NELSON, NATHAN ORMOND. Soil and waste management effects on phosphorus leaching in acid sandy soils of the North Carolina coastal plain. (Under the direction of Robert L Mikkelsen and J. Wendell Gilliam.)

Excess phosphorus applied to soils with low P adsorption capacities can potentially enter surface water via leaching and subsurface transport, thereby negatively impacting surface water quality. Currently proposed best management practices for inhibition of P leaching are limited to reducing the P application rates, which can decrease the economic viability of animal producers. The protection of water quality and sustainability of animal production are dependent on accurate descriptions of waste and soil management effects on P leaching. Development of new best management practices will benefit both the environment and animal producers. This requires further data and research to adequately describe the risk of P loss via leaching and determine the effects of new best management practices on P leaching. The objectives of this research are to: 1) monitor P concentrations in the soil solution of soils with long-term histories of swine lagoon effluent application and relate these P concentrations to easily quantifiable soil properties, 2) modify the GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) model P subroutines to more accurately reflect P sorption/desorption and validate the modified model with collected field data, 3) use the validated version of GLEAMS to determine cropping system and waste management effects on long-term P leaching losses, and 4) evaluate the use of alum (Al$_2$(SO$_4$)$_3$•14H$_2$O) additions to soil and waste as a best management practice to reduce P leaching.

Soil solution P concentrations were monitored at 45, 90, and 135 cm depths for 20 months in Autryville and Blanton soils under grazed pasture that had received swine waste for more than 20 years. Maximum soil solution P concentrations at 45 cm were in excess of 18 mg L$^{-1}$ in both soils. Soil solution P concentrations at 90 cm in the Blanton
soil were similar to that at 45 cm, indicating low P sorption. However, soil solution P concentrations at 90 cm in the Autryville soil averaged 0.05 mg L$^{-1}$ compared to 10 mg L$^{-1}$ at 45 cm. A split-line model related soil solution P concentration to the degree of P saturation (DPS), identifying a change point at 45% DPS. Phosphorus leaching losses were as high as 100 kg ha$^{-1}$ yr$^{-1}$ passing through 45 cm in the Autryville soil but less than 1 kg ha$^{-1}$ yr$^{-1}$ passing through 135 cm.

Modifying GLEAMS with the Langmuir equation to partition labile P between adsorbed and solution phases improved predictions of percolate P concentrations and soil P accumulation and increased model sensitivity to changes in crop and P management. Phosphorus-based waste applications decreased predicted P leaching by 20 kg ha$^{-1}$ yr$^{-1}$ compared to N-based waste applications. Eliminating all P applications decreased the predicted P leaching losses by less than 1 kg ha$^{-1}$ yr$^{-1}$ compared to P-based waste application.

The effectiveness of using alum to reduce P leaching was evaluated with an intact column leaching study, where 45 and 90 cm soil columns with Autryville and Blanton soils were leached for 60 weeks. Treatments consisted of a control (no P or alum addition), poultry litter, alum amended poultry litter, swine lagoon effluent, and swine lagoon effluent applied to alum-amended soil. The addition of alum to soil or waste consistently reduced P loss compared to continued P addition without alum, and in some cases decreased P leaching losses less than the control. Alum amendment to waste was a more effective best management practice to reduce P leaching losses than alum additions to soil followed by continued waste application. The effectiveness of direct alum additions to soil in reducing P leaching losses from swine lagoon effluent was dependent on soil type. Addition of salts contained in applied wastes caused temporary decreases in leachate P concentrations, which occasionally decreased leachate P concentrations below that of the control. The research results could be used to advise regulatory agencies and producers about management options that will reduce P leaching on soils that could pose an environmental risk.
SOIL AND WASTE MANAGEMENT EFFECTS ON PHOSPHORUS LEACHING IN ACID SANDY SOILS OF THE NORTH CAROLINA COASTAL PLAIN

by

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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

SOIL SCIENCE

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PERSONAL BIOGRAPHY

Nathan Ormond Nelson, son of Thomas Kruger and Susan Ormond Nelson, was born in Logan, UT on July 2, 1974. At age 3, he moved to Manhattan, KS where he grew up on a 30 ac. farm raising beef, fruits and vegetables, and an occasional pig. Nathan graduated from Manhattan High School in May of 1992 and began post secondary education at Ricks College in Rexburg, ID with a major in Botany. After graduating with an AAS from Ricks College in April of 1996, he moved back to Manhattan, KS and attended Kansas State University, majoring in Agronomy with an emphasis in soil and water science. Highlights of his stay at Kansas State University include an undergraduate research project in Soil Microbiology, participation in the Wheat State Agronomy Club and competing with the Kansas State Soil Judging Team. He graduated from KSU in December of 1998 with a BS in Agronomy and a secondary major in Natural Resource and Environmental Sciences. Nathan began a MS program at North Carolina State University in January 1999 under the direction of Rob Mikkelsen and graduated in December of 2000. As the NCSU Soil Science Dept. had treated him well, Nathan remained there in pursuit of his Ph.D. Highlights of his tenure at NCSU include teaching multiple teaching appointments with Soil Fertility Lecture and Labs, countless trips to his field sites in Sampson County and associated back-hoe operation (because nothing’s better than diggin’ in the dirt), and several field trips across North Carolina observing agriculture, industry, geography, and culture of the South. Other significant events occurring during his stay in NC include courting and marriage to his wife, Wendy Rasmussen, and the birth of their child, Nathan Reed Nelson.
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The road to completion of this research and dissertation has been long and I would have never arrived at the end without the help and encouragement of family, fellow students, and professors. I express deep gratitude to my committee, Drs. Gilliam, Mikkelsen, Parsons, and Skaggs, for their advice and council while allowing me the freedom to study topics of my choosing. I offer many thanks to Dr. Gumpertz for her statistical expertise and advice, not to mention her willingness to help me in spite of a less than perfect experimental design. I thank Smithfield foods for being so cooperative and allowing me open access to their farm; without their help this research could not have been accomplished. I am very appreciative of our lab workers, Josh, Lamont, Ellen, and James for their help in many lab and field operations. A special thanks to Eric for his dependability in collecting leachate samples and to Nykea for the hours she spent doing particle size analysis. I owe much gratitude to all the technicians in the Soil Science Department including Guillermo, Chris, Barrett, Kim, Peggy, Charles, and Mark for their technical assistance with field work, laboratory procedures, and analyses. Thanks to Dr. Havlin for his teaching advice and expertise, Dr. Robarge for offering different views, Dr. Cassel for allowing me to learn for myself, Dr. Hesterberg for his willingness to hear me out. Many thanks to Drs. Amoozegar, Kamprath, Israel, and Shi. Without the support of my parents and wife this would have never happened, I owe this success to all their encouragement and their faith that I could finish even when I thought I couldn’t. Thank you. I humbly thank God, my Heavenly Father, for the quiet miracles and unexpected inspiration that lead me to discoveries which I could not have made on my own.
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Phosphorus (P) is an essential nutrient for plant growth, and is therefore a common fertilizer in crop production. When managed properly, P additions in combination with appropriate rates of other fertilizers can reduce runoff and soil erosion by increasing crop growth. However, the mismanagement of P can increase the risk for P loss to surface water. (Sharpley et al., 1994; Sharpless, 1995).

Economic factors that encourage the judicious management of commercially purchased fertilizers are often nonexistent in large-scale animal production systems where the supply of waste-based nutrients frequently exceeds crop requirements. Because the objective of confined animal feeding operations is animal production rather than crop production, managers are more likely to view waste-based nutrient application as the disposal of an unwanted byproduct of their operation as opposed to a resource for improved crop growth. This attitude toward land application of agricultural wastes, combined with economic factors, has led to practices where more nutrients have been applied than the growing crops have required. For example, the average available N:P ratio of swine lagoon liquid is between 2:1 and 4:1 and the N:P ratio of common receiver crops ranges from 4:1 to 9:1, therefore manure applications designed to meet crop N requirements can over apply P by 2 to 3 times (Barker et al., 1994; Mikkelsen, 1997).

Excess P from N-based waste application increases the soil test P (STP) concentrations far beyond the crop requirements. Sharpley et al. (1999) found that cropland with a history of waste application had STP concentrations over 26 times greater than adjacent woodlands, compared to cropland without waste application that only had STP 5 times greater than adjacent woodlands. Ham (1999) also found increased STP in soils with long-term histories of waste application. These studies agree with Kleinman et al. (2000), Maguire et al. (2000), and Pierzynski et al. (1990), all of whom found positive correlations between excessively high STP and waste applications.
Furthermore, soils in regions of intensive animal agriculture have higher average STP than regions without animal production (Figure 1).

Figure 1. Soil test P and livestock population by county for North Carolina. Data source: NCSU Spatial Information Research Lab.

The excess P in waste-amended soils can potentially be transported from the field to adjacent surface water through rainfall runoff, soil erosion, and leaching (Hansen et al., 2002). For example, studies have shown positive correlation between STP in agricultural fields and the P concentration in eroded sediments (Daverde et al., 2003; Andraski and Bundy, 2003), runoff (Sharpley, 1995), and leachate (McDowell and Sharply, 2001). Increasing P inputs to surface water has a negative environmental impact because of the deleterious effects of P on water quality.
Environmental Impact of P on Surface Water

Excessive P inputs to surface water have been shown to degrade water quality in both fresh and salt water ecosystems. The primary water quality problems are associated with eutrophication, or the excessive growth of algae in response to increased concentrations of the nutrient limiting their growth. Following this excessive growth, or algae bloom, the algae die and sink to the lake or river bottom where the biomass is decomposed by other microorganisms. Because of the sudden flush of readily decomposable biomass, dissolved oxygen, which is required for the decomposition process, is removed from the water faster than it can be replaced through diffusion. This creates a condition know as hypoxia, where the dissolved oxygen concentration decreases below what is required by aquatic animals. When dissolved oxygen decreases below 2 mg L⁻¹, most fish and other aquatic animals begin to suffocate and will eventually die resulting in fish kills. A variety of factors associated with eutrophication degrade water quality, reducing its value as a drinking water source, its environmental functions, and its recreational uses (Table 1).

<table>
<thead>
<tr>
<th>Water quality problem</th>
<th>Contributing factors from eutrophication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water safety, taste, odor</td>
<td>Nutrients and suspended sediments degrade water quality and cause:</td>
</tr>
<tr>
<td></td>
<td>• Increased cost and difficulty of drinking water purification.</td>
</tr>
<tr>
<td></td>
<td>• Anoxic conditions and toxins produced in algal blooms that can cause fish kills and make water unsafe for birds and livestock.</td>
</tr>
<tr>
<td>Low species diversity</td>
<td>Stimulated growth of certain organisms cause:</td>
</tr>
<tr>
<td></td>
<td>• Decreases in number and size of population of other species</td>
</tr>
<tr>
<td></td>
<td>• The lake to become dominated by algae and coarse, rapid-growing fish.</td>
</tr>
<tr>
<td></td>
<td>• High quality edible fish, submerged macrophytes (large plants) and benthic (bottom-dwelling) organisms disappear.</td>
</tr>
<tr>
<td>Impairment of recreational use and navigation</td>
<td>Decaying algal biomass produces surface scums, odors, and increases populations of insect pests.</td>
</tr>
<tr>
<td></td>
<td>• Increased sedimentation decreases lake depth, and enhances vegetative growth that blocks navigable waterways;</td>
</tr>
</tbody>
</table>

Numerous experiments have been conducted to determine the limiting nutrient in fresh water and, with the exception of a few cases of very high P enrichment, P is the limiting nutrient in fresh water lakes, rivers, and reservoirs (Correll, 1998). Although many studies show nitrogen (N) to be the limiting nutrient in saltwater ecosystems, some recent studies argue that P is a limiting nutrient to some saltwater ecosystems. For example, Murrell et al. (2002) found that phytoplankton growth responses to N additions were always less than or equal to growth responses to P additions for estuarine water near the Gulf of Mexico. Other research studies have concluded that N is a short term limiting nutrient whereas P limits the long-term productivity of salt water ecosystems (Tyrell, 1999).

Phosphorus inputs to surface water can also promote outbreaks of toxic dinoflagellates, such as *Pfiesteria piscicida*. While in its toxic form, *Pfiesteria* growth has been shown to be strongly stimulated by P additions with little or no effect from N additions (Burkholder and Glasgow, 1997). Although it remains in its toxic form for a relatively short period, the growth during this period could have drastic effects on the amount of toxin released into the water and subsequently the number of fish killed. When *Pfiesteria* is in the non-toxic form it feeds on other algae present in the water and growth has been shown to be indirectly stimulated by increased abundance of algae prey in response to P inputs (Burkholder and Glasgow, 1997). Burkholder and Glasgow (1997) also found that non-toxic *Pfiesteria* abundance was significantly greater near wastewater discharge sites in the New River estuary, which had total P concentrations nearly double that of the control areas. Because of the primary role of P in the eutrophication of freshwater lakes and rivers as well as its potential effects on algae growth in saltwater, it is environmentally advantageous to encourage land management practices that reduce P inputs to water resources.

**Phosphorus Transport Pathways**

As previously mentioned, P can be transported from soils in agricultural fields to adjacent surface water through surface (runoff and erosion) or subsurface (leaching) pathways. Under typical agricultural practices, P remains concentrated in the surface
horizon, which leads to greater P loss through surface transport. Peterjohn and Corell (1984) found average annual total P (TP) concentrations of 5 mg L\(^{-1}\) in surface runoff leaving a corn field compared to only 0.01 mg L\(^{-1}\) in the sub-surface flow, which agrees with findings of Osborne and Kovacic (1993). Annual surface losses of P in watershed studies are frequently over 1 kg ha\(^{-1}\) and reported greater than 10 kg ha\(^{-1}\) (Smith et al., 1993; Pierson et al., 2001) compared to subsurface losses of 0.03 kg ha\(^{-1}\) (Randall et al., 2000). Because the primary mode of P transport for the majority of situations is through surface runoff and erosion, considerable research efforts have been made to describe and quantify management effects on surface losses of P. These studies include, but are not limited to, the effects of erosion control on P loss (Andraski et al., 2003; Daverde et al., 2003; Kimmell et al., 2001; Gaynor and Findlay, 1995; Richardson and King, 1995; Seta et al., 1993), reduced P loss with vegetated buffer strips (Uusi-Kamppa et al., 2000; Lee et al., 2000; Schmitt et al., 1999; Parsons et al., 1994; Daniels and Gilliam, 1996;), effects of STP on dissolved P in runoff (Andraski et al, 2003; Daverede et al., 2003; Andraski and Bundy, 2003; Sims et al., 2002; Sharpley, 1995), and effects of applied P sources on surface P loss (Kleinman and Sharpley, 2003; Eghball et al., 2002; Edwards and Daniel, 1993a, 1993b, 1993c).

Until recently, research describing management effects on P loss through leaching had received little attention because under typical agricultural practices soil P concentrations remain less than what is required for significant P leaching (Lemunyon and Daniel, 2002, Hansen et al., 2002; Sims et al., 1998). However, long-term animal waste applications have increased soil P concentrations to the point where P leaching is a potential environmental threat. For example, Ham (1999) documented soil P concentrations in sub-soils of waste application fields in the NC coastal plain that were 10 times greater than P concentrations in fields not receiving waste. Elevated sub-soil P from repeated waste applications has also been documented by Novak et al. (2002), Maguire et al. (2000), Sharpley et al. (1984a), King et al. (1990), and Mozaffari and Sims (1994).
Description of P Leaching Processes

In the most basic definition, P leaching is the downward movement of P in the soil profile, which is indicated by accumulation of soil-bound P or STP in lower soil horizons as observed by previously cited authors. This transport process is simply the product of the P concentration in the soil water and the soil water flux. The greatest potential for P leaching is obviously created by the combination of soils with high P concentrations in soil water and high volumes of percolate.

Inorganic P in the soil system is highly reactive with a variety of soil surfaces and solutes. Phosphorus can be precipitated as Ca-phosphates in alkaline to neutral soils or Al- and Fe-phosphates in more acidic soils. However, the majority of P in acidic soils is adsorbed to surfaces of clay particles, Al-oxides/hydroxides, and Fe-oxides/hydroxides. Phosphate adsorption can be simplified into two processes, a fast, reversible reaction of P adsorption to surface sites and a slow more irreversible reaction of P diffusion followed by precipitation (van der Zee and van Reimsdijk, 1988). These processes of adsorption/desorption control soil solution P concentration of acid soils. The classical method of describing the relationship between P adsorbed to soil and P concentration in soil solution is with P adsorption isotherms, which are mathematically characterized by a number of non-linear equations. Three of these equations will be discussed in brief here as they relate to current methods of studying P leaching. A more detailed explanation of these equations and others can be found in literature reviews conducted by McGechan and Lewis (2002) and McGechan (2002).

The Freundlich equation has the general form of

\[ Q = k_F C^b, \]

where \( Q \) is the quantity of P sorbed in mg kg\(^{-1}\), \( C \) is the concentration of P in solution in mg L\(^{-1}\), and \( k_F \) and \( b \) are fitting coefficients. The Freundlich equation produces very good fits to experimental data (Figure 2) but is less desirable because the fitting parameters do not correspond with the theoretical models of surface adsorption, namely the Freundlich equation predicts an infinite capacity of the soil to adsorb P.
The Langmuir equation is written as follows:

\[ Q = Q_{max} \frac{k_L C}{1 + k_L C}, \]  

(2)

where \( Q_{max} \) is the maximum amount of P adsorbed to the soil (mg kg\(^{-1}\)) assuming monolayer coverage and \( k_L \) is a constant related to the binding energy of P. The Langmuir equation has the advantage of describing a theoretical adsorption maximum but it does not always provide a good fit to experimental data (Figure 2). Koopmans et al. (2002) favored using the Langmuir equation because they stated that it adequately represented the fast sorption process which is hypothesized to control P release in runoff and drainage events.

![Figure 2. Freundlich, Langmuir, and two-surface Langmuir equations fit to adsorption data from a Norfolk Sandy loam. Coefficients for equations 1, 2, and 3 are as follows: \( k_F = 104 \), \( b = 0.309 \), \( Q_{max} = 194 \) mg kg\(^{-1}\), \( k_L = 1.45 \), \( Q_{max1} = 123 \) mg kg\(^{-1}\), \( k_{L1} = 3.59 \), \( Q_{max2} = 205 \) mg kg\(^{-1}\), and \( k_{L2} = 0.071 \) (Nelson, N.O., unpublished data).](image)

The defined P sorption maximum is particularly useful for P leaching research because it provides a basis for the definition of the degree of P saturation (DPS), which is the percent of total sorption sites that are occupied (i.e. \( 100 \times Q/Q_{max} \)). From a
functional standpoint, as the soil becomes saturated with P, or the DPS increases, the potential for P leaching increases. Phosphorus leaching occurs as the DPS of surface horizons increase to the point where P can be transported to underlying horizons. At the extreme, the entire soil profile would become saturated (DPS approaching 100) and P additions would leach without any retention. Although this scenario once seemed a far-fetched idea, current animal waste management practices have made it a fast approaching reality.

To overcome the poor fit of the Langmuir equation to some adsorption data, a two-surface Langmuir equation was developed, which is written as

$$Q = Q_{\text{max}1} \left[ k_{L1} C / (1 + k_{L1} C) \right] + Q_{\text{max}2} \left[ k_{L2} C / (1 + k_{L2} C) \right], \quad (3)$$

where $Q_{\text{max}1}$ and $Q_{\text{max}2}$ are adsorption maxima for two different adsorption sites with adsorption energies $k_{L1}$ and $k_{L2}$. In general, low energy adsorption sites ($Q_{\text{max}2}$) are approximately 3 times more plentiful than the high energy adsorption sites ($Q_{\text{max}1}$) but held at only 1/100 of the binding strength (i.e. $k_{L1} = 100 \times k_{L2}$). The two-site Langmuir equation retains the defined adsorption maximum and still provides good fits to experimental data (Figure 2). Furthermore, the description of two binding sites with different energies is useful from a theoretical standpoint, for example, Holdford et al. (1997) hypothesize that no P leaching should occur prior to $Q = Q_{\text{max}1}$.

The sorption capacity of soils provides a strong buffer to the P concentration in solution, maintaining low solution P concentrations through adsorption when the DPS is low and maintaining high solution P concentrations through desorption at high DPS. Because the previously mentioned slow, near irreversible adsorption process occurs simultaneously with the fast adsorption process, the subsequent desorption is incomplete and desorption curves (modeled with the same equations as adsorption curves) rarely follow the adsorption curve (McGechan and Lewis (2002). Beauchemin et al. (1996) found only 40% of adsorbed P was released from waste impacted soil in fast desorption. However, it is important to note that the mass of adsorbed P is two or more orders of magnitude larger than the mass of P in solution. For example, at ~60% DPS, the soil in Figure 2 contains 200 mg sorbed P kg\(^{-1}\) and only 3 mg solution P kg\(^{-1}\) (assuming 30%
moisture). Therefore 40% release of sorbed P still represents over 25 times the mass of P in solution. Although P desorption does not provide a complete release of adsorbed P, P desorption from P-saturated soils can maintain relatively high solution P concentrations even after P additions to the soil are eliminated.

Phosphorus sorption and desorption are affected by soil physical and chemical properties, and therefore the parameters in equations 1-3 are highly dependent on soil type. Phosphorus sorption tends to be greater in soils with greater surface area; therefore P sorption has been related to clay content (Sharpley et al., 1984b). Soils with greater clay contents often have greater amounts of Al- and Fe-oxides, which have high affinities for P (Khare et al., 2004). Dynamic soil chemical properties can also affect P sorption. For example, Coleman et al. (1960) found that P sorption to clay minerals increased with increasing exchangeable Al. Phosphorus sorption is also affected by soil pH (Barrow, 1984). Because determining P sorption coefficients for isotherms are time and labor intensive and must be independently determined for each soil and horizon of interest, they are generally unsuitable for large scale assessment of P leaching.

Simplified forms of the adsorption relationships can be made with quantity-intensity (Q/I) relationships, which relate a quantity of P adsorbed (i.e. STP) to its intensity (i.e. concentration in solution) (Koopmans et al., 2002; Beauchemin et al., 1996). Common Q/I relationships for assessing the risk of P leaching relate water extractable P (Pw) or CaCl2 extractable P (PCaCl2) to any number of standardized STP methods (i.e. Mehlich-3, Bray, or Olsen extractants). Several authors have found good linear correlations for Q/I relationships of Pw or PCaCl2 to STP for different soil types (Sharpley, 1995, Paulter and Sims, 2000; Andraski and Bundy, 2003). Other authors have found split-line graphs more appropriate; which indicate a STP concentration representing significant change-point, after which the slope of the relationship drastically increases (Figure 3) (Hesketh and Brooks, 2000; Koopmans et al., 2002). Koopmans et al. (2002) assert that the presence or absence of a change-point is dictated by the range of STP for the samples used and the extraction ratio used in determining of Pw or PCaCl2, where the change-point becomes more definitive with lower soil to solution ratios. In the natural setting, P leaching occurs at very low soil to solution ratios (< 1), therefore it
is expected that such a change point exists for P leaching. Maguire and Sims (2002a) and Hesketh and Brooks (2000) found significant change points in Q/I relationships between STP and dissolved P in leachate from intact soil columns. This agrees with Heckrath et al. (1995) who observed similar change-points when relating STP to P concentrations in tile drainage water. McGechan and Lewis (2002) assert that the change-point observed by these authors could correspond to the saturation of the high strength sorption capacity identified by the two-surface Langmuir equation.

Figure 3. Quantity-intensity relationship for dissolved reactive P (DRP) in leachate vs. Fe-oxide strip extractable P (a measure of STP), illustrating a change point as indicated by two different slopes. Source: Maguire and Sims. (2002a).

Quantity-intensity relationships with STP can vary significantly between soils as a result of different sorption properties (Andraski and Bundy, 2003), therefore better relationships are acquired by normalizing the STP on the basis of maximum sorption capacity, as done with DPS. The P sorption capacity of soils has been related to the amount of Al and Fe extracted by the ammonium-oxalate extraction procedure (Al$_{ox}$ and Fe$_{ox}$) (van der Zee et al., 1988; Freese et al., 1992). Therefore the P sorption capacity (mmol P kg$^{-1}$) can be estimated by the sum of Al$_{ox}$ and Fe$_{ox}$ (mmol kg$^{-1}$). Furthermore the DPS can be approximated as
DPS = \left[ \frac{\text{P}_{\text{ox}}}{(\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})} \right] \times 100, \quad (4)

where \( \text{P}_{\text{ox}} \) is ammonium oxalate extractable P (mmol kg\(^{-1}\)). There are variations on the form of equation 4 as some authors have found that the P sorption capacity of specific soils are better approximated by \( \frac{1}{2} \) the sum of \( \text{Al}_{\text{ox}} \) and \( \text{Fe}_{\text{ox}} \) (Schoumans and Groenendijk, 2000). Using DPS to quantify adsorbed P in Q/I relationships improves the correlation when multiple soils are included (Sims et al., 2002). These Q/I relationships still maintain the distinct change point, indicating a drastic increase in P leaching beyond a certain DPS. Some authors have proposed a critical DPS of 25% for regulatory action and environmental protection (Schoumans and Groenendijk, 2000), however, the change point for DPS vs. P concentration in leachate has been shown to occur closer to 50% DPS (Maguire and Sims, 2002b). The change-points described by these authors demonstrate that although P leaching is a rare occurrence at low STP, P movement rapidly increases as a soil nears P saturation.

Soil Characteristics Contributing to Greater Risks of P Leaching

Soils at high risk for P leaching are those that have low P adsorption capacities, regularly receive large amounts of P inputs, and have relatively large volumes of percolation. Soils with low pH and relatively small amounts of Al and Fe-oxides, such as organic soils and very sandy soils, have much lower P sorption capacities than other soils (Fox and Kamprath, 1971; Marconi and Nelson, 1984). For example, Izuno et al. (1991) found average P concentrations in excess of 1 mg L\(^{-1}\) in drainage water leaving the Everglades Agricultural Area, a region dominated by Histosols. Beauchemin et al. (2003) found higher P concentrations in tile drains for “low P sorbing soils” (sandy with low extractable Al) as compared with “high P sorbing soils.” Breuwsma et al. (1995) found a flow-weighted annual mean P concentration of 1 mg L\(^{-1}\) leaving tile drains in a region dominated by sandy soils and animal agriculture. The estimated P lost through the drains was 2.5 kg ha\(^{-1}\) yr\(^{-1}\).

The environmental significance of P leaching depends upon P entry into surface water, which is highly dependant upon the transport pathway of shallow ground water to
streams. Because drain lines and ditches in artificially drained fields by-pass the natural flow paths and decrease soil contact, much of the research on P leaching has focused on artificially drained soils (Sims et al., 1998). Although P transport from naturally drained fields would be slower and subject to adsorption onto soils in the shallow aquifer, there are still concerns that P applied to naturally drained soils with low sorption capacity may enter nearby surface water through leaching and transport in shallow groundwater.

