Lawns v. Forest	-1.67	2.13	0.12
Parks v. Forest	-1.30	2.13	0.21
Agriculture v. Parks	-5.91	2.14	<0.01*
Agriculture v. Forest	-2.91	2.16	0.01*



Figure 5.10. Distribution of Zn by land use. Note: bolded line is median value, O = outlier value, * = extreme value

Lead. Lead (Pb) is a metal indicative of anthropogenic pollution from sources such as car exhaust, paints and industrial emissions; although in southwest Missouri there are natural deposits of lead that have been mined on a limited basis (Shade, 2003). Its presence may help explain the presence of other trace metals such as copper and zinc, but not why they are correlated to TP. Both Tables 5.23 and 5.24 were made without data from site 32 (forested site) due to Pb contamination in the Wilson's Creek floodplain found by Shade (2003). Lead concentrations varied widely among lawns with a range from 14 ppm to 204 ppm and a very high coefficient of variation. Park sites also show elevated levels of lead that are significantly greater than either forest or agricultural sites (Table 5.24). Shade (2003) found background Pb concentrations to be 23 ppm while Rodgers (2005) found the background Pb concentrations to range from 17-30 ppm.

Using these concentrations as a comparison it can be seen that the lawns and parks in urban areas have been subject to Pb pollution, as have forested sites to a lesser degree. Agricultural areas had a significantly lower mean Pb concentration than the other land uses. The difference in mean Pb concentration between lawns and parks was not significant. Forested areas were significantly lower than parks, but not lawns. This is surprising in the case of forested areas which would be expected to have the least amount of pollution. The distribution of Pb shown in Figure 5.11 reveals that several lawn sites have Pb concentrations that are well outside the standard error bars.

Table 5.23. Descriptive statistics for Pb by land use.

Land Use	Mean	median	min	max	sd	cv%
Lawns	47.48	30.00	14.00	204.00	50.70	106.78
Parks	49.25	48.50	30.00	77.00	17.02	34.56
Agriculture	22.96	23.00	16.00	29.00	3.42	14.91
Forest	32.33	31.50	25.00	44.00	6.31	19.53

Table 5.24. Comparison of Pb concentration among land uses using a Two-Tailed t-Test.

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	3.05	2.02	<0.01*
Lawns v. Parks	-0.19	2.01	0.85
Lawns v. Forest	1.84	2.02	0.07
Parks v. Forest	3.23	2.14	<0.01*
Agriculture v. Parks	-5.30	2.20	<0.01*
Agriculture v. Forest	-4.82	2.14	<0.01*



Figure 5.11. Distribution of Pb by land use. Note: bolded line is median value, O = outlier value, * = extreme value

These sites are generally older homes near either a hospital or the Missouri State University campus. The distribution of Pb suggests that agricultural areas away from an urban area have experienced less pollution than even undisturbed forested sites within or near an urban area. Sites 9, 18, and 19 are located near the center of Springfield and have the highest Pb concentrations

Mercury. Mercury (Hg) is another metal used as a measure of atmospheric pollution. Rodgers (2005) found background Hg concentrations of 0.01-0.03 ppm in the study area. Mean Hg concentrations were highest for lawns (Table 5.25). Mean Hg concentrations are significantly lower at agricultural sites than all other land uses (Table 5.26). In fact, the agricultural sites were the only land use to be close to the background Hg concentrations. All other land uses show increases of at least 100%. Urbanized areas

such as parks and lawns show evidence of elevated Hg concentration with some lawns containing over 1ppm Hg (Figure 5.12). The proximity of some forested sample sites to urban areas may have resulted in a mercury signature similar to the urban areas and less like the rural agricultural lands. As with Cu and Zn the expected relationship of Hg contamination to proximity of the sample site to the power plant is not apparent. Sites 9, 18, and 19 are all in the center of the city near either St. Johns hospital or the Missouri State University campus.

Land Use	Mean	median	min	max	sd	cv%
Lawns	0.19	0.05	0.03	1.67	0.37	194.12
Parks	0.08	0.06	0.04	0.19	0.05	58.63
Agriculture	0.04	0.04	0.02	0.10	0.02	39.81
Forest	0.11	0.08	0.06	0.27	0.07	67.17

Table 5.25. Descriptive statistics for Hg by land use.

Table 5.26. Comparison of Hg concentration among land uses using a Two-Tailed t-Test.

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	2.52	2.02	0.02*
Lawns v. Parks	1.85	2.02	0.07
Lawns v. Forest	1.39	2.01	0.17
Parks v. Forest	-1.10	2.07	0.28
Agriculture v. Parks	-2.65	2.18	0.02*
Agriculture v. Forest	-3.25	2.14	0.01*



Figure 5.12. Distribution of Hg by land use. Note: bolded line is median value, O = outlier value, * = extreme value

Total Phosphorus

The spatial distribution of Total P (TP) in the Springfield area can be visualized by a map showing the average TP concentration of the two samples taken at each sample site for all land use classes (Figure 5.13). This map shows no readily apparent spatial pattern in TP concentrations for Greene County when all four sampled land use types are included. To analyze for possible differences in spatial patterns between land-uses descriptive statistics for TP concentrations are categorized by land use (Table 5.27) and compared using a box-plot (Figure 5.27).



Figure 5.13. Spatial Distribution of TP concentration (ppm) at sampling sites

The mean TP concentrations for all sampled sites in Greene County are shown in Table 5.27. The mean TP concentration for all sites was 602 ppm and ranged from 250 ppm to 1,200 ppm. Mean TP concentration for lawns was lower than all other land uses except for agriculture (Table 5.27). These differences in means were not significant except that forest sites were significantly higher in TP than lawns and agriculture (Table 5.28). The variability of TP was highest for forested sample sites (CV% = 41%) and lawns (CV% = 37%). Variability of TP was lowest for agricultural sites (CV% = 30%) and for Springfield city parks (CV% = 26%). While the range in variability among CV values is not large, the differences in variability may be partially explained by differences in management practices for each land use. Lawns would be expected to have a higher CV% due to the great variability of fertilizer inputs and management practices by homeowners. Of the 20 homes lawns sampled 5 were fertilized by a lawn care service,

Table 5.27.	Descriptive statistics for Total P (ppm) by land use.	

Land Use	n	mean	median	min	max	sd	cv%
Lawns	40	564	515	250	1200	208	37
Parks	12	649	605	480	1000	167	26
Agriculture	26	556	500	380	940	167	30
Forest	14	756	865	300	1170	310	41
All Samples	92	602	530	250	1200	220	36

	t-Statistic	t-Critical	P-value
Lawns v. Agriculture	0.17	2.00	0.86
Lawns v. Parks	-1.46	2.07	0.16
Lawns v. Forest	-2.16	2.11	0.05*
Parks v. Forest	-1.12	2.08	0.28
Agriculture v. Parks	-1.61	2.08	0.12
Agriculture v. Forest	-2.26	2.11	0.04*

Table 5.28. Comparison of TP concentration among land uses using a Two-Tailed t-Test.



Figure 5.14. Distribution of TP by land use. Note: Bolded line is median value, O = outlier value, * = extreme value.

8 were fertilized by the homeowner and 6 did not fertilize at all (Appendix A). One homeowner had just purchased the home and did not know the fertilization history of the lawn. In addition to different fertilizer types, each homeowner put on different amounts of fertilizer (only 2 of the 20 homeowners knew how much fertilizer they applied, either total or per unit area). The timing of application varied greatly between lawns with some applying in Autumn, others in the Spring and some in both seasons. Thus the processes of mineralization and immobilization of P in the soil would have had different lengths of time to affect P concentrations at the time of sample collection. The outlying values in Figure 5.14 come from sites 18 and 19. Both of these sites are in the center of Springfield. Although site 19 was fertilized, only one of the two samples had a high TP concentration (1200 ppm). It is possible that a non-even distribution of fertilizer would result in some areas of the lawn being more heavily fertilized than others. Although site 18 was not fertilized it did have the highest OM concentration among all lawn samples. The Agricultural sites 40 and 42 that have high TP concentrations do not show a corresponding elevated OM concentration. Samples taken at other landscape positions within the same fields at sites 40 and 42 had TP levels within one standard deviation of the agricultural mean. Thus these outlying values may be simply an uneven distribution of fertilizer in the field, or sampling effects.

The lower variability of agricultural sample sites is possibly due to the application of fertilizer for the purpose of reaching specified levels of nutrients in the soil needed for optimum forage growth. In Southwest Missouri 79% of agricultural fertilizer use is for the production of forage and hay (Greene et al., 2004). In order to know how much

fertilizer to apply, 45% of agricultural producers regularly utilize a soil test to recommend the proper amount of fertilizer to obtain optimum growth of their grass, which is predominantly tall fescue. The farm lands sampled in this study showed the same trend as shown in Greene et al. (2004) with two of the five landowners (40%) reporting that they utilized soil tests. Four of the five had fertilization records recording exactly how much and what kind of fertilizer was applied showing that agricultural producers have much better fertilization records than do residential homeowners. Agricultural producers in Greene County are aiming for a specific level of nitrogen and P in their soils needed by tall fescue and other forage grasses. This could account for the relatively low coefficient of variance for TP levels found in agricultural sites (Table 5.27) and the narrow distribution range for TP in agricultural sites (Figure 5.14).

Parks had the lowest CV% (26%) most likely because parks are not fertilized by the City of Springfield (Springfield Park Board, 2006). As a result the variability between parks could be due to natural differences between soils rather than differences in management. It may also be the influence of natural carbon (C) and OM cycling since the Springfield Parks department does not bag grass clippings or leaves (Springfield Park Board, 2006). Leaving this plant material in place returns the nutrients, OM, and carbon to the A-horizon. This may in part explain why parks would have a higher mean TP concentration than both lawns and agricultural land uses by showing that natural nutrient cycling may be more efficient than management in some areas. Although the differences in means among these three land uses were not statistically significant, it would be expected that both lawns and agricultural sites would have a higher mean TP concentration, but they don't.

Both lawns and agricultural fields receive additional P in the form of fertilizers while parks do not. It is therefore unexpected that lawns and agricultural areas should have a lower mean TP concentration. Unfortunately, the amount of fertilizer applied to each site was not quantifiable and this explanation is not supported by any empirical data.

Forested sites showed the greatest mean TP concentrations and the greatest variability in TP concentrations (Table 5.27). It is unclear why these sites would have the highest TP concentrations since they receive no additional inputs of P from fertilizers. Waschbusch et al. (1999) cite tree canopies as a primary source of P in their study of P in urban runoff and they found a very strong relationship ($R^2=0.93$) between percent of tree cover and P in runoff. Trees may have the same effect on soil P in the A-horizon of lawns or the O-horizon found in some wooded Ozark soils. Most of the P taken up by tree roots is transported via the xylem to the leaves (Schachtman, et al., 1998). When leaves fall and are decomposed into the A-horizon, much of the P that had been taken up and used by the leaves would be returned to the soil surface. Although no research was found on phosphorus content of leaves for different tree species, it would not be likely that all tree species would have the same amount of P in their leaves. Therefore any change in the dominant tree species of a particular area could result in significant differences in soil P for different forested areas. The high phosphorus levels could also be a product of the non-random nature of the site selection resulting in a biased sample.

Analysis of Sampled Pairs

As was mentioned in chapter four, two samples were collected at each site. The second sample (sample B) from each site was collected one meter from the first (sample A) in order to gain an idea of what the TP variability was within each site. Figure 5.15

shows a plot of the TP concentrations for sample A versus sample B for the 46 sites sampled in this study. With no variability in the sites there should be a one to one relationship, the slope of the regression line should be one as should the R^2 value. When considering all land uses the R^2 value is 0.83 (p<0.01) and the slope of the regression line is 0.91. Figure 5.15 suggests that the variability within sites is small overall. When looking at the land classifications individually, there is no apparent tendency of any one land use to show more variability than another. Of the 20 lawns sampled only two (site 9 and 19) showed much within lawn variability. Of the other land uses, only forested areas had one site (site 31) that shows any deviance from the generally one to one trend. These three sites have previously been mentioned as having been subject to heavy metal pollution and therefore may have been polluted by other elements including P. Even though later chapters will show that TP is highly correlated to OM, Figure 5.16 shows that the variance within each sample site does not vary in the same way as OM.



Figure 5.15. Sample pairs for each site.



Figure 5.16. OM versus TP for sample pairs (% difference).

Soil Color and Parent Material Effects

Iron (Fe) is generally considered to be the element primarily responsible for the differences in soil horizon color in southwest Missouri. It indicates the degree of weathering and redox conditions in the soil. In a well drained soil iron is in its oxidized state (Fe³⁺) and has a characteristically reddish color. Reduced iron (Fe²⁺) has a gray color which is characteristically found in soils that are saturated for significant periods of the year. Hue is a measure of the relative proportions of yellow and red colors in the soil with a 7.5 YR having more red than a 10YR hue.

It is important to note that in the present study, agriculture, parks, and forest sites each had only one site that had a hue of 7.5 YR, while 7 of the 20 lawn sites had a 7.5 YR hue. Table 5.28 shows that when divided into two groups based on soil hue (10 YR and 7.5 YR) the lawn sites with more reddish coloring (7.5 YR) had a significantly higher mean Fe concentration (p=0.02), significantly lower mean OM (p=0.02), and significantly higher mean Al (p=0.05) than the sites with a more brown (10 YR) hue. Lawns with a 7.5 YR hue also had significantly lower mean TP concentration (p=0.00) (Table 5.29). This indicates more soil disturbance at lawn sites by either soil mixing or topsoil removal during construction, resulting in increased exposure of alumina-silicate clay-rich subsoil at the soil surface.

Lawns with a hue of 7.5 YR showed a much stronger relationship of Fe to TP ($R^2 = 0.60$, p=<0.01) than did lawns with a hue of 10YR ($R^2 = 0.09$, p=0.13). The plots of Fe versus TP (Figure 5.19) show that the 7.5 YR sites represent the lower limit of TP concentrations. In 7.5 YR lawns Fe is better correlated to TP than OM because of the

relative absence of OM in 7.5 YR lawns as compared to 10 YR lawns, and its effect is diluted. The 7.5 YR lawns represent the lowest limit of OM in all samples (Figure 5.18).

Lawns with a 7.5 YR hue had approximately the same relationship of OM to TP $(R^2=0.57 \text{ p}=<0.01)$ as 10 YR lawns $(R^2=0.61, \text{ p}=<0.01)$. This is supported by the fact that there was no significant difference (p=0.96) in the mean age of lawns with a hue of 7.5 YR (28.7 yrs) and lawns with a 10YR hue (29.1 yrs). The slope of the regression line for 7.5 YR lawns (β_1 = 120.83) was also similar to that for 10 YR lawns (β_1 = 156.32). However, the 7.5 YR lawns generally had a lower TP concentration for a given OM content (Figure 5.18). This and the fact that Fe has a much stronger relationship to TP in

Table 5.29. Soil color influence on soil composition for	lawn samples.
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	Mean Values				
Hue	AI (%)	Fe (%)	OM (%)	Clay (%)	TP (ppm)
7.5 YR (n=14)	1.18	1.83	2.66	25.24	452.86
10 YR (n=26)	1.00	1.56	3.30	23.52	623.46
P-Value	0.05	0.02	0.04	0.12	0.00


Figure 5.17. Relationship of Fe to OM by soil hue in lawn soils.



Figure 5.18. Relationship of OM to TP by soil hue in lawn soils.



Figure 5.19. Relationship of Fe to TP by soil hue in lawn soils.

7.5 YR lawns (Figure 5.17) further emphasizes that the increased influence by Fe is due to the decreased level of OM. Thus it can be seen that the redder (7.5 YR) samples have TP that is related more to Fe, while the TP in more brown colored samples (10YR) is closely related to OM.

