

ABSTRACT

Title of Thesis: **EVALUATING SOIL PHOSPHORUS DYNAMICS OVER TIME**

Emileigh Rosso Lucas, Master of Science, 2017

Directed by: Professor Frank J. Coale
Department of Environmental Science and Technology

Agricultural nutrient management became mandatory in Maryland (MD) due to water quality concerns. Phosphorus (P) management is complex due to the stability of P in the soil, nutrient mass imbalance, and “legacy” P.

To explore how potential P application bans impact historically manured fields, agronomic and environmental soil tests were conducted on plots treated with five manure-P rates, then no P applications, spanning 15 years. Mehlich-3 extractable P (M3P) declined slowly and then generally did not change during the last six years. Phosphorus saturation declined slowly or not significantly. Excessive P soils had sufficient P for crop growth in solution.

Phosphorus saturation and M3P were compared in fifty sites across MD pre- and post- nutrient management planning. Results showed an increase in P concentration of Maryland agricultural fields. This response was logical, as better management would increase below-optimum P concentrations, and the regulations were not designed to draw down P.

EVALUATING SOIL PHOSPHORUS DYNAMICS OVER TIME

BY

EMILEIGH ROSSO LUCAS

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Advisory Committee:

Professor Frank Coale, Chair
Dr. Robert Kratochvil
Dr. Patricia Steinhilber

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LIST OF ABBREVIATIONS

Al- Aluminum
AmOx- Ammonium oxalate extraction
ASTP- Agronomic soil test phosphorus
BMP- Best management practice
Ca- Calcium
CMREC- Central Maryland Research and Education Center
DPS_{ox}: Degree of phosphorus saturation using ammonium oxalate extractable aluminum, iron, and phosphorus to calculate
K- Potassium
LESREC- Lower Eastern Shore Research and Education Center
Fe- Iron
FIV-P- Fertility index value phosphorus
M1P- Mehlich-1 extractable phosphorus
M3Al- Mehlich-3 extractable aluminum
M3Fe- Mehlich-3 extractable iron
M3P- Mehlich-3 extractable phosphorus
M3PSR- Phosphorus saturation ratio using Mehlich-3 extractable aluminum, iron, and phosphorus to calculate
MD- Maryland
Mg- Magnesium
MT- Manure treatment
N- Nitrogen
OM- Organic matter
OxAl- Ammonium oxalate extractable aluminum
OxFe- Ammonium oxalate extractable iron
OxP- Ammonium oxalate extractable phosphorus
P- Phosphorus
PSI- Phosphorus site index
WEP- Water extractable phosphorus
WREC- Wye Research and Education Center
WQIA- Water Quality Improvement Act

Chapter 1: Introduction

Overview

Agricultural nutrient management became mandatory in Maryland due to water quality concerns from agricultural nitrogen (N) and phosphorus (P) inputs. Management of P can be complex due to the stability of P in the soil and the effects of “legacy” P (i.e. P in the soil from historic applications, which continues to contribute to environmental P losses). Also, a nutrient mass imbalance exists due to the animal and human population concentration in the area, where more nutrients are coming in to feed these populations from commercially fertilized crops, but nutrient-rich manure is not easily transported back to the areas where the food was grown.

Due to this imbalance, many fields across the state became saturated with P while farmers continued to apply manure as part of their management practices, even when soil test P concentrations were already excessive, in order to avoid the costs of transporting manure and to benefit from the N and other nutrients it contains.

Elevated soil P may have also been a result of application of commercial P, exceeding crop uptake, to high value crops when agronomic soil test P (ASTP) was already optimum. In this scenario, farmers wanted assurance that the P supply from soil was adequate so that yield and quality of their crops were not compromised.

When ASTP was excessive, yet farmers desired to apply more P on their fields in Maryland, a mandatory P-risk analysis tool was used to predict the potential environmental impact. The results of this risk assessment could have prevented or allowed further P application.

Several research questions arose from these observations of agricultural nutrient management planning in Maryland:

- In scenarios where farms have a history of manure application, but have to stop applying manure for regulatory or other reasons, how does the P change in the soil under a standard cropping rotation for the Mid-Atlantic (if all other plant-required nutrients are provided with commercial fertilizers)?
- How available is the P in the soil to plants when no inputs of P have been made for an extended period of time?
- How have farms across the state of Maryland changed in terms of P status between voluntary and mandatory nutrient management planning?

Objectives

The objectives of these studies are:

- To explore the effects of five manure P treatment rates, followed by cessation of P applications for 15 years and continued crop removal, on ammonium oxalate-P (OxP), Mehlich-3-P (M3P), water extractable-P (WEP), and the degree of P saturation (DPS) at four sampling dates across the 15 years.
- To investigate the changes in M3P, OxP, DPS, and WEP using data from 50 fields across the state of Maryland sampled prior to nutrient management planning (1994) and after mandatory nutrient management was enforced for ten years (2012)

Rationale

More investigation is required to understand the effect of crop removal on P drawdown after various rates of P-loading. Also, little is known about how nutrient management planning changed soil P status across Maryland. Data on this subject would help clarify the impact of the policies in place.

Chapter 2: Long-term Drawdown of Soil Phosphorus after Manure Phosphorus Loading in Fields with Typical Mid-Atlantic Crop Rotation

Emileigh Rosso Lucas

Abstract

Rationale: A timeframe for phosphorus (P) drawdown from soils historically treated with manure at different rates, under standard cropping scenarios, is necessary due to political and environmental drivers in areas where agricultural nutrient contributions to surface water are regulated.