Novak et al. (2002) monitored shallow groundwater beneath a 10-year-old swine lagoon effluent spray field on an Autryville soil (loamy, siliceous, thermic Arenic Paleudults) and found that P concentrations remained near the detection limit of 0.04 mg P L\(^{-1}\) for an 8 year period. However, groundwater P concentrations beneath a 20-yr-old swine effluent spray field where soils were mapped as Blanton series (loamy, siliceous, semiactive, thermic Grossarenic Paleudults) had P concentrations in excess of 4 mg P L\(^{-1}\) (Figure 4) (Sloan and Gilliam, 1999, unpublished data). These high P concentrations were atypical when compared to other wells on the site, but demonstrate that excessive P applications to sandy soils can increase the P concentration in shallow groundwater, thereby creating the potential for it move laterally.

![Figure 4](image_url)  
**Figure 4.** Phosphate-P concentrations in shallow groundwater beneath a swine lagoon effluent spray field with long-term history of waste application (Sloan and Gilliam, 1999, unpublished data).
Previously cited studies of Ham (1999), Novak et al. (2002), and Sloan and Gilliam (1999, unpublished data) were conducted in the North Carolina Coastal plain; an area with extremely intensive animal production and correspondingly high STP (Figure 1). It is unlikely that these observations of P leaching represent isolated occurrences. For example, over 25% of the soils mapped in Sampson and Duplin counties have very low P adsorption capacities and are therefore susceptible to P leaching (Figure 5). Over 60% of the swine facilities in these counties are within 100 m of sandy soils (Arenic Udults, Grosarenic Udults, and Psamments), making it highly probable that waste is applied to soils at risk for P leaching. Furthermore, these same two counties contain 7.2 million broilers, 3.9 million swine, and 5.8 million turkeys, which produce an estimated 4,950 Mg of P beyond crop requirement each year (NCSU Spatial Information Research Lab, 2000).
The sustainability of the swine and poultry industries in the North Carolina Coastal Plain are very important economically, producing nearly 2 billion dollars in cash receipts in 2001 with over 1 billion dollars originating from Sampson and Duplin counties (NCDA, 2003). However, excess P losses to the surface water are unacceptable from an environmental standpoint. In response to updated NRCS nutrient management standards, Osmond et al. (2003) developed a phosphorus loss assessment tool to evaluate the risk of P loss from agricultural fields, including evaluation of the risk of P loss
through leaching. Producers with fields that are at risk for P leaching losses currently have only one best management practice to adopt, which is to decrease the P additions to the land. Decreasing the P additions could create a financial hardship by requiring producers to purchase additional land, expand waste application systems, install additional waste treatment systems, or decrease the size of their livestock holdings.

**Future Research Needs**

This situation demonstrates the need for further research concerning the soil and waste management effects on P leaching in acid sandy soils of the North Carolina Coastal Plain. There is a need for more research that describes the extent of P leaching in naturally drained soils; specifically data demonstrating the P concentration in the soil solution of soils with histories of long-term waste application, including relationships between leachate P concentrations and easily quantifiably soil properties. This will assist in quantifying the environmental risks of P leaching as well as determining a need for future research describing P transport in shallow ground water. As previously stated, P desorption from P saturated soils could potentially result in continued P leaching even after elimination of P addition. For example, Schoumans and Groenendijk (2000) and Breeuwsma et al. (1995) have estimated that P leaching could continue for 100 to 200 years given the current P status of soils in the Netherlands. Management recommendations and water quality regulations issued today must consider effects extending many years into the future. Therefore, there is a need for research describing the changes in leachate P concentrations and P distribution within the soil profile resulting from various management practices, such as continuation of current practices, changing to P-based waste application, or the complete cessation of P additions.

Animal producers are currently limited to a single option for reduction of P leaching losses – reduce P application rates. However, increasing a soil’s P sorption capacity could potentially reduce P leaching also. For example, Summers et al. (1996) found that amending soils with an Al containing industrial by-product improved soil fertility by reducing P leaching on sandy soils. Phosphorus leaching on acid sandy soils could also be controlled by treating the waste and/or soils with alum (Al₂(SO₄)₃•14H₂O).
Alum additions to poultry litter or to soil receiving swine lagoon effluent can immobilize P through precipitation or adsorption reactions, thereby minimizing leaching. Shreve et al. (1995) found that alum additions to poultry litter prior to land application reduced runoff P concentrations compared to untreated litter. Other authors have found similar results from treating soils with drinking water treatment residuals that contain alum or other forms of Al (Haustein et al., 2000; Codling et al., 2000; Hyde and Morris, 2000). These results justify further research on the use of alum as a best management practice for reducing P leaching in waste amended soils.

**Research Objectives**

The objectives of this research are threefold. First, to monitor P leachate concentrations in soils of a long-term swine lagoon effluent application field and relate these P concentrations to easily quantifiable soil properties, thus determining the extent of P leaching and controlling factors. Secondly, to use P concentrations and collected field data to validate a computer model capable of estimating P leaching. This includes modifying the model algorithms to better represent soil processes dictating P concentrations and movement in the soil and soil solution. This revised and validated model will then be used to evaluate long-term impacts of different soil and waste management practices, namely continuation of current practices, changing to P-based waste application, or the complete cessation of P additions. The final objective of this research is to evaluate the use of alum additions to soil and waste as a best management practice to reduce P leaching on sandy soils with low native P sorption capacities.
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Introduction

Phosphorus accumulation in soils with long-term histories of waste application has prompted increased attention to P loss from agricultural soils to surface water through leaching and subsurface transport, as described in a review of P leaching studies by Sims et al. (1998). Because artificial drainage systems accelerate drainage water transport to surface water bodies and decrease the interaction of drainage water with subsoils, the majority of research concerning P loss through leaching has focused on artificially drained soils. Sims et al. (1998) summarize results of over 20 studies that report on P leaching losses through agricultural drainage systems. Although many of the studies reviewed found low P losses in drainage waters, several studies found P concentrations in excess of 1 mg P L$^{-1}$. More recent studies have also found elevated P concentrations in drainage water from artificially drained soils (Gardner et al., 2002; Beauchemin et al., 2003).

Although less of an immediate environmental concern, P leaching losses from naturally drained soils can still pose an environmental threat, more particularly in sandy soils with low P sorption capacities that receive high P additions from animal waste (Breeuwsma and Silva, 1992; Sims et al., 1998). Novak et al. (2000) found P accumulations $>$ 100 mg Mehlich 3 P kg$^{-1}$ (M3P) soil down to 110 cm in sandy soils receiving swine lagoon effluent, however M3P decreased to near background levels (1-5 mg kg$^{-1}$) by 180 cm. Correspondingly, shallow ground water (3 m) had relatively low average P concentrations (< 0.05 mg P L$^{-1}$), most likely a result of P adsorption between the zone of high soil P and the ground water depth. It is advantageous to assess P leaching losses prior to observations of increased P concentration in ground water because once a soil profile accumulates high amounts of P, P leaching can continue for many years even when P additions have been reduced or eliminated (Breeuwsma and Silva, 1992; Breeuwsma et al., 1995; Schoumans and Groenendijk, 2000).
Recent studies using large intact soil columns, or field lysimeters, have found elevated P concentrations in leachate, with mean and maximum P concentrations ranging from 0.01 to 0.8 mg L\(^{-1}\) and 0.3 to 1.8 mg L\(^{-1}\) respectively (Djodjic et al., 2004; Godlinski et al., 2004; Turner and Haygarth, 2000; Leinweber et al., 1999). Leinweber et al. (1999) found positive correlations between surface (0-30 cm) soil P status and P concentrations in leachate while other authors did not. Djodjic et al. (2004) concluded that while surface soil P concentrations may be indicative of potential P release, sub soil properties, including P status, have a strong influence on P leaching. However Djodjic et al. (2004) did not report sub soil P status of the soils used in their study. Carefoot and Whalen (2003) found dissolved reactive P (DRP) concentrations from 0.01 to 0.17 mg L\(^{-1}\) in 60 cm deep piezometers, with low P status in corresponding sub-soil. Other studies have used Teflon suction cups or tension lysimeters to monitor P leaching through unsaturated zones in the soil profile at depths ranging from 15 to 180 cm (Bry et al., 2002; Andersen and Xia, 2001; Tischner et al., 1998; Andersen, 1994). These authors found P concentrations ranging from 0.01 to 0.2 mg L\(^{-1}\) in the leachate, with the majority of the samples having less than 0.05 mg P L\(^{-1}\). Some of the monitored soils had elevated soil P levels in the surface, but when reported, the P status of the soil in the immediate vicinity of the samplers was relatively low. Andersen and Xia (2001) found leachate P concentrations from 0.005 to 0.1 mg L\(^{-1}\) in soils with the degree of P saturation (DPS, \(P_{ox}(100)/(0.5(A_{ox} + Fe_{ox}))\), where \(P_{ox}\), \(A_{ox}\), and \(Fe_{ox}\) are oxalate extractable elements in mmol kg\(^{-1}\) soil) ranging from 20 to 50% in the surface but only 4 to 9% at depths of soil water sampling.

Although research shows that P movement is greatly increased with increasing soil P status, namely increasing DPS (Maguire and Sims, 2002, Sims et al., 2002), the current research on P leaching in naturally drained soils have focused on P concentrations in leachate collected at depths where soil P status is well below the P sorption capacity, thus leading to relatively low estimates of P leaching losses (Brye et al., 2002; Turner and Haygarth, 2000; Djodjic et al., 2004; Godlinski et al., 2004). The objectives of this research study are to monitor P leaching throughout the soil profile of soils with a long-term history of waste application and various degrees of P saturation,
relate P leaching losses to soil P status, and identify soil properties that are related to P retention.

**Materials and Methods**

**Site description**

The study was conducted on a 21-yr old farrow-to-wean swine facility in Sampson County, North Carolina that is managed typical to farms in the Coastal Plain region. Swine waste generated on the farm was treated in an anaerobic lagoon, after which excess lagoon liquid was irrigated on approximately 19 ha of Coastal Bermudagrass (*Cynodon dactylon* L.) pasture overseeded with Triticale (*X Triticosecale* Wittmack). Pastures were alternately grazed and cut for hay. Lagoon liquid, ranging from 50 to 100 mg P L\(^{-1}\), was irrigated at a rate of 300 kg available N ha\(^{-1}\) yr\(^{-1}\) throughout the growing season (February through December), which over applied P by 40 - 60 kg ha\(^{-1}\) yr\(^{-1}\) based on average P removal rates of 10 and 40 kg ha\(^{-1}\) yr\(^{-1}\) from pasture and hay fields respectively receiving swine lagoon effluent (Nelson and Mikkelsen, 2001). However, it is very likely that pre-regulation waste applications (first 10-15 years of farm operation) exceeded current applications.

In situ suction soil solution samplers (Appendix A) were installed in Autryville (loamy, siliceous, thermic Arenic Paleudults) and Blanton (loamy, siliceous, semiactive, thermic Grossarenic Paleudults) soils located on the farm. Two pits (1 m by 3 m by 1.5 m deep) were excavated in each soil and samplers were installed 0.4 m into the sidewalls of the pits so that samplers were beneath undisturbed soil. Two samplers were installed at 45, 90, and 135 cm in each pit, for a total of 24 samplers (2 soils, 2 pits, 2 reps, 3 depths). Slope in the immediate area of the pits was 0-3%, however the overall slope of the field was 4% with some areas as high as 9%.

Soil moisture was monitored in one pit in each soil with Campbell Scientific CS616 (Campbell Scientific, Logan UT) automated TDR probes inserted horizontally into the pit wall at 10, 45, 68, 90, 114, and 135 cm deep. TDR probes measured soil moisture every minute and the data-logger recorded the average soil moisture every 10 min. TDR probes were field calibrated during the first 3 months of operation by
determining gravimetric soil water content in soil samples taken within 1.5 m of the TDR probes. Precipitation and irrigation were continuously measured and recorded every 10 min. with a tipping bucket rain gauge (TE525, Campbell Scientific, Logan UT) mounted 50 cm from the ground surface. Vegetation around the rain gauge was kept trimmed to < 40 cm to avoid interference with rain and irrigation measurement. On farm irrigation records were used to separate irrigation events from precipitation. After installation of soil solution samplers and TDR probes, the pits were filled in and the area surrounding the pits was fenced off from the cattle. Each fall, Triticale was seeded inside the fenced area near the same time it was overseeded in the pasture. Vegetation over the samplers was cut and removed throughout the study to maintain the plots in the same condition as the surrounding pasture.

A continuous vacuum of -12 to -10 kPa was maintained in each sampler by means of a hanging water column as described by Riekerk and Morris (1983), thereby allowing for continuous sample collection when soil moisture tension (SMT) was less than -12 kPa. Soil solution samples were removed from the samplers once every 12 to 20 days from Sept. 2002 through April 2004, for a total of 42 sampling intervals. Because of low soil moisture and occasional sampler failure (Appendix A), 880 samples were collected out of a possible 1008. Samples were stored at < 4 °C and either frozen or analyzed within 2 weeks of collection. Soil solution samplers were equipped with 0.45 µm polyethersulfone membrane filters, resulting in the immediate filtering of all samples at the time of collection. Initial sampler testing showed that refiltering samples did not affect P concentration, therefore samples were not refiltered. Dissolved reactive P (DRP) concentration in all samples was determined colorimetrically using a Lachat QuickChem 8000 auto analyzer instrument (Lachat, 1995).

Soil analysis

Prior to pit excavation, 3 soil cores (9 cm by 90 cm) were removed from each pit for use in soil chemical and physical analyses. Soil cores were dissected into 5, 10, or 15 cm segments based on soil morphology. Additional soil samples were taken from the side walls of the excavated pits from 90 to 140 cm deep in 10 cm increments. Soil samples were air dried, ground, and passed through a 2 mm sieve prior to analyses.
Samples were extracted for Mechlich 3 P (M3-P) by shaking 2.5 cm$^3$ soil with 25 mL of Mehlich 3 solution for 5 min. and filtering through a Whatman No. 42 filter paper (Sims, 2000). Water extractable P ($P_w$) was determined by shaking 2 g oven dry soil (60 °C for 48 hr) with 20 mL distilled water for 1 hr, then centrifuging the sample for 10 min at 10,000 rpm, filtering the supernatant through a 0.45 µm filter, acidifying the sample with 1 drop 6 M HCl and freezing until analysis (Self-Davis et al., 2000). Oxalate extractable P, Fe, and Al ($P_{ox}$, $Fe_{ox}$, $Al_{ox}$) was determined by shaking 0.75 g soil with 30 mL 0.2 M ammonium oxalate/oxalic acid solution adjusted to pH 3 for 2 hr. in darkness. After shaking, samples were centrifuged at 6,000 rpm for 6 min. and filtered through Whatman No. 42 filter paper and stored in the dark until analysis (Schoumans, 2000). The degree of P saturation (DPS) was calculated as $P_{ox}(100)/\alpha (A_{ox} + F_{ox})$, where $P_{ox}$, $A_{ox}$, and $F_{ox}$ are oxalate extractable elements in mmol kg$^{-1}$ soil and $\alpha$ is 0.5 for non-calcareous sandy soils (van der Zee and van Riemsdijk, 1988; Schoumans and Groenendijk, 2000). Total P (TP) was determined by a modified sulfuric acid/hydrogen peroxide digestion procedure (Gasparatos and Haidouti, 2001). In brief, 5 mL concentrated sulfuric acid was added to 1 g of soil and 10 mL of distilled water. The mixture was slowly heated to 360 °C, where it remained for 4 hr. After cooling, 6 to 12 mL of 30% hydrogen peroxide was added and the mixture was brought to 200 °C for 2 hr. After cooling, the mixture was brought to 100 mL with distilled water, allowed to set for > 24 hr, and the supernatant removed for P analysis. Phosphorus concentration in M3-P, $P_w$, and TP solutions were determined colorimetrically using a Lachat QuickChem 8000 auto analyzer instrument (Lachat, 1995). Phosphorus, Al, and Fe concentration in the oxalate extracts were determined by ICP. Particle size analysis of all samples used for chemical analysis was determined by the pipette method (Gee and Bauder, 1986).

Intact soil cores 6 cm tall by 5.5 cm dia. were taken in triplicate from each horizon in each pit for determination of water retention, hydraulic conductivity, and bulk density. Water retention functions were determined with laboratory methods described by Klute (1986) and fit to moisture release curves with a modified form of the van Genuchten equation (Appendix B; Fayer and Simmons, 1995). Saturated hydraulic conductivity was determined using the constant head method as described by Klute and
Dirksen (1986). Unsaturated hydraulic conductivity functions were determined using saturated hydraulic conductivity and the van Genuchten method (Appendix B; van Genuchten, 1980). Analysis of variance and contrasts for pair-wise comparisons of soil analysis and leachate were performed with SAS proc glm (SAS Institute, 1998). Moisture release curves were fit with SAS proc nlin (SAS institute, 1998)

**Determination of percolate volume**

Percolation volume for each sampling interval was determined using a water balance method, given as

\[ \Delta S = (P+I) - ET + D, \]  

where \( \Delta S \) is the change in storage (cm), \( P \) is precipitation (cm), \( I \) is irrigation (cm), \( ET \) is evapotranspiration, and \( D \) is the drainage (cm). A negative value for \( D \) indicates drainage is down and a positive value for \( D \) indicates upward flux of the soil water.

Runoff was assumed to be negligible because the field was planted in pasture with good ground cover and the surface soil had very high saturated hydraulic conductivities (> 35 cm hr\(^{-1}\)); furthermore, there were no visual indications of runoff in the vicinity of the field plots.

Computationally, a water balance was determined separately for each soil layer, given as

\[ BAL_1 = \Delta S_1 - (P+I) + PET_1, \]  

for the surface soil layer and

\[ BAL_i = \Delta S_i + D_{i-1} + PET_i, \]  

for subsurface soil layers. Where \( BAL_i \) is the water balance for layer \( i \), \( PET_i \) is the potential evapotranspiration removed from layer \( i \) (cm), and other terms are as previously defined. Potential evapotranspiration (PET) was determined by multiplying the reference ET by a crop coefficient. The reference ET was determined with the FAO56 Penman-Monteith combination method on an hourly time step (Allen et al., 1998). Crop growth was divided into three growth stages with three transition periods,
where each growth stage had a different crop coefficient (Table 1) (Chamblee et al., 1995; Allen et al., 1998). The fraction of PET removed from each soil layer \((PET_i)\) was determined as

\[
PET_i = \lambda_i \text{PET},
\]

where \(\lambda_i\) are distribution coefficients 0.6, 0.32, 0.05, 0.02, 0.01, and 0 for soil layers 1 through 6 respectively, which were determined according to the root distribution function

\[
y = 1 - 0.5^{z/m},
\]

where \(y\) is the fraction of roots above depth \(z\) and \(m\) is the half-depth or depth at which \(y = 0.5\) (Federer et al., 2003). The parameter \(m\) was set at 15 cm based on research from Hays et al. (1991), Beyrouty et al. (1990), and Bonachela (1996).

**Table 1.** Growth stages and evapotranspiration crop coefficients for coastal bermudagrass overseeded with triticale pasture/hay mix.

<table>
<thead>
<tr>
<th>Growth Stage</th>
<th>Dates</th>
<th>crop coefficient†</th>
</tr>
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<tbody>
<tr>
<td>initial</td>
<td>Jan 1 – Feb. 14</td>
<td>0.63</td>
</tr>
<tr>
<td>development</td>
<td>Feb. 15 – March 16</td>
<td>0.63 – 1.0</td>
</tr>
<tr>
<td>mid-season</td>
<td>March 17 – July 31</td>
<td>1.0</td>
</tr>
<tr>
<td>late-season</td>
<td>Aug. 1 – Sept. 15</td>
<td>1.0 – 0.85</td>
</tr>
<tr>
<td>end</td>
<td>Sept. 15 – Nov. 31</td>
<td>0.85</td>
</tr>
<tr>
<td>dormancy</td>
<td>Dec. 1 – Dec. 31</td>
<td>0.85 – 0.63</td>
</tr>
</tbody>
</table>

* determined from Chamblee et al. (1995)
† determined after method described by Allen et al. (1998)

Using Equations 2 and 3, drainage from each layer was computed as

\[
D_i = BAL_i, \quad BAL_i \leq U_{\text{max}(i)},
\]

\[
D_i = U_{\text{max}(i)}, \quad BAL_i > U_{\text{max}(i)},
\]

where \(U_{\text{max}(i)}\) is the maximum upward flow of soil water that could have occurred during the sampling interval (cm).
If the water table depth was greater than the monitoring depth (145 cm) then the maximum upward flow of water into a soil layer \( (U_{\text{max}(i)}) \) was determined by estimating average flux between the midpoints of consecutive soil layers on a daily basis using Darcy’s law,

\[
q = -K(h_i) \cdot \frac{[(h_{i+1}) + z_{(i+1)}] - (h_i + z_i)}{(z_{i+1} - z_i)},
\]

(7)

where \( q \) is soil water flux (cm hr\(^{-1}\)), \( K(h) \) is the unsaturated hydraulic conductivity as a function of \( h \) (cm hr\(^{-1}\)), \( h \) is the soil moisture tension at the center of layer \( i \) (cm), and \( z \) is the distance from the surface to the center of layer \( i \) (cm). Moisture release curves were used to determine \( h \) from average daily volumetric soil moisture content as measured by TDR. The \( h \), with the corresponding \( K(h) \) relationship, was used to determine an appropriate \( K \). Because \( K(h) \) and moisture release relationships were different for each layer, the geometric mean interlayer conductivity \( (K) \) was used in Equation 7 (Equation 8, Haverkamp and Vauclin, 1979).

\[
K = (K_i \cdot K_{(i+1)})^{1/2}
\]

(8)

When the average daily flux calculated by Equation 7 was positive, then the maximum upward flow for that day was determined by multiplying \( q \) by 24 hr, otherwise maximum upward flow was set equal to 0.

If the water table was less than the monitoring depth (as determined by volumetric water content equal to saturation) then the maximum upward flux of water was estimated using the steady state relationship between upward flux and water table depth (Figure 1). The steady state upward flux/water table depth relationships were determined with the SOILPREP computer program from the DRAINMOD model (Workman et al., 1994), which employs the method described by Skaggs (1981). The \( U_{\text{max}} \) was determined for each layer as the upward flux from the water table to the mid point of the layer multiplied by 24 h. Daily estimates of \( U_{\text{max}(i)} \) were summed for each sampling interval.
Actual evapotranspiration removed from each layer \((AET_i)\) was determined as

\[
AET_i = -\Delta S_i + (P+I) + D_i, \quad i = 1, \\
AET_i = -\Delta S_i - D_{i-1} + D_i, \quad i > 1, \tag{9}
\]

where \(D_i\) is as computed in Equation 6. Notice that for \(D_i \leq U_{\text{max}(i)}\), \(AET_i = PET_i\).

Phosphorus losses at each sampling depth were calculated by multiplying the P concentration in leachate by the calculated drainage for each sampling interval. Annual P losses were computed by summing the P losses for each sampling interval through the entire year.

**Results and Discussion**

*Soil phosphorus distribution*

Both Autryville and Blanton soils showed significant P accumulations in the upper 75 cm of the soil profile, with M3-P concentrations 40 to 90 times background concentrations for similar soils (Figure 2; Novak et al., 2000). There was a significant soil*depth interaction for \(P_w\), M3-P, \(P_{\text{ox}}\) and TP \((p < 0.001)\). Concentrations of \(P_w\) and M3-P followed the same general trend, where the Autryville soil had higher concentrations than the Blanton in the upper 75 cm \((p < 0.05)\), the Blanton soil had
higher concentrations from 85 to 115 cm ($p < 0.05$), and the soils had similar P concentrations at 125 cm and below ($p > 0.05$).

![Figure 2](image-url)

**Figure 2.** Mehlich 3 P (M3-P, solid lines) and water extractable P ($P_w$, dashed lines) concentrations with depth in the Autryville and Blanton soils (95% confidence limits (CL) represent ± 43 and 3 mg kg$^{-1}$ M3-P and $P_w$ respectively).

Concentrations of $P_{ox}$ and TP are higher in the upper 75 cm of the Autryville soil compared to the Blanton ($p < 0.05$), but were similar below 85 cm ($p > 0.05$) (Figure 3). Although patterns of P accumulation in the two soils are very different, they suggest that the upper horizons of the soils have reached the phosphorus sorption capacity. Oxalate extractable P ($P_{ox}$) concentrations do not significantly decrease from the surface values until 1 m in the Blanton soil ($p > 0.05$), where $P_{ox}$ is a measure of adsorbed P (van der Zee and van Riemsdijk, 1988), thus suggesting this soil has reached its P sorption capacity. In the Autryville soil, $P_{ox}$ concentrations initially decrease down to 40 cm, followed by a large increase between 40 and 60 cm, thus suggesting that the decrease between 20 and 40 cm is a result of a lower P sorption capacity of the E horizon.
Figure 3. Total P (TP, solid lines) and oxalate extractable P (P\(_{\text{ox}}\), dashed lines) concentrations with depth in the Autryville and Blanton soils (95% confidence limits (CL) represent ± 74 and 56 mg kg\(^{-1}\) TP and P\(_{\text{ox}}\) respectively).

The sum of Al\(_{\text{ox}}\) and Fe\(_{\text{ox}}\), a useful indicator of the P sorption capacity of soils (Breeuwsma and Silva, 1992), ranged from 5 to 50 mmol kg\(^{-1}\) in the Autryville soil and from 2 to 24 mmol kg\(^{-1}\) in the Blanton soil, which would suggest that these soils have comparably lower P adsorption capacities than other soils of the Mid-Atlantic Coastal Plain (Sims et al., 2002). The P accumulation at 60 cm in the Autryville soil corresponds to the depth of the Bt horizon, at which depth Al\(_{\text{ox}}\) and Fe\(_{\text{ox}}\) concentrations also increase (Figure 4a). The DPS was greater than 90% in the upper 70 cm of the Autryville soil and the upper 100 cm of the Blanton soil (Figure 4b), indicating that the soils are at or near the P sorption capacity in these horizons. For soil horizons with > 90% DPS, multiple regression analysis was used to determine the amount of variation in the soil P status that could be explained by Al\(_{\text{ox}}\) and Fe\(_{\text{ox}}\). Oxalate extractable Al and Fe explained 99% of the variability in P\(_{\text{ox}}\) for soil samples with > 90% DPS (Table 2), while Al and Fe individually explained 98% and 46% of the variability respectively. Oxalate extractable Fe failed to explain a significant portion of the variation in P\(_{\text{w}}\), M3-P and TP when Al\(_{\text{ox}}\) was included in the model (Table 2), where Al\(_{\text{ox}}\) explained 76, 95, and 98% of the variability respectively. This is in agreement with other research that shows the majority of P in Coastal Plain soils is associated with Al (Novais and Kamprath, 1978).
Figure 4. (a) Oxalate extractable Al ($A_{ox}$, solid lines), oxalate extractable Fe ($F_{ox}$, dashed lines), and (b) degree of P saturation (DPS) with depth in the Autryville and Blanton soils (95% confidence limits (CL) represent ± 88 and 30 mg kg$^{-1}$ $A_{ox}$ and $F_{ox}$ respectively and ± 8% DPS).