Soil Classification

Sample sites were located on 17 of the 33 different soil series as mapped in Greene County by Hughes (1982). Although mean TP concentrations differed between sites on different soil series, normalizing the TP data by OM removed most of the variance in TP levels (Figure 5.20). When normalized by OM the mean TP/OM ratio was 193. The variance between the TP/OM ratios is likely due as much to the small sample size for each series as to actual differences. Due to the low sample size when grouping by soil series, none of the differences in the TP/OM ratio were statistically significant at the 0.05 level. This pattern of the TP/OM ratio being close to 190 was also evident when grouped by soil suborders (Figure 5.21). The same TP/OM ratio is shown for lawn samples only (Figure 5.22). These charts provide further strong evidence that OM is a primary controller of TP in soil regardless of soil order, or soil series in the study area. However, it is important to point out the soil series composition and morphology in Hughes (1982) may differ significantly from the top soil sampled due to mapping errors and disturbance by construction, grading, or landscaping.



Figure 5.20. Mean TP and mean TP/OM ratio by soil series name.



Figure 5.21. Mean TP and mean TP/OM ratio for all sites by soil suborder. Note: one site classified as a Haplaquoll was included as a Hapludoll for simplicity.



Figure 5.22. Mean TP and mean TP/OM ratio for lawns by soil suborder.

Summary

In this study the surface soil texture of most sample sites was silt loam with the remainder classified as silty clay loam. The sand fraction was less than 10% for all but two samples. Silt ranged from 52% to79% and clay ranged from 11% to 39%. Due to its large surface area and colloidal charge, clay is probably the most important size fraction in controlling chemical processes in soil. The mean clay fraction was significantly lower in agricultural land uses when compared to lawns, parks and forests. The mean Organic matter content was also lower in agricultural land uses possibly reflecting the permanent removal of plant mass in forage and hay. This difference was significant for parks and forest, but not quite significant for lawns (p=0.06). The pH of surface soil was significantly lower for lawns than all other land uses suggesting that more acidic B-horizon material is now at the soil surface due to A-horizon removal or mixing during construction.

The important elements Al, Fe and Ca all show similar patterns of distribution among land uses. Parks and forest land uses each have higher mean concentrations of Al, Fe, and Ca than either lawns or agricultural sites. Agricultural sites had significantly lower mean Al and Fe concentrations than lawns with no difference in mean Ca concentration. The differences in clay contents can explain some of the differences in Al and Fe since these metals are closely associated with clay. The exposure of subsoil during construction can explain why lawns have higher Al and Fe concentrations than the other land uses, but not why there's no significant difference in the mean Al and Fe concentrations among lawns, parks and forest. The distribution of both Cu and Zn mirror that of lead indicating that these two heavy metals may have an anthropogenic pollution

source. The distribution of mercury simply indicates that the urban areas have experienced higher pollution rates than the agricultural sites.

Total phosphorus concentrations showed no systematic spatial pattern and less than expected variation among the land use conditions. Lawn and agricultural samples examined here showed virtually no difference in mean TP concentrations. While Parks had a higher mean TP concentration than lawns or agricultural sites the difference was not significant. Only forested areas had higher mean TP concentrations in part due to higher organic matter from leaf decomposition.

The redder hue of many lawn soils is a further indication of soil disturbance and mixing of subsoil during construction. Soils with a hue of 7.5 YR had a stronger relationship of Fe to TP than did lawns with a 10YR hue. The OM and TP concentrations had their lowest limit in lawns with a 7.5 YR hue.

Total phosphorus concentrations varied greatly among soil suborders and soil series. However when TP concentration was divided by OM the resulting ratio was consistently valued at between 170 and 200 lending extra weight to the argument that OM is a primary controller of TP in soil.

CHAPTER 6

RESULTS AND DISCUSSION: GEOCHEMICAL RELATIONSHIPS

Any attempts to understand and model the behavior and fate of phosphorus in the soil and runoff water of Greene County must begin with an analysis of the relationships among TP concentrations and soil components that may compose the total phosphorussoil composition relationship in this physiographic region.

Total Phosphorus Correlation Analysis

This section examines the correlation of the previously discussed soil properties and geochemical elements to the TP concentration in soil samples for all land uses. Scatter plot are used to show the linearity of the relationship between it and TP. Table 6.1 shows that the correlation of each of the previously discussed soil constituents to TP depends greatly on land use. Figure 6.1 shows the strength and direction of the TP relationship using Pearson's R. Neither phosphorus nor any of the other elements were analyzed sequentially; therefore all correlations are between the total amounts of the element present.

	All sites (n=92)		Lawns (n=40)		Parks (n=12)		Ag (riculture n=26)	Forest (n=14)	
	R ²	p-value	R ²	p-value	R ²	p-value	R ²	p-value	R ²	p-value
OM (%)	.508	<.01	.648	<.01	.840	<.01	.231	.01	.416	.01
clay (%)	.124	<.01	.016	.43	.108	.30	.082	.16	.697	<.01
рН	.002	.63	.001	.89	.076	.39	.222	.02	.149	.17
AI (%)	.142	<.01	.017	.43	.042	.52	.014	.57	.798	<.01
Fe (%)	.030	.10	.031	.28	.126	.26	.047	.29	.857	<.01
Ca (%)	.210	<.01	.361	<.01	.494	.01	.018	.52	.611	<.01
Cu (ppm)	.606	<.01	.768	<.01	.442	.02	.375	<.01	.574	<.01
Zn (ppm)	.412	<.01	.617	<.01	.436	.02	.516	<.01	.257	.06

Table 6.1. Relationship of soil constituents to TP.



Figure 6.1. Relationship of soil constituents to TP. Note: values given are Pearson's R

Texture. It has been shown in this study that sand fraction did not differ among land uses, thus the differences in texture are mainly the result of varying clay contents in the sample. The relationship of clay to TP is very weak for all land uses except for forested sites (Table 6.1 and Figure 6.1). Since Al and clay are highly correlated the same explanation may be used for clay as to why it is not related to TP. Clay was also significantly (p=<0.01) associated with Fe for lawns (R² = 0.29), parks (R² = 0.94), and forest (R² = 0.53) illustrating the influence of weathering on Greene county soils. The relationship fo Clay to TP is shown in Figure 6.2. For forested sites clay also has the strongest relationship to TP of the soil sediment components, stronger than OM or pH. Only the geochemical components, Al and Fe, both of which are associated with clay minerals, have a stronger correlation to TP for forested sites. This is evidence that disturbance of the surface soil has masked the natural relationship of clay and TP. Forested areas, that have not been disturbed show a strong relationship of clay to TP.



Figure 6.2. Relationship of clay to TP.

Organic Matter. The most important positive relationship found in this study was between OM and TP. A strong relationship between OM and TP would be expected because one of the products of OM decomposition is phosphate (Bohn et al., 1985). The decomposition of OM in soil provides 50% to 60 % of the phosphate of unfertilized soils in temperate climates (Bohn et al., 1985). The relationship of OM to TP for all sites combined is fairly strong (R^2 =0.508) with OM explaining about 51% of the variance in TP concentrations. However, the relationship of OM to TP varies greatly among land uses, probably due to differences in fertilizer inputs, physical disturbances and exchangeable cation concentrations that can mask the natural association of OM and TP (Figure 6.3). Table 6.1 shows that OM had the strongest relationship with TP in lawns and parks. Although the correlation was weaker for forest and agricultural sites the relationship was significant for all land uses at the 0.01 level. The strong relationship of OM to TP in parks is fairly straightforward since parks in Springfield do not receive any fertilizer. Most of the P present in the soil would necessarily come from OM.

The logarithmic relationship of OM to TP (Figure 6.4) shows a slightly better relationship between the variables than just the arithmetic plot. For all land uses the R^2 value increases to 0.568 when the log-log relationship is considered (Figure 6.4). Likewise a log-log relationship improves the correlation of OM to TP for lawns somewhat from 0.65 to 0.69. Agricultural sites show the best improvement in R^2 values, increasing from 0.231 to 0.348 for a log-log relationship. The correlational coefficient decreased slightly for parks from 0.84 to 0.814 while forest improved slightly to 0.455 from 0.416. This indicates that the logarithmic value of OM may be a slightly better predictor of TP than simply the arithmetic value, but the difference is very small.

Lawns show a wider scatter in plots of OM versus TP (Figure 6.3), but they still follow the same basic trend of increasing TP with increasing OM. Although many of the homeowners do not fertilize their lawns, the lawns that receive fertilizer would be expected to have a higher TP concentration for a given OM content thus weakening the relationship. Agricultural sites have the weakest relationship of OM to TP. The addition of fertilizer onto fields might obscure the natural relationship of OM to TP.

Agricultural sites did not differ significantly from lawns or parks in TP concentrations (Table 5.27), but they do have a significantly lower OM content than parks (Table 5.9). This trend suggests that the TP present in agricultural fields is associated with other sources than just OM. Since agricultural producers are attempting to reach a target level of soil P for their crops the addition of fertilizer would elevate TP levels in agricultural sites regardless of OM content. When looking at the log-log chart

forested sites show that in the absence of fertilizer inputs OM can be a good predictor of TP, as was also found in park samples (Figure 6.4).

The large surface area and colloidal properties of OM make it one of the primary controllers of cation exchange and other chemical reactions in soil (Bohn et al., 1985; Evangelou, 1998). The association of phosphate to OM can be a function of bridging by metal cations (Evangelou, 1998). Had the extraction been performed sequentially, it could be known whether or not the TP held by OM-cation bridges could have an affinity for the organic phase. However, since only total values are known, the association of TP with the metals such as Al, Fe, Ca, Cu, and Zn that can form the cation bridges may be overshadowing the relationship of TP to OM (Table 6.1).



Figure 6.3. Relationship of OM to TP.



Figure 6.4. Logarithmic relationship of OM to TP.

The accuracy of the predictive value of this relationship can be measured using a confidence interval (Figures 6.5-6.8). Lawns had 58% of the actual values within the 95% CI. Parks show the best fit of the collected data to the predicted 95% CI with 92% of the sample points falling within the CI limits. Only 54% of agricultural sites and 50% of forested sites had points within the 95% CI.



Figure 6.5. 95% confidence interval for lawns.



Figure 6.6. 95% confidence interval for parks.



Figure 6.7. 95% confidence interval for agriculture.



Figure 6.8. 95% confidence interval for forest.

Acidity-pH. The only significant correlation between pH and TP at the α =0.05 level was for agricultural sites, but the correlation was very weak with an R² of only 0.22 (Table 6.1). Agricultural producers have a target pH that is optimum for forage production. By utilizing soil tests the agricultural producers in this study are for the most part trying to reach approximately the same pH and P levels in their soil resulting in a correlation that does not exist for other land uses. Figure 6.9 shows the relationship of acidity-pH to TP.



Figure 6.9. Relationship of pH to TP.

Aluminum. Similar to clay, Aluminum is most closely related to TP in the samples from forested sites (Table 6.1). Aluminum in all other land uses has no strong relationship with TP (Table 6.1 and Figure 6.10). Lawns, agricultural areas and parks have all had the upper soil surface disturbed by humans to some extent. The lack of a relationship with aluminum in these sites may be a result of a disruption of the natural relationship either through physical mixing or the effect of chemical inputs in the past that have had a swamping effect on the aluminum signature. The disruption of the Al-TP relationship by mixing is supported in that the two land uses with the least amount of physical disturbance, forest and parks, show a much higher correlation of Al to clay (R = 0.974 and 0.971 respectively, p=<0.01) than do the more physically disturbed lawns and agriculture sites (R = 0.667 and 0.773 respectively, p=<0.01). However this cannot be a complete explanation as the mean clay percentage did not differ between forested sites, lawns, and parks.

Iron. The relationship between Fe and TP was not significant for lawns, parks or agricultural sites. However, the iron in forested sites showed the strongest relationship to TP of any other variable (Table 6.1). Figure 6.11 shows a wide scatter in the plots of Fe concentration versus TP concentration for lawns, parks and forest, but a strong linear relationship for forested sites.



Figure 6.10. Relationship of Al to TP.



Figure 6.11. Relationship of Fe to TP.

Calcium. Calcium has very little relationship with TP in lawns, parks or agricultural sites (Table 6.1). However there is a significant relationship between Ca and TP at forested sample sites (Table 6.1 and Figure 6.12). This may suggest that under undisturbed conditions TP may have a correlation to Ca. A logarithmic plot of Ca versus TP (Figure 6.13) reveals a strong linearity for all land uses suggesting that there may be more of a relationship between Ca and TP than a linear regression equation would indicate.



Figure 6.12. Relationship of Ca to TP.



Figure 6.13. Logarithmic relationship of Ca to TP.

Copper. Surprisingly, Cu had one of the strongest relationships with TP. Although Cu had a stronger overall relationship to TP than did OM (Table 6.1), OM is probably a much more important source of P and is a much stronger influence on the chemical reactions of P in soil. Copper is a micronutrient that is only of minor importance in controlling soil reactions. Copper was measured by the same method as TP and thus serial correlation can be expected. Also there is a possibility that the source of the Cu may be pollution, or that Cu an P are attracted to the same binding sites in the soil.

Although the overall relationship of Cu to TP was strong ($R^2 = 0.61$, p=<0.01), not all land uses had an equally strong correlation. Figure 6.14 shows a plot of the relationship between Cu and TP for each land use. For the more urbanized land uses lawns had the strongest correlation of Cu to TP and parks had a weak relationship of Cu with TP (Table 6.1). These two land uses had significantly higher concentrations of Cu than did agricultural sites (Tables 5.19 and 5.20). Agricultural sites also had a low correlation of Cu to TP (Table 6.1). The relationship of Cu to TP may be weakest in agricultural sites because agricultural fertilizers that supply phosphorus do not include micronutrients like Cu (Robertson, 2006). Therefore, any phosphorus applied in fertilizer would not be associated with applied Cu. Since agricultural sites do not receive anthropogenic Cu inputs the Cu present must be naturally occurring. Figure 6.14 illustrates that even though Cu and TP are highly correlated only one of the agricultural sites shows higher Cu concentrations than the 15 ppm found by Rodgers (2005).

To test the possibility that Cu in lawns and parks could be associated with pollution, the relationship between lead (Pb) and Cu was examined. Lead is usually associated with anthropogenic pollution sources such as car exhaust, paints and industrial emissions; although in southwest Missouri there are natural deposits of lead that have been mined on a limited basis (Shade, 2003). Figure 6.15 shows the relationship of Cu to Pb for each land use class. Lawns and parks had the highest mean concentration of Pb (47.5ppm and 49.3 ppm respectively) although lawns and parks both had only a moderate relationship of Cu to Pb ($R^2 = 0.65$, p = < 0.01 and $R^2 = 0.48$, p = < 0.01 respectively). Figure 6.15 shows that for a given increase in Pb concentrations there is a greater increase in Cu concentrations for these two land uses than for forest or agricultural sites. The slope of the regression equations for lawns and parks was $\beta_1 = 2.86$ and 9.02 respectively.



Figure 6.14. Relationship of Cu to TP.

While the slope of the regression equations for forest sites was much steeper (β_1 =33.94). Agricultural areas had no significant relationship of Cu to Pb and no regression equation fit (R²=0.022, p=0.47). Many of the lawns and parks show Pb concentrations greater than the 23 ppm background lead concentrations found in the area (Shade, 2003). Agricultural areas have a mean Pb concentration of 22.96, almost exactly the background levels found in Shade (2003). This strongly indicates that the more rural agricultural areas have not received major pollution, or any Cu associated with metal pollution. Some of the urban areas may have been slightly enriched by Cu deposited with other heavy metals from anthropogenic sources.