Table 2. Selected output from analysis of variance tables for multiple regressions of $P_w$, M3-P, $P_{ox}$, and TP with $A_{ox}$ and $F_{ox}$.

<table>
<thead>
<tr>
<th></th>
<th>$P_w$</th>
<th>M3-P</th>
<th>$P_{ox}$</th>
<th>TP</th>
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Type III SS

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<tr>
<td>Fe</td>
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<td>0.122</td>
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34
**Drainage**

The study contained both wet and dry intervals relative to 30-yr average precipitation (Figure 5). Precipitation was less than average during the first few months and last few months of the study. The year 2003 was a wet year with 150 cm of precipitation, compared to average annual precipitation of 124 cm. Despite the high rainfall in 2003, irrigation continued because the producer had to dispose of the excess lagoon liquid. The relative AET (AET/PET) for individual sampling intervals was as low as 0.5 and 0.2 in the Autryville and Blanton soils respectively during the dryer months, but the relative AET for the entire study period was greater than 0.9 for both soils (Figure 6).

![Figure 5](image-url)  
*Figure 5.* Monthly precipitation and irrigation during the study compared to the 30-yr average precipitation.
Figure 6. The average daily precipitation plus irrigation, potential evapotranspiration (PET), and actual evapotranspiration (AET) during each of the sampling intervals for pasture grown on Autryville and Blanton soils.

In accordance with the higher precipitation, there was also more drainage in 2003 than in similar time periods of 2003 or 2004 (Table 3). Drainage volumes were similar between the Blanton and Autryville soils with the largest difference occurring in the summer of 2003, where the rising water table decreased drainage rates in the Blanton soil for the sampling interval ending on May 30 and then decreased drainage rates in the Autryville soil for the sampling intervals ending on July 24 and August 1 (Figures 7 and 8). However, cumulative drainage volumes for the summer months (May – August) remained similar between the soils (Table 3).
Table 3. Precipitation, irrigation, evapotranspiration, and drainage by depth in the Autryville and Blanton soils.

<table>
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<td>Precip. (cm)</td>
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<td>36</td>
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<td>Irr. (cm)</td>
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<td>Autryville ET (cm)</td>
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<td>Blanton ET (cm)</td>
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<td>-9</td>
<td>-13</td>
<td>-35</td>
<td>-21</td>
<td>-10</td>
<td>-88</td>
</tr>
</tbody>
</table>
Figure 7. Drainage and precipitation + irrigation rates at each of the sampling intervals for the Autryville soil. Note: sign on drainage axis indicates direction of flow.

Figure 8. Drainage and precipitation + irrigation rates at each of the sampling intervals for the Blanton soil. Note: sign on drainage axis indicates direction of flow.
The water table was in the upper 135 cm of the Autryville soil for a brief period during the summer of 2003 (Figure 9) and in the upper 135 cm of the Blanton soil for the majority of the sampling period (Figure 10). During these periods the assumption of no lateral water movement would most likely not have been valid for the saturated portions of the soil profile. Because the water balance did not account for lateral entry or exit of water, the drainage calculated during these periods would represent the net flux out of the uppermost saturated layer, but not necessarily in the vertical direction. Therefore, the drainage into the underlying soil layers and the corresponding water balance for those layers may be incorrect. To ascertain the extent of possible error introduced into the drainage calculations by the presence of the water table within the depth of measurements, the volume of drainage from each soil layer, that was calculated to have occurred when the layer was saturated or the overlying layers were saturated, was determined (Table 4). The possible errors in the calculated drainage due to lateral flow were minimal for the Autryville soil and the upper layers of the Blanton soil. Drainage out of the 114 and 135 cm layers of the Blanton are considered best approximations given the circumstances.

**Figure 9.** Soil moisture (solid lines) at three depths and water table depth (WTD, dashed line) in the Autryville soil during the study period.
Figure 10. Soil moisture (solid lines) at four depths and water table depth (WTD, dashed line) in the Blanton soil during the study period.

Table 4. Percent of total drainage calculated for the study period that occurred when the soil layer was saturated or when the overlying soil layer(s) were saturated.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Calculated drainage when layer is saturated Autryville</th>
<th>Calculated drainage when preceding layer is saturated Autryville</th>
<th>Blanton</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>45</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>68</td>
<td>0</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>1</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>114</td>
<td>12</td>
<td>38</td>
<td>1</td>
</tr>
<tr>
<td>135</td>
<td>17</td>
<td>71</td>
<td>12</td>
</tr>
</tbody>
</table>

Phosphorus concentrations in leachate

The average leachate DRP concentration at 45 cm in the Autryville soil was over two orders of magnitude greater than DRP concentrations at 90 and 135 cm (Table 5). By contrast, leachate DRP concentrations were elevated in the Blanton soil down to 90 cm, but were below the detection limit (0.03 mg L⁻¹) at 135 cm. Although the DPS in
the Autryville soil is greater than or equal to the DPS in the Blanton soil above 70 cm, leachate DRP at 90 cm is over 2 orders of magnitude less than the Blanton soil, thus confirming the importance of considering sub soil properties when estimating the fate and transport of P (Djodjic et al., 2004).

Table 5. Mean DRP concentrations in leachate collected in Autryville and Blanton Soils from September 1, 2002 to April 4, 2004.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Autryville mean</th>
<th>CL † ±</th>
<th>Blanton mean</th>
<th>CL ±</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg L⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>10.04</td>
<td>1.98</td>
<td>8.41</td>
<td>3.53</td>
</tr>
<tr>
<td>90</td>
<td>0.05</td>
<td>0.04</td>
<td>6.42</td>
<td>2.50</td>
</tr>
<tr>
<td>135</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>

† 95% confidence limit of the mean

The leachate DRP concentrations at 45 cm followed the same general trend for both soils throughout the course of the study (Figure 11). In the Blanton soil, leachate DRP at 90 cm generally remained slightly less than the DRP at 45 cm and changes in DRP concentration tended to lag behind the changes observed at 45 cm. Dissolved reactive P concentrations at 90 cm in the Autryville soil remained relatively low for most of the study period, with the exception of February through April 2004, where concentrations were as high as 0.2 mg L⁻¹. Similarly, leachate DRP concentrations at 135 cm remained below the detection limit for most of the study except in spring 2004 (Figure 12). The high variability of P concentrations throughout the sampling period is consistent with results from other studies (Heckrath et al., 1995, Bry et al., 2002). Increased drainage from overlying soils could potentially transport excess P from animal waste applications to the lower horizons, however changes in leachate DRP concentrations did not seem to follow a consistent pattern with either drainage or waste applications (Figures 13 and 14). This is in contrast to Stamm et al. (1997) and Hodgkinson et al (2002) who found increased P concentrations in drainage water following dairy and swine waste applications. However, these authors concluded that P concentrations increased after waste application because of preferential flow through the
soil. It is likely that preferential flow is not a significant transport pathway in the poorly structured sandy soils of the present study, thus explaining the lack of correlation between waste applications and changes in DRP concentrations of leachate.

**Figure 11.** Dissolved reactive P (DRP) concentrations in leachate collected at 45 cm in the Autryville soil and at 45 and 90 cm in the Blanton soil.
Figure 12. Dissolved reactive P (DRP) concentrations in leachate collected at 90 and 135 cm in the Autryville soil and at 135 cm in the Blanton soil.

Figure 13. Dissolved reactive P (DRP) concentrations at 45 cm in the Autryville soil with corresponding drainage rates from the overlying soil layer (0-20 cm; bars) and waste applications.
Figure 14. Dissolved reactive P (DRP) concentrations at 45 cm in the Blanton soil with corresponding drainage rates from the overlying soil layer (0-20 cm; bars) and waste applications.

The DRP concentrations at 45 cm in the Autryville soil and 45 and 90 cm in the Blanton soil all decreased dramatically during the summer of 2003, which could be a result of climate or crop management factors. Precipitation in May and July of 2003 was over double the 30-year average (Figure 5). The high drainage rates at the end of May 2003 would reduce the soil to solution ratio, which has been shown to decrease P concentrations in quantity-intensity relationships (Koopmans et al., 2002; Hesketh and Brooks, 2000). Further complicating the interpretation, the producer applied lime to the pasture in early April 2003, as the surface soil pH values were 4.8 and 4.6 for Autryville and Blanton soils respectively. Displaced Al and neutralized hydroxyl-Al species resulting from lime addition could have also been the cause of decreased DRP concentrations in the leachate (Robarge and Corey, 1979).

Split-line models describing two linear relationships on either side of a threshold have been used to relate DPS, or other measures of soil P status, to $P_w$ and/or leachate DRP for use in defining environmental thresholds for P leaching (Nair et al., 2004, Maguire and Sims, 2002; Koopmans et al., 2002; Hesketh and Brooks, 2000). Similarly,
a split-line model was fit to the average leachate DRP measured from each soil*pit*depth combination and the corresponding DPS, with the model as follows:

\[
DRP = a_0 + b_0DPS, \quad \text{for } DPS \leq d_0
\]

\[
DRP = a_1 + b_1DPS, \quad \text{for } DPS > d_0
\]

(12)

\[
b_0 = \left[ \frac{(a_1 - a_0) + b_1d_0}{d_0} \right]
\]

(13)

where \(d_0\) is the change point and \(b_0\) and \(b_1\) are the slopes prior to and following the change point respectively. Fitting split-line model identified a change point in the relationship between leachate DRP and the soil DPS at 45\% DPS, after which the DRP concentration increased rapidly with increasing DPS (Figure 15). This change point is slightly lower than the change point of 56\% identified by Maguire and Sims (2002), which is most likely due to the lack of data points between 43 and 95\% DPS. The relationship between \(P_w\) and DPS was also fit with the split-line model, identifying a change point at 59\% DPS (Figure 16). The increase in the slope of the \(P_w\) vs. DPS relationship after the change point was much less than that in the DRP vs. DPS relationship, as indicated by a smaller \(b_1:b_0\) ratio (Table 6). The smaller \(b_1:b_0\) ratio is a result of the smaller soil to solution ratio for the \(P_w\) extraction. Koopmans et al. (2002) calculated that soil to solution ratios of 1:0.3 and 1:10 should have \(b_1:b_0\) ratios of 110 and 7.1 respectively, which are in general agreement with soil to solution and \(b_1:b_0\) ratios found in Table 6. Koopmans et al. (2002) also calculated that the change point should decrease with decreasing soil to solution ratio, which is contrary to what was found in this study. However, this discrepancy could also be because there are no data points between 43 and 95\% DPS in the DRP vs. DPS relationship, thus suggesting that the change point would have been greater had there been more data points between the extremes. Although change points identified in this study agree with results of Maguire and Sims (2002), they are greater than the change point of 20\% DPS found by Nair et al. (2004) and the change point of 25\% DPS suggested by research in The Netherlands (Breeuwsma et al., 1995; Schoumans and Groenendijk, 2000).
Figure 15. Relationship between the average leachate DRP concentration and soil DPS with corresponding split-line model.

![Graph showing the relationship between DRP concentration and DPS]

Figure 16. Relationship between water extractable P (Pw) concentration and DPS for Autryville and Blanton soils with corresponding split-line model.

![Graph showing the relationship between Pw concentration and DPS]

Table 6. Parameter estimates for the split-line models fit to the relationships between leachate DRP and DPS and Pw and DPS.

<table>
<thead>
<tr>
<th>Dependent variable</th>
<th>$d_0$</th>
<th>$a_0$</th>
<th>$b_0$</th>
<th>$a_1$</th>
<th>$b_1$</th>
<th>soil to solution ratio</th>
<th>$b_1:b_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRP</td>
<td>45.3</td>
<td>0.014</td>
<td>0.001</td>
<td>-6.32</td>
<td>0.14</td>
<td>1:0.1†</td>
<td>170</td>
</tr>
<tr>
<td>Pw</td>
<td>58.6</td>
<td>-0.60</td>
<td>0.097</td>
<td>-14.16</td>
<td>0.33</td>
<td>1:10</td>
<td>3.4</td>
</tr>
</tbody>
</table>

† estimated based on average water content of 0.16 cm$^3$ cm$^{-3}$ for the study period and bulk density of 1.6 g cm$^{-3}$
**Mass losses of dissolved phosphorus**

Phosphorus losses at 45 cm were 109 and 75% of the P applied to the Autryville and Blanton soils respectively during the study period (Table 7). Average crop P removal for bermudagrass hay/pasture is approximately 30 kg P ha\(^{-1}\), assuming half of the forage is grazed and half is removed as hay (Nelson and Mikkelsen, 2001), indicating that >150% of the excess P applied to the Blanton soil was leached past 45 cm and >120% of the excess P was leached past 90 cm in 2003. Phosphorus loss in excess of P application indicates P desorption occurred during the greater than average drainage events in the summer of 2003. This indicates P desorption from P saturated soils will buffer solution P concentrations and P leaching may continue to occur even in the absence of P applications, which has been confirmed in P desorption studies (Beauchemin et al., 1996). Although 111 kg P were lost from the upper 45 cm of the Autryville soil only 0.4 kg were lost past 90 cm because of P adsorption between 45 and 90 cm, equating to a 5% increase in the mass of adsorbed P (P\(_{ox}\)) at that depth. Because the DPS is greater than 95% above 70 cm, it is possible that the P adsorption would occur between 70 and 80 cm, where the soil P status is below the P sorption capacity, which would increase P\(_{ox}\) by 27% and raise the DPS from 70 to 98%.

**Table 7.** Phosphorus additions from waste application and P losses through leaching in an Autryville and Blanton soil.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste Application</td>
<td>18.4</td>
<td>67.9</td>
<td>15.4</td>
<td>101.8</td>
</tr>
<tr>
<td>Leaching Losses</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Autryville</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45 cm</td>
<td>7.6</td>
<td>99.4</td>
<td>4.0</td>
<td>111.1</td>
</tr>
<tr>
<td>90 cm</td>
<td>0.0</td>
<td>0.3</td>
<td>0.0</td>
<td>0.4</td>
</tr>
<tr>
<td>135 cm</td>
<td>0.0</td>
<td>0.2</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Blanton</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45 cm</td>
<td>12.4</td>
<td>62.1</td>
<td>4.9</td>
<td>79.4</td>
</tr>
<tr>
<td>90 cm</td>
<td>5.1</td>
<td>46.5</td>
<td>2.9</td>
<td>54.5</td>
</tr>
<tr>
<td>135 cm</td>
<td>0.0</td>
<td>0.2</td>
<td>0.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Phosphorus losses calculated for the P saturated soil horizons in this study are much greater than the P losses determined by other studies, which range from < 0.1 to 3.2 kg P ha\(^{-1}\) yr\(^{-1}\) (Leinweber et al., 1999; Djodjic et al., 2004; Godlinski et al., 2004; Bry et al., 2002; Sims et al., 1998), with the exception of a tile drained organic muck soil where losses were as high as 31 kg ha\(^{-1}\) yr\(^{-1}\) (Duxbury and Peverly, 1978). However, P losses in the soil horizons that were below the DPS are well within the reported range. This demonstrates that significant vertical P movement can occur in the upper portions of a soil profile even when leachate P concentrations in the deeper depths are near detection limits.

Future P losses from the Autryville soil were estimated using an annual mass balance approach for each layer in which soil samples had been taken. The year-end P mass in each layer \(i\) (\(Pfi\); kg ha\(^{-1}\)) was calculated as

\[
Pfi = Poi + PAi - PCi - PLi
\]

where \(i\) indicates soil layer 1 through 16 with bottom depth 15, 25, 35, 45, 55, 60, 65, 70, 75, 80, 90, 100, 110, 120, 130, and 140 cm. Initial P (\(Poi\)) was set equal to the mass of Pox (kg ha\(^{-1}\)) determined in soil samples taken in May 2002. Phosphorus additions (\(PAi\)) were equal to average annual P additions from waste application (70 kg P ha\(^{-1}\)) for the surface layer and set equal to P leaching losses from the previous layer (\(i-1\)) for all subsequent soil layers. Crop P uptake (\(PCi\)) was equal to the average P removal from bermudagrass hay and pasture cropping systems (30 kg ha\(^{-1}\); Nelson and Mikkelsen, 2001) and was distributed within the soil profile according to root distribution as given by Equation 1. Phosphorus leaching losses (\(PLi\)) were estimated as the product of DRP concentration in leachate (as determined by the relationship in Figure 15) and the drainage out of the layer. Annual drainage at a depth of 135 cm for 2003 was 75 cm, however precipitation was 26 cm above the long-term annual average of 124 cm yr\(^{-1}\) for the region (Table 3). Therefore, estimated average annual drainage from the soil profile was reduced to 49 cm. Drainage for layers above 135 cm was estimated based on the relative drainage observed for the study period. Where relative drainage was determined as the volume of drainage at any depth divided by the volume passing 135 cm, i.e. 2.1,
1.5, 1.12, 1.05, 1.03, 1.01, and 1.0 for soil layers ending at 0, 20, 58, 81, 100, 125, and 140 cm deep respectively (Table 3).

If waste applications continue at 70 kg P ha$^{-1}$ yr$^{-1}$, then DRP concentrations in the leachate at 90 cm in the Autryville soil will be expected to begin rising in 2004 and reach a peak of 9.7 mg L$^{-1}$ in 2033, then stabilize at 7.7 mg L$^{-1}$ near 2090 (Figure 17). Leachate DRP concentrations at 135 cm would begin rising in 2034 and reach a peak of 9.6 mg L$^{-1}$ in 2055, then stabilize around 8 mg L$^{-1}$ in 2100. Phosphorus loads follow similar trends, where maximum P loss past 135 cm is 48 kg ha$^{-1}$ yr$^{-1}$ in 2055, stabilizing at 40 kg ha$^{-1}$ yr$^{-1}$ by 2100 (Figure 18). By comparison, if P applications were stopped today, leachate DRP concentrations would still increase in years 2004 and 2032 at 90 and 135 cm depths respectively, reaching peak concentrations near the same as if P applications continued. These increased P concentrations would be a result of P desorption from the overlying soil horizons that are at or even in excess of the P sorption capacity (Figure 4). Similarly, Breeuwsma and Silva (1992) estimated increases in leachate P concentrations until year 2045 in The Netherlands, despite the prohibition of excess P loading after the year 2000.

![Figure 17. Estimated leachate DRP concentrations at 45, 90, and 135 cm in the Autryville soil under continued P application (solid points) and discontinued P application (open points).](image-url)
In contrast to the scenario of continued P applications, in the absence of P applications, leachate DRP concentrations would decrease as the soils DPS is lowered by crop P uptake and P leaching, returning to near background concentrations by year 2100. Even if P applications were stopped today, P losses at 135 cm would exceed 40 kg ha\(^{-1}\) yr\(^{-1}\) in 2055. Total P losses past 135 cm over the next 100 years are estimated to be 2850 kg ha\(^{-1}\) if P applications continue compared to 1370 kg ha\(^{-1}\) if P applications were stopped today. The eventual fate of this P would depend upon soil properties below 135 cm and the flow dynamics of the shallow groundwater.

Predictions of soil P distribution by this simple model compare favorably with other models. For example, the predicted P front is a steep gradient as indicated by the rapid increase in P concentrations (Figure 17) and the steep gradient in DPS (Figure 19), which agrees with more complex models using numerical solutions to the convective dispersive equation (De Willigen et al., 1982). Although leachate DRP concentrations are higher than predicted by other models, the Al\(_{ox}\) and Fe\(_{ox}\) concentrations in this soil are relatively low compared to the soils used in the other models (Schoumans and Groendijk, 2000, De Willigen et al., 1982). However, P losses predicted by Equation 12 do not include P loss from the irreversible fixation of P through diffusion of P into soil.
aggregates, which can account for 0 to 9 kg P ha\(^{-1}\) yr\(^{-1}\) (Schoumans and Groenendijk, 2000). Therefore, these predicted losses are rough approximations and should be confirmed through the use of more complex models that account for the various P transformations that may occur in soils.

Figure 19. Estimated change in DPS in the Autryville soil under continued P application (a) and discontinued P applications (b).

Conclusions

Soil P distribution in P saturated soil horizons are strongly correlated to oxalate extractable Al. Annual P applications of 40 to 60 kg excess P ha\(^{-1}\) yr\(^{-1}\) for 20 years resulted in elevated P concentrations in leachate below the root zone. Relatively significant P movement occurred in the upper horizons of P saturated soils while soil solution P concentrations remained very low in the lower horizons. Therefore, accurate assessments of P leaching must incorporate P status and P sorption capacity of the entire soil profile, not just the surface horizons.
A split-line model adequately described the relationship between average DRP concentration in leachate and the DPS, identifying a change point at 45% DPS. Increases in adsorbed P above 45% DPS have 170 times greater impact on leachate P concentrations compared to soils with less than 45% DPS. A change point of 59% DPS was determined for the $P_w$ vs. DPS relationship, suggesting that more data points for the leachate DRP vs. DPS relationship may be needed to more precisely identify the change point.

Phosphorus leaching losses in excess of surplus P additions were observed, indicating that P desorption is contributing up to 50% of current P leaching losses at 45 cm and greater than 15% of leaching losses at 90 cm in the Blanton soil. There is a potential for 1370 kg P ha$^{-1}$ to be leached from the Autryville soil over the next century even if P applications were stopped today. This demonstrates the need to consider long-term leaching losses when calculating potential environmental impacts of P loss from agricultural soils with low P sorption capacity. Further work with more complex models would be useful in identifying the future impacts of current P management strategies.
References


Introduction

Application of agricultural wastes to supply crops with N requirement often over-applies P, resulting in P accumulation and leaching (Chapter 2, Novak et al., 2000; Sims et al., 1998). Phosphorus accumulated in soils with low P sorption capacities, such as acid sandy soils of the NC Coastal Plain, can be released through desorption and result in elevated leachate P concentrations even when current P inputs are less than crop removal (Breeuwsma and Silva, 1992). Because excess P inputs to surface waters promote cultural eutrophication, thereby leading to water quality degradation, it is important to adequately assess the effects of soil and waste management practices on P losses, including P leaching losses. However, conventional field studies for comparison of management effects on P leaching are difficult to conduct. Spatial variability of soils, including variability in soil horizonation and variability in soil P status resulting from differences in past management, complicates the experimental design and poses problems for adequate replication of the experiment. Furthermore, P sorption-desorption reactions buffer solution P concentrations; therefore, the effects of different management practices may not be apparent in short-term monitoring studies. Alternatively, field scale computer simulation models can be used to compare long-term effects of contrasting management practices. Although computer simulation models are not constrained by the same time or experimental design parameters as conventional field studies, the equations and parameters used must adequately reflect the natural processes governing P transport.

There are a variety of simulation models presently available that have been used to predict P losses through surface transport processes. However, because P leaching is a more recent concern, many of these models do not simulate vertical P movement within the soil profile. For example, the Soil and Water Assessment Tool (SWAT) only allows P leaching to occur from the top 10 cm of the soil profile (Neitsch et al., 2002). Other models, such as the Erosion Productivity Impact Calculator (EPIC), do not
consider dissolve P in soil solution and therefore do not provide for a means of predicting P leaching (Williams, 1995). The Root Zone Water Quality Model (RZWQM) predicts leaching of other agricultural chemicals, but does not currently have P cycling subroutines incorporated into the model structure (Ma et al., 2000). The Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) model uses P cycling subroutines very similar to those used in EPIC, but it includes the prediction of dissolved P concentrations in percolation water (Knisel, 1993).

The few attempts at simulating P leaching with GLEAMS have produced mixed results. Shirmohammadi et al. (1998) found that with proper selection of initial parameter values, GLEAMS produced reasonable estimates of dissolved P mass losses through tile drain lines. However, dissolved P was only 25% of the total P losses, where the particulate P loss was simulated with the addition of a new submodel incorporated into the existing hydrology component. Yoon et al. (1994) found that GLEAMS predicted a constant low (0.02 mg P L$^{-1}$) P concentration in leachate that was within the range of measured data but did not reflect the weekly variability in measured data. Stone et al. (2001) found that although GLEAMS predicted leachate P concentration within the range of measured data, the model leachate P predictions were completely unresponsive to changes in waste application rates over 8 year simulations. Furthermore, GLEAMS predictions of soil P accumulation and distribution within the soil profile were very poor. Measured data showed that continued waste application produced small increases in surface soil P concentrations and large increases in sub-soil P concentrations, consistent with other studies of P loading on soils with low P adsorption capacities (Sims et al., 1998). However GLEAMS predicted P accumulation in excess of 4500 mg kg$^{-1}$ in surface soils (compared to measured P concentrations of less than 500 mg kg$^{-1}$) and no change in soil P concentration in sub-soil horizons. Similar to leachate P concentrations, model predictions of subsoil P concentrations were unresponsive to changes in waste application rates (Stone et al., 2001). These studies suggest that GLEAMS may be able to adequately predict low leachate P concentrations typical of conventional agricultural systems, but GLEAMS P leaching predictions are unreliable when excessive P loading increases soil P status nears the P sorption capacity, as is the case for situations involving
animal waste application. This inadequacy in the P subroutines was noted by the GLEAMS developers who cautioned against using GLEAMS to simulate P losses from fields receiving animal waste (Knisel, 1993).

Under prediction of solution P concentrations would cause GLEAMS to underestimate P leaching losses and misrepresent the effects of waste management practices on current and future P leaching losses. Furthermore, under predicting P leaching would result in unrealistic P accumulation in surface soils, as was noted by Stone et al. (2001). Therefore, long-term predictions of surface P losses from agricultural systems with over-applications of P would also be inaccurate. The objectives of this research are to modify the P sub-routines in GLEAMS to improve P leaching predictions, validate the model using field monitoring data, and use the validated model to compare the effects of future management practices on P leaching losses from acid sandy soils receiving swine lagoon effluent.

Model Description

GLEAMS was developed in the 1980s based on the CREAMS (Chemicals, Runoff and Erosion from Agricultural Management Systems) model, which was developed from 1978 to 1980 (Knisel and Williams, 1995; Knisel, 1980). GLEAMS has been commonly used to predict movement of P and other contaminants from field scale agricultural systems (Yoon et al., 1994; Garnier et al., 1998; Zacharias and Heatwole, 1994; Webb et al., 2001). The water balance method employed by GLEAMS has been shown to provide adequate predictions of long term (annual) runoff and percolation although there is a poor correlation with short term field data (Knisel et al., 1991; Nicks, 1998; Ma et al., 1998). GLEAMS was selected to model P leaching in the present study because it already had P leaching mechanisms integrated into its structure, the hydrologic character of the field site studied corresponds with the intended field characteristics for the GLEAMS model, and the source code was readily available, thereby facilitating modifications to P subroutines.

The P cycle in GLEAMS consists of both organic P and inorganic P pools. The inorganic P pools will be described here as they relate to P leaching. Complete
descriptions of the P cycle can be found in the model documentation and related model
descriptions (Jones et al., 1984; Knisel, 1993; Williams, 1995; Lewis and McGechan, 2002). GLEAMS has three inorganic P pools: labile, active, and stable. Labile P is the
plant available portion, analogous to anion exchange extractable P. Labile P is in fast
equilibrium with active P, and active P is in turn in a slow equilibrium with stable P.
This is designed to represent two phase P adsorption: quick reversible P adsorption
(labile P to active P), and slow near irreversible adsorption (active P to stable P). At
equilibrium, the stable P pool is four times the size of the active P pool (regardless of
soil properties) and the size of the labile P pool is proportional to the active P pool
according to the following equation:

\[ P_{labile} = P_{active} \left( \frac{PSP}{1 - PSP} \right) \] (1)

where PSP is the phosphorus sorption coefficient. The PSP is defined conceptually as
the fraction of applied fertilizer that remains labile after a 6-month incubation with
multiple wetting and drying cycles. Within the model, PSP is estimated from regression
equations, with different equations for calcareous soils, slightly weathered soils and
highly weathered soils. For highly weathered soils, such as udults, PSP is estimated as a
function of clay content according to the following equation:

\[ PSP = 0.46 - 0.0916(\ln(\% \text{ clay})) \] (2)

PSP increases with decreasing clay content. Labile P pool is larger than the active P
pool for PSP > 0.5, or % clay < 0.65%. The labile P pool is less than one half of the
active P pool when % clay is > 4.0 % and less than one fifth of the active P pool when %
clay is > 25%. PSP is constrained to lower and upper limits of 0.05 and 0.75
respectively.

Labile P is partitioned between solid phase and liquid phase according to the
equation:

\[ k_d = Q/C \] (3)
where $Q$ is the concentration of labile P on the solid phase, $C$ is the concentration of P in the solution phase (mg L$^{-1}$) and $k_d$ is a partitioning coefficient that is estimated with the following equation:

$$k_d = 100 + 2.5(\% \text{ clay})$$  \hspace{1cm} (4)

As can be seen in the above equations, the relationship between $C$ and $Q$ is a straight line with slope of $1/k_d$. Furthermore, the relationship between labile P and active P is a straight line, as is the relationship between the active and stable P pools. The end result of the these combinations of equations is a straight line relationship between adsorbed P and solution P concentration, as opposed to the non-linear relationship typical of P adsorption isotherms (Figure 1). Although this relationship may be suitable at low soil P concentrations, it can potentially under predict the P concentrations at high soil P levels.

![Solution P vs Adsorbed P](image)

**Figure 1.** Langmuir adsorption isotherm fit to adsorption data for a Norfolk sandy loam A horizon (unpublished data) compared to leachate P concentrations predicted with the GLEAMS P equations at 15, 50, and 150 days following P application and the predicted equilibrium concentration.
Site and Soil Characterization

Phosphorus concentrations in leachate at 45, 90, and 135 cm were monitored for 20 months (September 2002 through April 2004) in Autryville (loamy, siliceous, thermic Arenic Paleudults) and Blanton (loamy, siliceous, semiactive, thermic Grossarenic Paleudults) soils that had received swine lagoon effluent for 21 years. Soil solution was continuously collected with suction samplers and removed from the samplers every 5 to 20 days. Swine lagoon effluent was irrigated at an average rate of 11 cm yr\(^{-1}\) and supplied 250-300 kg available N and 60 – 80 kg P ha\(^{-1}\) yr\(^{-1}\). Soils were planted in Coastal Bermudagrass (\textit{Cynodon dactylon} L.) pasture overseeded with Triticale (\textit{X Triticosecale} Wittmack) and grazed by cattle. Leachate collection sites (20 to 40 m\(^2\)) were fenced off from the rest of the pasture and grass was occasionally cut and removed throughout the study. In addition to collection of leachate soil moisture was monitored in each soil with Campbell Scientific CS616 (Campbell Scientific, Logan UT) automated TDR probes inserted horizontally at 10, 45, 68, 90, 114, and 135 cm deep. TDR probes measured soil moisture every minute and the data-logger recorded the average soil moisture every 10 min. Precipitation and irrigation were continuously measured and recorded every 10 min with a tipping bucket rain gauge (TE525, Campbell Scientific, Logan UT) mounted 50 cm from the ground surface. Additional site characteristics and details on leachate collection are available in Chapter 2.

Soils were sampled in six replicates from the surface to 140 cm deep in 5, 10, or 15 cm increments depending on soil morphology. Soils were analyzed for Mehlich-3 P (M3-P), water extractable P (P\(_w\)), total P, oxalate extractable P, Fe, and Al (P\(_{ox}\), Fe\(_{ox}\), and Al\(_{ox}\)), and particle size distribution as described in Chapter 2. Select soil samples were analyzed for anion-exchange extractable P (AEP) using BDH anion exchange membranes (BDH product no. 55164 2S, BDH Laboratory Supplies, BH151TD, Poole, England) following the procedure of Saggar et al. (1990). Briefly, anion exchange membranes were prepared by shaking with 0.5 M NaHCO\(_3\) adjusted to pH 8 for 30 min, repeated twice, then rinsed with distilled water by shaking for 5 minutes, repeated three times. Soil (1 g) was extracted by shaking with 30 mL of distilled water with two anion exchange membrane strips (24 cm\(^2\) surface area each) for 16 hours. Phosphorus was
eluted by shaking membranes in 30 mL of 0.5 N NaCl for 1 h. Phosphorus concentrations in leachate, Mehlich-3, anion exchange, and diluted soil digest solutions were determined colorimetrically using a Lachat QuickChem 8000 auto analyzer instrument (Lachat, 1995). Phosphorus, Al, and Fe in oxalate extracts were determined by ICP. Additional details of soil analysis can be found in Chapter 2.

**Model Modifications**

Two separate methods were used to modify the partitioning of labile P between solution and adsorbed phases, a simplified empirical approach based on the degree of phosphorus saturation (DPS) and a theoretical approach based on the Langmuir equation. **Empirical modification**

The DPS, or amount of adsorbed P relative to the adsorption capacity, can be estimated as $P_{ox}(100)/(\alpha(Al_{ox} + Fe_{ox}))$, where $P_{ox}$, $Al_{ox}$, and $Fe_{ox}$ are oxalate extractable elements in mmol kg$^{-1}$ soil and $\alpha$ is 0.5 for non-calcareous sandy soils (van der Zee and van Riemsdijk, 1988; Schoumans and Groenendijk, 2000). Research has shown a non-linear relationship between DPS and leachate P concentrations, where the slope increases as the DPS approaches 100% (Schoumans and Groenendijk, 2000; Maguire and Sims, 2002; Nair et al., 2004). This increase in slope would correspond to decrease in the $k_d$ defined in Equation 3. Therefore, GLEAMS was modified such that $k_d$ became a dynamic variable dependent upon the DPS rather than a static variable determined by the clay content.

The empirical relationship between $k_d$ and DPS was determined from a related column leaching study, where intact soil columns removed from the site used for the current study were leached for 60 weeks either in the absence of P additions or receiving applications of swine waste or poultry litter (Chapter 4). At the end of 60 weeks, the leachate P concentrations ranged from 0.03 to 20 mg P L$^{-1}$. The AEP concentration and DPS of soil from the bottom 10 cm of each column was determined and, with the corresponding leachate P concentration, the $k_d$ was calculated according to Equation 3. Using these data, a relationship between $k_d$ and DPS was determined for use in the modified GLEAMS model (Figure 2). Although $P_{ox}$ is not predicted by GLEAMS,
predictions of total soil P were used to estimate $P_{\text{ox}}$ by means of a regression equation determined from experimental data (Figure 3). The use of the empirically modified P subroutine requires the user to provide two inputs not previously required by GLEAMS 3.0, namely $A_{\text{lox}}$ and $F_{\text{ox}}$ for each soil horizon, which can be determined in a single soil extraction procedure (Schoumans, 2000).

**Figure 2.** Relationship between the P partitioning coefficient ($k_d$) and the degree of P saturation (DPS) for Autryville and Blanton soils.

**Figure 3.** Relationship between oxalate extractable P and total P for Blanton and Autryville soils.
**Langmuir modification**

The change in labile P mass during a leaching event in any layer of soil can be described with the differential equation

\[ \frac{d \text{P}_{labile}}{dt} = -C f/10, \]  

where \( \text{P}_{labile} \) is kg labile P ha\(^{-1} \), \( C \) is solution P concentration (mg L\(^{-1} \)), \( f \) is water flux (cm d\(^{-1} \)), and \( t \) is time in days. The mass balance of \( \text{P}_{labile} \) in any soil layer is

\[ \text{P}_{labile} = C \theta z/10 + Q \rho_b z/10, \]  

where \( \theta \) is the soil water content (cm\(^3\) cm\(^{-3} \)), \( z \) is the layer thickness (cm), \( Q \) is the adsorbed labile P (mg kg\(^{-1} \)), and \( \rho_b \) is the soil bulk density (g cm\(^{-3} \)). Adsorbed labile P (\( Q \)), or reversibly adsorbed P, in equilibrium with solution P concentration \( C \), can be described by the Langmuir equation

\[ Q = Q_{max} \left[ \frac{k_L C}{1+k_L C} \right], \]

where \( Q_{max} \) is the adsorption maximum (mg kg\(^{-1} \)) and \( k_L \) is the Langmuir adsorption constant (van der Zee et al., 1987, Koopmans et al., 2002). Substitution of Equation 7 into Equation 6 yields

\[ \text{P}_{labile} = C \theta z/10 + Q_{max} \left[ \frac{k_L C}{1+k_L C} \right] \rho_b z/10, \]

which can be further rearranged to produce the following quadratic equation:

\[ 0 = k_L \theta C^2 = (Q_{max} k_L \rho_b + \theta - \text{P}_{labile} k_L 10/z) C - \text{P}_{labile} 10/z. \]

Equation 9 can then be solved for \( C \) with the quadratic formula as

\[ C = \frac{-b + (b^2 - 4ac)^{1/2}}{2a} \]

where

\[ a = k_L \theta \]
\[ b = Q_{max} k_L \rho_b + \theta - \text{P}_{labile} k_L 10/z \]
\[ c = -\text{P}_{labile} 10/z. \]

Rewriting Equation 5 as a finite difference approximation yields

\[ -\frac{\text{P}_{labile} - \text{P}_{labile-\Delta t}}{\Delta t} = C f/10, \]  

(11)
which can be solved for the mass of labile P at time $t$ ($P_{\text{labile-}t}$) as

$$P_{\text{labile-}t} = P_{\text{labile-}(t-\Delta t)} - \Delta t \times C \times f / 10.$$  \hspace{1cm} (12)

The theoretical approach to modifying GLEAMS solves Equation 12 for labile P at the end of each day ($t = 1$) by substituting Equation 10 in place of $C$ and substituting $P_{\text{labile-}(t-\Delta t)}$ in place of $P_{\text{labile}}$ in variables $b$ and $c$ of Equation 10. Errors from using the finite difference approximation method and substitution of $P_{\text{labile-}(t-\Delta t)}$ in place of $P_{\text{labile}}$ were found to be negligible when $\Delta t$ was decreased to $1/100$ d, thereby adequately representing Equation 6. The mass of P leached, $P_{\text{leached}}$ (kg ha$^{-1}$) is determined by the difference between $P_{\text{labile}}$ at the start of the day ($t = 0$) and $P_{\text{labile}}$ at the end of the day ($t = 1$). Average daily P concentration in the leachate, $C_{av}$ (mg L$^{-1}$) is then determined as

$$C_{av} = P_{\text{leached}} \times 10 / \text{PERC},$$  \hspace{1cm} (13)

where $\text{PERC}$ is the percolation volume in cm ha$^{-1}$. When $\text{PERC} = 0$, then $C_{av}$ is equal to $C$ determined by Equation 10.

Use of the Langmuir modified P subroutine requires the user to provide estimates of $k_L$ and $Q_{\text{max}}$ for each soil horizon. The maximum adsorption capacity for reversibly adsorbed P ($Q_{\text{max}}$) is proportional to the sum of $\text{Al}_{\text{ox}}$ and $\text{Fe}_{\text{ox}}$

$$Q_{\text{max}} = \beta_m (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})^{31},$$  \hspace{1cm} (14)

where 31 is the atomic weight of P and $\beta_m$ is 0.2 for soils receiving heavy waste applications, or 0.135 for other agricultural soils (van der Zee et al., 1987; van der Zee et al., 1988). Koopmans et al. (2002) showed that the mass balance of labile P can be combined with the Langmuir equation and solved for $k_L$ to yield the following:

$$k_L = (T - vC) / (gQ_{\text{max}}C + vC^2 - TC),$$  \hspace{1cm} (15)

where $T$ is the mass of reversibly sorbed P (mg), $v$ is the volume of water (L), and $g$ is the mass of soil (kg). Reversibly sorbed P is determined as the amount of P desorbed in the presence of an infinite sink, such as AEP or Fe-oxide strip P (van der Zee et al., 1988). For the present study, 0.43(M3-P) was found to provide a good estimate of AEP.
The P concentration in solution \((C)\) in equilibrium with reversibly adsorbed P on mass of soil \((g)\) can be estimated as the P concentration in the \(P_w\) extract (Koopmans et al., 2002). Therefore, \(k_L\) can be determined from AEP, \(P_w\), and \(Q_{max}\), where \(T = AEPg, C = P_w(g/v)\), and \(g\) and \(v\) are respectively the soil mass and volume of extractant used to determine \(P_w\), given units for AEP and \(P_w\) are mg kg\(^{-1}\).

Because GLEAMS v. 3.0 already requires labile P, analogous to AEP, as a user input, use of the Langmuir modification requires the user to determine three additional soil parameters, namely \(A_{ox}\), \(Fe_{ox}\), and \(P_w\), which can be determined in two separate soil extractions (Schoumans, 2000; Self-Davis et al., 2000). Modifications to the GLEAMS source code for the two approaches for determination of leachate P are listed in Appendix D.

The goodness of fit between the measured data and the predicted values was evaluated with Pearson product moment correlation coefficients determined with SAS proc corr (SAS institute, 1998). The division of soil horizons into computational layers used by GLEAMS did not always correspond directly to the depths at which measured data was collected. Therefore, weighted averages of predicted values were computed using GLEAMS predictions for computational soil layers that were within the depth of sample observations.

**Model Inputs**

*Climate data*

Climate parameters were primarily acquired from the North Carolina Department of Agriculture, Horticultural Crops Research Station (HCRS), at Clinton, NC, which was located 16 km from the research site. Mean monthly maximum and minimum temperatures and mean solar radiation from 2000 – 2003 as reported at HCRS were used for all simulations. Inputs for daily mean air temperature and daily precipitation were taken from the HCRS historical record from Jan 1971 to May 2004, filling in occasional periods of missing data from Kinston, NC and Whiteville, NC monitoring stations. Simulations over the course of the monitoring period (September 2002 – May 2004) used precipitation and irrigation records recorded on site, in combination with other
parameters as previously described. Simulations of past P accumulation and future P losses used the HCRS daily precipitation and temperature data from 1971 through 2003 as a representation of long-term weather patterns typical of the research site. Simulations involving applications of swine lagoon effluent included irrigation amounts in the precipitation file.

**Crop rotations**

Three crop rotation files were used for the simulations to represent i) the “field plot” rotation, simulating field plot conditions as close to actual during the monitoring period; ii) the “hay” rotation, simulating typical hay removal from a Coastal Bermudagrass hay field overseeded with a winter annual with of 4 hay harvests per year; and iii) the “grazing” rotation, simulating a grazed Coastal Bermudagrass / winter annual pasture with 11 harvests from February to October varying from 19 to 30 days apart. Crop characteristics for the field site were unavailable; therefore, best estimates were used from the GLEAMS database, published values, and expert opinions (Table 1).

**Table 1.** Select crop characteristics used for GLEAMS inputs for the field plot, hay, and grazing rotations.

<table>
<thead>
<tr>
<th></th>
<th>potential yield† (Mg ha⁻¹⁻)</th>
<th>Maximum LAI‡</th>
<th>% N at maturity††</th>
<th>N:P ratio‡‡</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Autryville</td>
<td>Blanton</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Field plot and Hay rotations</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coastal Bermudagrass</td>
<td>6.3</td>
<td>5.4</td>
<td>4.5</td>
<td>2.4</td>
</tr>
<tr>
<td>winter annual</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>2.4</td>
</tr>
<tr>
<td>Grazing rotation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coastal Bermudagrass</td>
<td>4.4</td>
<td>3.8</td>
<td>3</td>
<td>2.4</td>
</tr>
<tr>
<td>winter annual</td>
<td>2.8</td>
<td>2.8</td>
<td>2.2</td>
<td>2.4</td>
</tr>
</tbody>
</table>

† Based on realistic yield expectations for the given soil series in North Carolina
‡ Burns, J., Professor of Crop Science at NCSU, personal communication
†† Zublena, 1991
‡‡ Pierzynski and Logan, 1993

**Waste application data**

Waste application dates and nutrient concentrations from on farm records during the monitoring period were used in the GLEAMS input file, with corresponding applications rates as determined by an automated rain gauge. During the 20 month
monitoring period 411 kg available N ha\(^{-1}\) (using a 50% availability coefficient) and 102 kg P ha\(^{-1}\) were applied to the site in the form of irrigated swine waste. Average swine waste N and P concentrations from 2 years of farm records were used to estimate swine waste nutrient concentrations for simulations of past P accumulation and future P losses (Table 2). Swine waste applications for the P accumulation period were equal to 240 kg available N ha\(^{-1}\) yr\(^{-1}\), or 100% of the crop N requirement as determined by realistic yield expectations for a hay crop, ignoring the reduction in yield from grazing and the N contribution from the grazing cattle. This method of swine waste application is considered a conservative estimate of pre-regulation waste applications. For simulations predicting future P losses, N-based swine applications applied 100% of crop N requirement from swine waste to hay crops and a 25% reduction in waste application to grazed pastures, practices typical of current waste management. Simulations of P-based waste applications applied swine lagoon effluent based on estimated annual P removal of the growing crop, as outlined in the NRCS Nutrient Management Conservation standard, code 590 (NRCS, 1999).

Simulations involving grazing required estimates of the number of cattle grazing, the amount of waste produced, and nutrient concentrations in the waste. The number of cattle grazing the pasture was estimated based on the expected yield, where cattle required daily dry matter intake equal to 2.5% of their body weight (Burns, J., personal communication). It was estimated that cattle produced 0.061 kg waste kg\(^{-1}\) animal mass d\(^{-1}\), with average nutrient concentrations as listed in Table 2 (Barker et al., 1994). Waste applications from the cattle were distributed over the 10 month grazing period according to estimated annual patterns of crop growth and yield.

<table>
<thead>
<tr>
<th>application</th>
<th>rate yr(^{-1})</th>
<th>Total N</th>
<th>Organic N</th>
<th>NH(_4)-N</th>
<th>Total P</th>
<th>Organic P</th>
<th>Organic Matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>cattle manure†</td>
<td>19.4 Mg ha(^{-1})</td>
<td>0.67</td>
<td>0.40</td>
<td>0.19</td>
<td>0.10</td>
<td>0.053</td>
<td>10.3</td>
</tr>
<tr>
<td>swine lagoon liquid</td>
<td>9.1 cm (^{*})</td>
<td>0.059</td>
<td>0.011</td>
<td>0.048</td>
<td>0.071</td>
<td>0.0015</td>
<td>0.14</td>
</tr>
</tbody>
</table>

† from by Barker et al. (1994) and Barnett (1994).
* 6.9 cm for simulations of future P losses with grazing,
Soils data

The soil parameter inputs were generally obtained by direct measurement or, when direct measurement was labor intensive, parameters were estimated using related soil parameters directly measured on the site and correlations developed from limited sample sizes (Table 3). Field capacity was determined as the soil water content 24 hours after large precipitation events. Field capacity and wilting point were adjusted slightly through minimal calibration. Field capacity and wilting point were within the range suggested by GLEAMS for the given soil textural classes. Other parameters were determined as noted in Table 3.
Table 3. Soil properties used as inputs for GLEAMS simulations of P leaching in Autryville and Blanton soils.

<table>
<thead>
<tr>
<th>depth to bottom of horizon (cm)</th>
<th>silt</th>
<th>clay</th>
<th>OM†</th>
<th>Total N‡</th>
<th>Total P</th>
<th>labile P††</th>
<th>Qmax</th>
<th>Alox</th>
<th>Feox</th>
<th>kL</th>
<th>PSP‡‡</th>
<th>field capacity</th>
<th>wilting point</th>
<th>Poro-osity†††</th>
<th>Ksat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autryville</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>7.9</td>
<td>2.2</td>
<td>1.95</td>
<td>917</td>
<td>537</td>
<td>139</td>
<td>159</td>
<td>19.6</td>
<td>6.0</td>
<td>0.9</td>
<td>0.73</td>
<td>0.21</td>
<td>0.10</td>
<td>0.42</td>
<td>35</td>
</tr>
<tr>
<td>55</td>
<td>9.9</td>
<td>2.8</td>
<td>0.27</td>
<td>131</td>
<td>351</td>
<td>94</td>
<td>95</td>
<td>13.2</td>
<td>2.2</td>
<td>1.3</td>
<td>0.66</td>
<td>0.18</td>
<td>0.10</td>
<td>0.37</td>
<td>6.6</td>
</tr>
<tr>
<td>80</td>
<td>10.7</td>
<td>10.4</td>
<td>0.33</td>
<td>160</td>
<td>667</td>
<td>144</td>
<td>171</td>
<td>24.4</td>
<td>3.1</td>
<td>0.9</td>
<td>0.58</td>
<td>0.24</td>
<td>0.15</td>
<td>0.39</td>
<td>5.6</td>
</tr>
<tr>
<td>130</td>
<td>8.7</td>
<td>6.8</td>
<td>0.15</td>
<td>71</td>
<td>157</td>
<td>10</td>
<td>66</td>
<td>8.6</td>
<td>2.0</td>
<td>1.8</td>
<td>0.26</td>
<td>0.13</td>
<td>0.06</td>
<td>0.42</td>
<td>12</td>
</tr>
<tr>
<td>140</td>
<td>12.9</td>
<td>8.7</td>
<td>0.13</td>
<td>63</td>
<td>130</td>
<td>2</td>
<td>73</td>
<td>9.6</td>
<td>2.3</td>
<td>1.1</td>
<td>0.09</td>
<td>0.20</td>
<td>0.06</td>
<td>0.37</td>
<td>1.6</td>
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<tr>
<td>Blanton</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>15</td>
<td>2.8</td>
<td>1.2</td>
<td>1.64</td>
<td>867</td>
<td>311</td>
<td>64</td>
<td>86</td>
<td>9.9</td>
<td>3.9</td>
<td>0.5</td>
<td>0.76</td>
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<td>0.41</td>
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<tr>
<td>30</td>
<td>3.3</td>
<td>1.2</td>
<td>0.53</td>
<td>261</td>
<td>256</td>
<td>67</td>
<td>74</td>
<td>9.6</td>
<td>2.4</td>
<td>1.6</td>
<td>0.69</td>
<td>0.15</td>
<td>0.06</td>
<td>0.37</td>
<td>23</td>
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<tr>
<td>90</td>
<td>3.4</td>
<td>1.4</td>
<td>0.15</td>
<td>74</td>
<td>179</td>
<td>47</td>
<td>49</td>
<td>6.6</td>
<td>1.3</td>
<td>1.7</td>
<td>0.66</td>
<td>0.13</td>
<td>0.06</td>
<td>0.39</td>
<td>20</td>
</tr>
<tr>
<td>125</td>
<td>2.6</td>
<td>1.4</td>
<td>0.11</td>
<td>53</td>
<td>139</td>
<td>33</td>
<td>46</td>
<td>5.8</td>
<td>1.6</td>
<td>2.4</td>
<td>0.62</td>
<td>0.12</td>
<td>0.06</td>
<td>0.40</td>
<td>37</td>
</tr>
<tr>
<td>135</td>
<td>3.5</td>
<td>3.8</td>
<td>0.16</td>
<td>76</td>
<td>94</td>
<td>3</td>
<td>60</td>
<td>6.2</td>
<td>3.5</td>
<td>1.4</td>
<td>0.16</td>
<td>0.18</td>
<td>0.06</td>
<td>0.35</td>
<td>10</td>
</tr>
</tbody>
</table>

† Organic matter, estimated as 1.724(organic carbon), where organic carbon was determined by combustion (Knisel and Davis, 2000)
‡ determined by combustion
†† estimated as 0.43(M3-P) (Appendix C)
‡‡ P sorption coefficient calculated as given in text
††† Porosity estimated as 1 – (ρb/2.65)

---

The table above lists soil properties used as inputs for GLEAMS simulations of P leaching in Autryville and Blanton soils. The properties include depth to the bottom of the horizon, silt, clay, OM (organic matter), Total N, Total P, labile P, Qmax, Alox, Feox, kL, PSP, field capacity, wilting point, porosity, and Ksat. The values are provided for different depths in centimeters, with the properties measured in specific units as indicated.
Percolate P concentrations calculated by the preceding equations are dependent on the size of the labile P pool, and therefore dependent on PSP. Although GLEAMS determines PSP from clay content (Equation 2), an improved estimate of PSP can be made by back calculating PSP given reliable estimates of labile P, organic P, and total P are available. From, the P mass balance we have

\[ P_{\text{total}} = P_{\text{organic}} + P_{\text{stable}} + P_{\text{active}} + P_{\text{labile}} \]  

(16)

Given the stable P pool is 4 times the size of the active P pool, Equations 1 and 5 can be combined to yield

\[ P_{\text{total}} - P_{\text{organic}} = 4P_{\text{labile}}((1 - PSP)/PSP) + P_{\text{labile}}((1 - PSP)/PSP) + P_{\text{labile}} \]  

(17)

Equation 6 can then be solved for PSP as follows:

\[ PSP = 1/(((P_{\text{total}} - P_{\text{organic}})/(5P_{\text{labile}})) + 4/5) \]  

(18)

Although organic P can be difficult to determine, it can be estimated using relationships between organic P and total N given by Sharpley et al. (1984), which are also used for initialization of P pools in GLEAMS (Knisel and Davis, 2000). The PSPs calculated by Equation 18 for the given site are included in Table 3.