The relationship of Cu and Pb for forested areas was examined without data from site 32 since it was collected in the floodplain of Wilson's Creek within Wilson's Creek National Battlefield. Floodplain sediment from that area has been shown to have high levels of Pb from the wastewater treatment plant upstream, and from urban runoff (Shade, 2003). The mean Pb concentration for the remaining 12 forest samples was 32.33 ppm. This was significantly higher than agricultural sites p = <0.01), significantly lower than parks (p = < 0.01), and not quite significantly lower than lawns (p = < 0.07). Although the mean Pb concentration was not different between lawns and forested samples, Figure 6.15 shows that the trend line would be nearly vertical meaning that a large increase in Pb would not result in a large increase in Cu despite the strong relationship between the two ($R^2 = 0.77$, p<0.01). Figure 6.15 shows that even the highest concentrations of Cu do not relate to a Pb concentration greater than 44 ppm for forested areas whereas lawns and parks show many sites that have Pb concentrations greater than 50 ppm. This is also a strong indication that a higher proportion of copper found in urban lawn and park samples is from anthropogenic pollution sources that also release Pb. Thus, the strong correlation of Cu to P in the more urban land uses would suggest that at least some of the TP in the soil is from pollution sources that also deposit the Pb and Cu. Copper concentrations in the soil probably do not exert a strong chemical control on TP as do other soil components, and the effect of Cu on the concentration of TP is not fully explainable. For these reasons, Cu is not considered to be very useful for the development of regression models to predict soil TP concentrations despite its high correlation to TP.



Figure 6.15. Relationship of Pb to Cu. Note: chart was made without site 26.

Zinc. Zinc follows many of the same trends as the previously discussed with Cu. Zinc has a moderate relationship with TP for lawns (Table 6.1). Unlike Cu however, agricultural sites had a moderate relationship of Zn to TP ($R^2 = 0.516$) although the slope of the regression line was still very steep ($\beta_1 = 10.77$) indicating that the Zn concentrations in agricultural areas would not exceed 75 ppm regardless of TP levels. Although the relationship between Zn and TP is statistically significant for agricultural sites it does little to explain the differences in TP concentrations for those sites. Agricultural fertilizers do not contain any additional Zn (Robertson, 2006) and the relationship between the two would therefore be expected to reflect the naturally occurring correlations between Zn and TP rather than anthropomorphically influenced relationships. Park soils showed a weak statistical relationship of Zn to TP, while that for lawns was strong. Both of these land uses however, have a regression slope that is less steep ($\beta_1 = 5.14$ and 3.58 respectively) than agricultural sites indicating that a unit increase in TP is associated with a larger increase in Zn. The relationship for forested sites was not significant (p=0.06). Four samples from two of the forest sites, sites 31 and 32 show extremely high Zn concentrations (Figure 6.16). Both of these sites are close to Wilson's Creek in the Battlefield which suggests they may have been exposed to heavy metal pollution from upstream.

Considering the close correlation between Zn and Cu for all land uses and the close correlation between Pb and Zn for all land classes except agriculture (Tables 6.3, 6.5, 6.7, 6.9), it is plausible that the presence of Zn is due to pollution by the same heavy metal sources as Cu. The Springfield power plant to the southwest of Springfield was close to several of the forested sites and could be a possible source of airborne heavy metals such as Cu and Zn. Also, the solder on older drainage pipes contains Pb, Cu, and Zn (Mantei, 2006). The deterioration of this solder and its leaking into the soil could also be a common pollutant source for these three metals.



Figure 6.16. Relationship of Zn to TP.



Figure 6.17. Logarithmic relationship of Zn to TP.

Physical Site Characteristics

Selected physical attributes were recorded at each site to give an idea of any nonchemical influences on mean TP concentration. Since there were two samples taken at each site, the mean TP of those samples was used for regression analysis with site characteristics. Those attributes measured are included in Table 4.2. Of the measured attributes only fertilization, irrigation, slope, tree cover, and lawn age are discussed. Table 6.2 displays the relationship between the physical attributes of age, slope and tree cover measured at each site to the TP concentration.

Fertilization Practices. The most important site factor that was attempted to be measured is fertilizer history. Landowners of both lawns and agricultural sites were asked about how much fertilizer was applied, what kind of fertilizer was applied, and how often was it applied. The amount, timing, and type of fertilizer undoubtedly have an effect on mean TP concentrations in the topsoil, but most homeowners could not give details on the fertilization history of their lawns. Agricultural producers all had records of fertilizer history, but only one was willing to give details. No relationship could therefore be drawn between fertilizer history and mean TP (or water extractable P) due to lack of quantifiable data. Of the 20 lawns sampled, 85% of homeowners were unable to report either the amount of fertilizer applied which is slightly lower than the 94% found by Varlamoff (2001). Although six of the eight homeowners could give the brand name of the fertilizer that was used, only two could report the amount that was applied. Only eight of the homeowners who did not utilize a lawn care service were able to report the frequency with which fertilizer was applied. Of the five who utilized a lawn service none

	Lawns			Parks	Ag	riculture	Forest		
	R ²	p-value	R ²	p-value	R ²	p-value	R ²	p-value	
Age	.430	<.01	N.D	N.D	N.D	N.D	N.D	N.D	
Slope	.152	.09	.090	.56	.168	.16	.274	.23	
Tree Cover	.000	.97	.001	.95	N.D	N.D	N.D	N.D	

Lubic dilli iterationship of physical site attributes to 11	Table 6.2.	Relationship	p of	physical	site	attributes	to	TP
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N.D. indicates no quantifiable data

could say for sure how often fertilizer was applied. Most fertilizer companies in the Springfield area apply fertilizer 5 to 7 times per year as a standard treatment for lawns that are irrigated (TrueGreen, 2006). Non-irrigated lawns receive less fertilizer in the spring and summer. However, even if the homeowner had known the application frequency, the amount and type of fertilizer varies greatly between companies. For lawns that utilize a lawn care service (sites 4, 7, 10, 12, and 15) the mean TP concentration was 494 ppm. The eight lawns (sites 1, 2, 3, 5, 6, 13, 14, and 19) whose owners used fertilizer, but did not use a service had a higher mean TP value of 543 ppm. This difference was not significant at the α =0.05 level (p=0.58).

Irrigation. Irrigation history of the lawns presented a similar problem of quantification. Three homeowners could quantify the irrigation frequency in terms of times per week the lawn was watered. Two had automatic in-ground irrigation systems that watered everyday in the summer and one watered the lawn three times per week. Of the other 17 homeowners, nine never irrigated, three irrigated rarely, two irrigated some, two irrigated often and one watered as needed. Although irrigation frequency impacts soil moisture status and therefore time to runoff initiation, its correlation to TP and water extractable P could not be determined.

Tree Cover. For parks, agriculture, and forest sites tree coverwas one of only two quantifiable attributes. An attempt was made to quantify tree canopy coverage using a likert scale with a numeric rank assigned to each category. However, this variable could only be tested for lawns and parks since all forest sites had complete tree cover (assigned a rank of 3) and all agriculture sites had no tree cover (assigned a rank of 0). With no range of variance for forest and agricultural sites there was no predictive value in using tree cover. For lawns and parks where tree cover did vary somewhat no significant relationship with TP was found (Table 6.2). This was unexpected in the case of tree cover considering that Waschbusch et al. (1999) found a very strong correlation between tree cover and both dissolved P ($R^2 = .93$) and total P ($R^2 = .94$) in urban runoff in Madison, Wisconsin. Soil P and P in runoff have a known relationship (Sharpley, 1995; Pote et al., 1996; Pote et al., 1999; Sharpley at al., 2001; Torbert et al., 2002; Schroeder et al., 2004). Therefore it is somewhat surprising that a variable that is so strongly correlated to DP and TP in runoff in the Michigan study would have absolutely no relationship to total soil P in the present study.

Slope. Slope was the only other quantifiable variable available for parks, agriculture, and forest sites. Unlike tree cover, slope was a variable that could be collected at all sites and had a wide enough range for use a predictor variable. Slope had no significant correlations to TP for any of the land uses (Table 6.2).

Lawn Age. For lawns it was possible also to measure the age of the lawn by asking homeowners the age of the house. It was expected that the age of the home may have an influence on TP due to older homes having more time for OM to accumulate in the surface soil since the end of construction. Age may also reflect differing construction

techniques since older homes did not typically have as much land disturbance during construction. The age of the lawn was the only variable significant relationship to TP of any physical attribute for lawns. The strength of this relationship may be founded in the relationship of OM to TP. As the time increases since construction of the home OM that was removed with the topsoil in construction has time to re-develop. Figures 6.18 and 6.19 respectively show the distribution of OM and TP for different ages of lawns sampled. This demonstrates that as the time since construction increases so does OM content and the associated phosphorus. The strength of the relationship of OM to TP is also illustrated by a plot of the ratio of OM to TP (Figure 6.20) which shows that when normalized by OM, the differences in TP concentrations are no longer as evident. This is further supported by the USDA-NRCS who have found that 63% of new lawns in the Springfield area require additional P, while only 35% of lawns greater than 20 years needed additional P for grass maintenance (JRBP, 2006).



Figure 6.18. Distribution of OM for lawns by age.



Figure 6.19. Distribution of TP for lawns by age.



Figure 6.20. Ratio of OM to TP for lawns by age.

Linear Regression Models

The previous sections have examined the relationship between soil TP and the geochemical variables, clay composition, and physical site attributes. The final analytical step is to attempt to create a regression model to predict TP for the different land uses and explain the distribution of TP.

For each land use a Pearson Correlation Matrix is shown for all variables used to predict TP concentrations. Stepwise linear regression models were used to predict TP in ppm. Any variables correlated to each other with an R-value higher than 0.70 were not used together in the same model to limit inaccuracies due to co-variation. A model summary table is also given to explain the correlational coefficient R^2 , standard error, percent error, significance of the model, model intercept (b₀), and each predictor variable

slope (b_1) along with significance to the model. Zinc and copper were not included as a variable in any model since they are minor metals in the soil and not drivers of chemical reactions. Zinc and Copper are included in the Pearson's Correlation matrices only for descriptive purposes. Stepwise regression modeling was performed on all soil, physical, and geochemical variables found in Tables 6.1 and 6.2 for each land use type.

Lawn Soils

Table 6.3 is a Pearson Correlation matrix showing the R-value of the relationship between all variables at the 0.01 and 0.05 significance levels. Table 6.4 summarizes several regression models developed using different soil, physical and geochemical variables. The regression model used was the one with the lowest standard error and highest R^2 -value.

The model that best fit the data for lawns was a single parameter model utilizing only OM to predict TP. This model has an R^2 value of 0.613 and a standard error (SE) of 131 ppm. Comparing a plot of actual TP with predicted TP shows an R^2 -value if 0.61 which shows the model is moderately accurate in predicting TP concentrations in lawn soil (Figure 6.21). Plotting the residuals versus the predicted value shows an R^2 of 0.00 which emphasizes the unbiased nature of the model (Figure 6.22). It does not trend toward over or underestimating the TP value. The errors are distributed evenly about zero. This distribution and the cluster of points similar to the prediction plot emphasize that the variability is similar to that of the original data. Organic matter accounts for 61% of the variance among lawns, again emphasizing the importance of OM as a primary control of soil P. **Agriculture Soils.** The variables that went into the agricultural model are different from those used for lawns. Table 6.5 is a Pearson Correlation matrix showing the R-value between variables at both the 0.01 and 0.05 significance levels. It illustrates the fact that only a few variables were significantly correlated to TP, and none of these relationships was very strong. Table 6.6 is a summary of several models utilizing one and two predictor variables to model TP.

The best model for agricultural sites in terms of the highest R^2 value and lowest SE was the two parameter model. This model utilizes both OM % and pH to predict TP. Although it has a weak relationship with TP for agricultural sites, OM still has a better correlation to TP than any other variable. The role of OM as both a source and sink for P has already been discussed.

	ОМ	Clay	Age	Slope	рН	TP	Fe	AI	Ca	Cu	Zn
ОМ	1										
Clay	0.080	1									
Age	0.538	0.459	1								
Slope	-0.282	-0.121	-0.725	1							
рН	-0.156	-0.359	-0.268	0.262	1						
ТР	0.783	0.128	0.656	<u>-0.377</u>	-0.023	1					
Fe	0.091	0.540	0.600	-0.256	-0.233	0.175	1				
AI	-0.006	0.666	0.291	-0.061	-0.195	0.129	0.792	1			
Ca	0.674	-0.094	0.246	-0.040	0.463	0.601	0.033	-0.070	1		
Cu	0.776	0.137	0.700	-0.306	-0.034	0.876	0.381	0.286	0.614	1	
Zn	0.768	0.010	0.587	-0.242	0.193	0.786	0.216	-0.010	0.776	0.845	1

Table 6.3. Pearson Correlation matrix for lawn samples. (n=40)

Bold = correlation is significant at the 0.01 level (two-tailed) <u>Underline</u> = correlation is significant at the 0.05 level (two-tailed)

Table 6.4. Linear regression model summaries for lawn samples. Mean TP = 564 ppm (n= 40)

Model	R ²	SF	% Frror	Sia	bo	b,	b _a
			2.1.01	o.g.	~0	OM (%)	N 2
Organic Matter	0.613	130.9	23	0.00	74.07	158.28	
						(0.000)*	
1 Parameter						Age (yrs)	
Physical Attribute	0.430	140.8	25	0.00	345.45	6.31	
						(0.000)*	
2 Parameter						Ca (%)	Age (yrs)
Physical Attribute +	0.493	135	24	0.00	269.30	246.06	5.70
Geochemical						(0.067)*	(0.000)*

* Number in parentheses is the significance of the variable



Figure 6.21. Predicted TP vs. actual TP (ppm) for lawn regression model.



Figure 6.22. Residual plots for lawn soil model.

The model also includes pH which plays an important role in controlling the species of phosphate that is found in the soil (Bohn, et al., 1985). Different species of phosphate would have different charges and therefore different ionic potential. This would increase the affinity of different phosphate species for different elemental phases. However, since this analysis was done only on total phosphorus and phosphorus was not split into different fractions it is not clear why pH would be associated with TP in agricultural samples.

Comparing predicted TP (ppm) and actual TP (ppm) from the model shows an R² value of only 0.44 and a standard error (SE) of 128.5 ppm, showing that the model is only marginally accurate at predicting TP concentrations in agricultural areas (Figure 6.23). The model does reflect the general trend, but has some fairly large residual values. An accurate and quantifiable measure of farmers' fertilizer applications could possibly be the
most important variable influencing TP, but this was unavailable for the present study. A model that could include quantifiable fertilization history may prove to be far more accurate. Plotting the residuals versus the predicted TP concentration shows an R^2 value of 0.00 which initially would indicate that the variability is similar to the original data. However, a plot of the residuals (Figure 6.24) shows the errors vary somewhat systematically when the residuals are negative, indicating that when the model overestimates the TP concentration it does so in a systematic way.

Parks Soils. The models for predicting TP in samples collected at city parks are in Tables 6.7 and 6.8. Table 6.7 is a Pearson Correlation matrix showing the R-value between predictive variables at the 0.01 and 0.05 significance levels. Table 6.8 displays two different models using 1 soil component or geochemical variable to obtain the model that best fits the data with the highest R^2 value and the lowest SE.

Table 6.5. Pearson Correlation matrix for agriculture samples. (n=26)

	ОМ	Clay	Slope	рН	TP	Fe	AI	Ca	Cu	Zn
ОМ	1									
Clay	0.070	1								
Slope	<u>0.410</u>	-0.274	1							
рН	-0.024	-0.777	0.283	1						
TP	<u>0.475</u>	0.286	0.408	<u>-0.471</u>	1					
Fe	-0.293	0.288	-0.158	0.027	-0.218	1				
AI	0.026	0.773	-0.171	-0.336	0.117	0.285	1			
Ca	-0.028	-0.667	0.332	0.757	-0.133	0.060	-0.342	1		
Cu	0.089	0.402	0.038	-0.727	0.612	-0.023	0.055	-0.523	1	
Zn	0.174	0.694	-0.071	-0.833	0.718	0.020	0.403	-0.547	0.870	1

Bold = correlation is significant at the 0.01 level <u>Underline</u> = correlation is significant at the 0.05 level

Table 6.6. Linear regression model summaries for agriculture samples. Mean TP = 556 ppm (n= 26)

			%				
Model	R ²	SE	Error	Sig.	b ₀	b₁	b ₂
						OM (%)	
Organic Matter	0.226	147.6	27	0.01	193.9	133.74	
_						(0.014)*	
2 parameter						OM (%)	pН
Soil composition	0.437	128.5	23	0.00	1025.2	130.61	-120.73
						(0.007)*	(0.007)*

* Number in parentheses is the significance of the variable



Figure 6.23. Predicted TP vs. actual TP (ppm) for agriculture regression model.



Figure 6.24. Residual plots for agriculture soil model.

The model that best fits the data for park samples is a one parameter model utilizing OM to predict TP in soil. The relationship between OM and P has already been discussed. This model has a R^2 value of 0.84 and a standard error (SE) of 70.15 ppm. Comparing the predicted value of TP from the model with the actual TP values shows the same R^2 of 0.84 indicating that the model is accurate in predicting TP concentrations (Figure 6.25). A plot of the predicted TP values versus the regression model residuals shows no systematic variation about the zero line (Figure 6.26). That and an R^2 of 0.00 shows that the variance for the model is very similar to that of the original data. As the main predictor variable, OM explains 84% of the variance, further emphasizing the importance of the relationship between OM and TP in the soil. **Forest Soils.** Tables 6.9 and 6.10 contain information used to create the regression models for forest sites. Table 6.9 is a Pearson Correlation matrix displaying the R values between the examined variables at the 0.01 and 0.05 significance levels. Table 6.10 summarizes several models that utilize 1 to 3 predictor variables including soil composition, geochemistry, and physical site attributes to obtain the model with the best fit in terms of the highest R^2 value and the lowest standard error. Both tables were made without data from site 32. Site 32 displayed extreme concentrations of heavy metals, TP, and other predictor variables.

	ОМ	Clay	Slope	рН	ТР	Fe	AI	Ca	Cu	Zn
ОМ	1									
Clay	-0.474	1								
Slope	0.397	-0.890	1							
рН	0.116	-0.520	0.387	1						
ТР	0.917	-0.328	0.291	0.276	1					
Fe	-0.516	0.971	-0.825	-0.522	-0.355	1				
AI	-0.363	0.971	-0.852	-0.544	-0.206	0.968	1			
Ca	0.684	-0.609	0.357	<u>0.619</u>	0.703	-0.663	-0.519	1		
Cu	0.425	0.413	-0.348	0.098	0.665	0.377	0.490	0.223	1	
Zn	0.385	0.249	-0.298	0.394	0.661	0.174	0.290	0.435	0.916	1

Table 6.7. Pearson Correlation matrix for park samples. (n=12)

Bold = correlation is significant at the 0.01 level Underline = correlation is significant at the 0.05 level

Table 6.8. Linear regression model summaries for parks. Mean TP = 649 ppm (n= 12)

	_		%			
Model	R ²	SE	Error	Sig.	b ₀	b ₁
						OM (%)
Organic Matter	0.840	70.15	11	0.00	272.13	98.13
						(0.000)*
1 parameter						Ca
Geochemical	0.494	124.7	19	0.01	535.12	80.31
						(0.011)*

* Number in parentheses is the significance of the variable



Figure 6.25. Predicted TP vs. actual TP (ppm) for parks regression model.



Figure 6.26. Residual plots for parks soil model.

The model with the best fit for forest samples was the two parameter soil component and geochemical model (Table 6.10). This model uses OM content and Fe concentration to predict TP in soil. Although clay % and slope also made a model that fit the data well, it was not the best, and the high correlation of clay, OM, slope, and Fe indicates that they should not be included together in the same model. The relationship between OM and TP has already been explained. In the highly weathered Ozark soils most of the readily soluble cations have been leached out of the profile leaving more insoluble cations of iron, aluminum, and silica. In the kaolinitic clay of the Ozarks much of this residual aluminum and silica make up the single layer lattice structure of the clay. In the higher pH and well aerated surface soil the Fe is more readily oxidized into Fe³⁺ which is one of the elements of hydrolysates (Mason, 1952). Through hydrolysis the iron can bind with water by attaching to the oxygen and causing the hydrogen to dissociate

from the water molecule. This causes the precipitation of insoluble Fe oxide hydroxide structures that can absorb other cations and anions such as phosphate into its structure. Both forms of iron, Fe^{2+} and Fe^{3+} , can also bind directly with $H_2PO_4^-$, HPO_4^{-2-} , PO_4^{-3-} complex anions, or serve as cation bridges enabling clay colloids to adsorb the phosphate anions (Bohn et al., 1985). The OM-Fe model has an R² value of 0.95 and a standard error (SE) of 79.4 ppm. Comparing the predicted value of TP from the model with actual TP also shows an R² of 0.95 which indicates the model is very accurate at predicting TP concentrations (Figure 6.27). A plot of predicted TP values versus the regression model residuals (Figure 6.28) shows that the variance of the predicted values is similar to the original data. This model further emphasizes that OM is a main predictor of TP for all land uses.

	ОМ	Clay	Slope	рΗ	TP	Fe	AI	Ca	Cu	Zn
ОМ	1									
Clay	0.866	1								
Slope	0.503	0.563	1							
рН	-0.057	0.101	0.627	1						
ТР	0.780	0.857	0.781	0.295	1					
Fe	0.567	0.736	0.890	0.461	0.924	1				
AI	0.894	0.978	0.633	0.093	0.898	0.791	1			
Са	0.849	0.942	0.682	0.277	0.912	0.825	0.950	1		
Cu	0.441	0.621	0.747	0.538	0.849	0.885	0.635	0.681	1	
Zn	0.082	0.274	0.607	0.590	0.433	0.642	0.279	0.449	0.563	1

Table 6.9. Pearson Correlation matrix for forest sites.(n=12)

Bold = correlation is significant at the 0.01 level <u>Underline</u> = correlation is significant at the 0.05 level

Note: Table was made without data from site 32

Table 6.10. Linear regression model summaries for forest sites. Mean TP = 720 (n= 12)

			%				
Model	R ²	SE	Error	Sig.	b ₀	b ₁	b ₂
						OM (%)	
Organic Matter	0.608	211.1	29	0.00	125.31	155.08	
_						(0.003)*	
1 parameter						Clay (%)	
Soil composition	0.734	173.9	24	0.00	- 106.17	32.86	
-						(0.000)*	
1 parameter						Fe (%)	
Geochemical	0.854	128.8	18	0.00	- 609.63	855.07	
						(0.000)*	
2 Parameter						Clay (%)	Slope (%)
Soil composition +	0.865	130.7	18	0.00	- 130.52	23.42	23.74
Physical Attribute						(0.003)*	(0.016)*
2 Parameter						OM (%)	Fe (%)
Soil Composition					-		
+	0.950	79.4	11	0.00	589.53	74.91	657.41
Geochemical						(0.002)*	(0.000)*

* Number in parentheses is the significance of the variable

Note: Models were made without data from site 32 due to very high heavy metal concentrations indicating the possibility of P pollution. Mean TP with site 32 was 756 ppm.



Figure 6.27. Predicted TP vs. actual TP (ppm) for forest regression model.



Figure 6.28. Residual plots for forest soil model.

Composite Model

Predictor variables were combined into one composite model to see if a single model could effectively predict TP for all land use classes. This composite model was created using predictor variables included in the individual models for all land use classes. Table 6.11 is a Pearson Correlation matrix displaying the R values between the examined variables at the 0.01 and 0.05 significance levels. The results of this analysis showed that the TP concentration in the soil could be predicted only moderately well ($R^2 = 0.56$, p <0.01) using Ca, clay, and OM contents (Table 6.12). The composite model was more accurate than the agricultural model only. The three-variable model was only marginally more accurate than using OM alone (Table 6.12). In general the individual land use models yield a better prediction of TP than a composite model. Figure 6.29 shows the relationship of predicted TP values to measured TP concentrations. A plot of predicted TP values versus the regression model residuals shows that the variance of the predicted values is similar to the original data and that the residuals do not vary systematically around zero (Figure 6.30).

	TP	AI	Ca	Fe	рН	Clay	ОМ
TP	1						
AI	0.376	1					
Ca	0.458	0.042	1				
Fe	0.175	0.753	-0.123	1			
рН	0.051	-0.183	0.439	-0.199	1		
Clay	0.352	0.883	-0.080	0.651	-0.341	1	
OM	0.713	0.274	0.537	0.013	-0.022	0.259	1

Table 6.11. Pearson Correlation matrix for all sites. (n=92)

Bold = correlation is significant at the 0.01 level <u>Underline</u> = correlation is significant at the 0.05 level

Table 6.12. Linear regression model summaries for all sites. Mean TP = 602 (n= 92)

			%					
Model	R ²	SE	Error	Sig.	b ₀	b ₁	b ₂	b ₃
						OM (%)		
Organic Matter	0.508	154.9	25.7	0.00	178.71	133.70		
						(0.000)*		
							Clay	
3 Parameter						Ca (%)	(%)	OM (%)
Soil Comp +	0.558	148.4	24.6	0.00	20.54	55.8	9.24	10.67
Geochem + Phys						(0.049)*	(0.005)*	(0,000)*

* Number in parentheses is the significance of the variable



Figure 6.29. Predicted TP vs. actual TP (ppm) for all sites.



Figure 6.30. Residual plots for all soil models.

Summary

Significant correlations of soil properties and geochemical elements to TP varied greatly among land uses. Organic matter was the only predictive variable to have a significant relationship to TP for all land uses. A summary of the predictive variable used in the regression model for each land use is found in Table 6.13.

In lawn samples, TP was significantly correlated to OM, Ca, Cu, Zn, and lawn age. Organic Matter had the strongest relationship to TP for lawns. Organic matter is an important source of P (Bohn, 1985). Organic matter also provides important binding sites for cations that can precipitate with phosphates (Evangelou, 1998). Organic matter was the only predictor variable used in a regression model for lawns which explained 61% of the variance of TP in lawns. Unexplained variance in the model may be due to fertilization rates, fertilizer type, and natural variability. Total phosphorus at agricultural sites had a significant relationship with OM, pH, Cu and Zn. Since Cu and Zn are probably only correlated with TP and are not acting as a major control on P reactions in the soil, they were not included in a regression model. Organic matter and pH together explained 44% of the variance of TP for agricultural sites. Organic matter was a much less important predictor variable for agricultural sites than for other land uses and explained only 23% of the variance of TP. However, it still had the strongest correlation of any other predictor variables to TP. Since neither pH or Ca concentration were significantly different from other land uses, it is unclear why it would be important in predicting TP for agricultural areas.

Statistical analysis of park samples shows that TP was significantly correlated with OM, Ca, Cu and Zn. Organic matter alone explained 84% of the variance in TP for parks also, making it the primary predictive variable for the regression model.

			%				
Land Use	Model	R ²	Error	Sig.	b ₀	b₁	b ₂
						OM (%)	
Lawns	Organic Matter	0.613	23	0.00	74.07	158.28	
	_					(0.000)*	
	2 parameter					OM (%)	рΗ
Agriculture	Soil composition	0.437	23	0.00	1025.2	130.61	-120.73
_	-					(0.007)*	(0.007)*
						OM (%)	
Parks	Organic Matter	0.840	11	0.00	272.13	98.13	
						(0.000)*	
	2 Parameter					OM (%)	Fe (%)
Forest	Soil Composition +	0.950	11	0.00	-589.53	74.91	657.41
	Geochemical					(0.002)*	(0.000)*

Table 6.13. Summary of regression models for all land uses.

* Number in parentheses is the significance of the variable

Organic mater content and Fe were the parameters most important in predicting TP for Forest sites. Organic matter alone explained 61% of the variance in TP for forest soils while OM and Fe combined explained 95% of the variance. Although they were not included in the best regression model, there was one soil component and one physical attribute that were highly correlated to TP. Clay had a very high correlation to TP and could alone explain 73% of the variance and combined with slope they explained 87% of the variance in TP concentrations. The importance of the correlation of OM to TP has been discussed. The relationship of Fe to TP is not known, only that there is a significant correlation.

CHAPTER 7

RESULTS AND DISCUSSION: WATER EXTRACTABLE PHOSPHORUS

Previous studies found a strong relationship between soil P and DP in storm runoff in both agricultural and residential lawn settings (Sharpley, 1995; Torbert et al., Waschbusch et al, 1999; Garn, 2002; 2002; Schroeder et al., 2004). These studies all caution that any predictive results not be generalized beyond the soil type and geographic area in which they were conducted. In addition, experimental relationships may be method specific and standardized by any means. The present study previously discussed some of the mechanisms by which TP is chemically and physically bound in the soil. If soil binding capacity is greater than the ability of water to desorb P, then dissolved P levels in runoff would be expected to be low. However, if storm runoff is able to release soil P as dissolved load then there is a possibility that this runoff can contribute to P enrichment in receiving waters. De-ionized water extraction was conducted in the present study to gain a better understanding of how much P could be released from the soil by interaction with storm runoff.

Land Use Trends

Mean TP concentrations of the soil sample subset selected for de-ionized (DI) water extraction analysis were slightly higher than the mean TP of all samples for each of the land use classes except forest. The subsets differed from the overall mean TP concentration for each land use class by only +/- 8%, although none of these differences

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		DI Subset		All Samples	p-value
	(n)	Mean TP	(n)	Mean TP	two- tailed
Lawns	14	606	40	564	0.55
Parks	3	703	12	649	0.77*
Agriculture	5	586	26	556	0.74*
Forest	4	735	14	756	0.92*

 Table 7.1.
 Mean TP of samples selected for DI extraction.

* Caution should be taken when interpreting the differences due to small sample size.

Table 7.2. Summary of water extractable P results	5.
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	Mean Filtrate TP (mg/L)	Mean Soil WEP (ppm)	Mean Soil TP (ppm)	Mean % of TP as WEP
Lawns	0.96	23.95	606	4.05
Parks	0.81	20.22	703	2.88
Agriculture	0.68	16.90	586	2.78
Forest	0.59	14.87	735	2.08

were significant (Table 7.1). This indicates that the selections were a representative sample for each land use category. After the 1:25 soil: water solution had been shaken, the filtered water was analyzed for total dissolved P. Table 7.2 shows the mean total dissolved phosphorus (TDP) in the filtrate, the mean DI water extractable phosphorus in the soil (WEP), and the percentage of the total P in the soil as WEP.

The mean concentration of TDP (mg/L) in the filtrate was not significantly different among the four land use classes. This was not surprising considering the small sample sizes for the three land uses besides lawns. Since the WEP concentration of the soil is a function of multiplying the filtrate concentration by 25, there were also no significant differences in soil WEP among land uses. The WEP (calculated absolute amount of P extracted by water) in this study was well within the 0.044 to 1.8 mg/L range

found in Torbert et al. (2002) and Schroeder et al. (2004). It is very important to note that the percentage of TP that was extractable by DI water was significantly higher in lawn samples than in all other land uses. For lawn samples the mean fraction of TP as WEP was 4.05%. This is 1.5-2 times higher than other land uses.

This difference in WEP % is not due to TP concentrations since soil TP concentrations of lawns were not significantly higher than any other land use (Table 5.28) as would be expected if homeowners were applying too much fertilizer and this excess was stored in the upper soil. The percentage of WEP in lawns that had been fertilized (4.72%) was slightly higher than WEP % in lawns that had not been fertilized (3.57%). However this difference was not quite statistically significant (p=0.08). This is supported by Garn (2002) who also found no significant difference in P concentrations in runoff from fertilized lawns.