Results and Discussion

Hydrology correlation

GLEAMS offers the option of using either the Penman-Monteith or Priestly-Taylor methods for calculation of daily potential evapotranspiration. The option for using the Penman-Monteith method to calculate potential evapotranspiration (PET) was selected because results were in better agreement with independent calculations of PET and actual evapotranspiration (AET) for this site as described in Chapter 2. Furthermore, the Penman-Monteith method resulted in lower error sums of squares for soil water content predictions than the Priestly-Taylor method. Although the estimates of PET and AET calculated by Penman-Monteith method were less than the Priestly-Taylor method, they were greater than calculations with the FAO-56 Penman-Monteith combination method (Figure 4, Allen et al., 1998).
As previously mentioned inputs for field capacity and wilting point were adjusted through minimal model calibration (maximum of 2 iterations) to improve the visual comparison of the predicted soil water content to the measured soil water content. Although the correlation coefficients were low, the predicted soil water content tended to follow the same general trend as observed data for the upper soil horizons (Figure 5, Table 4). Predicted soil water content in the lower horizons was unresponsive to climate and cropping conditions, generally remaining at field capacity, and showed poor correlation with observed data. Predictions of percolation rates during sampling intervals (41 intervals of 5 to 20 days each) for upper soil horizons were well correlated with independent estimations of percolation rates employing a water balance approach in conjunction with measured field data as described in Chapter 2 (Figure 6, Table 4). The summer of 2003 was unusually wet which caused a perched water table within the root
zone. The presence of the water table within the root zone could have produced errors in percolation rates predicted by GLEAMS as well as estimates computed with field data for the lower soil horizons, thus contributing to the poor correlations for these depths. However, GLEAMS predictions of overall percolation volumes during the monitoring period were reasonably close to the estimates using field data (Table 5).

Figure 5. Comparison of measured and predicted daily soil water content in the Autryville soil at 10 cm (a) and 45 cm (b).
Table 4. Pearson moment correlation coefficients ($r$) and associated p-values ($p$) for correlations between predicted and measured soil water content and percolations rates either predicted by GLEAMS or calculated with field data.

<table>
<thead>
<tr>
<th>bottom depth (cm)</th>
<th>soil water content</th>
<th>percolation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Autryville</td>
<td>Blanton</td>
</tr>
<tr>
<td></td>
<td>$r$</td>
<td>$p$</td>
</tr>
<tr>
<td>20</td>
<td>0.65</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>57</td>
<td>0.56</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>80</td>
<td>0.35</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>100</td>
<td>0.24</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>125</td>
<td>0.01</td>
<td>0.883</td>
</tr>
<tr>
<td>140</td>
<td>0.00</td>
<td>0.922</td>
</tr>
</tbody>
</table>

Figure 6. Comparison of percolation (Perc.) rates predicted by GLEAMS with estimates using a water balance method and field data at 20 (a, b), 80 (c, d) and 140 (e, f) cm in the Autryville soil.
Table 5. Total percolation from September 2002 through April 2004 for Autryville and Blanton soils as predicted by GLEAMS and estimated by a water balance method using field data.

<table>
<thead>
<tr>
<th>bottom depth of horizon (cm)</th>
<th>Autryville</th>
<th>Blanton</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GLEAMS</td>
<td>water balance</td>
</tr>
<tr>
<td>20</td>
<td>127</td>
<td>135</td>
</tr>
<tr>
<td>57</td>
<td>94</td>
<td>100</td>
</tr>
<tr>
<td>80</td>
<td>86</td>
<td>95</td>
</tr>
<tr>
<td>100</td>
<td>86</td>
<td>92</td>
</tr>
<tr>
<td>125</td>
<td>86</td>
<td>91</td>
</tr>
<tr>
<td>140</td>
<td>86</td>
<td>91</td>
</tr>
</tbody>
</table>

Evaluation of modified phosphorus subroutines

Percolate P concentrations were predicted with the unmodified GLEAMS model, the empirically modified P subroutine, and the Langmuir modified subroutine. Because the method used to collect field leachate continuously collected soil water solution throughout the sampling intervals, flow-weighted average predicted P concentrations were used for comparisons with observed P concentrations. Percolate P concentrations predicted by the unmodified model were much less than observed values in the Autryville 45-cm (A-45), Blanton 45-cm (B-45), and Blanton 90-cm (B-90) soil horizons, where observed percolate P concentrations exceeded 15 mg L\textsuperscript{-1} (Figures 7 and 8). However, percolate P concentrations predicted by the unmodified model were close to observed values in the Autryville 90-cm (A-90), Autryville 135-cm (A-135), and Blanton 135-cm (B-135) soil horizons, where observed percolate P concentrations were between 0.01 and 0.2 mg L\textsuperscript{-1}. The empirical and Langmuir modifications resulted in higher predicted percolate P concentrations than the unmodified model, which were generally within range of the observed values with the exception of predictions for the A-90 horizon. The predicted P concentrations in the A-90 horizon from the empirically modified model ranged from 1.5 to greater than 8 mg L\textsuperscript{-1}, which were much greater than observed values. The Langmuir modification also over predicted percolate P concentrations for the A-90 horizon, however, the predicted values were only slightly greater than observed (Figure 7b). The predicted P concentrations from the modified
models showed greater variability over time than did the unmodified model, but they still failed to capture the variability of the observed data, resulting in poor colorations between predicted and observed values for individual observations (Figures 7 and 8).

Figure 7. Comparison of predicted and observed percolate P concentrations at 45 (a), 90 (b), and 135 (c) cm in an Autryville soil. Empirical model predictions for A-90 were not included in the figure because they far exceeded observed data (see text for explanation).
Figure 8. Comparison of predicted and observed percolate P concentrations at 45 (a), 90 (b), and 135 (c) cm in a Blanton soil.

Correlations between predicted and observed percolate P concentrations were much better when data were averaged over the study period. Although the average percolate P concentrations predicted by the unmodified model were highly correlated with average observed concentrations (Table 6), the predicted values were far from the
1:1 line (Figure 9). The magnitude of the average percolate P concentrations predicted by the Langmuir modification were very close the observed concentrations, as indicated by the lack of significant difference between means (Table 6). The Langmuir modification also resulted in the highest correlation between average predicted percolate P concentrations and average observed concentrations. Results of comparisons between mass P losses over the course of the study period were very similar to those described for P concentrations.

Table 6. Average percolate P concentrations for observed data and model predictions with corresponding Pearson moment correlation coefficients ($r$).

<table>
<thead>
<tr>
<th>depth (cm)</th>
<th>Observed</th>
<th>for observed</th>
<th>Unmodified</th>
<th>Empirical</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autryville</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>10.0</td>
<td>2.0</td>
<td>1.0 (&lt;0.01)‡</td>
<td>16.5 (&lt;0.01)</td>
<td>10.0 (0.94)</td>
</tr>
<tr>
<td>90</td>
<td>0.05</td>
<td>0.04</td>
<td>0.09 (0.03)</td>
<td>4.1 (&lt;0.01)</td>
<td>0.18 (&lt;0.01)</td>
</tr>
<tr>
<td>135</td>
<td>0.02</td>
<td>0.004</td>
<td>0.02 (0.07)</td>
<td>0.03 (0.07)</td>
<td>0.03 (0.01)</td>
</tr>
<tr>
<td>Blanton</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>8.4</td>
<td>3.5</td>
<td>0.45 (&lt;0.01)</td>
<td>4.6 (0.04)</td>
<td>5.7 (0.09)</td>
</tr>
<tr>
<td>90</td>
<td>6.4</td>
<td>2.5</td>
<td>0.46 (&lt;0.01)</td>
<td>3.4 (0.03)</td>
<td>7.6 (0.22)</td>
</tr>
<tr>
<td>135</td>
<td>0.02</td>
<td>0.002</td>
<td>0.03 (0.02)</td>
<td>0.03 (&lt;0.01)</td>
<td>0.04 (&lt;0.01)</td>
</tr>
</tbody>
</table>

$r$ [0.937 0.756 0.960] 95% confidence interval for the mean of the observed concentrations. ‡ probability of the population of data from which observed concentrations were taken having a population mean equal to the predicted concentrations (as determined by a two-tailed $t$-test).

Figure 9. Predicted vs. observed average percolate P concentrations.
Phosphorus accumulation in the soil profile was predicted by estimating pre-waste application soil P concentrations based on background P concentrations for similar soils as reported by Novak et al. (2000) (Table 7). Because the initial soil P concentrations were approximated, as were the waste applications, the model was run until the soil profile P mass in the simulations was near the current soil profile P mass of 7900 and 4150 kg P ha\(^{-1}\) for the Autryville and Blanton soils respectively. This required 80 and 31 years of simulations for approximate accumulations of 4400 and 1850 kg P ha\(^{-1}\) for the Autryville and Blanton soil respectively, although the swine farm was only in existence for 20 years prior to sampling. Simulations required more than 20 years to accumulate soil P mass equivalent to the present conditions because actual waste applications possibly exceeded the estimated rates prior to implementation of regulations and initial soil P concentrations were estimated based on soils without prior history of crop production.

<table>
<thead>
<tr>
<th></th>
<th>Autryville</th>
<th></th>
<th>Blanton</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizon</td>
<td>total P</td>
<td>labile P</td>
<td>Horizon</td>
<td>total P</td>
</tr>
<tr>
<td>bottom cm</td>
<td>mg kg(^{-1})</td>
<td></td>
<td>cm</td>
<td>mg kg(^{-1})</td>
</tr>
<tr>
<td>18</td>
<td>200</td>
<td>3.2</td>
<td>15</td>
<td>180</td>
</tr>
<tr>
<td>55</td>
<td>120</td>
<td>1.6</td>
<td>30</td>
<td>130</td>
</tr>
<tr>
<td>80</td>
<td>240</td>
<td>0.4</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>130</td>
<td>130</td>
<td>0.4</td>
<td>125</td>
<td>90</td>
</tr>
<tr>
<td>140</td>
<td>130</td>
<td>0.4</td>
<td>135</td>
<td>90</td>
</tr>
</tbody>
</table>

The unmodified version of GLEAMS over-predicted P accumulation in the soil surface and predicted little to no change in P accumulation below 40 cm for either soil type, similar to results described by Stone et al. (2001) (Figures 10 and 11). Both the empirical and Langmuir modifications greatly improved comparison of the predicted and observed soil P concentrations. The empirically modified model failed to accurately predict the P accumulation between 60 and 80 cm in the Autryville soil, and therefore over predicted P leaching in the lower soil depths (Figure 10).
Figure 10. Predicted P accumulation with unmodified (a, b), empirically modified (c, d), and Langmuir modified (e, f) GLEAMS models in the Autryville soil after 1, 20, 50, and 80 years of P applications under grazing.
Figure 11. Predicted P accumulation with unmodified (a, b), empirically modified (c, d), and Langmuir modified (e, f) GLEAMS models in the Blanton soil after 1, 10, 20, and 31 years of P applications under grazing.
The Langmuir modified model did a better job of predicting the P accumulation between 55 and 60 cm in the Autryville soil than did the empirical model, and predicted continued P accumulation at that depth up to 90 years of simulation with very little P movement below 90 cm, where as the empirical model did not predict continued P accumulation in the Autryville Bt beyond 80 years of waste application (data not shown).

In the Blanton soil, the empirically modified model only predicted P movement to 95 cm, whereas P accumulations were observed as deep as 115 cm (Figure 11). Although the Langmuir model predicted P movement to 105 cm, it still under-predicted P concentrations between 80 and 120 cm. This under-prediction is potentially because of over-predictions of organic P concentrations in the surface, which do not contribute to P leaching. This is indicated by the accurate predictions of labile P concentrations in the surface but yet over predictions of total P at these same depths (Figure 11 e and f).

Predicted soil P concentrations from the Langmuir modification had the best correlation with observed values (Table 8). The over prediction of soil P concentrations at lower depths in the Autryville soil and under predictions of soil P concentrations at lower depths in the Blanton soil by the empirical modification corresponds to the tendancy for it to over predict solution P concentrations in the Autryville soil and under predict solution P concentrations in the Blanton soil (Table 6).

Table 8. Pearson moment correlation coefficients for predicted soil P accumulation vs. observed.

<table>
<thead>
<tr>
<th>P subroutine</th>
<th>Total P</th>
<th>Labile P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Autryville</td>
</tr>
<tr>
<td>unmodified</td>
<td>0.33</td>
<td>0.66</td>
</tr>
<tr>
<td>empirical</td>
<td>0.94</td>
<td>0.90</td>
</tr>
<tr>
<td>Langmuir</td>
<td>0.96</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Autryville</td>
</tr>
<tr>
<td></td>
<td>0.41</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>0.94</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>0.97</td>
<td>0.97</td>
</tr>
</tbody>
</table>
Predictions of future P losses

Because the Langmuir modification provided a better correlation with measured data for both soil solution P concentration and soil P accumulation, it was used to predict future P losses under different P management practices. Management practices chosen for evaluation were as follows:

i) Swine waste applied to grazed pasture at a rate of 200 kg available N ha$^{-1}$ yr$^{-1}$ and 50 kg P ha$^{-1}$ yr$^{-1}$.

ii) Swine waste applied to bermudagrass hay overseeded with a winter annual at a rate of 270 kg available N ha$^{-1}$ yr$^{-1}$ and 65 kg P ha$^{-1}$ yr$^{-1}$.

iii) Swine waste applied to bermudagrass hay overseeded with a winter annual at a rate equal to the P removal by the harvested crop (P-based waste application), 270 kg available N ha$^{-1}$ yr$^{-1}$ and 36 kg P ha$^{-1}$ yr$^{-1}$.

iv) No P additions to bermudagrass hay overseeded with a winter annual. Nitrogen additions continued at 270 kg available N ha$^{-1}$ yr$^{-1}$.

For scenarios iii and iv swine waste applications continued at the normal rate but with a reduced P concentration, assuming that the producer would utilize waste treatment technologies to remove P from the lagoon effluent.

As previously mentioned, phosphorus sorption coefficients ($PSP$) were back calculated from available soils data. The back-calculated $PSP$s showed a strong correlation with DPS, increasing to an average of 0.65 when DPS was greater than 90% (Appendix C). The low $PSP$s in the lower horizons resulted in higher P accumulations than would be expected based on the $Al_{ox}$ and $Fe_{ox}$ concentrations. For example, van der Zee and van Riemsdijk (1988) found that the P sorption capacity ($PSC$) of sandy non-calcareous soils could be approximated by $PSC = 0.5(Al_{ox}+Fe_{ox})$, where $PSC$, $Al_{ox}$, and $Fe_{ox}$ are in mmol kg$^{-1}$ soil. Comparison between the $PSC$ of the Autryville soil profile with the predicted P accumulation after continued waste application, shows an increase in soil P concentration at 85 cm although the $PSC$ decreases with depth (Figure 12). This increase is a result of the decrease in the back-calculated $PSP$ (Table 3). To correct this error, $PSP$ was set to a minimum of 0.62, the $PSP$ predicted at 90% P saturation, which improved the predicted P accumulation with respect to $PSC$ (Figure 12). Because
this could over-predict P desorption, GLEAMS simulations comparing the management practices were made both with PSP as listed in Table 3 and with the minimum PSP set to 0.62. However, it is likely that the latter method would better predict P concentrations in the presence of excessive P loading that would tend to increase the DPS.

![Figure 12. Phosphorus accumulation in the Autryville soil after 50 additional years of waste application to grazed pasture as predicted with back calculated PSP and with a minimum PSP of 0.62 in comparison with the PSC based on Al\textsubscript{ox} and Fe\textsubscript{ox}.](image)

Predicted average annual percolate P concentrations at 45 and 90 cm remained between 4 and 8 mg L\textsuperscript{-1} for the grazing scenario (Figure 13), similar to currently observed concentrations in the Blanton soil and slightly less than observed values at 45 cm in the Autryville soil. Simulations restricting PSP to ≥ 0.62 showed P concentrations at 135 cm gradually increasing in both soils, reaching concentrations near that predicted for 45 and 90 cm after 25 years in the Blanton soil and 35 years in the Autryville soil. There was a large difference in predicted P concentrations depending on the choice of PSP, where predicted percolate P concentrations using the back calculated PSP remained near 0 at 135 cm for both soils. However, setting PSP ≥ 0.62 represents the potential P loss given the limited P sorption capacity of these soils.
Figure 13. Predicted future percolate P concentrations in Autryville (a) and Blanton (b) soils under continued waste application on grazed pasture. Open symbols are predictions with minimum PSP of 0.62.

Changing to a hay removal cropping system resulted in decreased predicted percolate P concentrations at all depths, but still predicted potential increases over time in percolate P concentrations at 135 cm in both soils, with average annual concentrations above 2 mg L\(^{-1}\) after 50 years of waste application (Figure 14). The predicted average annual percolate P concentration at 135 cm in the Blanton soil after 50 years of waste application was greater than in the Autryville soil, reflecting differences in P sorption capacity between the two soils.
Figure 14. Predicted future percolate P concentrations in Autryville (a) and Blanton (b) soils under continued waste application on Bermudagrass harvested for hay. Open symbols are predictions with minimum PSP of 0.62.

Changing to P based waste applications further reduced predicted percolate P concentrations at all depths (Figure 15). Although P additions were not in excess of crop removal, percolate P concentrations at 135 cm increased throughout the simulation as a result of P desorption from overlying soil horizons. Eliminating P additions resulted in predicted P concentrations decreasing to near zero at 45 cm after 30 years in the Blanton soil and after 50 years in the Autryville soil (Figure 16). However, there was little difference between the predicted percolate P concentrations at 135 cm for simulations with P-based waste application compared to simulations without P additions.
Figure 15. Predicted future percolate P concentrations in Autryville (a) and Blanton (b) soils under continued waste application equal to crop P removal on Bermudagrass harvested for hay. Open symbols are predictions with minimum PSP of 0.62.

Figure 16. Predicted future percolate P concentrations in Autryville (a) and Blanton (b) soils without any P applications on Bermudagrass harvested for hay. Open symbols are predictions with minimum PSP of 0.62.
Corresponding to the highest predicted percolate P concentrations, the grazed pasture simulation had the highest predicted average annual P leaching loss for the last 10 years of the 50-year simulations (Table 9). Predicted annual P leaching losses were more variable than the percolate P concentrations because of the variability in annual percolate volume, which ranged from 86 to 18 cm for the 34 years of climate data used for the simulations. At 135 cm, maximum predicted annual P leaching losses of 28 and 43 kg ha\(^{-1}\) occurred in the grazed pasture simulations for Autryville and Blanton soils respectively \((PSP \geq 0.62)\).

Table 9. Predicted average annual P leaching losses at 135 cm in Autryville and Blanton soils for the last 10 years of 50-year simulations of four different crop and waste management systems using the Langmuir modified version of GLEAMS.

<table>
<thead>
<tr>
<th>crop rotation</th>
<th>waste management</th>
<th>Autryville</th>
<th>Blanton</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>back calculated</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PSP</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$PSP \geq 0.62$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>grazed pasture</td>
<td>N-based</td>
<td>0.1</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.6</td>
<td>24.4</td>
</tr>
<tr>
<td>Bermudagrass hay</td>
<td>N-based</td>
<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.4</td>
<td>12.7</td>
</tr>
<tr>
<td>Bermudagrass hay</td>
<td>P-based</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Bermudagrass hay</td>
<td>no P applied</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

As would be expected, the maximum and average annual P leaching losses and the percolate P concentrations decreased as the quantity of excess P applied to the soil decreased. Regardless of soil type, the grazed pasture simulation resulted in the highest predicted P losses and the Bermudagrass hay without P additions resulted in the lowest P losses. However, there appeared to be a soil × management practice interaction, where P losses in the Blanton soil ranged from 230 to 539 kg ha\(^{-1}\) and P losses from the Blanton soil ranged from 117 to 839 kg ha\(^{-1}\) over the course of the simulation time \((PSP \geq 0.62)\). Simulations with P additions in excess of crop P removal, the predicted P losses at 135 cm from the Blanton soil exceeded that from the Autryville soil (Table 10). This corresponds to the lower P sorption capacity of the Blanton soil as indicated by lower
Al_{ox}, Fe_{ox}, and resultant lower $Q_{max}$. Conversely, when simulated P additions were less than or equal to crop P removal, predicted P loss at 135 cm was greater in the Autryville soil than in the Blanton soil ($PSP \geq 0.62$). This indicates that the higher P sorption capacity of the Autryville may buffer the soil solution P concentration against changes induced through P management strategies.

**Table 10.** Predicted total P loss at 135 cm in Autryville and Blanton soils for 50-year simulations of four different crop and waste management systems using the Langmuir modified version of GLEAMS.

<table>
<thead>
<tr>
<th>Crop Rotation</th>
<th>Waste Management</th>
<th>Autryville</th>
<th>Blanton</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>back calculated</td>
<td>$PSP$</td>
<td>$PSP \geq 0.62$</td>
</tr>
<tr>
<td></td>
<td>$kg \cdot ha^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graded pasture</td>
<td>N-based</td>
<td>7.1</td>
<td>67.0</td>
</tr>
<tr>
<td>Bermudagrass hay</td>
<td>N-based</td>
<td>6.4</td>
<td>34.0</td>
</tr>
<tr>
<td>Bermudagrass hay</td>
<td>P-based</td>
<td>6.4</td>
<td>18.6</td>
</tr>
<tr>
<td>Bermudagrass hay</td>
<td>no P applied</td>
<td>6.4</td>
<td>15.9</td>
</tr>
</tbody>
</table>

These results may have implications beyond simply demonstrating that decreased P additions reduce P leaching losses. For example, it may be argued that soils with higher P sorption capacity can receive greater P additions without risks of P leaching. As illustrated by the observed field data, although the Autryville soil had higher soil P concentrations in the surface, P concentrations at 90 cm were less than in the Blanton soil. However, in longer term simulations, the Autryville has the potential to lose more P than the Blanton soil in absence of P additions because the accumulated P provides a large buffer against changes in solution P concentration. Further improvements in the GLEAMS P subroutines, such as better characterization of soil P pools and associated fluxes (i.e. improved determination of $PSP$), would help evaluate these issues.
Conclusions

Modifying GLEAMS with the Langmuir equation to partition labile P between adsorbed and solution phases greatly improved predictions of percolate P concentrations. As a result, GLEAMS predictions of soil P accumulation were also improved. Although the Langmuir modification greatly improved correlations between predicted and observed average percolate P concentrations, it failed to adequately predict the variation in P concentrations for time periods less than a year. An alternate method of modifying GLEAMS with an empirical relationship between the phosphorus partitioning coefficient \( k_d \) and the DPS also improved comparisons of predicted and observed percolate P concentrations and soil P distribution, but did not provide the same level of correlation with observed data as did the Langmuir equation. The Langmuir modification requires the user to provide estimates of \( Q_{\text{max}} \) and \( k_L \) for each soil horizon, which can be ascertained through determination of ammonium oxalate extractable Al and Fe and water extractable P, in conjunction with the estimate of labile P concentration which was a previously required input.

The Langmuir modified model was sensitive to simulated changes in crop and P management, an attribute which was notably lacking from the unmodified version of GLEAMS (Stone et al., 2001). Predicted P leaching losses decreased with decreasing P applications for Autryville and Blanton soils that had previously received waste applications. However, decreasing P applications below crop removal did not result in large decreases in the predicted P leaching losses compared to P-based waste application (< 1 kg P ha\(^{-1}\) yr\(^{-1}\)). Soil properties, including soil P concentration and maximum labile P adsorption capacity \( (Q_{\text{max}}) \), affected the predicted P leaching losses.

The Langmuir modified version of GLEAMS was sensitive to the phosphorus sorption coefficient \( (PSP) \), which determines the relative size of the labile P pool. Additional research is needed to identify an appropriate method of determining \( PSP \) with respect to soil P concentrations and other soil properties. Potential methods of modifying the determination of \( PSP \) may be based on the DPS.
References


– CHAPTER IV –

Waste and Alum Effects on Phosphorus Leaching in Acid Sandy Coastal Plain Soils

Introduction

Long-term P applications in excess of crop requirements have been shown to increase the degree of P saturation (DPS) in sandy soils and result in substantial P leaching within the root zone (Chapter 2; Novak et al., 2000). Correspondingly, there is rising concern that continued P application to soils with low P sorption capacity may result in P loading to shallow groundwater and potential transport to streams through lateral flow or artificial drainage systems (Chapter 3; Sims et al., 1998). Because P loading into surface waters can induce cultural eutrophication (Correll, 1998) and P leaching from waste amended soils can potential provide long-term P loading to surface waters (Breeuwsma and Silva, 1992), P leaching losses have been considered in P loss assessment tools developed in response to the revised NRCS nutrient management policy (Mallarino et al., 2002; Osmond et al., 2003; NRCS, 1999). To protect against environmental degradation, these P loss assessment tools limit P applications when there is a high risk of P losses. However, this can decrease the economic productivity of animal producers who rely on land application methods for waste treatment and disposal.

The investigation of cropping system and waste application effects on P leaching losses are valuable in developing guidelines for best management practices (BMPs) that might reduce P losses, thereby protecting both the environment and economic productivity of animal producers. Research studies have shown that P source and application rates influence P leaching losses (Leinweber et al., 1999; Brye et al., 2002; Heckrath et al., 1995; Godlinski et al., 2004). Leinweber et al. (1999) found that fertilized grasslands lost more P through leaching than arable crop land due to higher drainage and P concentrations. Although soils without P additions had the lowest P losses, treatments with the highest P application rates did not have the highest P leaching losses. Other research indicates that P leaching losses were related to the ratio between P
applications and crop P removal, where larger ratios indicate larger P leaching losses (Godlinski et al., 2004). Heckrath et al. (1995) also found the lowest P leaching losses in treatments without P fertilizer application. However, P leaching for treatments receiving P applications depended on P source, where mineral P applications resulted in greater P leaching than farmyard manure applied at equivalent P rates. Although manipulation of P applications can affect P leaching losses, this does not provide animal producers with much flexibility when disposing of animal waste.

Chemical amendment of animal wastes can reduce P solubility, thereby limiting its mobility in the environment (Codling et al., 2000; Dao, 1999; Moore and Miller, 1994). Moore and Miller (1994) found that addition of Al, Ca, and Fe containing compounds to poultry litter decreased soluble P by 88, 99, and 99% respectively. Although Ca and Fe chemicals provided for a greater decrease in P solubility, addition of Al in the form of alum (Al₂(SO₄)₃•14H₂O) provided an added benefit of reduced ammonia volatilization (Moore et al., 1995). Alum additions to poultry litter reduce the P solubility by forming amorphous Al-hydroxide compounds, which have a high P sorption capacity (Peak et al., 2002; Hunger et al., 2004). Because of the reduced P solubility in alum-treated waste, runoff water from fields receiving alum-treated waste has dramatically lower dissolved P concentrations than that from fields receiving conventionally treated waste (Shreve et al., 2000; Moore et al., 2000; Smith et al., 2001).

Direct soil application of Al or Fe can also reduce P mobility and availability. Application of Al and Fe containing chemicals, such as drinking water treatment residuals, to waste amended soils has been shown to reduce P loss in runoff water compared to soils not receiving Al and Fe additions (Haustein et al., 2000; Gallimore et al., 1999; Dayton et al., 2003). Furthermore, addition of drinking water treatment residual to high P soils can decrease P desorption to water, as shown by decreases in water soluble P concentrations ranging from 80 to 99% (Codling et al., 2000; Hyde and Morris, 2000; Peters and Basta, 1996). Similarly, addition of Al-containing residuals can increase the soil’s P sorption capacity (Novak and Watts, 2004), which agrees with research showing that P sorption capacity is correlated to Al concentration (van der Zee...
and van Riemsdijk, 1988). These studies support the hypothesis that Al addition to waste or soil may be effective in reducing P leaching.

Limited research has been conducted to determine the effectiveness of chemical amendments for controlling P leaching losses. Summers et al. (1996) found that the addition of bauxite residue (10-20 Mg ha\(^{-1}\)) reduced P leaching by 60% in 10-cm deep soil columns leached for a 90-d period. Elliott et al. (2002) found that drinking water treatment residuals containing Al, Fe, or Ca decreased P leaching in re-packed sandy soil columns (45 cm deep) that were leached for 120 days. Although these studies show that chemical additions can decrease P leaching, further research is needed to determine the long-term efficacy of chemical additions in reducing P leaching. Furthermore, little is known about the effectiveness of chemical additions in reducing P leaching in soils with high soil P concentrations from previous waste applications. The objectives of this research are to determine the effects of alum additions to either poultry litter or soil on P leaching in soils with long-term history of P additions.

**Materials and Methods**

Waste and alum effects on P leaching were studied using intact soil columns to which P source and alum treatments were applied in a modified randomized complete block design of 5 treatments, two soils, two depths, and four replications. Treatments consisted of a control (no P or alum addition, CN), poultry litter (PL), alum amended poultry litter (PLA), swine lagoon effluent (SL), and swine lagoon effluent applied to alum-amended soil (SLA).

*Soil columns*

Intact soil columns (9 cm dia. by 45 and 90 cm in length) were removed from Autryville (loamy, siliceous, thermic Arenic Paleudults) and Blanton (loamy, siliceous, semiactive, thermic Grossarenic Paleudults) soil series with a hydraulic soil sampling unit (Giddings Probe) equipped with a 10 cm dia. steel tube containing a polyethylene terephthalate copolymer (PTEG) liner, which enabled removal and transportation of soil columns while minimizing disturbance. The Autryville soil contained <5% clay from the surface to 50 cm and 6 to 13% clay from 50 to 90 cm. The Blanton soil contained
<2% clay from the surface to 90 cm. Six 90-cm soil columns, in addition to the 40 required for the experiment, were removed from each soil for pre-experimental chemical analysis. Soils had received swine waste for >30 years and showed evidence of significant P accumulation (Table 1). Additional site and soil characterization is found in Chapter 2.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Autryville</th>
<th>Blanton</th>
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<tbody>
<tr>
<td></td>
<td>M3P †</td>
<td>P_ox</td>
</tr>
<tr>
<td>0-15</td>
<td>329</td>
<td>406</td>
</tr>
<tr>
<td>15-25</td>
<td>298</td>
<td>329</td>
</tr>
<tr>
<td>35-45</td>
<td>224</td>
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<td>55-60</td>
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<td>60-70</td>
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<td>70-80</td>
<td>205</td>
<td>252</td>
</tr>
<tr>
<td>80-90</td>
<td>73</td>
<td>96</td>
</tr>
</tbody>
</table>

† M3P, Mehlich 3 P; P_ox, oxalate extractable P; TP, total P; Al_ox, oxalate extractable Al; Fe_ox, oxalate extractable Fe; DPS, degree of P saturation

Columns were prepared in the lab by removing the top 15 cm of soil, screening it through a 8 mm sieve to remove plant roots and residue, and mixing 0.42 and 0.34 g Ca(OH)_2 kg soil\(^{-1}\) for the Autryville and Blanton soils respectively. Four randomly selected columns from each soil and length also received 1.7 g alum (Al\(_2\)(SO\(_4\))\(_3\)•14H\(_2\)O) kg soil\(^{-1}\) and an additional 0.69 g Ca(OH)_2 kg soil\(^{-1}\), for use as the SLA treatment. Calcium hydroxide was added to increase the surface soil pH of the Autryville and Blanton soils from 4.7 and 4.5 respectively to approximately 5.5, and additional lime was added to alum-amended soil to counteract the acidity produced by the alum as determined by pre-experimental analysis (Appendix E). Alum amendment supplied 350 kg Al ha\(^{-1}\), the molar equivalent of approximately 400 kg P ha\(^{-1}\), which is the quantity of excess P applied to these soils over 6 years when under pasture management with swine lagoon effluent applied to meet the N requirement. This Al application rate is within the range applied in field experiments (Haustein et al., 2000; Gallimore et al., 1999), but less
than that used in laboratory experiments (Codling et al., 2000; Peters and Basta, 1996; Hyde and Morris, 2000). After mixing, soil from the top 15 cm was repacked in the columns in 3-cm increments to the same bulk density prior to disturbance. Repacking the surface of the columns allowed for the incorporation of lime and/or alum and decreased the void space between the soil column and the liner, thus minimizing preferential flow.

Leaching process

Disposable filter units with polystyrene bodies and 0.45 μm polyethersulfone membrane filters were used to collect leachate and maintain a constant soil moisture tension at the bottom of each column (Appendix A). Columns were leached by adding 2.8 cm of distilled water per week to the surface and maintaining a constant vacuum of -25 kPa in the filter units with an electric vacuum pump. The leaching rate of 2.8 cm week⁻¹ produces 33.6 cm of drainage in 12 weeks, which is equivalent to estimates of annual rainfall excess (i.e. rainfall minus evapotranspiration and runoff) for these soils and their corresponding crop and climate (Osmond et al., 2003). Therefore, each 12-week period is one simulated year of leaching. Columns were leached for an initial 7 weeks prior to waste applications and for 60 weeks following the first addition of waste. Soils had high hydraulic conductivity (10 to 40 cm hr⁻¹) and applied water infiltrated rapidly. Visual observations indicated minimal wall flow in the upper 15 cm and the absence of wall flow below 15 cm. This was confirmed by adding a Br tracer to all columns (Appendix F).

Because initial P concentrations in the leachate from the soil columns was highly variable prior to treatment application, columns were separated into a second blocking pattern based on initial P concentrations, thus modifying the original randomized complete block design based on soil, length and physical position of the column in the laboratory. The CN, PL, PLA, and SL treatments were randomly assigned to soil columns within the second blocking pattern. For statistical analysis, the SLA treatments were assigned to appropriate initial P blocks.

Waste was applied to soil columns at a rate of 67 kg P ha⁻¹ every 12 weeks, which approximates the annual excess P applied to grazed pasture when swine lagoon
effluent is applied to meet N requirements, where P removal from grazing is 10 kg P ha\(^{-1}\) yr\(^{-1}\) (Nelson and Mikkelsen, 2001). Poultry litter used for the study was from a commercial broiler house that had raised 14 flocks using sawdust bedding prior to sample collection (Table 2). Poultry litter from the same source was amended with alum at a 1:1 molar Al:P ratio by gradually adding 0.6 M alum solution to the litter. Both amended and unamended litters were brought to 20% moisture by volume (60% by weight) and incubated for 3 months at room temperature prior to the experiment. After incubation, the litter was stored at < 4 °C for the duration of the experiment. Litter applications were made once every 12 weeks, simulating annual waste applications. Swine lagoon effluent was periodically collected from a commercial farrow-to-wean swine operation and stored at 4 °C for up to 24 weeks (Table 2). Swine waste was added once every 3 weeks, simulating 4 applications per year. All waste applications were made 3 days following addition of water to the columns. Water applications to SL and SLA treatments were reduced on the waste application weeks so that all columns received equal volumes of liquid.

Table 2. Chemical analysis of the swine lagoon effluent (SL1, SL2, and SL3) and poultry litter (PL and PLA) used as P sources for the column treatments.

<table>
<thead>
<tr>
<th>N</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>Al</th>
<th>S</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg L(^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>542</td>
<td>87.4</td>
<td>839</td>
<td>135</td>
<td>28.2</td>
<td>269</td>
<td>49.1</td>
<td>3.3</td>
<td>0.46</td>
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<tr>
<td>SL2</td>
<td>896</td>
<td>72.3</td>
<td>829</td>
<td>174</td>
<td>29.1</td>
<td>264</td>
<td>23.8</td>
<td>4.7</td>
<td>0.47</td>
</tr>
<tr>
<td>SL3</td>
<td>738</td>
<td>70.8</td>
<td>816</td>
<td>154</td>
<td>29.7</td>
<td>254</td>
<td>34.9</td>
<td>3.6</td>
<td>0.44</td>
</tr>
<tr>
<td>PL</td>
<td>41.8</td>
<td>17.0</td>
<td>32.0</td>
<td>32.3</td>
<td>6.3</td>
<td>8.5</td>
<td>0.3</td>
<td>5.0</td>
<td>0.3</td>
</tr>
<tr>
<td>PLA</td>
<td>37.4</td>
<td>15.1</td>
<td>26.2</td>
<td>26.7</td>
<td>5.3</td>
<td>7.3</td>
<td>13.1</td>
<td>23.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>

\(\dagger\) SL1, SL2, and SL3 are swine lagoon effluents used for weeks 0-23, 24-47, and 48-60 respectively; PL, poultry litter; PLA, poultry litter amended with alum

Leachate was removed from sample collection devices each week at the time of water addition and stored at < 4 °C until analysis. Because leachate collection devices were equipped with 0.45 µm polyethersulfone membrane filters, leachate was
immediately filtered at the time of collection. Initial sampler testing showed that refiltering samples did not affect P concentration, therefore samples were not refiltered. Dissolved reactive P (DRP) concentration in all samples was determined colorimetrically using a Lachat QuickChem 8000 auto analyzer instrument (Lachat, 2001). Select samples were analyzed for total dissolved P using an in-line persulfate digestion procedure (Lachat QuickChem method 10-115-01-3-A, Lachat, 2001), and dissolved Ca, Mg, Fe, Al, and Si with the ICP. Electrical conductivity and pH of select samples were also determined. Bromide analysis of leachate was performed with Lachat QuickChem method 12-135-21-2-A, Lachat, (2001).

Soil analysis

Prior to chemical analyses, all soil samples were air dried, ground, and passed through a 2 mm sieve. Samples were extracted for Mehlich 3 P (M3-P) by shaking 2.5 cm³ soil with 25 mL of Mehlich 3 solution for 5 min. and filtering through a Whatman No. 42 filter paper (Sims, 2000). Oxalate extractable P, Fe, and Al (Pox, Feox, Alox) were determined by shaking 0.75 g soil with 30 mL 0.2 M ammonium oxalate/oxalic acid solution adjusted to pH 3 for 2 hr. in darkness. After shaking, samples were centrifuged at 6,000 rpm for 6 min. and filtered through Whatman No. 42 filter paper and stored in the dark until analysis (Schoumans, 2000). The degree of P saturation (DPS) was calculated as $P_{ox}(100)/\alpha(Alox + Feox)$, where $P_{ox}$, $Alox$, and $Feox$ are oxalate extractable elements in mmol kg⁻¹ soil and $\alpha$ is 0.5 for non-calcareous sandy soils (van der Zee and van Riemsdijk, 1988; Schoumans and Groenendijik, 2000). A 20-g sample was taken from 1-3 cm deep from each soil column after 24 and 48 weeks of leaching to determine pH in 1:1 soil water solution.

Soil microbial biomass P (MBP) was determined on samples taken at 24 weeks and 60 weeks. Soil microbial biomass P was determined as the difference of Bray extractable P in CHCl₃ fumigated and non-fumigated samples (Wu et al., 2000, He et al., 2003). In brief, soil samples were collected moist, stored at < 4°C, and brought to room temp in a 6-hr pre-incubation prior to analysis (Winter et al., 1994). Duplicate 5-g soil samples were placed in separate vacuum chambers. One of the vacuum chambers, containing an open container of CHCl₃, was evacuated several times to fumigate the
samples. Following 24-h fumigation period, the CHCl₃ was removed and the fumes were evacuated several more times. All samples were extracted with 25 mL of Bray exacting solution (0.025 M HCl in 0.03M NH₄F) for 30 min. and filtered through Whatman No. 42 filter paper. Extracts were stored at < 4°C until analysis. Phosphorus concentration in M3-P and Bray extracts were determined colorimetrically using a Lachat QuickChem 8000 auto analyzer instrument (Lachat, 1995). Phosphorus, Al, and Fe concentration in the oxalate extracts were determined by ICP.

Statistical analysis

Statistical analysis was performed with SAS proc mixed for repeated measures analysis of variance and SAS proc glm all other analysis of variance (SAS Institute, 1998). A log₁₀ transformation was used to equalize variance of leachate DRP over time and between treatments. Although back-transformation of means produces a biased estimate of the mean, it produces an unbiased estimate of the median, therefore back-transformation of mean logDRP results are referred to as estimates of the median DRP. Mass P losses also required log₁₀ transformations.

Results

Soluble phosphorus loss

Prior to adding treatments, five soil columns from the Autryville 90-cm soil columns had initial DRP concentrations one to two orders of magnitude higher than the other 15 soil columns. The leachate DRP concentrations in these five columns were 0.74 to 2.7 mg L⁻¹ compared to other columns which had an average of 0.04 mg L⁻¹. Furthermore, leachate that was collected at 90 cm in the Autryville soil during an in situ field study averaged 0.05 mg DRP L⁻¹ (Chapter 2). Data analysis with or without these columns had little effect on the significance of treatment effects for other soil and length combinations and minimal effect on the overall significance of model effects in the ANOVA F-tests. However, omitting these columns from the data analysis did eliminate some significant contrasts for Autryville 90 cm soil columns where treatment means were overwhelmingly influenced by one column in the treatment. Therefore, these columns were omitted from the data analysis.
Analysis of variance showed a significant soil × length × treatment × time interaction ($p < 0.001$). Phosphorus concentrations in the leachate just prior to waste application were similar between treatments in each soil × length combination, with the exception of the SLA treatment, which had lower P concentrations from alum additions to the soil (Figure 1). Within two weeks after waste application, the DRP concentration in 45-cm columns decreased drastically in all waste amended treatments, reaching a low at week 5. In contrast, the control exhibited a more gradual decline over time. The DRP concentration in PL and PLA treatments rebounded, then declined again following the next waste application. Although the leachate DRP concentration in the SL and SLA treatments did not rebound to the same extent as the PL and PLA treatments, there was a 3-week cyclical trend that corresponded to the 3-week waste application interval (Figure 1). Similar trends were also evident in the 90-cm columns (Appendix G).

**Figure 1.** Dissolved reactive P (DRP) concentration in leachate from 45-cm Autryville (a) and 45-cm Blanton (b) soil columns receiving various waste and alum treatments.
To simplify the detection of long-term trends and facilitate repeated measures ANOVA for data throughout the entire experiment, the leachate DRP concentrations for each column were averaged over 12-week periods, where each period simulated one year of P additions and leaching. Although the Autryville soil had higher initial leachate DRP concentrations at 45-cm length than the Blanton, by the end of the experiment concentrations from the Blanton soil were greater than the Autryville (Figure 2). Leachate DRP from 90-cm Blanton soil columns was slightly less than from the 45-cm Blanton soil columns, whereas leachate DRP from the 90-cm Autryville soil columns was one to two orders of magnitude less than all other columns (Figure 2).

Treatment effects on leachate DRP concentrations within each period and over the course of the experiment are most simply expressed with a series of contrast statements (Table 3). In general, CN treatments had higher leachate DRP concentrations than waste-amended soil columns for the first period, but by periods 4 and 5, PL and SL treatments had higher leachate DRP concentrations than the control for the Blanton soil. Although there was not a significant difference in leachate DRP concentrations in the CN treatment compared to the PL and SL treatments in the Autryville soil, there was a trend for the difference between CN and PL+SL treatments to decrease throughout the experiment, becoming negative by period 5 (Figure 2, Table 3). Leachate DRP concentrations from CN treatments were greater than or equal to that from alum treatments for all soils and time periods with the exception of the Blanton 45 cm columns receiving SLA treatment in period 5. Furthermore, waste-amended columns with alum consistently had significantly lower leachate DRP concentrations than waste-amended columns in absence of alum treatment, demonstrating that alum amendments to soils or wastes can reduce P leaching losses.
Figure 2. Leachate DRP concentrations for Autryville 45 cm (a), Autryville 90 cm (b), Blanton 45 cm (c), and Blanton 90 cm (d) soil columns (vertical bars represent ± 1 standard error). Back-transformation of data is indicated on the secondary ordinate, note the log scale.
Table 3. Estimates of contrasts† between treatment effects on logDRP in leachate collected from Autryville and Blanton soil columns at 45 and 90 cm for each 12 week period.

<table>
<thead>
<tr>
<th></th>
<th>Period 1</th>
<th>Period 2</th>
<th>Period 3</th>
<th>Period 4</th>
<th>Period 5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Autryville 45 cm</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control vs. waste without alum</td>
<td>0.19 (0.06)**</td>
<td>0.14 (0.07)*</td>
<td>0.12 (0.07)</td>
<td>-0.01 (0.09)</td>
<td>-0.15 (0.09)</td>
</tr>
<tr>
<td>Control vs. waste with alum</td>
<td>0.26 (0.06)***</td>
<td>0.14 (0.07)*</td>
<td>0.16 (0.07)*</td>
<td>0.20 (0.09)*</td>
<td>0.22 (0.09)*</td>
</tr>
<tr>
<td>Waste w/ alum vs. waste w/o alum</td>
<td>-0.07 (0.05)</td>
<td>0.00 (0.05)</td>
<td>-0.04 (0.06)</td>
<td>-0.20 (0.07)**</td>
<td>-0.37 (0.08)***</td>
</tr>
<tr>
<td>Poultry vs. swine (without alum)</td>
<td>0.15 (0.07)*</td>
<td>0.08 (0.08)</td>
<td>0.05 (0.09)</td>
<td>0.01 (0.10)</td>
<td>0.04 (0.11)</td>
</tr>
<tr>
<td>Poultry vs. swine (with alum)</td>
<td>0.23 (0.07)**</td>
<td>0.11 (0.08)</td>
<td>0.11 (0.09)</td>
<td>0.20 (0.10)*</td>
<td>0.17 (0.11)</td>
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<td><strong>Autryville 90 cm</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Control vs. waste without alum</td>
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<td>-0.02 (0.08)</td>
<td>-0.08 (0.09)</td>
<td>-0.12 (0.10)</td>
<td>-0.15 (0.11)</td>
</tr>
<tr>
<td>Control vs. waste with alum</td>
<td>0.02 (0.07)</td>
<td>0.05 (0.07)</td>
<td>0.05 (0.09)</td>
<td>0.04 (0.10)</td>
<td>0.04 (0.11)</td>
</tr>
<tr>
<td>Waste w/ alum vs. waste w/o alum</td>
<td>0.03 (0.06)</td>
<td>-0.07 (0.06)</td>
<td>-0.14 (0.07)x</td>
<td>-0.16 (0.08)x</td>
<td>-0.19 (0.09)*</td>
</tr>
<tr>
<td>Poultry vs. swine (without alum)</td>
<td>0.07 (0.10)</td>
<td>0.17 (0.10)x</td>
<td>0.24 (0.11)x</td>
<td>0.25 (0.13)x</td>
<td>0.21 (0.14)</td>
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<tr>
<td>Poultry vs. swine (with alum)</td>
<td>0.01 (0.08)</td>
<td>0.12 (0.08)</td>
<td>0.11 (0.09)</td>
<td>0.12 (0.11)</td>
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<tr>
<td>Control vs. waste without alum</td>
<td>0.17 (0.06)*</td>
<td>-0.08 (0.07)</td>
<td>-0.20 (0.07)*</td>
<td>-0.41 (0.09)***</td>
<td>-0.48 (0.09)***</td>
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<tr>
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<td>0.04 (0.08)</td>
<td>-0.04 (0.09)</td>
<td>-0.06 (0.09)</td>
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<tr>
<td>Waste w/ alum vs. waste w/o alum</td>
<td>-0.04 (0.05)</td>
<td>-0.08 (0.05)</td>
<td>-0.24 (0.06)***</td>
<td>-0.37 (0.07)***</td>
<td>-0.42 (0.08)***</td>
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<tr>
<td>Poultry vs. swine (without alum)</td>
<td>0.16 (0.07)*</td>
<td>0.01 (0.08)</td>
<td>-0.08 (0.09)</td>
<td>-0.19 (0.10)x</td>
<td>-0.21 (0.11)</td>
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<tr>
<td>Poultry vs. swine (with alum)</td>
<td>0.13 (0.08)</td>
<td>0.10 (0.08)</td>
<td>0.06 (0.09)</td>
<td>-0.21 (0.10)*</td>
<td>-0.36 (0.11)**</td>
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<td>0.16 (0.07)*</td>
<td>0.10 (0.08)</td>
<td>-0.03 (0.09)</td>
<td>-0.28 (0.09)***</td>
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<td>Control vs. waste with alum</td>
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<td>0.20 (0.07)***</td>
<td>0.20 (0.08)*</td>
<td>0.18 (0.09)*</td>
<td>0.15 (0.09)</td>
</tr>
<tr>
<td>Waste w/ alum vs. waste w/o alum</td>
<td>-0.10 (0.05)x</td>
<td>-0.05 (0.05)</td>
<td>-0.10 (0.06)</td>
<td>-0.21 (0.07)***</td>
<td>-0.43 (0.08)***</td>
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<tr>
<td>Poultry vs. swine (without alum)</td>
<td>0.10 (0.07)</td>
<td>0.11 (0.08)</td>
<td>0.14 (0.09)</td>
<td>0.09 (0.10)</td>
<td>-0.02 (0.11)</td>
</tr>
<tr>
<td>Poultry vs. swine (with alum)</td>
<td>0.12 (0.08)</td>
<td>-0.06 (0.08)</td>
<td>-0.06 (0.09)</td>
<td>-0.08 (0.10)</td>
<td>-0.19 (0.11)x</td>
</tr>
</tbody>
</table>

† contrasts are stated such that the estimate of contrast X vs. Y is equal to logX – logY. Back-transformation of the estimate is equivalent to the ratio of the medians. Standard errors of estimates are in parenthesis.

×, *, **, *** indicate significance at α = 0.1, 0.05, 0.01, and 0.001 respectively.
Leachate DRP concentrations from PL treatments were greater than or equal to that from SL treatments in the Autryville soil ($p=0.1$). Although PL treatments had higher leachate DRP concentrations than SL treatments for the first period in the Blanton 45 cm columns, this trend was reversed by the fifth period and DRP concentrations in leachate from SL treatments were greater than in PL treatments ($p=0.1$). This indicates that P leaching from poultry litter applications would be greater than from swine waste applications on the Autryville soil, but the reverse would be true for the Blanton soil.

Direct alum amendments to the soil were more effective at controlling P leaching in the Autryville soil than in the Blanton soil. By period 5, the leachate DRP concentration from the SLA treatment was greater than the control ($p<0.05$) in the Blanton 45 cm columns but less than the control ($p<0.01$) in the Autryville 45 cm columns (Figure 2). This effect is further illustrated by the difference in leachate DRP concentrations between PLA and SLA treatments. Leachate DRP from PLA treatments was equal to or greater than from SLA treatments in the Autryville soil, which contrasts the Blanton soil where leachate DRP from SLA treatments was greater than from PLA treatments (Figure 3). This indicates that direct soil amendment with alum was more effective at reducing P leaching in the Autryville soil than in the Blanton soil, regardless of the fact that the Autryville soil had higher soil P concentrations throughout the upper 45 cm than did the Blanton soil (Table 1).

![Figure 3](image-url)

**Figure 3.** Difference between log(DRP) concentrations in PLA treatments compared to SLA treatments for 45 and 90 cm Autryville (A) and Blanton (B) soil columns.
Mass phosphorus loss

Treatment effects on P mass losses were similar to effects on leachate DRP concentration, where there was a significant soil × length × treatment × time interaction ($p < 0.01$), with all lower level interactions involving time also significant ($p < 0.01$). There was a wide range of median P mass losses, where Autryville 90-cm columns had the lowest P losses (0.1 – 0.3 kg ha$^{-1}$ period$^{-1}$) and Blanton 45-cm soil columns had the highest P losses, up to 64 kg ha$^{-1}$ for SL treatment in the fifth 12-week period. The soil × treatment × time interaction is well illustrated by P mass losses (Table 4). Initially, P losses from poultry treated columns were greater than from swine waste treated columns. By the end of the experiment, P losses from swine and poultry treatments were similar in the Autryville soil, however, P losses from swine treatments were greater than from poultry in the Blanton soil (Table 4).

Table 4. Median P mass losses and corresponding contrasts for treatments applied to Autryville and Blanton 45-cm soil columns during the first and last 12-week periods (periods 1 and 5).

<table>
<thead>
<tr>
<th></th>
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<th>Autryville</th>
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<td>24.4</td>
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<tr>
<td>SL</td>
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Contrasts

<table>
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<th>contrast estimates $\dagger$</th>
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</thead>
<tbody>
<tr>
<td>CN vs. PL &amp; SL</td>
<td>0.17 (0.07)* 0.16 (0.07)* -0.15 (0.09) -0.48 (0.09)***</td>
</tr>
<tr>
<td>PL &amp; PLA vs. SL &amp; SLA</td>
<td>0.20 (0.05)*** 0.16 (0.05)** 0.11 (0.08) -0.28 (0.08)***</td>
</tr>
<tr>
<td>CN vs. PL &amp; SLA</td>
<td>0.24 (0.07)*** 0.20 (0.07)** 0.22 (0.09)* -0.07 (0.09)</td>
</tr>
<tr>
<td>PL &amp; SL vs. PLA &amp; SLA</td>
<td>-0.07 (0.05) -0.04 (0.05) -0.37 (0.08)*** -0.42 (0.08)***</td>
</tr>
<tr>
<td>PL vs. SL</td>
<td>0.16 (0.08)* 0.17 (0.08)* 0.04 (0.11) -0.20 (0.11)</td>
</tr>
<tr>
<td>PLA vs. SLA</td>
<td>0.23 (0.08)** 0.15 (0.08) 0.17 (0.11) -0.36 (0.11)**</td>
</tr>
</tbody>
</table>

$\dagger$ Equivalent to kg ha$^{-1}$ yr$^{-1}$, where each period simulated 1 year of P application and leaching

$\dagger$ contrasts are stated such that the estimate of contrast X vs. Y is equal to logX − logY. Back-transformation of the estimate is equivalent to the ratio of the medians. Standard errors of estimates are in parenthesis.