The significantly higher WEP % in lawns may be due to differences in pH. Figure 7.1 was made using samples from all four land use types and clearly shows that as the soil pH increases the % of WEP increases. Lawn soils did have significantly lower pH levels. Figure 7.1 therefore supports the finding that lawns would have a greater percentage of TP released as WEP. This result is somewhat difficult to explain since lower pH soils should tend to bind P to both Al (and clay) and Fe, and in high pH soils P would tend to bind more to Ca (Bohn et al., 1985) This should render P less soluble at the more extreme pH levels. The more neutral pH levels should release more P, not less. Since pH is related to Fe, the possibility of Fe control on percent WEP was also tested, but showed no clear trend (Figure 7.2). Aluminum was also tested to see if it might be

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Figure 7.1. Soil pH control of WEP% for all land uses.



Figure 7.2. Soil Fe (%) control of WEP% for all land uses.

related to the WEP percentage (Figure 7.3). There was no clear trend of increasing, or decreasing WEP percentage with increasing in Al concentration.

Calcium may exert some control over WEP percent with lower Ca concentrations showing a tendency to have a higher WEP percentage (Figure 7.4). This trend supports the pH trend (Figure 7.1) showing lower WEP percentage with higher pH. These plots indicate that WEP percentage is highest with lower pH, and lower Ca concentrations. In most soils as weathering progresses Ca concentrations decrease and Al concentrations



Figure 7.3. Soil Al (%) control of WEP% for all land uses.



Figure 7.4. Soil Ca (%) control of WEP % for all land uses.

increase, resulting in lower pH (Bohn et al., 1985). This study shows that these are all indicative of increased release of soil P into DI water. This is contrary to Minor et al. (1997) who state that at lower pH, Al and Fe tend to bind P and Ca bind P at higher pH levels. However, they are looking only at plant available P which is only in the inorganic form. The ammonium persulfate digestion method used to analyze the water extraction in the current study measures both organic and inorganic forms of P. It may be that the organic forms of P were preferentially extracted by the water leaving the inorganic P bound to Al and Fe at lower pH and Ca at higher pH. Figures 7.1 to 7.4 suggest that pH may play a more important role in P release than the Pearson correlation suggests and that pH may be controlled more by carbonates rather than Al and Fe. To further test the influence of soil pH on WEP the distribution of pH for WEP samples was plotted (Figure 7.5). When grouped by land use it is apparent that lawns have lower Ph values in general as compared to other land uses as shown for all samples in Figure 5.5. This indicates that the higher WEP concentrations and the higher WEP% may be due, at least partially, to differences in soil pH. However, Figure 7.6 shows that when WEP is plotted over soil pH lawn samples still have higher WEP concentrations for a given pH. When WEP % is plotted over soil pH the same pattern emerges. For a given soil pH, lawn samples have a higher WEP% than other land uses, especially in the pH range of 6 to 7. Figures 7.6 and 7.7 indicate that although pH may influence WEP and WEP%, other factors such as fertilization, soil disturbance history, and unmeasured effects probably increase the WEP concentrations in lawns.



Figure 7.5. Soil pH control of WEP by land use



Figure 7.6. Relationship of pH to WEP by land use



Figure 7.7. Relationship of pH to WEP% by land use

The relationship between soil TP (ppm) and WEP (ppm) for all samples is shown in Figure 7.8. As expected, an increase in soil WEP was generally associated with an increase in soil TP. The linear relationship was significant (p= 0.00), but was not as strong (R^2 = 0.49) as would be expected from previous research where this relationship was much stronger (Schroeder, 2004; Pote et al, 1999). A curvilinear regression equation was tried to see if the data could be fit better than with a linear regression function. The curvilinear line for all data points had a slightly better fit (R^2 = 0.56) and was just as statistically significant (p= 0.00) even though it too was lower than would be expected from previous research. The relationship of WEP to TP and all other previously discussed predictor variables can be seen in Table 7.3. This table shows that the relationships of each variable to WEP for a given land use is very different than with TP (Table 6.1).

	Lawns (n=14)		Parks (n=3)		Agriculture (n=5)		Forest (n=4)	
	R ²	p-value	R ²	p-value	R ²	p-value	R ²	p-value
TP (ppm)	.436	.01	.891	.21	.987	<.01	.494	.30
Fraction of TP (%)	.327	.03	.086	.81	.938	<.01	.271	.48
OM (%)	.376	.02	.886	.22	.906	.01	.140	.63
Clay (%)	.061	.39	.931	.17	.003	.94	.158	.60
рН	.243	.07	.123	.77	.004	.92	.585	.24
AI (%)	.126	.21	.847	.26	.013	.85	.180	.58
Fe (%)	.037	.51	.986	.07	.561	.15	.553	.26
Ca (%)	.029	.56	.986	.07	.021	.81	.143	.62
Cu (ppm)	.181	.13	.229	.68	.000	.99	.982	<.01
Zn (ppm)	.236	.08	.634	.41	.029	.78	.584	.24

Table 7.3. Relationship of predictor variables to WEP.



Figure 7.8. Relationship of TP to WEP for all land uses.

Lawn Soils

For lawn soils the linear relationship between TP and WEP had an R^2 value of 0.46 and a p-value of 0.01. A polynomial regression line improved the R^2 to 0.75 with a p-value of 0.001 (Figure 7.9). In addition to fitting the data more closely, an exponential regression function reflects the idea of a WEP limit as is also shown by the curve of TP vs. WEP percent in Figure 7.9. It may be argued that the end point of Figure 7.9 is weighting the trend line into a curvilinear shape when it may really be linear. From the distribution of points in Figure 7.9 it appears that a linear regression function may work if the high end point is omitted. The data for this point is from site 18 which has been previously discussed as having very high levels of pollutants as well as extremely high

TP concentrations (1050 ppm). It appears that this site is heavily weighting the regression line into a curvilinear form. The linearity of the relationship of TP to WEP is shown in Figure 7.10 without site 18. The R^2 value for this linear relationship is 0.61 with a significance of 0.00, showing that a linear function may be appropriate for this relationship even though the R^2 value for the curvilinear function is still higher.

All other predictor variables previously discussed in chapter 6 were also compared with WEP to find if any had a significant relationship (Table 7.3). Only OM had a significant relationship with WEP in selected lawn samples (p=0.02), but it was not very strong ($R^2=0.38$).



Figure 7.9. Comparison of WEP to TP for lawns.



Figure 7.10. Relationship of soil TP to WEP without site 18.

The relationship of TP to the % of WEP was found to be curvilinear rather than linear when all the lawn samples are evaluated. The % of WEP increases with TP until it reaches a certain threshold, and then begins to decrease (Figure 7.11). The curvilinear relationship between TP and WEP% had an R² value of 0.54 and a p-value of 0.01. Most of the sampled lawn soil fell within the range of 300 to 700 ppm that was discussed previously. This is reflected in the cluster of points within this range that have a WEP fraction of 3-6%. The cluster of data points in Figure 7.11 are the same sites as in Figure 7.10. These sites show a linear relationship between TP and WEP and in Figure 7.8 they have a mean of 4.6% WEP. Figure 7.11 indicates that the samples in the 300-700 ppm TP range have no relationship between TP and percent WEP. When the data from the extreme TP values is added then as TP concentrations increase from this cluster the WEP percentage begins to decrease. This indicates a curvilinear relationship, or one that has a maximum. As TP concentrations increase beyond 700 ppm there is a limit to WEP concentration in lawn soil that will not be exceeded even if the TP concentration continues to increase. Based on the current data this maximum for WEP is approximately 35 ppm (see also Figure 7.18). Analysis of the three extreme TP values shows that those sites have either high OM, or very low OM which is controlling the TP concentrations.



Figure 7.11. Relationship of TP to WEP % for lawns.

Even though OM can account for the very high and very low points on this graph, there are also important management variables, such as exact fertilizer application that this model can't account for. Further research will need to be done to determine if water extractable TP is a good indicator of TP in Ozark soils or of P in runoff.

Agricultural Soils

Agricultural sites had by far the strongest correlation between TP and WEP (Figure 7.12). With an R^2 value of 0.987 the amount of WEP can predicted based solely on TP. This also means TP can also be predicted based on DI water extraction analysis. The percent WEP and OM were the only other predictor variables that had a significant relationship to WEP (Table 7.3).

Unlike Lawns and Parks, the relationship of TP and the percentage of WEP was linear rather than curvilinear (Figure 7.13). There was no decrease in the percent of WEP with an increase in TP indicating that as the amount of TP in the soil increases there is an increasing amount of WEP available to runoff water. However, the percentage of WEP is significantly lower for a given TP concentration in agricultural areas than in lawns (Table 7.4). It is important to note again that all agricultural sites sampled had low to moderate grazing/haying intensity. The relationships of TP to WEP and WEP % would be much more complicated in heavily grazed areas or confined animal feeding operations (CAFO's).



Figure 7.12. Comparison of WEP to TP for Agriculture.



Figure 7.13. Relationship of TP to WEP percentage for agriculture.

Park Soils

There was a very strong relationship between WEP and TP for sample sites in parks (Figure 7.14). The R^2 value for this relationship was 0.89, but due to the small sample size (n=3) the relationship was not statistically significant at the 0.05 level (p=0.21). Although this is a strong relationship that looks promising in its predictive value, more research is needed with a larger sample size to determine if the relationship is truly significant, or if the present results are anomalous. These initial results indicate that for parks, the amount of P in runoff may be predictable based on soil P. There were also no significant relationships between WEP and any other predictor variables (Table 7.3). Clay, Ca, and Fe might have had significant relationships if the sample size were larger.

The relationship between TP and the percentage of WEP is not clear from the data available. Like Figure 7.11 for lawns, there appears to be a curvilinear relationship between TP and the percentage of WEP for parks (Figure 7.15). However, the subsample tested was not large enough to yield significant results. With a quadratic regression function and a sample size of three there are zero degrees of freedom. The result is a significance level that is undefined making an evaluation of the relationship impossible. A linear regression function yields an R^2 of 0.09 and a p-value of 0.81 showing that the relationship is not linear.



Figure 7.14. Comparison of WEP to TP for parks.



Figure 7.15. Relationship of TP to WEP % for parks.

Forest Soils

Total Phosphorus did not have a significant relationship with WEP for forest sites (Figure 7.16). This relationship had an R^2 of 0.49 and a p-value of 0.30. Surprisingly, the only predictor variable to have a significant relationship with WEP was Cu concentration (Table 7.3). The relationship of Cu to WEP had an R^2 of 0.98 and a p-value <0.01. Copper did not have a very strong correlation to TP for forest sites (Table 6.1), so it is unknown why it would have such a strong correlation to WEP. It may simply be a result of the small sample size.

Even though no regression line was significant (due again to a small n), the curvilinear regression line fit best with an R^2 of 0.37 and a p-value of 0.79 (Figure 7.17). Similar to the other land uses this relationship shows that in general WEP percentage may rise, peak, and then fall again. A linear relationship between TP and WEP percent yields an R^2 value of 0.058 and a significance value of 0.76.



Figure 7.16. Comparison of WEP to TP for forest sites.



Figure 7.17. Relationship of TP to WEP % for forest sites.

Phosphorus Mobility

Water extractable P percentage was significantly higher in lawns than the WEP percentage for parks (p= 0.02), agriculture (p= 0.00), and forest samples (p= 0.00). The potential significance of this finding to the understanding of urban runoff quality is very important. This indicates that runoff from a lawn could yield a greater amount of P as WEP than could runoff from another land use type with the same amount of soil TP. This form of P is most available for transport to local streams and for plant and algal utilization. Table 7.4 illustrates this point by showing the different WEP concentrations of land uses with virtually the same TP concentrations.

The potential of soil P to be transported to a waterway is a function of both runoff volume and the ability of runoff water to extract P from the soil. This study did not address runoff volume. The analysis of de-ionized water extractable P (WEP) yielded some important implications for loss of P in runoff for different land uses. In this study the concentrations of WEP in soil were greatest for lawns and parks (20 ppm and 24 ppm respectively). This is nearly 1.5 times higher than agricultural and forest lands which had lower concentrations of 17 ppm and 15 ppm respectively. Due to the low sample sizes of water analysis these differences were not significant. However, the difference in the mean percentage of TP that was extractable by de-ionized water was significant among land uses.

The curvilinear relationship between TP and WEP % points to a maximum limit of phosphorus sorption by runoff water for lawns, parks, and forest in the TP range of 500 to 800 ppm. The curvilinear relationship between TP and WEP percent for these three land uses means that there may be a limit to the amount of P that can be extracted

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TP					Lawns Difference in WEP%		
(ppm)	Site #	Land Use	TDP %	TDP (ppm)	TP % Difference	Relative Increase	
410	11	Lawn	4.07	16.68	+1 66%	1.7x	
400	45	Agriculture	2.41	9.65	+1.00%		
500	1	Lawn	5.41	27.05		2.1x	
	23	Park	2.53	12.65	+2.82%		
	43	Agriculture	2.59	12.96			
630	8	Lawn	4.75	29.95	+1 67%	1.5x	
	41	Agriculture	3.08	19.38	±1.07 /0		

Table 7.4. TP concentration paired analysis of WEP % by land use.

by water of 6%, 3.5% and 3% of TP for lawns, parks, and forest sites respectively. Agricultural sites showed a linear relationship between TP and WEP % indicating there is no maximum limit of Phosphorus sorption by runoff water in the samples tested. The maximum TP concentration for agricultural sites was 940 ppm. Higher TP concentrations would need to be tested to see if there is a curvilinear relationship between TP and WEP percent for agricultural sites.

It is evident that the majority of lawns fall within the 300 to 700 ppm range of soil TP. Figure 7.18 is a combination of Figures 7.9 and 7.12 and shows that at approximately 950 ppm TP the two land uses will have the same WEP of around 35 ppm which is the limit of WEP found in this study. At moderate TP concentrations (approximately 300 to 800 ppm) lawns will have higher concentrations of WEP than agricultural areas. This study shows that the majority of lawns fall within this range. In this range the WEP % for lawns is 1.7 to 2.8 times higher than that of agricultural soils (Table 7.4). Since this is the range where lawns have a higher proportion of WEP, it is reasonable to conclude that the lawns sampled in this study can contribute more WEP per unit area than can agricultural areas.

Even if the relationship of TP to WEP in lawns is really linear, it still shows that the WEP for lawns is going to be higher than for agricultural sites. Figure 7.19 is a composite of Figures 7.10 and 7.12. It is significant to point out that the slope of the regression line for lawns (0.437) is virtually parallel to the slope for agricultural sites (0.439) but with a b_0 value that is 8 ppm higher. This indicates that lawns are going to have a higher WEP concentration regardless of the shape of the regression function. When all land uses are added to one graph it can clearly be seen that lawn sites have a higher WEP concentration than all others (Figure 7.20).



Figure 7.18. Soil TP versus WEP for lawns and agricultural sites.


Figure 7.19. Trend of TP to WEP without site 18.



Figure 7.20. Soil TP related to WEP for all land uses.

Summary

In this study no statistically significant differences were found in mean WEP among the four land uses. This is not surprising considering the low sample sizes involved in the DI water extraction analysis. Even though the difference was not statistically significant urban lawns and parks typically had higher WEP concentrations that were 1.5-2 times higher than agricultural or forested areas. With a larger n, future research may find that these differences are statistically significant.

Lawns also had a significantly higher percentage of WEP (the percent of TP that was extracted by DI water) than all of the other land uses. There was no significant difference in WEP percentage among parks, agriculture, and forest land uses. This implies that for a given TP concentration in the soil more P is available to runoff in lawns than other land uses due in part to a lower pH, higher Al concentration, and lower Ca concentration. Although pH does appear to influence WEP and WEP%, the differences among land use are also influenced by other important factors that make lawns have higher WEP concentration and WEP%. Therefore lawns could be contributing more P in runoff to surface waters than other land uses even though there is no difference in the amount of soil TP among the four land us classes. For both lawn and agricultural sites the concentration of soil TP was the variable most strongly correlated to WEP concentration and statistically significant. A strong correlation of TP to WEP was also found for parks, but this was not significant due to a small sample size. Unexpectedly, Cu was the only variable significantly correlated to WEP in forest samples.