*, **, ***; indicate significance at $\alpha = 0.05, 0.01, and 0.001$ respectively
Changes in soil phosphorus concentrations

There was considerable variability in the post-experiment soil analysis, therefore significant treatment effects were only apparent in at 0-5 and 5-15 cm depths and treatment × soil interactions were not significant for any of the soil analysis measured. The control treatment decreased the M3P and DPS where other treatments increased the M3P and DPS (Figure 4). The PLA treatment only increased M3P and DPS in the 0-5 cm depth, whereas other waste treatments resulted in increases at 5-15 cm depth. The SLA treatment resulted in a larger increase in M3P at 0-5 cm than the SL treatment, but produced a similar increase in DPS. Although the PLA treatment increased the 0-5 cm Al concentration over two fold compared to the initial Al concentration, it still increased the DPS by 35%. Both PL and PLA treatments resulted in larger increases in DPS in the surface 0-5 cm than did the swine waste treatments ($p < 0.001$).

![Figure 4](image-url)  
**Figure 4.** Change in M3P and DPS from initial values (final-initial) at the zero to 5 and 5 to 15 cm depth. Bars represent ± 1 standard error of the mean and asterisks indicate means are significantly different from 0 at $\alpha = 0.5$ (*), 0.01 (**), and 0.001 (***).
Discussion

The relatively high leachate DRP concentrations from the CN treatments for the 45 cm columns and Blanton 90 cm soil columns are a result of P desorption from P the P-saturated soils. There were seldom significant differences between the leachate DRP concentrations from CN treatments for Autryville 45, Blanton 45 and Blanton 90 cm soil columns. However, the considerably lower leachate DRP concentrations from the Autryville 90-cm soil columns are a result of greater Al and Fe concentrations and lower DPS in the lower portion of the soil columns, thereby increasing sorption of P that was translocated from overlying soil layers (Table 1).

Although the consistent pattern of decreased leachate DRP concentrations following waste application was unexpected, other research studies have observed similar effects. Heckrath et al. (1995) observed that although plots receiving manure had Olsen-P concentrations similar to plots receiving inorganic P fertilizer, the drainage water P concentrations from manured plots were significantly less. McDowell and Sharples (2000) found that leachate DRP concentrations 1 year following manure applications were greater than leachate DRP concentrations 3 weeks following manure applications. In a column leaching experiment, Hergert et al. (1981) found that DRP concentrations decreased following the addition of an aqueous manure extract and then increased to concentrations greater than pre-waste application. Possible explanations for reduced DRP concentrations following waste application include i) increased microbial activity and P immobilization due to addition of C and N source, ii) shift from inorganic P to organic P in leachate resulting from changes in microbial activities, iii) precipitation of P minerals due to addition of Ca and/or Mg in waste, and iv) change in P sorption characteristics from waste addition.

The addition of a readily available C source has been shown to increase microbial P uptake and P turnover in soils (Kouno et al., 2002), which could potentially impact quantity and forms of P in leachate. Glucose additions to soils have been found to increase MBP and cause concurrent decreases in inorganic soil P concentrations (Cole et al., 1978). However, measurement of treatment effects on MBP failed to support this hypothesis for the present study. Although there was a significant treatment × soil effect
on MBP at 24 weeks, MBP in waste-amended soils was less than the control with the exception of the Autryville P treatment (Figure 5). At 60 weeks, there were no significant differences in MBP between treatments. Furthermore, typical C:P ratios in poultry litter and swine lagoon liquid are < 25:1 and < 10:1 respectively (Barker et al., 1994), much less than the 300:1 ratio typically associated with P immobilization (Havlin et al., 1999). There was no difference between the DRP and total P concentrations in leachate for weeks 19 through 21 (data not shown), indicating that the observed decreases in leachate DRP were not a result of a shift from inorganic P to organic P in leachate caused by possible waste-induced changes in microbial activities. Therefore, it is unlikely that the difference between the leachate DRP concentrations in the control vs. the waste amended soils is a result of waste effects on microbial activity.

![Figure 5.](image)

**Figure 5.** Microbial biomass P (MBP) in the surface soil of Autryville and Blanton soils after 24 and 60 weeks of leaching as affected by poultry and swine additions (bars represent standard error).

Appreciable quantities of K, Ca, Mg, and Na were present in the waste sources and therefore added to the soil columns with the P additions (Table 2). Increasing salt concentrations in soils, particularly Ca, can decrease P desorption and potentially induce precipitation of Ca-phosphate minerals (Lehr and Van Weselmael, 1952; Clark and
Peech, 1955), which could explain the decreases in leachate DRP concentrations. The electrical conductivity (EC) of column leachate was inversely related to the P concentrations in waste amended soils ($p < 0.001$; Figure 6), a trend also observed by Hergert et al. (1981). These salt additions could have decreased leachate DRP by either inducing the precipitation of Ca-phosphates or displacing exchangeable Al. Displaced Al could precipitate Al-phosphates or Al-hydroxides, which could in turn adsorb dissolved P. To distinguish which of these possible mechanisms might be controlling the reduction in leachate DRP, a sub-set of samples, including CN and PL treatments, were further analyzed for Al, Fe, Ca, Mg, and Si (Figure 7). These analysis, in conjunction with DRP, pH, and EC, were used as inputs for the chemical speciation program MINTEQA2 v. 4.02 (USEPA, 2000), where ionic strength was estimated as 0.013*EC (Griffin and Jurinak, 1973). Solution pH was very similar between the CN and PL treatments and ranged between 3.5 and 4.6 during weeks 1-12 (Table 5) however, the pH values are considered a best approximation as they were determined after the samples had been frozen for 18 months.

![Graph](attachment:image.png)

**Figure 6.** Average electrical conductivity (EC, solid lines) and DRP (dashed lines) for the leachate from 45-cm Autryville soil columns during the first 12 weeks of leaching following waste application ($n=4$).
**Figure 7.** Changes in the elemental composition of leachate from the PL treatment during 12 weeks of leaching following waste application for the 45-cm Autryville soil columns (n=2).

**Table 5.** Solution pH for select leachate samples from Autryville 45-cm CN (n=1) and PL (n=2) treatments for 12 weeks following the first waste application

<table>
<thead>
<tr>
<th></th>
<th>1†</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<th>7</th>
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<td>4.1</td>
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<td>3.6</td>
<td>3.7</td>
<td>4.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>

† Weeks after first application of waste

MINTEQA2 calculated that the leachate solutions were under saturated by >1000 times with respect to Ca- and Mg-phosphates (Table 6). However, the soil solution was supersaturated with respect to Variscite (AlPO₄•2H₂O) and near or above saturation with respect to Diaspore (β-AlOOH). This suggests that increases in Al concentration in soil solution could induce precipitation of either of these minerals, which would both decrease P concentrations in solution. Precipitation of Variscite would decrease P concentrations for the obvious reasons. Precipitation of Diaspore would create new adsorptive surfaces, which would react with dissolved P. Al-hydroxide minerals similar to Diaspore have been found to have a high affinity for P, with adsorption maxima near
25 mg P g⁻¹ Al-hydroxide (Khare et al., 2004). Increases in P adsorption capacity and corresponding decreases in solution P concentrations have been observed as a result of Ca additions to Al saturated clay minerals and Al saturated ion exchange resins (Coleman et al., 1960; Robarge and Corey, 1979). Bhat and O’Callaghan (1980) found that P sorption on soils treated with pig slurries were greater than twice that of soils treated with inorganic P sources.

**Table 6.** Saturation indices for select minerals as calculated by chemical speciation of leachate solutions from the Autryville 45-cm soil columns with MINTEQA2.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Control 1†</th>
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<tbody>
<tr>
<td>Diaspore</td>
<td>0.3</td>
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<td>-0.3</td>
<td>-0.8</td>
<td>-0.7</td>
<td>-1.5</td>
<td>-0.1</td>
<td>-1.0</td>
<td>-1.2</td>
<td>-1.1</td>
<td>1.2</td>
<td>1.3</td>
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<tr>
<td>Gibbsite</td>
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<td>1.0</td>
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</table>

† Weeks after first application of waste
‡ IAP is the ion activity product and K is the solubility constant for the respective minerals. Saturation indices (SI) less than -1 suggests the solution is undersaturated with respect to the mineral, -1 < SI < 0 suggests the solution is saturated with respect to the mineral, and SI > 0 suggests that the solution is supersaturated with respect to the mineral (Essington, 2003)

However, saturation indices in Table 6 do not provide definitive proof of mineral precipitation or presence in the soil. MINTEQA2 calculations were limited to ion pairs for the select ions in Figure 7 and therefore neglected to consider effects of other metals and anions on PO₄³⁻ and Al³⁺ activities. Furthermore, complex interactions between dissolved organic matter and Al³⁺ and Ca²⁺ were not considered, which could either decrease or increase Al³⁺ activities. Organic acids can complex Al³⁺ and thereby
decrease Al activity in soil solutions (van Hees et al., 2001). However, increasing Ca$^{2+}$ concentrations have been found to decrease dissolve organic carbon in soil solutions, which could decrease total Al in solution yet increase Al$^{3+}$ activity (Romkens et al., 1996). Calcium influence on dissolved organic matter could be one explanation for the decrease in Al and Fe concentrations in Figure 7. Despite its shortcomings, the solution speciation provides useful information lending to a feasible explanation for the influence of neutral salt additions on solution P concentrations in relation to the observed decreases in DRP shortly following waste additions (Figure 1).

The effect of neutral salts on leachate DRP concentrations helps to clarify some of the treatment × soil interactions. The Autryville soil had greater Al$_{ox}$ concentrations, and therefore a greater potential to supply Al to solution as compared to the Blanton soil (Table 1). The Autryville soil also has greater clay content which would indicate a higher CEC and potentially larger quantity of exchangeable Al. Therefore, it stands to reason that the addition of neutral salts to the Autryville soil would have a larger impact on DRP concentrations resulting from displacement of exchangeable Al$^{3+}$. This is a possible explanation for the reduced effect of waste application on leachate DRP in the Autryville soil as compared to the Blanton soil.

Although the amount of total P that is water soluble in swine lagoon liquid is near 80% compared to 25% in poultry litter (Barker et al., 1994), DRP concentrations from PL treatments in the Autryville soil were greater than or equal to that from SL treatments. This lack of difference could be a result of greater salt additions from swine lagoon liquid and therefore a potential to displace larger quantities of exchangeable Al$^{3+}$ as compared to the poultry litter (Table 2). However, the Blanton soil has lower CEC and lower Al$_{ox}$ concentrations and therefore the additional salt in the SL treatments compared to PL treatments did not have the same impact on leachate DRP concentrations as was observed in the Autryville soil (Figure 1).

Alum amendments to poultry litter were effective at reducing P leaching compared to conventionally treated poultry litter applications, as seen by lower leachate DRP concentrations from PLA treatments compared to PL treatments in all soils by period 5 ($p < 0.05$). This agrees with Elliott et al. (2002), who found that Al
amendments to municipal biosolids reduced P leaching losses. Although alum amendments to poultry litter were equally effective at reducing P leaching in both soils, the effectiveness of alum amendments directly to the soil on reducing P leaching from applied swine lagoon liquid was affected by soil type. Initial DPS at 0-15 cm was similar for both soils and it would be expected that equal Al additions would cause an equal increase in P sorption capacity between the two soils, therefore having a similar effect on P leaching losses. There is a possibility that differences in soil pH could have affected P sorption-desorption reactions, where increasing the soil pH decreases P sorption capacities of Al-hydroxide minerals (Oh et al., 1999). After 42 weeks of leaching, the surface pH of the Blanton soil was 5.2 compared to 5.0 in the Autryville soil (Appendix F). However this small difference in pH is not likely the cause of the observed difference in treatment effects. Therefore, available data did not offer an explanation for this observed treatment effect.

Corresponding to decreased P leaching losses, PLA and SLA treatments increased surface M3P values above the PL and SL treatments. Because only 33 cm of water leached through the soil columns for each simulated year, opposed to 123 cm of average annual rainfall that would infiltrate the soil surface in the soil’s natural environment, absolute increases in soil P for this study may not reflect what would occur in a field environment. However, relative differences in P leaching due to alum treatments are valuable for comparisons. Therefore, long-term use of alum amendments could lead to elevated soil-test P levels in the surface soil. Although water soluble P and corresponding runoff P concentrations may be lower in Al amended soils (Codling et al., 2000), total P losses from erosion could potentially be greater due to larger quantities of adsorbed P. Therefore, additional precautions should be taken to assure minimal soil loss from application fields where alum or Al containing materials are used as best management practices to reduce either P leaching or P runoff losses.

**Conclusions**

Alum additions to poultry litter were effective in reducing P leaching losses compared soil columns receiving conventional litter and in some cases decreased P
leaching losses to less than the control. The effectiveness of direct alum additions to soil in reducing P leaching losses from swine lagoon effluent was dependent on soil type. In the Autryville soil, alum additions to the soil reduced P leaching losses from applied swine lagoon effluent and maintained leachate DRP concentrations less than or equal to the control. However, in the Blanton soil, alum additions to the soil initially decreased P leaching from swine lagoon effluent, but resulted in P leaching greater than the control after 60 weeks of leaching. Alum amendment to waste appears to be a more effective best management practice to reduce P leaching losses than alum additions to soil followed by continued waste application. Although the alum effectiveness varied, the addition of alum consistently reduced P loss compared to continued P addition without alum. Alum amendments to either soil or waste resulted in greater soil P levels at 0-5 cm deep than waste application alone. Therefore, additional caution should be taken to reduce erosion when alum is used as a best management practice.

Addition of salts contained in applied wastes caused temporary decreases in leachate P concentrations, which occasionally decreased leachate DRP below that of the control. The effect of changes in salt concentration on the leachate P concentration is possibly dependent upon the soil’s ability to supply Al$^{3+}$ to solution through either exchange reactions or dissolution of poorly crystalline Al-hydroxides. Further research needs to be done to determine the effects of salt concentration in wastes on P leaching, P sorption capacity of soils, and the long-term stability of adsorbed P in waste amended soils.
References


Polyethersulfone Membrane Filters for Sampling Soil Water from Intact Soil Columns and Field Studies for Phosphate Analysis

Introduction

The principal of collecting soil solution samples from unsaturated soil was first described by Briggs and McCall (1904). In brief, soil solution samples are collected by applying a suction to the soil that is greater than the matrix tension of the soil water. The suction is applied across a hydrophilic porous material with a high bubble point. When the porous material is moist, capillary forces hold water in the pores thereby preventing the passage of air yet allowing the passage of water. Suction is applied to the soil by applying a vacuum to the collection vessel, thus creating a gradient between a sample collection vessel and the bulk soil. In response to this applied gradient, soil water flows from the soil, through the porous material, into the collection vessel. Devices that employ this method of sampling are generally referred to as soil solution samplers, although many other names exist (Litaor, 1988).

Porous ceramic plates or cups have historically been the most common material used for constructing soil solution samplers (Liator, 1988, Grossmann and Udluft, 1991). Although the ceramic is durable and relatively inexpensive, it is unsuitable for sampling soil solution for phosphate analysis because P is adsorbed and desorbed as the solution passes through the ceramic plate or cup. In laboratory studies, ceramic cups have adsorbed 20 to 80% of the P from a solution of 1 mg P L$^{-1}$, followed by desorption of P upon introduction to distilled water (Bottcher et al., 1984; Zimmerman et al., 1978). Field studies have also shown that soil solution P concentrations are altered by ceramic soil solution samplers (Andersen, 1994).

Other porous materials have been used in constructing soil solution samplers and have been found to have minimal impacts on soil solution composition. Several studies have shown that soil solution samplers constructed with PTFE do not adsorb P (Bottcher et al., 1984; Andersen, 1994). Although PTFE soil solution samplers have been implemented in field scale research (Andersen, 1994; Andersen and Xia, 2001), it has
been noted that their high cost is a limiting factor in wide scale use (Litaor, 1988). Bry et al. (2002) used soil solution samplers constructed of stainless steel to monitor P leaching. Stainless steel porous plates are also used in laboratory column leaching studies by Fremanich et al. (1991) and Woodbury et al. (1996). Again, high cost may be a limiting factor for using stainless steel porous plates. A limited number of studies have employed membrane filters of various compositions for sampling soil solution (Driscoll et al., 1985; Magesan et al., 1995; Tischner et al., 1998).

Recently there has been increased interest in determining the P concentration in leachate and drainage waters from intact soil cores for use in quantity-intensity relationships (Hesketh and Brookes, 2000; McDowell and Sharpley, 2001; Maguire and Sims, 2002). The common method cited in these studies has been to use gravity drainage to collect water from the bottom of the columns. On occasion, collected leachate volumes have reportedly been un-equal between columns or some columns have failed to produce any leachate (Maguire and Sims, 2002). The application of suction to the bottom of the columns may reduce these problems.

Polyethersulfone membranes, commonly used for filtration, are chemically inert and have a high bubble point (>200 kPa at 0.45 µm pore size) and could therefore be used in a soil solution sampler in place of a porous plate or cup. Advantages of using membrane filters in place of porous plates include (i) a uniform pore size—thereby eliminating the need for sample filtration, (ii) chemically inert, (iii) relatively inexpensive. However, membrane filters may dry out in conditions of low soil moisture, or become clogged with soil particles, thereby rendering them inoperable for sample collection. The objective of this study is to determine the suitability of polyethersulfone membranes for the extraction of soil solution in field studies and intact soil columns for phosphate analysis. Experiments were conducted to determine the following: (i) the range of soil water tension in which the samplers would collect soil solution samples, (ii) the range of soil water tension where the samplers would maintain a vacuum, i.e. water would remain in the membrane pores such that air could not pass through the membrane, and (iii) the change in flow rate after membranes were exposed to soil.
Materials and Methods

The experiments in this study evaluate the use of membrane filters in an in-situ soil solution sampler for field use and a soil solution sampler for collecting leachate from large intact soil columns.

**In-situ soil solution sampler**

The samplers were constructed from polysulfone membrane filter holders (Nalgene cat. no. 300-4000) that were modified for use as soil solution samplers by cutting the upper chamber off and adding a sample collection line through one of the two side arms and a vacuum line to the other (Figure 1a). Samplers were equipped with polyethersulfone membranes with 0.45 µm pore size and 45 mm dia. Six samplers were tested for P adsorption by rinsing 25 mL of distilled water through three samplers and 25 mL of 1 mg L⁻¹ P solution through the other three samplers. The rinsing was repeated three times for each sampler. After each rinsing, the sampler was emptied and the solution was collected for P analysis. Phosphorus concentrations were determined colorimetrically using a Lachat QuickChem 8000 auto analyzer instrument (Lachat, 1995).

**Figure 1.** (a) Modified filter holder used for an in-situ soil solution sampler and (b) disposable filter unit attached to the end of an intact soil column (sample collection container not shown).
The soil moisture range in which the soil solution samplers could function was evaluated by installing samplers in ceramic pots containing loamy sand, sandy loam, and sandy clay loam textured soils. The membrane of the sampler was approximately 10 cm below the soil surface. The experiment was a randomized complete block design with 4 replicates. Soils were saturated from the bottom up, after which a -10 kPa vacuum was applied to the samplers with a 100 cm hanging water column. Soil moisture tension (SMT), sample collection rate, and vacuum pressure were monitored while soils drained and dried for a period of 27 days. Once all samplers failed to hold a vacuum, the soils were re-saturated to determine if vacuums could be re-established by re-wetting the membranes. Flow rates were determined before and after the sampler instillation to determine if filters were clogged by the soil. Statistical analysis was done with SAS PROC GLM procedure for determining analysis of variance (ANOVA) and multiple comparisons using the Tukey test (SAS Institute, 1998).

**Field evaluation**

In-situ soil solution samplers were evaluated in the field by installing them in Autryville (loamy, siliceous, thermic Arenic Paleudults) and Blanton (loamy, siliceous, semiactive, thermic Grossarenic Paleudults) soils planted in coastal bermudagrass (*Cynodon dactylon* L.) pasture (Table 1). Two pits (1 m by 3 m by 1.5 m deep) were excavated in each soil and samplers were installed 0.4 m into the sidewalls of the pits so that samplers were beneath undisturbed soil. Two samplers were installed at 45, 90, and 135 cm in each pit, for a total of 24 samplers (2 soils, 2 pits, 2 reps, 3 depths). Pits were also equipped with Campbell Scientific CS616 (Campbell Scientific, Logan UT) automated TDR probes to monitor soil moisture. A continuous vacuum of -12 to -10 kPa was maintained in each sampler by means of a hanging water column as described by Riekerk and Morris (1983). Soil solution samples were removed from the samplers once every 12 to 20 days for 18 months, for a total of 40 sampling periods and 960 samples collected. Samplers were considered to have held a vacuum for the sampling period if the hanging water column was still holding at the end of the sampling period. Intact soil cores 6 cm tall by 5.5 cm dia. were taken in triplicate from each horizon in each pit and used to determine moisture release curves for the soil. Moisture release
curves fit with the Fayer and Simmons (1995) modification of the van Genuchten equation were used to determine SMT from TDR readings.

Table 1. Soil descriptions for Autryville and Blanton soils used for field evaluation of in-situ soil solution samplers.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autryville</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Horizon</td>
<td>Depth (cm)</td>
<td>Description</td>
</tr>
<tr>
<td>Ap</td>
<td>0-20</td>
<td>Dark brown sand (2 % clay), weak fine granular structure</td>
</tr>
<tr>
<td>E</td>
<td>20-58</td>
<td>Brownish yellow sand (2-4 % clay), weak medium granular structure</td>
</tr>
<tr>
<td>Bt</td>
<td>58-80</td>
<td>Yellowish brown sandy loam (6-14 % clay) weak medium subangular blocky structure</td>
</tr>
<tr>
<td>Bw</td>
<td>80-100</td>
<td>Yellowish brown loamy sand (8-9 % clay) weak fine subangular blocky structure</td>
</tr>
<tr>
<td>E’</td>
<td>100-130</td>
<td>Brownish yellow sand (4-7 % clay) single grained loose</td>
</tr>
<tr>
<td>B’t</td>
<td>130-150+</td>
<td>Yellowish brown sandy loam (5-15% clay), weak fine subangular blocky structure</td>
</tr>
<tr>
<td>Blanton</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ap</td>
<td>0-20</td>
<td>Dark brown sand (1-2 % clay), weak fine granular structure</td>
</tr>
<tr>
<td>E</td>
<td>20-125</td>
<td>Brownish yellow sand (1-3 % clay), single grained, loose</td>
</tr>
<tr>
<td>Bt1</td>
<td>125-150+</td>
<td>Yellowish brown sandy loam (5-8 % clay), weak fine subangular blocky structure</td>
</tr>
</tbody>
</table>

Soil solution extraction from intact soil columns

Disposable filter units (Nalgene cat. no. 169-0045) with polystyrene bodies and 0.45 μm polyethersulfone membrane filters were used to collect leachate and maintain a constant SMT at the bottom of intact soil columns. Intact soil columns 88 mm diameter were collected from Blanton and Autryville soils and trimmed to 45 or 90 cm in length. Filter units were placed on the bottom of each column and sealed with a 1 mm rubber gasket (Figure 1b). Columns were leached for 60 weeks by adding 2.8 cm of water per week to the surface and maintaining a constant vacuum of -25 kPa in the filter units with an electric vacuum pump. Leachate was collected on a weekly basis. Following the 60
week period, the flow rate in selected filter units was compared to new units by passing 50 mL of water through the filter under a -10 kPa vacuum.

**Results**

The average P concentration of rinse solution from membrane filters rinsed with distilled water was less than the detection limit of 0.02 mg P L\(^{-1}\), indicating that neither the membranes or filter units released P. The average P concentration of the rinse solution from membrane filters rinsed with P solution (1 mg L\(^{-1}\)) was 1.02 mg P L\(^{-1}\). The difference between the rinse solution before and after passing through the filters is less than the variability expected by the P analysis procedure; therefore, we conclude that P concentration was not affected by the sampler.

The minimum SMT for sample collection ranged from –4 to –12 kPa and was not affected by soil texture (p > 0.1) (Table 2). Although the analysis of variance (ANOVA) f-test was not significant, multiple comparison analysis with the Tukey test did show a difference between the minimum SMT for sample collection from the loamy sand and sandy clay loam soils (p < 0.05). Therefore, there is a tendency for the samplers to stop collecting samples at higher SMT in sandy soils as compared to finer textured soils.

There was a significant effect of soil texture on the SMT range in which samplers maintained vacuum (p < 0.001), where samplers lost vacuum at only -23 kPa SMT in the loamy sand soil but maintained vacuum up to -77 kPa SMT in the sandy loam. However, it is possible that the tensiometers did not accurately measure the SMT in the loamy sandy due very low unsaturated hydraulic conductivity. Re-wetting the soils and thereby re-wetting the membranes allowed a vacuum to be re-established in all samplers.
Table 2. Performance of suction lysimeters in three soils.

<table>
<thead>
<tr>
<th>Soil Texture</th>
<th>loamy sand</th>
<th>sandy loam</th>
<th>sandy clay loam</th>
<th>95% CI (+/-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>minimum SMT for sample collection (kPa)</td>
<td>-4</td>
<td>-10</td>
<td>-12</td>
<td>4</td>
</tr>
<tr>
<td>minimum SMT for maintaining vacuum (kPa)</td>
<td>-23</td>
<td>-77</td>
<td>-69</td>
<td>6</td>
</tr>
<tr>
<td>leachate collection rate (mL cm(^{-2}) hr(^{-1}))</td>
<td>1.1</td>
<td>1.8</td>
<td>1.6</td>
<td>1.0</td>
</tr>
<tr>
<td>flow rate prior to installation (mL cm(^{-2}) hr(^{-1}))</td>
<td>385</td>
<td>387</td>
<td>345</td>
<td>42</td>
</tr>
<tr>
<td>flow rate after installation (mL cm(^{-2}) hr(^{-1}))</td>
<td>97</td>
<td>193</td>
<td>177</td>
<td>60</td>
</tr>
</tbody>
</table>

\(a\) CI – confidence interval  
\(b\) SMT – soil moisture tension  
\(c\) leachate collection rate was determined by the amount of soil solution collected in the first three hours of leachate collection (between 0 and –2 kPa SMT).

Samplers collected soil solution at an average rate of 1.5 mL cm\(^{-2}\) hr\(^{-1}\) during the first 3 hr following saturation (0 to -2 kPa SMT). The membranes became partially clogged when samplers were placed in the soil, as indicated by the decreased flow rate after removal. However, this decrease would not affect soil solution sampler function because the flow rate greatly exceeds the leachate collection rate (Table 2).

During the 18 month field evaluation, the SMT ranged from 0 to -52 kPa depending upon the horizon in which the samplers were located (Table 3). In the Blanton soil, sample volumes tended to increase when SMT was greater than -5 and -10 kPa for the 45 and 90 cm depths respectively (Figures 2 and 3). The samplers at 135 cm in the Blanton soil were near the seasonally high water table. Rainfall during the sampling period was greater than average; therefore the soil was saturated at this depth for most of the sampling period which resulted in very large sample volumes (Figure 4). The samplers at 45 cm in the Autryville soil tended to collect more sample when the SMT was greater than -6 kPa (Figure 5). Samplers at 90 and 135 cm collected considerably less soil solution after October 2003, even though the SMT was similar to the previous year (Figures 6 and 7). The cause of the decrease is not known. The membrane filters could have become partially clogged following heavy rains in June and July, but this will have to be determined after they are removed from the site.
Table 3. Range of soil moisture tension (SMT) for each horizon during the 18 month field evaluation period with corresponding average sample volumes for collected soil solution samples.

<table>
<thead>
<tr>
<th>soil</th>
<th>depth (cm)</th>
<th>SMT (kPa)</th>
<th></th>
<th></th>
<th>sample vol. (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>maximum</td>
<td>minimum</td>
<td>mean</td>
<td>mean</td>
</tr>
<tr>
<td>Autryville</td>
<td>45</td>
<td>-4.9</td>
<td>-13.9</td>
<td>-7.6</td>
<td>42</td>
</tr>
<tr>
<td>Autryville</td>
<td>90</td>
<td>0.0</td>
<td>-8.0</td>
<td>-6.6</td>
<td>50</td>
</tr>
<tr>
<td>Autryville</td>
<td>135</td>
<td>0.0</td>
<td>-25.5</td>
<td>-10.7</td>
<td>102</td>
</tr>
<tr>
<td>Blanton</td>
<td>45</td>
<td>-4.1</td>
<td>-9.3</td>
<td>-6.5</td>
<td>47</td>
</tr>
<tr>
<td>Blanton</td>
<td>90</td>
<td>0.0</td>
<td>-51.6</td>
<td>-13.8</td>
<td>100</td>
</tr>
<tr>
<td>Blanton</td>
<td>135</td>
<td>0.0</td>
<td>-4.8</td>
<td>-1.3</td>
<td>305</td>
</tr>
</tbody>
</table>

Figure 2. Soil moisture tension (line) and volume of soil solution collected (bars) at 45 cm in the Blanton soil.
Figure 3. Soil moisture tension (line) and volume of soil solution collected (bars) at 90 cm in the Blanton soil.

Figure 4. Soil moisture tension (line) and volume of soil solution collected (bars) at 135 cm in the Blanton soil.
Figure 5. Soil moisture tension (line) and volume of soil solution collected (bars) at 45 cm in the Autryville soil.

Figure 6. Soil moisture tension (line) and volume of soil solution collected (bars) at 90 cm in the Autryville soil.
The hanging water columns remained in operation about 90% of the time. Most of the hanging water columns that failed could be accounted for by cracked tubing or disturbance from wildlife, those which could not be attributed to these factors were assumed to be a result of dried membrane filters or general sampler failure. During the first year of operation, the only sampler failures were in Blanton soils at 45 and 90 cm depths, which both had a 9% failure rate. Samplers at 45 cm in the Blanton soil tended to fail at SMT < -8.5 kPa, however the vacuum could be re-established when the SMT increased, indicating that the cause of failure may have been dried membrane filters. This also demonstrates that if a membrane dries, increases in soil moisture content can sufficiently wet the membrane and allow re-establishment of vacuum. The sampler failures in the Blanton 90 cm depth were all the same sampler and were not correlated to SMT, indicating that it may be a defective sampler. Sampler failure rates increased in the second year of operation, where one of the four samplers at both 45 and 90 cm depths in the Blanton soil consistently failed. Two additional samplers consistently
failed after 15 months in the field, one at 90 cm and the other 135 cm in the Autryville soil. The cause for the sampler failures has not been determined because the samplers are still in the field.

The in-situ sample collection rate for samplers located at 90 cm in the Blanton soil was determined on two separate occasions. On May 30, 2003 the average sample collection rate for was 4.1 mL cm\(^{-2}\) hr\(^{-1}\) with the SMT equal to or greater than 0 kPa. On June 13, 2003, shortly after the water table dropped below 90 cm, the average sample collection rate was 0.4 mL cm\(^{-2}\) hr\(^{-1}\) with the SMT at -4.1 kPa. This agrees well with the leachate collection rates in Table 2, indicating that after 10 months the samplers at 90 cm in the Blanton soil operate with similar efficiency to samplers that have just been installed.

Although there were some sampler failures, the overall sampling procedure was successful in collecting soil water solution suitable for phosphate analysis. Samplers collected greater than 5 mL of soil solution 84% of the time. Membrane filters have promising possibilities for more widespread use in sampling soil water solution, as was found by Driscoll et al. (1985), who successfully employed membrane filters in sampling soil water solution in a shorter field study (5 months). Refinements in sampler design could overcome problems that may have contributed to the complete failure of some of the samplers for the present study.

*Disposable membrane filter units*

Individual testing of the disposable membrane filter units attached to intact soil columns indicated that only one of 80 filter units failed to maintain a vacuum. Upon removal and inspection, this filter unit was found to have been punctured by a root protruding beyond the bottom of the column. The root was trimmed and a new filter placed on the column. There was a 0% failure rate for the remainder of the 15 month collection period. The flow rate for filters following use in the column leaching study was 550 mL cm\(^{-2}\) hr\(^{-1}\), which was not different from the flow rate of new filters (710 mL cm\(^{-2}\) hr\(^{-1}\), p > 0.1), thus indicating that the filters did not clog during the experiment. The lack of clogging compared to the in-situ soil solution samplers (Table 2) may be explained by the reduced disturbance of the soil at the soil-membrane interface.
was minimal disturbance of soil structure at the soil-membrane interface when membrane filter units were attached to the columns. However, installation of the in-situ soil solution samplers resulted in disturbance of 1-2 cm of soil immediately above the sampler.

**Conclusions**

Polyethersulfone membrane filters were successfully employed in sampling soil solution from unsaturated soil in field and laboratory experiments. Unlike conventional ceramic plates, the membranes did not adsorb or desorb P. Because the membranes do not chemically alter the soil solution, they could possibly be used for a wider range of applications than the standard ceramic plates. The membrane pores remained water-filled to -77 kPa SMT in the laboratory and less than -50 kPa SMT in the field, thereby allowing for continuous sampling of the soil solution. Although some membranes did become partially clogged, the flow rate remained higher than would be expected for soil solution flux in unsaturated soils. Experiments testing the longevity of soil water samplers with membrane filters in field applications showed very good success for the first year of sampling, after which 4 of the 24 samplers failed to work. Improvements in sampler design may improve the durability for implementation in field experiments. Disposable filter units worked nearly flawlessly in place of suction plates to maintain unsaturated conditions in intact soil columns. The filter units facilitated easy collection of soil water from the intact soil columns without altering the chemical composition of the percolate.
References


Nalgene Labware, Nalge Nunc International, International Department, 75 Panorama Creek Drive, Rochester, NY 14625. U.S.A.


Water Retention and Hydraulic Conductivity of Autryville and Blanton Soils

(Chapter II)

Methods

Intact soil cores 6 cm tall by 5.5 cm dia. were taken in triplicate at five depths in each pit excavated in the Blanton and Autryville soils (Chapter 2), for a total of 6 cores from each depth and soil. Intact soil cores were first used for determination of hydraulic conductivity, then allowed to air dry prior to determination of water retention. Bulk density was also determined as part of the water retention analysis.

Saturated hydraulic conductivity was determined using the constant head method as described by Klute and Dirksen (1986). Soil cores were slowly saturated from the bottom up over the course of 24 h. A constant head of 4 to 4.2 cm was maintained and the volume of water flowing through the cores during three 0.5 to 2.0 h periods was measured.

Water retention functions were determined with laboratory methods described by Klute (1986). Briefly, soil cores were saturated from the bottom up for a minimum of 48 hours then equilibrated for a minimum of 24 hours at 0, 0.3, 1.0, 2.8, 5.8, 9.8, 19.6, 33.4, and 49.1 kPa of pressure, where the volume of water drained at each pressure was determined. After the last pressure, the soil cores were dried at 105°C for 48 h, weighed, and ground to pass a 2 mm sieve. Ground soils were used to determine soil moisture after equilibration of saturated samples at 500 and 1500 kPa of pressure in a pressure plate apparatus.

Water Retention

Moisture release curves were fit to data using the Brooks and Cory, van Genuchten, and Fayer and Simmons modified van Genuchten equations (Brooks and Corey, 1964; van Genuchten, 1980; Fayer and Simmons, 1995). The Brooks and Corey
and van Genuchten methods were also used to determine unsaturated hydraulic conductivity in relations to soil moisture tension given the saturated hydraulic conductivity and corresponding moisture release curve (Brooks and Corey, 1964; van Genuchten, 1980). The moisture release curves and hydraulic conductivity/soil moisture tension relationships were also determined using the method of Millington and Quirk (data not presented, Millington and Quirk, 1961). Moisture release curves were fit to experimental data with SAS proc nlin (SAS institute, 1998).

**Brooks and Corey**

\[
\begin{align*}
  h > h_b & \quad \theta = \theta_s, \\
  h \leq h_b & \quad \theta = \left(\frac{h_b}{h}\right)^{\lambda} \left(\theta_s - \theta_r\right) + \theta_r, \\
\end{align*}
\]

(1)

where

- \(\theta\) = soil water content (cm\(^3\) cm\(^{-3}\))
- \(\theta_s\) = soil water content at saturation (cm\(^3\) cm\(^{-3}\))
- \(h\) = soil water tension (kPa)
- \(h_b\) = fitting parameter representing the air entry water tension
- \(\lambda\) = fitting parameter
- \(\theta_r\) = fitted parameter representing the residual soil water content

**van Genuchten**

\[
\theta = \left(\left(1 + (\alpha p)^n\right)^{-\left(1 -\left(\frac{1}{n}\right)\right)}\right)\left(\theta_s - \theta_r\right) + \theta_r,
\]

(2)

where

- \(\theta\) and \(\theta_s\) are as previously defined
- \(p\) = soil matrix suction (cm water)
- \(\alpha\) = fitting parameter
- \(n\) = fitting parameter
- \(\theta_r\) = fitted parameter representing the residual soil water content

**Fayer and Simmons**

\[
\begin{align*}
  p > p_c & \quad \theta = \left(1 - \left(\ln\left(p\right)/\ln\left(p_m\right)\right)\right)\theta_s + \left(\theta - \left(1 - \left(\ln\left(p\right)/\ln\left(p_m\right)\right)\right)\theta_s\right)\left(1 + (\alpha p)^n\right)^{(1-n)}, \\
  p \leq p_c & \quad \theta = \theta_s, \\
\end{align*}
\]

(3)

where

- \(\theta\) and \(\theta_s\) are as previously defined
- \(p\) = soil matrix suction (cm water)
- \(\alpha\) = fitting parameter
- \(n\) = fitting parameter
- \(\theta_r\) = fitted parameter
### Table 1. Moisture release parameters for the Brooks and Cory method.

<table>
<thead>
<tr>
<th>soil</th>
<th>Depth (cm)</th>
<th>θₛ (cm cm⁻³)</th>
<th>λ</th>
<th>θᵣ (cm cm⁻³)</th>
<th>hₗ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autryville</td>
<td>8-14</td>
<td>0.36</td>
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</tr>
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<td></td>
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<td>-1.77</td>
</tr>
<tr>
<td>Blanton</td>
<td>8-14</td>
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<td>0.90</td>
<td>0.034</td>
<td>-2.10</td>
</tr>
<tr>
<td></td>
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<td>1.32</td>
<td>0.027</td>
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<td></td>
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<td>1.54</td>
<td>0.034</td>
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<tr>
<td></td>
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<td>0.30</td>
<td>0.53</td>
<td>0.054</td>
<td>-1.69</td>
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</tbody>
</table>

### Table 2. Moisture release parameters for the van Genuchten equation.

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<thead>
<tr>
<th>soil</th>
<th>Depth (cm)</th>
<th>θₛ (cm cm⁻³)</th>
<th>θᵣ (cm cm⁻³)</th>
<th>n</th>
<th>α</th>
</tr>
</thead>
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<tr>
<td>Autryville</td>
<td>8-14</td>
<td>0.35</td>
<td>0.018</td>
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<td>67-73</td>
<td>0.30</td>
<td>0.054</td>
<td>1.53</td>
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<td></td>
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<td>2.25</td>
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<tr>
<td></td>
<td>124-130</td>
<td>0.31</td>
<td>0.047</td>
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<tr>
<td>Blanton</td>
<td>8-14</td>
<td>0.37</td>
<td>0.041</td>
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<tr>
<td></td>
<td>39-45</td>
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<tr>
<td></td>
<td>130-136</td>
<td>0.29</td>
<td>0.057</td>
<td>1.64</td>
<td>0.037</td>
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</table>

### Table 3. Moisture release parameters for the Fayer and Simmons modified van Genuchten equation

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<tr>
<th>soil</th>
<th>Depth (cm)</th>
<th>θₛ (cm cm⁻³)</th>
<th>θᵣ (cm cm⁻³)</th>
<th>n</th>
<th>α</th>
<th>pₘ (cm water)</th>
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</thead>
<tbody>
<tr>
<td>Autryville</td>
<td>8-14</td>
<td>0.34</td>
<td>0.22</td>
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<td>4.03E+04</td>
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<td>39-45</td>
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<td>67-73</td>
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<td>2.42E+05</td>
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<td>4.28E+04</td>
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<td>39-45</td>
<td>0.32</td>
<td>0.11</td>
<td>4.91</td>
<td>0.024</td>
<td>4.17E+04</td>
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<td>0.16</td>
<td>2.27</td>
<td>0.032</td>
<td>3.02E+06</td>
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</table>
Unsaturated Hydraulic Conductivity

*Brooks and Cory*

\[ h > h_b \quad K = K_s, \]
\[ h \leq h_b \quad K = K_s \left( \frac{h_b}{h} \right)^{2+3\lambda}, \]

where

- \( K \) = hydraulic conductivity (cm h\(^{-1} \))
- \( K_s \) = saturated hydraulic conductivity (cm h\(^{-1} \))
- \( h \) = soil water tension (kPa)
- \( h_b \) = fitting parameter representing the air entry water tension
- \( \lambda \) = fitting parameter

*van Genuchten*

\[ K(h) = K_s \left\{ 1 - (\alpha p)^{mn} \left[ 1 + (\alpha p)^n \right]^{-m} \right\} \left[ 1 + (\alpha p)^n \right]^{-ml} \]

where

- \( K(h) \) = hydraulic conductivity (cm h\(^{-1} \))
- \( K_s \) = saturated hydraulic conductivity (cm h\(^{-1} \))
- \( p \) = soil matrix suction (cm water)
- \( \alpha \) = fitting parameter
- \( n \) = fitting parameter
- \( m = (1 - 1/n) \)
- \( l \) = pore connectivity parameter - estimated to be 0.5 for many soils

<table>
<thead>
<tr>
<th>soil</th>
<th>Depth (cm)</th>
<th>( K_s ) (cm h(^{-1} ))</th>
<th>( l )</th>
<th>( m )</th>
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<td>130-136</td>
<td>9.9</td>
<td>0.5</td>
<td>0.39</td>
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</table>
References


**Figure 1.** Relationship between anion exchange extractable P (AEP) and Mehlich extractable P (M3-P) for 80 soil samples taken at 35-45 cm and 80-90 cm deep from Autryville and Blanton soils.

\[
y = 0.4314x \\
R^2 = 0.78
\]

**Figure 2.** Relationship between back-calculated phosphorus sorption coefficient (PSP) and the degree of P saturation (DPS) for 180 soil samples taken at 0 to 140 cm deep from Autryville and Blanton soils.

\[
y = 0.2147\ln(x) - 0.3431 \\
R^2 = 0.93
\]
Empirical Modification

New variables

\[ CAli = (mg kg^{-1}) \] oxalate extractable Al in layer \( i \), user input that remains constant throughout the model run time.

\[ CFe_i = (mg kg^{-1}) \] oxalate extractable Fe in layer \( i \), user input that remains constant throughout the model run time.

\[ CPADSi = (mg kg^{-1}) \] adsorbed P in layer \( i \), to be calculated on a daily time step

\[ DPSi = (%) \] degree of P saturation in layer \( i \), to be calculated on a daily time step.

Calculations

1. Determine \( CPADSi \) in one of two ways
   a. \[ CPADSi = 1000(PMINPi + PLABi)/SOILMSi \]
   b. \[ CPADSi = 0.724[1000(SOILPi + PMINPi + PLABi + SORGPi)/SOILMSi] - 34.5 \]

2. Determine \( DPSi \):

\[ DPSi = 100(CPADSi(1/31))/\left[0.5(CAli(1/27) + CFe_i(1/55.8))\right] \]

3. Determine \( CPKD_i \). Replace existing equation (which is calculated once for the entire model run) \( CPKD_i = 100 + 2.5 CL_i \), with the following equation (which will be re-evaluated for every timestep).

\[ CPKD_i = 339.75\exp(-0.0363DPSi), \]

4. Determine \( (Cav)_p \) and \( CPLABW_1 \), and \( CPLABW_{2...i} \) as the model currently does.

Langmuir Modification

New variables

\[ CPLABMi = (mg kg^{-1}) \] maximum quantity of adsorbed P, user input that remains constant throughout the model run time.

\[ k_{Li} = (L mg^{-1}) \] Langmuir adsorption constant, user input that remains constant throughout the model run time.
Calculations for layer 1

1. Determine labile P in layer 1 after percolation event
   a. Determine $PLAB_{it}$
      $$PLAB_{it} = - \left( \frac{PERC_i}{10} CPLABW_i (\Delta t) - PLAB_{it-1} \right)$$
      do from $t=0$ to $t=1$ for each day, $\Delta t=1/100$, where:
      $$CPLABW_i = (-b_i + (b_i^2 - 4a_i c_i)^{1/2})/(2a_i)$$
      $$a_i = k_{L1} solPOR_{1/10}$$
      $$b_i = CPLABM_{1} k_{L1} (1 - solPOR_{1}(2.65/10)) + solPOR_{1/10} - PLAB_{1} k_{L1}$$
      $$c_i = - PLAB_{1}$$
   b. $PERCLP_{1} = PLAB_{1t0} - PLAB_{1t=1}$
   c. $CLPW_{1} = PERCLP_{1}(10)/PERC_{1}$
   d. $H2OCLP_{1} = (PLAB_{1t0} - PLAB_{1t=1}) (10)/PERC_{1}$

1. Determine labile P mass remaining in layer 1 after leaching (same as GLEAMS)
   $$PLAB_{1} = (PLAB_{1})_0 - PERCLP_{1}$$

2. Subtract $PERCLP_{1}$ from $PLAB_{1}$

3. Determine $ROP$, runoff labile P (kg ha$^{-1}$), – same as GLEAMS
   $$ROP = H2OCLP_{1} (RUNOFF/10)$$

4. Determine SEDLP, sediment associated labile P in runoff (kg ha$^{-1}$)
   $$SEDLP = (SY) (ER) (1e-6) \left[ CPLABM_{k_{L11}} H2OCLP_{1} / (1+k_{L1} H2OCLP_{1}) \right]$$

5. Determine labile P mass remaining in layer 1 after runoff (same as GLEAMS)
   $$PLAB_{1} = (PLAB_{1})_0 - ROLP - SEDLP - PRLPMS_{1}$$

Calculations for layers 2 through i

1. Determine labile P in layer $i$ prior to percolation event
   a. $PLAB_{i} = PLAB_{i} + (PERCLP_{i-1})$

2. Determine labile P in layer $i$ after percolation event
   a. Determine $PLAB_{it}$
      $$PLAB_{it} = - \left( \frac{PERC_i}{10} CPLABW_i (\Delta t) - PLAB_{it-1} \right)$$
      do from $t=0$ to $t=1$ for each day, $\Delta t=1/100$, where:
      $$CPLABW_i = (-b_i + (b_i^2 - 4a_i c_i)^{1/2})/(2a_i)$$
\[ a_i = k_L \frac{SWC_i}{10} \]
\[ b_i = (CPLABM_i k_L (1000/\text{SOILMS}) + SWC_i/10 - PLAB_i k_L) \]
\[ c_i = -PLAB_i \]

b. \( \text{PERCLP}_i = PLAB_{i0} - PLAB_{i1} \)
c. \( \text{CLPW}_i = \text{PERCLP}_i(10)/\text{PERC}_i \)

1. Determine labile P mass remaining in layer \( i \) after leaching (same as GLEAMS)
\[ PLAB_i = (PLAB_i)_0 - \text{PERCLP}_i \]
Lime requirement and acid buffering capacity of the top 15 cm of the Autryville and Blanton soils was determined by developing a titration curve for each soil. The titration curve was developed by adding 10 mL of solution containing various concentrations of acid or base to 10 g of soil. Acid was added as dilute solutions of HCl and base was added as dilute solutions of Ca(OH)$_2$. Acid buffering capacity was determined with one column from each soil and replicated 4 times. Lime requirement was determined using 5 replicates, where each replicate was a different soil column. The titration graph is shown in Figure 1.

![Titration curves for the A horizon of an Autryville and Blanton soil.](image)

**Figure 1.** Titration curves for the A horizon of an Autryville and Blanton soil.
The acidifying effect of alum \( \text{Al}_2(\text{SO}_4)_3\cdot14\text{H}_2\text{O} \) was evaluated in factorial study with 3 rates of alum (0, 0.84, and 1.69 g kg\(^{-1}\)) and 4 rates of lime (0, 1.5, 2.5, and 3.5 cmol base kg\(^{-1}\)) replicated 4 times with each soil. Soils were mixed with treatments at a 1:1 soil solution ratio and shaken over night, after which samples were centrifuged and the pH was determined in supernatants (Figure 2).

![Figure 2. Effect of alum and lime additions on pH in a 24-h equilibration study.](image)

Based on results in Figures 1 and 2, a final experiment was used to determine the effect of the proposed lime and alum amendments on soil pH and water soluble P of the Autryville and Blanton soils. Control, Lime, and Alum+Lime treatments (Table 1) were added 250 g soil samples, the soils were brought to 16% moisture by weight, and soils were incubated for 12 days at room temperature. Samples were periodically mixed and checked for moisture content during the incubation. After incubation, sub samples were removed for determination of pH and water extractable P. Lime and alum treatments
significantly increased the soil pH to an average of 5.4 for the Autryville soil and Blanton limed soil, which is within the expected pH range for pasture soils in NC (Figure 3). The Blanton Alum+Lime was slightly higher than the other alum and lime treatments, however, this range of difference was considered acceptable and treatments were applied to columns.

Table 1. Treatments to determine the effect of alum and lime on soil pH and water extractable P.

<table>
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<tr>
<th></th>
<th>Autryville</th>
<th>Blanton</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alum</td>
<td>Ca(OH)₂</td>
</tr>
<tr>
<td>Control</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Lime</td>
<td>0.0</td>
<td>0.42</td>
</tr>
<tr>
<td>Alum+Lime</td>
<td>1.7</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Figure 3. Effect of alum and lime additions on soil pH for Autryville (A) and Blanton (B) soils (columns with the same letter are not different at \( p = 0.05 \) level).
Although the addition of lime decreased the water extractable P by 20 and 26% in the Autryville and Blanton soils respectively ($p<0.01$), the addition of alum further decreased the water extractable P by 75 and 84% respectively. Therefore, the alum additions are adequate to significantly decrease water extractable P (Figure 4).

**Figure 4.** Effect of alum and lime additions on water extractable P in Autryville (A) and Blanton (B) soils (all means are significantly different $p=0.01$ level).
A Br tracer was added to the soil columns used for the experiment described in Chapter IV to determine if there was any significant preferential flow occurring between the soil columns and the liner walls. Potassium Br (KBr) solution containing 50 mg Br L-1 was added to the soil columns 56 weeks after the first addition of waste (at the beginning of week 9 for period 5). Leachate was collected approximately 1, 2, 3, 5, 7, 14, 28, and 29 days following Br, where regular weekly additions of distilled water continued as normal. Bromide analysis of leachate was performed with Lachat QuickChem method 12-135-21-2-A.

If columns were drained to equilibrium with -25 kPa suction applied to the base, then the Autryville 45 (A45), Blanton 45 (B45), Autryville 90 (A90), and Blanton 90 (B90) soil columns would contain approximately 2.8, 6.5, 4.1, and 8.6 cm of water respectively. Assuming piston flow, a leaching rate of 2.8 cm of water per week would take 2.5, 2, 4.5 and 3.2 weeks for each Br addition to move completely through the soil columns respectively, with first Br detection at 1.5, 1, 3.5, and 2.2 weeks respectively.

The first Br detections occurred in the A45 and B45 soil columns 2 d after Br addition, with peak Br concentrations occurring 21 d after Br addition (Figure 1). The first Br detection in the A90 and B90 soil columns occurred 28 and 21 days after Br addition. Because the experiment was ended 29 days after Br addition, further leachate collection was not possible. Bromide recovery from the A45 and B45 columns was approx. 75 and 85% respectively by 29 d following addition (Figure 2). Bromide recovery from the A90 and B90 soil columns was only 12 and 55% respectively.

Wall flow was considered to be negligible because only minimal amounts of Br were detected prior to when piston flow would have predicted first occurrence of the solute.
Figure 1. Relative Br concentration in leachate from Autryville 45 (A45), Autryville 90 (A90), Blanton 45 (B45), and Blanton 90 (B90) -cm soil columns following Br addition.

Figure 2. Relative Br mass occurring in leachate from the Autryville 45 (A45), Autryville 90 (A90), Blanton 45 (B45), and Blanton 90 (B90) -cm soil columns following Br addition.
Figure 1. Dissolved reactive P (DRP) concentration in leachate from 90-cm Autryville (a) and 90-cm Blanton (b) soil columns receiving various waste and alum treatments.
Figure 2. Change in $P_{ox}$ and $A_{ox}$ from initial values (final-initial). Bars represent ± 1 standard error of the mean and asterisks indicate means are significantly different from 0 at $\alpha = 0.5$ (*), 0.01 (**), and 0.001 (**).
Figure 3. Soil pH in Autryville and Blanton soil columns at 0-3 cm depth after 24 (a) and 48 (b) weeks of leaching (error bars represent ± 1 standard error of the mean).