Lawn, park, and forest sites appear to have a curvilinear relationship between soil TP and WEP percentage. The percentage of soil TP released by DI water appears to

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increase, reach a maximum point and then begin to decrease again with increasing soil TP concentrations. This indicates there may be a maximum concentration of WEP in water that was found to be about 35 ppm in this study. Agricultural sites did not show this curvilinear relationship between TP and WEP percent. This may have been because no agricultural sites were tested with a high enough TP concentration for the WEP percent to decrease. When compared among the land uses lawn sites clearly have a higher concentration of WEP for a given soil TP concentration. Figure 7.17 makes it fairly safe to say that there is a gradation in what land uses can contribute the most WEP. Lawns have the highest WEP concentrations followed by agriculture, then parks, and forests have the lowest concentration of WEP.

CHAPTER 8

CONCLUSIONS

Previous studies have shown that storm water runoff can transport P from urban and agricultural soils into waterways. The results of this study suggest that residential lawn soils may be an important of source of P enrichment in surface waters of the Ozarks. Previous studies relating soil phosphorus to runoff P have looked primarily at agricultural land use (Sharpley, 1995; Pote et al., 1999; Torbert et al., 2002). The few studies that looked at urban land use found lawns to be a significant source of P (Waschbusch et al., 1999; Garn, 2002). However, these studies were not able to compare the phosphorus concentrations among different land uses in the same geographic area. This study examined the TP and water extractable P concentrations in the upper 5 cm of soil for four land uses throughout Greene County, Missouri in an attempt to identify land uses which may contribute significant amount of P in storm water runoff

Soil Total Phosphorus

Mean total phosphorus concentrations in surface soil do not differ significantly between most land uses in Greene County.

Agricultural fields and residential lawns had the lowest mean TP concentrations in the soil and differed by only eight ppm over a range of 250 to 1200 ppm. The mean TP for parks was higher, but not significantly so. Forested areas had the highest TP concentrations, but were only significantly higher than lawns and agricultural land uses. It is unclear why the two land uses that are the least intensively managed and have no anthropogenic P inputs should have the highest concentration of TP in the soil. But, it

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may be related to organic matter and pH of the soil surface. Lawns and agricultural areas have virtually the same TP concentrations and are both managed relatively intensely. It is well documented that P in the soil surface is correlated to P in runoff in agricultural fields. The lack of significant difference in soil P between agricultural areas and lawns would suggest that lawns could be at least as important a contributor of P to surface waters proportional to the area of urban ground coverage.

Geochemical Modeling

The reliability of predicting total phosphorus concentrations using a combination of geochemical, soil composition, and physical variables depends on land use type. This study used multi-variable regression modeling to predict TP concentrations for each land use. Predictor variables for these models included soil composition, geochemical, and site attribute data. These models show that a wide range of factors were related to TP concentrations in the soils studied here. The best regression equations for each land use were: for lawn soils, OM (R^2 = 0.61, SE= 130.9 ppm); agricultural soils, OM and pH (R^2 = 0.44, SE= 128.5 ppm); park soils, OM (R^2 = 0.84, SE= 70.15 ppm); and forest sites, OM and Fe (R^2 = 0.95, SE= 79.4 ppm). These models show that OM is a prime controller of TP in most land uses. TP is highly predictable in parks and forest areas, but lawns and agricultural land uses have other influences on TP as shown by the relatively lower R^2 values.

Water Extractable Phosphorus

The percentage of TP that is extractable by water is significantly greater for lawns than all other sampled land uses. The mean percentage of TP that is extractable by water as dissolved P is significantly greater in lawns (4.05%) than in the other three land uses

studied. This does not include P transported on eroded sediment. For agricultural, parks, and forest land uses, the mean water extractable P ranged from 2.08 to 2.88% and the differences among them were not significant. This initial finding is very important to understanding P loss in runoff and indicates that lawns could be contributing more P in runoff water than other land uses given equal soil TP and equal area. Thus for a given soil TP concentration, more P is available for dissolved transport in runoff from lawns than in other land uses. This may be especially important considering the lower infiltration rates of lawns due to high clay fill and compaction during construction as well as their high connectivity to streams via impervious area and storm water drainage ways. The soil pH and Ca concentration partially control WEP with lower pH and lower Ca concentration tending to have higher WEP concentrations. However, for a given pH value lawns still had higher WEP and WEP% than other land uses indicating that other influences besides soil pH affect WEP concentrations. This requires further research on the influence of pH on P. 75% of lawns in this study have a TP concentration between 300 ppm and 700 ppm. Within this range of soil TP, the relationship between soil TP and WEP is linear and all lawn sites within this range had higher WEP concentrations than any other land use type examined. Although data from this study suggests that lawns can contribute more P than agricultural areas, these conclusions can only be generalized to pastures that have had no poultry litter or sewage sludge applied.

Implications For Future Research.

The majority of literature on P loading in surface waters names agricultural areas as the main source of P. Although agricultural areas may be an important source of P, this study has shown that urban areas have the potential to contribute P in runoff from

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lawns. However, there are important issues that need to be addressed by future research before any management decisions can be made to address P in urban runoff. The understanding of the associations between P and geochemical predictors is not as clear as it could be because the soil analysis was only for total element amounts. Affinity of those elements to P therefore cannot be separated into different geochemical phases since sequential phase extraction was not utilized. This makes some of the geochemical associations difficult to explain since there is no information on the exchangeable, carbonate, Al/Fe oxide, or organic forms of P. Perhaps the most important predictor of WEP could be fertilizer inputs of both agricultural and lawn land uses. However, landowner fertilizer records were not well documented for this study. Any future work needs to focus on quantification of these variables.

Verification of the relationship between soil P and runoff P is needed in this region. Data on phosphorus levels is storm runoff must be collected from different land uses and their catchments analyzed for soil phosphorus. Much of the P loss from land surfaces is a function of runoff volume as well as P concentration. A study of the runoff volumes from different land uses is needed to examine if lawns have a significantly higher volume of runoff for a given rainfall event which might increase the P loss from residential areas. This future study should also analyze the P concentrations in storm runoff to find if they are correlated to water extractable P from the soil. This could provide a means of predicting runoff P concentrations. Any subsequent research must also make a stronger effort to quantify the amount of P applied in fertilizer for use as a predictor variable in any regression model predicting either water extractable P or P in runoff.

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Previous studies of the relationship between soil P and runoff P have focused on only one land use type in a particular geographic area and the majority of these studies are conducted only on agricultural land, leaving a lack of data on P enrichment from residential and urban land uses. The present study has attempted to examine the potential loss of P from four different land uses in the same physiographic setting.

The results of this study are only a preliminary overview of the potential for P loss on runoff from grassed land uses in the Springfield, Missouri area. These results should not be generalized to different geographic settings, land uses or soil types.

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APPENDIX A

SPATIAL AND MANAGEMENT DATA

	Northing	Easting					
Site	UTM	UTM	Land Use	Slope	Irrigation	Fertiliza	tion
	NAD83	NAD83		%		Type	Amount
	Zone 15	Zone 15					
1	4109618	472751	Lawn	17.1	Frequent	13-13-13	N.O.
2	4110561	474390	Lawn	0.8	Never	Scott's 27-5-5	-
3	4109294	476198	Lawn	2.1	Never	Weed 'n Feed	-
4	4108235	476344	Lawn	6.9	Rarely	Lawn Service	-
5	4114330	473997	Lawn	3.2	Never	Weed 'n Feed	
6	4122151	474007	Lawn	10.5	Some	30-3-4	N.O.
7	4108827	477021	Lawn	3.4	Frequent	Lawn Service	-
8	4114994	474931	Lawn	8	Never	-	-
9	4116644	474545	Lawn	3.5	Never	-	-
10	4114025	482839	Lawn	3.4	Rarely	Lawn Service	-
11	4114743	470357	Lawn	7.5	Never	-	-
12	4114468	481465	Lawn	0.1	Some	-	-
						Wal-Mart	
13	4112866	477162	Lawn	2.3	Never	Sale	-
14	4117876	467528	Lawn	5.3	Rarely	Unknown	-
15	4111243	470933	Lawn	6	Frequent	Lawn Service	-
16	4116510	472433	Lawn	9.3	Never	-	-
17	4112214	472975	Lawn	4.7	Never	-	-
18	4114648	475947	Lawn	3.8	Never	-	-
19	4117344	475597	Lawn	1.1	Some	ortho lawn food	-
20	4111667	480131	Lawn	15	Never	-	-
21	4115880	474823	Park	3.7	Never	-	-
22	4116207	473427	Park	1.7	Never	-	-
23	4113684	470786	Park	1.6	Never	-	-
24	4113900	470777	Park	10.5	Never	-	-
25	4111227	478855	Park	4	Never	-	-
26	4122205	474186	Park	9.5	Never	-	-
27	4113487	470022	Forest	11.5	Never	-	-
28	4107255	471140	Forest	14.3	Never	-	-
29	4108971	478569	Forest	13.9	Never	-	-
30	4106525	463366	Forest	8.4	Never	-	-
31	4106220	463982	Forest	17.9	Never	-	-
32	4106209	463960	Forest	2.8	Never	-	-
33	4122968	461584	Forest	0.1	Never	-	-
34	4130482	478671	Agriculture	2.9	Never	N.O.	N.O.
35	4130396	478618	Agriculture	4.9	Never	N.O.	N.O.
36	4106831	465111	Agriculture	1.9	Never	N.O.	N.O.
37	4106849	465163	Agriculture	9.2	Never	N.O.	N.O.
38	4106894	465234	Agriculture	0.2	Never	N.O.	N.O.
39	4119650	485703	Agriculture	2	Never	N.O.	N.O.

Note: N.O. indicates landowner had fertilization records, but they were not obtained

Site	Northing UTM	Easting UTM	Land Use	Slope	Irrigation	Fertiliza	ation
	NAD83	NAD83		%		Туре	Amount
	Zone 15	Zone 15					
40	4119981	485550	Agriculture	16.9	Never	N.O.	N.O.
41	4120076	485417	Agriculture	1.5	Never	N.O.	N.O.
42	4117728	453048	Agriculture	1.4	Never	24-8-8	250 lbs/ac
43	4117882	453195	Agriculture	5.8	Never	24-8-8	251 lbs/ac
44	4117822	453440	Agriculture	0.9	Never	24-8-8	252 lbs/ac
45	4122965	461766	Agriculture	2.4	Never	N.O.	N.O.
46	4122878	461760	Agriculture	4.4	Never	N.O.	N.O.

Note: N.O. indicates landowner had fertilization records, but they were not obtained

APPENDIX B

SOIL COMPOSITION AND GEOCHEMISTRY

	<u> </u>	Sand	Silt	Clay	Organic	pН	AI	Са	Cu	Fe	Р	Pb	Zn
Site	Sample	%	%	%	Matter %	-	%	%	ppm	%	ppm	ppm	ppm
4	А	4.54	73.04	22.42	2.95	6.1	1.03	0.34	12	1.5	500	26	38
1	В	5.31	72.22	22.47	2.65	5.9	0.98	0.34	12	1.5	480	22	31
2	Α	10.19	68.59	21.23	2.85	5.5	0.97	0.26	11	1.4	510	25	34
2	В	8.76	67.15	24.10	3.11	5.3	1.24	0.3	15	1.8	550	25	36
2	Α	4.45	72.80	22.76	2.05	4.8	0.97	0.13	11	1.8	500	31	31
3	В	4.74	71.83	23.43	2.26	5.5	1.37	0.16	16	2.2	520	35	36
1	А	5.26	62.72	32.03	3.81	4.8	1.41	0.27	13	2.1	560	29	45
4	В	4.97	65.83	29.21	3.80	4.9	1.67	0.28	18	2.1	590	30	53
5	А	7.21	67.49	25.30	2.60	6.6	1.14	0.37	14	2.2	490	50	52
5	В	7.27	64.47	28.26	2.47	6.2	1.55	0.34	17	2.4	510	59	70
6	А	4.84	73.03	22.12	2.52	6.8	0.78	0.33	12	1.1	490	41	87
0	В	5.05	74.26	20.70	2.47	6.7	1.02	0.34	13	1.4	460	36	77
7	Α	2.93	79.25	17.82	2.79	7.0	1.11	0.4	13	1.5	580	16	34
'	В	3.45	75.01	21.54	2.86	6.8	0.86	0.47	10	1.2	600	17	33
8	А	3.28	69.42	27.30	3.64	5.1	1.16	0.31	15	1.6	630	37	60
0	В	3.26	66.73	30.01	3.49	5.3	0.88	0.3	12	1.3	630	38	58
٥	А	24.36	51.98	23.65	3.82	6.9	1.06	1.09	16	2.2	620	180	162
3	В	9.63	67.57	22.80	5.20	6.4	0.99	0.66	24	2.2	890	185	207
10	Α	6.00	70.22	23.78	3.24	6.0	0.99	0.32	10	1.5	570	23	43
10	В	8.04	67.34	24.62	3.09	5.9	0.92	0.29	11	1.4	550	24	56
11	А	7.43	70.73	21.85	2.44	6.2	0.78	0.3	9	1.5	410	20	32
	В	6.12	73.23	20.65	2.52	6.1	0.8	0.26	9	1.4	420	20	30
12	А	16.16	62.04	21.80	2.61	6.9	0.83	0.33	8	1.2	370	15	23
12	В	17.87	60.36	21.77	2.48	7.1	0.95	0.32	9	1.3	370	14	26
13	Α	4.35	69.62	26.03	2.86	5.3	1.02	0.22	14	1.6	450	30	34
10	В	4.18	68.74	27.08	2.42	5.1	1.05	0.22	12	1.6	470	30	37
1/	Α	7.62	70.35	22.03	3.08	5.9	0.82	0.28	9	1.6	360	24	27
14	В	7.35	70.64	22.00	2.41	5.4	0.78	0.22	8	1.5	360	27	26
15	А	5.43	70.33	24.23	2.48	7.3	1.00	0.46	11	1.4	370	20	51
15	В	6.52	69.37	24.11	2.42	7.5	1.04	0.63	11	1.6	380	19	33
16	Α	4.45	72.80	22.76	3.00	5.8	1.09	0.32	16	1.7	730	38	59
10	В	4.74	71.83	23.43	3.24	6.4	1.09	0.33	18	1.8	790	41	68
17	Α	4.72	66.92	28.37	3.37	6.1	1.28	0.42	12	1.9	600	32	46
	В	7.90	62.51	29.59	3.46	6.3	1.6	0.51	13	2.3	600	47	48
18	Α	6.04	73.40	20.56	5.91	6.2	0.87	1.01	26	1.5	1050	197	158
10	В	5.65	72.23	22.12	6.91	6.4	0.87	1.21	25	1.3	1050	204	170
10	Α	5.75	67.19	27.06	3.56	7.1	1.2	0.73	21	1.7	1200	74	131
13	В	5.39	67.66	26.95	3.35	7.1	1.21	0.58	20	1.8	830	76	120
20	Α	8.43	67.45	24.12	1.46	7.3	1.08	0.62	8	1.5	260	20	23
20	В	7.10	70.18	22.73	1.42	7.6	1.05	0.31	9	1.6	250	22	24
21	A	3.79	66.74	29.46	3.42	5.7	1.33	0.33	13	1.9	530	33	48
21	В	3.37	64.53	32.11	4.42	5.5	1.77	0.38	17	2.3	620	41	59
22	Α	4.55	61.14	34.31	3.88	6.8	1.78	0.78	22	2.5	790	64	101
	В	3.97	66.97	29.06	3.52	6.7	1.43	0.71	18	1.9	690	56	91
22	A	6.75	64.19	29.06	2.39	7.2	1.28	0.41	16	2	500	34	75
20	В	7.03	64.12	28.86	2.67	6.8	1.44	0.47	16	2.2	580	37	71

0:1-	0	Sand	Silt	Clay	Organic	рΗ	AI	Ca	Cu	Fe	Р	Pb	Zn
Site	Sample	%	%	%	Matter %	-	%	%	ppm	%	ppm	ppm	ppm
0.1	А	6.36	77.32	16.33	2.62	7.1	0.75	0.48	11	1.4	490	30	34
24	В	6.40	76.04	17.56	2.79	6.6	0.76	0.34	11	1.3	480	31	36
	А	7.84	69.69	22.47	3.14	7.5	1.05	2.81	16	1.5	600	58	84
25	В	8.85	67.15	24.01	3.38	7.5	1.18	3.05	15	1.6	610	56	74
	А	7.28	77.35	15.37	7.09	7.3	0.63	2.65	18	1	900	77	84
20	В	12.12	76.40	11.48	7.07	7.3	0.64	4.63	17	0.9	1000	74	83
27	А	4.02	70.57	25.41	4.03	6.9	1.2	0.7	23	1.7	920	38	76
21	В	3.40	69.92	26.68	4.25	6.8	1.14	0.78	18	1.7	910	38	80
20	А	4.18	56.50	39.32	7.37	6.7	1.93	1.5	16	1.8	1130	33	86
20	В	4.04	56.72	39.24	6.59	6.4	1.92	1.13	16	1.8	1060	32	78
20	А	7.74	73.86	18.40	3.54	6.9	0.77	0.43	12	1.4	610	25	41
29	В	8.73	75.36	15.91	3.17	6.8	0.89	0.44	11	1.6	590	27	47
20	А	6.10	71.78	22.13	2.94	6.9	0.85	0.48	12	1.3	390	31	40
30	В	6.62	70.02	23.36	2.72	7.1	0.95	0.51	11	1.3	420	31	43
21	А	9.05	66.24	24.71	3.19	7.4	1.11	0.91	19	1.9	820	44	341
51	В	6.74	59.54	33.72	3.73	7.3	1.6	1.18	22	2.1	1170	39	142
22	А	18.50	55.45	26.05	2.58	7.5	1.3	1.96	31	1.8	980	75	214
32	В	14.94	58.03	27.03	3.00	7.2	1.34	1.9	29	1.7	970	72	205
33	А	6.03	78.27	15.70	2.69	6.7	0.58	0.36	7	0.9	320	25	25
- 55	В	5.86	77.03	17.11	1.99	5.9	0.67	0.22	7	1.2	300	25	24
34	А	6.66	70.74	22.60	2.67	7.0	0.95	0.49	8	2.3	500	28	29
54	В	5.57	70.47	23.96	2.68	6.6	0.98	0.42	8	2.1	500	25	28
35	А	2.73	78.34	18.93	2.40	6.7	0.8	0.31	9	1.1	460	16	22
- 55	В	3.21	79.10	17.69	2.65	6.7	0.76	0.34	10	1.1	500	17	24
36	Α	6.71	76.82	16.47	2.84	7.1	0.88	0.44	9	1.3	500	22	26
00	В	6.66	75.66	17.67	2.96	7.2	0.78	0.48	9	1.3	450	21	25
37	A	9.08	73.88	17.03	3.11	7.2	0.83	0.67	9	1.2	520	22	27
07	В	8.83	72.32	18.86	4.62	7.3	0.84	0.53	10	1.3	510	23	26
38	Α	7.19	73.88	18.93	2.29	7.1	0.92	0.3	11	1.4	460	28	28
00	В	7.52	73.56	18.93	2.30	6.9	0.94	0.32	12	1.5	480	29	30
39	A	4.32	77.89	17.79	3.21	6.6	0.77	0.39	8	1.4	530	22	23
00	В	4.78	76.68	18.54	2.88	6.9	0.81	0.39	8	1.4	550	23	26
40	A	5.23	77.17	17.60	3.29	7.2	0.87	0.74	11	1.3	870	19	33
	В	6.03	76.25	17.72	3.26	7.2	0.87	0.71	12	1.3	920	20	35
41	A	8.26	70.13	21.61	3.00	6.9	0.96	0.43	10	1.4	630	26	40
	В	9.00	69.70	21.30	3.02	6.8	0.97	0.48	10	1.4	660	27	39
42	A	9.95	67.74	22.32	2.92	5.4	0.82	0.24	19	1.3	940	24	58
	В	11.12	67.14	21.73	3.04	5.5	0.79	0.26	19	1.4	880	24	56
43	A	7.83	73.35	18.82	2.32	6.6	0.81	0.17	16	1.7	500	23	40
	В	7.46	69.70	22.84	2.09	6.0	0.9	0.18	17	1.9	490	27	44
44	A	1.16	72.98	25.86	2.16	5.7	1.04	0.21	10	1.4	520	18	39
	В	1.15	74.01	24.84	2.42	6.2	1.05	0.25	11	1.4	530	19	43
45	A	10.53	75.55	13.92	1.99	7.7	0.77	1.2	7	1.6	380	24	18
	В	9.51	75.29	15.21	1.97	7.8	0.78	0.99	8	1.7	400	23	19
46	A	10.54	74.41	15.05	2.15	7.4	0.74	0.6	8	1.4	390	24	18
	В	9.86	73.83	16.31	1.83	7.5	0.75	0.54	7	1.5	380	23	17

APPENDIX C

TRIPLICATE GEOCHEMICAL ANALYSIS FOR TOTAL PHOSPHORUS

Sito	Sampla	AI	Са	Cu	Fe	Р	Pb	Zn
Sile	Sample	%	%	ppm	%	ppm	ppm	ppm
	Α	0.78	0.33	12	1.14	490	41	87
6	В	1.02	0.34	13	1.37	460	36	77
	С	0.78	0.32	13	1.18	480	41	91
	Α	0.82	0.28	9	1.62	360	24	27
14	В	0.78	0.22	8	1.49	360	27	26
	С	0.86	0.28	9	1.6	370	26	28
	А	1.05	2.81	16	1.49	600	58	84
25	В	1.18	3.05	15	1.57	610	56	74
	С	1.15	2.91	16	1.56	620	61	85
	А	1.3	1.96	31	1.77	980	75	214
32	В	1.34	1.9	29	1.73	970	72	205
	С	1.36	2.03	31	1.86	1030	78	212
	А	0.77	1.2	7	1.61	380	24	18
45	В	0.78	0.99	8	1.71	400	23	19
	С	0.75	1.25	9	1.7	400	23	18

Site	Land Use	Mean P (ppm)	SD	CV%
6	Lawn	485	7.07	1.46
14	Lawn	365	7.07	1.94
25	Park	610	14.14	2.32
32	Forest	1005	35.36	3.52
45	Agriculture	390	14.14	3.63

APPENDIX D

HYDROMETER TRIPLICATE ANALYSIS

Site	Sample	% Sand	% Silt	% Clay	Clay Mean (%)	Clay SD	Clay CV%
	А	8.43	67.45	24.12			
20	В	8.41	67.54	24.05	24.10	0.04	0.18
	С	8.92	66.95	24.13			
	А	6.40	76.04	17.56			
24	В	6.01	75.05	18.94	18.05	0.77	4.28
	С	6.02	76.33	17.65			
	А	14.94	58.03	27.03			
32	В	14.95	59.26	25.79	27.90	2.65	9.51
	С	14.49	54.63	30.88			
	А	7.19	73.88	18.93			
38	В	7.48	72.43	20.09	19.50	0.58	2.98
	С	7.49	73.01	19.49			
	A	9.51	75.29	15.21			
45	В	10.45	76.89	12.66	13.88	1.28	9.22
	С	10.62	75.60	13.78			

APPENDIX E

ORGANIC MATTER TRIPLICATE ANALYSIS

Site	Sample	OM%	Mean	SD	CV%	
	А	3.03				
2	В	2.78	2.85	0.14	4 80	
2	С	2.71	2.05	0.14	4.09	
	D	2.89				
	А	2.92				
10	В	3.45	3.24	0.30	0 30	
10	С	3.04	5.24	0.50	9.59	
	D	3.54				
	А	3.65				
10	В	4.52	1 11	0.36	8 73	
19	С	4.22	4.14	0.50	0.75	
	D	4.18				
	А	2.60				
24	В	3.03	2.62	0.31	11 70	
24	С	2.55	2.02	0.51	11.70	
	D	D 2.29				
	А	6.87				
26	В	6.85	7 09	0.30	4 30	
20	С	7.50	7.09	0.00	4.50	
	D	7.16				
	А	2.58				
32	В	2.69	2.58	0.00	3 68	
52	С	2.46	2.50	0.09	5.00	
	D	2.57				
	А	2.80				
34	В	2.39	2.68	0 10	7 25	
54	С	2.81	2.00	0.19	1.25	
	D	2.70				
	А	2.41				
38	В	2.34	2 20	0.11	4 70	
50	С	2.24	2.23	0.11	4.70	
	D	2.17				
	А	2.15				
12	В	2.13	2.00	0.09	3.03	
43	С	2.11	2.09	0.00	<u> </u>	
	D	1.97				

APPENDIX F

ACIDITY-pH DUPLICATE ANALYSIS

Site	Sample	рН	Mean	SD	CV%	
2	Α	5.3	E 25	0.07	1 22	
2	В	5.4	5.35	0.07	1.32	
7	Α	7.0	7.05	0.07	1.00	
'	В	7.1	7.05	0.07	1.00	
0	А	6.9	6.05	0.07	1.02	
9	В	7.0	0.95	0.07	1.02	
11	А	6.2	6.2	0.00	0.00	
11	В	6.2	0.2	0.00	0.00	
15	Α	7.5	7 45	0.07	0.95	
10	В	7.4	7.45	0.07	0.35	
18	Α	6.2	6 25	0.07	1 13	
10	В	6.3	0.20	0.07	1.10	
20	A	7.3	73	0.00	0.00	
20	В	7.3	7.0	0.00	0.00	
21	Α	5.7	5.6	0 14	2 53	
21	В	5.5	0.0	0.14	2.00	
26	Α	7.3	73	0.00	0.00	
20	В	7.3	7.0	0.00	0.00	
29	A	6.8	6 75	0.07	1 05	
20	В	6.7	0.70	0.07	1.00	
31	A	7.4	7 35	0.07	0.96	
01	В	7.3	7.00	0.07	0.00	
33	A	6.7	6 65	0.07	1.06	
	В	6.6	0.00	0.01		
35	A	6.7	6 65	0.07	1.06	
00	В	6.6	0.00	0.07	1.00	
39	A	6.9	6.9	0.00	0.00	
	В	6.9				
42	A	5.4	5.4	0.00	0.00	
	В	5.4	•		0.00	
44	A	5.7	5.95	0.35	5.94	
	B	6.2	0.00	0.00	0.01	

APPENDIX G

WATER EXTRACTION ANALYSIS

				Mean		
Land Use	Site	Sample	P (mg/L)	(mg/L)	STD	CV%
		A	1.08			
Lawn	1	В	1.15	1.08	0.07	6.06
		С	1.02			
Lowp	2	A	1.25	1 20	0.05	2.62
Lawn	2	В	1.32	1.29	0.05	3.03
		A	0.71			
Lawn	5	В	0.62	0.64	0.05	7.42
		С	0.61			
		A	0.97			
Lawn	6	В	0.95	0.91	0.09	9.53
		С	0.81			
		Α	1.05			
1	7	В	1.09	1.00	0.00	E 44
Lawn	1	С	1.15	1.08	0.06	5.41
		Lab Duplicate	1.02			
		A	1.22			
Lawn	8	В	1.17	1.20	0.03	2.10
		С	1.20			
		Α	1.34			
1	0	В	1.51	4.05	0.40	0.00
Lawn	9	С	1.32	1.35	0.12	0.09
		Lab Duplicate	1.23			
		A	1.22			
Lawn	10	В	1.15	1.16	0.06	5.02
		С	1.11			
		A	0.69			
Louro	11	В	0.68	0.67	0.02	4 10
Lawn	11	С	0.64	0.07	0.03	4.19
		Lab Duplicate	0.61			
		A	0.67			
Lawn	13	В	0.77	0.71	0.05	7.35
		С	0.69			
		A	0.79			
Lawn	17	В	0.95	0.84	0.10	11.35
		С	0.79			
		A	1.12			
Lawn	18	В	1.12	1.15	0.06	5.54
		С	1.23			
		A	0.19			
Lawn	20	В	0.18	0.18	0.01	5.43
		С	0.17			
		A	0.56			
Park	23	В	0.49	0.51	0.05	9.60
		С	0.47			

Note: Site 2 is not a triplicate due to experimenter error

				Mean		
Land Use	Site	Sample	P (mg/L)	(mg/L)	STD	CV%
		А	0.86			
Park	25	В	0.79	0.82	0.04	4.46
		С	0.81			
		А	1.06			
Park	26	В	1.09	1.10	0.05	4.76
		С	1.16			
		А	1.06			
Forest	27	В	1.03	1.04	0.02	1.70
		С	1.03			
		А	0.63			
Forest	28	В	0.62	0.61	0.02	3.02
		С	0.59			
		А	0.44			
Forest	29	В	0.46	0.47	0.03	6.21
		С	0.50			
		А	0.25	0.26		
Forest	33	В	0.27		0.01	3.41
		С	0.26			
		А	1.15			
Agriculture	40	В	1.19	1.18	0.03	2.49
		С	1.21			
		А	0.83			
Agriculture	41	В	0.75	0.78	0.05	5.93
		С	0.74			
		А	0.54			
Agriculture	43	В	0.50	0.52	0.02	3.40
		С	0.52			
		А	0.52			
Agriculture	44	В	0.49	0.52	0.03	5.98
_		С	0.55			
		А	0.46			
Agriculture	45	В	0.34	0.39	0.07	17.64
		С	0.35			

APPENDIX H

WATER EXTRACTION QUALITY ASSURANCE/QUALITY CONTROL DATA

	Calibration	Calibration P
	Standards	(mg/L)
RBL	0.000	0.011
TP1	0.010	0.045
TP2	0.020	0.069
TP3	0.050	0.144
RBL	0.000	0.038
TP4	0.100	0.283
TP5	0.200	0.547
TP6	0.500	1.340
RBL	0.000	0.017
LCC	0.100	0.097
QCC	0.100	0.085



Spectrophotometer Calibration Curve

Calibration Checks

Blank	-0.0011
LCC	0.100
QCC	0.087
Blank	-0.001
LCC	0.100
QCC	0.097
Blank	-0.003
Blank	0.003
LCC	0.103
QCC	0.095
Blank	-0.001

APPENDIX I

UN-DISCUSSED GEOCHEMICAL DATA
Site	Comple	As	Ва	Be	Со	Hg	κ	La	Mg	Mn
Site	Sample	ppm	ppm	ppm	ppm	ppm	%	ppm	%	ppm
1	Α	7	160	0.6	12	0.14	0.14	20	0.11	1120
1	В	5	150	0.5	14	0.06	0.14	20	0.1	1130
2	Α	<2	170	0.5	15	0.04	0.15	20	0.08	1395
2	В	3	200	0.6	19	0.04	0.2	20	0.1	1545
2	Α	7	170	0.5	21	0.03	0.14	20	0.09	1635
5	В	7	220	0.6	24	0.03	0.22	20	0.11	1715
1	Α	8	130	0.6	12	0.06	0.15	20	0.09	1020
4	В	6	160	0.6	12	0.06	0.21	20	0.12	1065
5	Α	11	190	0.7	22	0.05	0.18	20	0.11	1675
5	В	8	240	0.7	23	0.05	0.21	20	0.11	1905
	A	6	140	0.5	11	0.12	0.11	20	0.07	1045
6	В	7	150	0.6	13	0.08	0.17	20	0.09	1030
	С	5	140	0.6	13	0.12	0.13	20	0.08	1040
7	A	4	150	0.6	9	0.03	0.22	20	0.13	954
	В	5	130	0.6	9	0.03	0.15	20	0.11	918
8	A	5	170	0.5	5	0.06	0.22	20	0.12	466
0	В	6	150	0.5	5	0.06	0.14	20	0.1	455
q	A	2	180	0.6	15	0.08	0.11	10	0.11	1205
5	В	10	180	0.6	14	0.52	0.16	10	0.1	1110
10	A	7	140	0.5	12	0.04	0.13	20	0.09	1030
10	В	5	140	0.5	12	0.04	0.13	20	0.09	1045
11	A	4	130	0.5	14	0.04	0.09	20	0.08	1065
	В	4	130	0.5	13	0.03	0.1	20	0.07	1010
12	A	5	110	0.5	9	0.03	0.1	20	0.12	738
12	В	6	130	0.5	11	0.03	0.11	20	0.12	911
13	A	7	150	0.5	15	0.04	0.1	20	0.09	1085
	В	5	160	0.6	16	0.04	0.11	20	0.09	1240
	A	3	120	0.5	14	0.04	0.09	20	0.06	1030
14	В	6	110	0.5	15	0.04	0.09	20	0.06	1005
	С	5	120	0.5	15	0.04	0.09	20	0.07	1055
15	Α	6	140	0.6	13	0.03	0.12	20	0.1	1020
	В	5	160	0.6	13	0.03	0.11	20	0.11	1115
16	A	7	220	0.6	17	0.33	0.17	20	0.1	1670
	В	3	250	0.6	18	0.38	0.16	20	0.1	1825
17	A	6	160	0.7	16	0.05	0.13	20	0.1	1395
	В	5	220	0.8	19	0.06	0.13	30	0.1	1965
18	A	3	180	0.5	8	1.67	0.11	20	0.12	871
	В	5	170	0.5	7	1.36	0.11	20	0.13	865
19	A	5	180	0.5	10	0.83	0.21	10	0.12	728
	В	2	160	0.6	11	0.97	0.19	10	0.12	764
20	A	<2	170	0.6	14	0.03	0.12	20	0.09	1225
	В	2	170	0.6	15	0.03	0.11	20	0.09	1320
21	A	7	170	0.8	14	0.05	0.16	20	0.09	1135
	В	3	160	1	13	0.06	0.16	30	0.11	1070
22	A	5	210	1	14	0.09	0.18	30	0.12	1510
~~~	В	3	200	0.8	10	0.09	0.17	20	0.1	1195

Site	Commis	As	Ba	Be	Со	Hg	K	La	Mg	Mn
Site	Sample	ppm	ppm	ppm	ppm	ppm	%	ppm	%	ppm
	Α	3	280	0.9	22	0.05	0.15	20	0.09	2030
23	В	3	290	0.9	21	0.04	0.17	30	0.1	2020
24	Α	4	190	0.6	17	0.04	0.13	20	0.07	1735
24	В	3	190	0.6	17	0.04	0.14	20	0.07	1720
	Α	5	190	0.7	14	0.11	0.15	20	0.09	1730
25	В	5	180	0.6	15	0.06	0.17	20	0.09	1525
	С	3	190	0.7	14	0.1	0.16	20	0.1	1755
26	Α	2	110	<0.5	6	0.19	0.1	10	0.12	511
20	В	<2	110	<0.5	5	0.14	0.1	10	0.16	481
27	Α	<2	280	1	17	0.08	0.16	50	0.1	2630
21	В	<2	260	0.9	17	0.08	0.16	40	0.09	2210
28	Α	<2	150	1	11	0.09	0.24	40	0.16	1710
20	В	3	140	1	11	0.08	0.23	40	0.15	1565
20	Α	3	390	1.1	13	0.07	0.11	30	0.07	2800
23	В	4	510	1.4	14	0.07	0.12	30	0.08	3680
30	Α	4	230	0.8	14	0.07	0.12	20	0.08	2220
50	В	2	250	0.8	16	0.07	0.15	30	0.09	2480
31	Α	4	210	0.9	16	0.1	0.16	30	0.13	1950
51	В	4	250	1.1	15	0.11	0.22	40	0.13	2760
	A	3	170	0.8	12	0.27	0.13	30	0.11	1415
32	В	<2	170	0.8	12	0.27	0.14	30	0.12	1395
	С	<2	180	0.8	12	0.29	0.13	30	0.12	1435
33	A	3	180	0.6	11	0.06	0.1	20	0.07	1490
55	В	<2	160	0.7	11	0.06	0.09	20	0.07	1550
34	A	12	140	0.6	8	0.03	0.1	20	0.12	1105
54	В	3	150	0.6	9	0.03	0.1	20	0.13	1040
35	A	3	140	0.5	8	0.03	0.11	20	0.08	1115
00	В	<2	140	0.5	8	0.04	0.1	20	0.08	1170
36	A	4	160	0.5	14	0.03	0.12	20	0.13	1545
00	В	5	160	0.5	13	0.03	0.12	20	0.13	1525
37	A	<2	160	0.5	11	0.04	0.12	20	0.14	1415
0.	В	3	150	0.5	11	0.05	0.13	20	0.14	1410
38	A	6	190	0.5	14	0.03	0.12	20	0.12	1705
	В	2	180	0.5	13	0.04	0.12	20	0.12	1655
39	A	2	150	0.6	17	0.04	0.1	20	0.08	1475
	В	<2	160	0.6	17	0.04	0.1	20	0.09	1480
40	A	<2	180	0.7	13	0.04	0.15	20	0.1	1880
	В	<2	180	0.7	12	0.06	0.15	20	0.11	1770
41	A	<2	160	0.7	14	0.05	0.11	20	0.08	1530
	В	<2	160	0.7	14	0.05	0.13	20	0.09	1540
42	A	<2	210	0.7	13	0.08	0.1	20	0.08	1920
	В	4	170	0.7	14	0.1	0.1	20	0.09	1595
43	A	<2	230	0.8	14	0.05	0.1	20	0.08	2110
	В	2	240	0.8	16	0.06	0.12	20	0.09	2240
44	A	<2	140	0.6	7	0.04	0.11	20	0.1	909
	В	<2	140	0.6	8	0.04	0.14	20	0.1	939

Site	Sample	As	Ва	Be	Со	Hg	K	La	Mg	Mn
		ppm	ppm	ppm	ppm	ppm	%	ppm	%	ppm
	А	6	110	0.5	9	0.02	0.06	20	0.07	819
45	В	3	110	0.5	9	0.04	0.07	20	0.08	775
	С	4	100	0.5	9	0.03	0.06	20	0.07	786
46	А	<2	130	0.7	16	0.03	0.07	20	0.06	1165
	В	2	140	0.7	18	0.03	0.06	20	0.06	1235

Site	Samula	Мо	Ni	S	Sc	Sr	Ti	V
Site	Sample	ppm	ppm	%	ppm	ppm	%	ppm
1	А	2	14	0.03	2	10	0.02	28
1	В	2	15	0.03	2	9	0.02	27
2	А	1	14	0.04	2	9	0.02	29
2	В	4	20	0.03	2	12	0.03	34
3	А	2	15	0.02	2	8	0.03	36
3	В	4	23	0.02	2	10	0.03	47
1	А	1	16	0.04	2	8	0.02	42
4	В	3	20	0.04	3	10	0.03	42
Б	А	2	18	0.03	2	13	0.03	49
5	В	3	23	0.03	3	13	0.03	51
	А	1	8	0.02	1	8	0.02	21
6	В	3	14	0.02	2	10	0.03	26
	С	1	13	0.02	1	8	0.02	23
7	А	3	17	0.03	2	11	0.02	24
	В	1	11	0.03	2	9	0.01	21
0	А	3	17	0.04	2	14	0.02	30
8	В	1	12	0.04	1	11	0.02	26
0	А	3	17	0.05	2	17	0.02	37
9	В	1	15	0.06	2	20	0.02	37
10	Α	2	10	0.03	2	8	0.02	27
10	В	1	10	0.03	2	8	0.02	26
	Α	2	9	0.02	1	7	0.02	26
11	В	1	11	0.02	1	8	0.02	27
10	Α	1	10	0.02	1	10	0.02	21
12	В	1	10	0.02	2	11	0.02	24
40	Α	2	13	0.02	2	8	0.02	31
13	В	1	13	0.03	2	8	0.03	33
	Α	2	12	0.02	2	7	0.02	30
14	В	1	11	0.02	1	7	0.02	30
	С	2	12	0.02	2	7	0.02	30
45	Α	1	11	0.02	2	9	0.02	27
15	В	2	11	0.02	2	10	0.02	29
10	Α	1	17	0.03	2	15	0.02	34
16	В	2	19	0.03	2	11	0.02	34
47	Α	1	16	0.03	3	10	0.02	38
17	В	2	20	0.05	3	11	0.02	43
40	А	1	11	0.1	1	19	0.01	28
18	В	2	12	0.1	1	21	0.01	24
40	Α	1	11	0.06	2	22	0.02	31
19	В	2	12	0.05	2	17	0.02	32
	Α	1	11	0.02	2	20	0.02	31
20	В	1	12	0.02	2	10	0.02	31
~	Α	1	14	0.06	2	9	0.02	43
21	В	1	18	0.07	3	10	0.02	45
	Α	2	21	0.06	3	11	0.02	47
22	В	1	15	0.06	3	10	0.02	38

Sita Sample		Мо	Ni	S	Sc	Sr	Ti	V
Site	Sample	ppm	ppm	%	ppm	ppm	%	ppm
23	А	1	22	0.03	3	10	0.02	48
25	В	1	21	0.03	3	10	0.02	47
24	А	1	15	0.04	1	10	0.02	28
24	В	1	18	0.04	2	10	0.02	28
	А	1	16	0.05	2	17	0.02	30
25	В	1	15	0.05	2	19	0.02	34
	С	1	16	0.06	2	18	0.02	30
26	А	1	10	0.1	1	21	0.01	16
20	В	1	10	0.1	1	27	0.01	16
27	А	2	46	0.05	3	13	0.02	32
21	В	1	22	0.05	2	14	0.02	32
20	А	1	20	0.08	3	12	0.02	33
20	В	<1	20	0.07	3	11	0.02	34
20	Α	1	24	0.03	1	17	0.02	28
29	В	1	20	0.04	1	19	0.02	31
20	А	1	18	0.03	2	12	0.02	25
30	В	1	18	0.03	2	12	0.02	27
24	А	1	29	0.05	2	15	0.02	31
31	В	1	29	0.06	3	15	0.02	35
	А	1	25	0.05	2	17	0.02	30
32	В	1	22	0.06	2	16	0.02	30
	С	2	25	0.05	2	17	0.02	30
20	Α	1	8	0.03	1	13	0.02	19
33	В	2	8	0.03	1	10	0.02	20
24	Α	1	7	0.04	2	10	0.01	46
34	В	2	9	0.04	2	9	0.01	41
0.5	Α	1	9	0.04	1	8	0.01	19
35	В	2	11	0.04	1	8	0.01	19
	Α	1	10	0.04	1	9	0.02	24
36	В	1	11	0.04	1	8	0.02	23
07	Α	1	10	0.04	1	9	0.02	22
37	В	1	9	0.05	1	10	0.02	23
	Α	2	13	0.03	1	10	0.03	25
38	В	1	14	0.05	1	11	0.03	26
	Α	2	8	0.05	1	7	0.02	26
39	В	2	8	0.05	1	8	0.02	27
40	Α	2	12	0.06	1	11	0.02	23
40	В	2	12	0.07	1	13	0.02	23
	Α	1	12	0.05	1	7	0.02	26
41	В	1	13	0.05	2	7	0.02	25
40	Α	2	14	0.05	1	8	0.02	22
42	В	2	16	0.06	1	9	0.02	23
40	A	2	16	0.03	1	6	0.03	28
43	В	1	18	0.03	1	7	0.03	30
	Ā	1	12	0.03	2	8	0.02	24
44	В	1	12	0.04	2	8	0.02	24

Sito	Sample	Мо	Ni	S	Sc	Sr	Ti	V
Sile		ppm	ppm	%	ppm	ppm	%	ppm
	Α	2	8	0.03	1	9	0.02	31
45	В	2	6	0.04	1	10	0.02	32
	С	4	10	0.03	1	9	0.02	31
46	Α	1	8	0.04	1	8	0.02	28
40	В	2	9	0.03	1	6	0.02	28

**APPENDIX J** 

## SAMPLE SITE SOIL TAXONOMIC CLASSIFICATION

Site #	Series name	Sub-Group
1	Pembroke silt loam	Mollic Paleudalf
2	Keeno and Eldon cherty silt loams	Mollic Fragiudalf & Mollic Paleudalf
3	Keeno and Eldon cherty silt loams	Mollic Fragiudalf & Mollic Paleudalf
4	Wilderness and Goss cherty silt loams	Typic Fragiudalf & Typic Paleudalf
5	Newtonia silt loam	Typic Paleudoll
6	Goss cherty silt loam	Typic Paleudalf
7	Wilderness and Goss cherty silt loams	Typic Fragiudalf & Typic Paleudalf
8	Newtonia silt loam	Typic Paleudoll
9	Pembroke silt loam	Mollic Paleudalf
10	Wilderness cherty silt loam	Typic Fragiudalf
11	Creldon silt loam	Mollic Fragiudalf
12	Peridge silt loam	Typic Paleudalf
13	Pembroke silt loam	Mollic Paleudalf
14	Keeno and Eldon cherty silt loams	Mollic Fragiudalf & Mollic Paleudalf
15	Eldon cherty silt loam	Mollic Paleudalf
16	Keeno and Eldon cherty silt loams	Mollic Fragiudalf & Mollic Paleudalf
17	Keeno and Eldon cherty silt loams	Mollic Fragiudalf & Mollic Paleudalf
18	Creldon silt loam	Mollic Fragiudalf
19	Creldon silt loam	Mollic Fragiudalf
20	Goss cherty silt loam	Typic Paleudalf
21	Lanton silt loam	Cumulic Haplaquoll
22	Lanton silt loam	Cumulic Haplaquoll
23	Pembroke silt loam	Mollic Paleudalf
24	Pembroke silt loam	Mollic Paleudalf
25	Cedargap silt loam	Cumulic Hapludoll
26	Wilderness and Goss cherty silt loams	Typic Fragiudalf & Typic Paleudalf
27	Goss-Gasconade Complex	Typic Paleudalf & Lithic Hapludoll
28	Viraton silt loam	Typic Fragiudalf
29	Wilderness and Goss cherty silt loams	Typic Fragiudalf & Typic Paleudalf
30	Wilderness cherty silt loam	Typic Fragiudalt
31	Huntington silt loam	Fluventic Hapludoll
32	Huntington silt loam	Fluventic Hapludoll
33	Wilderness cherty silt loam	
34	Secesh-Cedargap silt loams	Ultic Hapludalf & Cumulic Hapludoll
35	Parsons and Sampsel silt loams	Mollic Albaqualf & Typic Argiaquoli
36	Wilderness cherty silt loam	
37	Goss cherty silt loam	I ypic Paleudalf
38	Secesh-Cedargap silt loams	Ultic Hapludalf & Cumulic Hapludoll
39	Needleye silt loam	
40	Goss cherty silt loam	I ypic Paleudalf
41	Cedargap silt loam	
42	vviiderness cherty silt loam	
43	Peridge silt loam	I ypic Paleudalt
44	Huntington silt loam	Fluventic Hapludoll
45	VVIIderness cherty silt loam	
46	Wilderness cherty silt loam	Typic Fragiudalf