Objectives: This study was conducted to observe changes in soil P concentration and the degree of P saturation following a build-up of P from manure sources, when no further P applications were made, in mid-Atlantic soils at points in time across a fifteen year timeframe from the final manure application.

Methods: Soil P was measured using Mehlich-3 (M3P), Ammonium oxalate (OxP), and water extractable P (WEP) methods. The degree of P saturation was calculated using ammonium oxalate (DPS_{ox}), as well as Mehlich-3 (M3PSR), extracted concentrations of P, iron (Fe), and aluminum (Al). The study was conducted at three University of Maryland research farms that have the following soil classifications: a Mattapex silt loam (fine-silty, mixed, active, mesic Aquic Hapludults) and a Nassawango silt loam (fine-silty, mixed, semiactive, mesic Typic Hapludults), which had both been treated with broiler litter, and a Donlonton fine sandy loam (fine-loamy, glauconitic, mesic Aquic Hapludults), which had been treated with dairy manure. Manure was applied at five treatment rates annually from 1994 to 1997, and this study examined the soils in 2001, 2004, 2006, and 2012.

Results: The effects of the manure treatments were clearly visible in all of the analyses across all years of the study. The M3P concentrations significantly declined for all treatments from 2001 to 2012, with only a few exceptions. The effects of the manure treatments were still present in 2012, as the soil concentrations for these treatments were in the same respective order, and were significantly different from each other in most cases, with some convergence occurring between adjacent treatments. The highest manure treatment resulted in M3P concentrations of greater than 200 mg kg^{-1} at all sites after 15 years of no further P application. Little to no significant decrease was observed in M3P, DPS_{ox} , M3PSR, or WEP from 2006 to 2012 at all sites.

Conclusion: Mehlich-3 P and the P saturation (DPS_{ox} and M3PSR alike) exhibited little to no decline, posing challenges for animal producers who have high-P fields from historic manure application, but still need to manage animal waste under P application restrictions. The data suggest there is sufficient available P in solution to sustain crop growth in scenarios where M3P is in the range where P application may be limited by a Phosphorus Site Index (PSI) or similar tool.

Introduction

Phosphorus (P) nutrient pollution to surface water has drawn global attention in recent years; particularly that from non-point agricultural sources. While P is an essential nutrient for plant growth, when applied to fields in excess, erosion occurs due to environmental conditions or certain management practices, or extreme weather events occur, P may be transported off-field and may enter surface water through various channels. If P is limiting for algal growth in a water body, small increases in the concentration of dissolved P in the water can cause rapid algal growth in a process called eutrophication. When this algal growth, and subsequent decomposition, deprives the water of oxygen and creates poor conditions for submerged aquatic vegetation, therefore creating an uninhabitable environment for many species (Boynton, 2000). The Chesapeake Bay Foundation estimated that roughly 50% of the non-point P pollution to the Chesapeake Bay comes from agricultural sources (Chesapeake Bay Foundation, 2012). The Water Quality Improvement Act (WQIA) was passed by the Maryland General Assembly in 1998. This act was passed in response to research indicating the poor state of the health of the Bay and catalyzed by the presumed association between nutrient pollution and *Pfiesteria* outbreaks in the Chesapeake Bay watershed (Sims and Coale, 2002). The WQIA required mandatory nutrient management planning, based on both nitrogen (N) and P, which had previously only been voluntary.

Nutrient management for P from agricultural sources is challenging for several reasons. Water quality response to changes in P management in agriculture could be slow, even with reductions in agronomic soil test P (ASTP) in the field (Hamilton, 2012; Sharpley et al. 2013), due to the presence of “legacy P.” Legacy P contributions to

surface water were described by Kleinman et al. (2011) as P that originated from historic P applications and desorbed from soils or sediments to water. Historically manure was applied at a rate to satisfy the N requirements of plants, leading to an over-application and accumulation of P, which can continue to contribute to P in the soil solution over time. Additionally, best management practices (BMP's) designed to trap particulate P and keep it from entering watersheds can act as a source of P under certain conditions (Kleinman et al., 2011). Areas designated to "trap" P, often implemented as best management practices on farms (e.g. buffer strips), may act as a large source for legacy P, despite management changes that reduce P inputs. Stutter et al. (2009) sampled field soils and adjacent vegetated buffer strip soils in the Tarland catchment in Scotland. They determined through laboratory incubation and leaching experiments that vegetated buffer strips possess characteristics that encourage biological and geochemical processes that convert soil P to readily leachable forms. They speculated that changes in management of these buffer strips, such as regular removal of vegetation, may reduce the potential of excess P build-up and leaching. Also, due to the chemical nature of P, elevated ASTP concentrations may persist for long periods of time, as some pools of soil P remain tightly bound with iron (Fe), aluminum (Al), calcium (Ca), and organic matter.

Tools to evaluate individual fields for environmental P risk were developed, due to the concern that ASTP alone is not always the best indicator of environmental quality. The source component (i.e. soil P or P in soil amendments) is only part of the risk; transport of P is also required in order to impair water quality. Different P transport pathways exist based on site characteristics and the environment. Transport can occur through erosion of P bound to soil particles, dissolved P in surface runoff, and dissolved

P in subsurface flow (Sharpley et al., 2001). Using this concept, P indices have been developed in different regions to evaluate the risk of P loss to surface water (Coale et al., 2002; Lemunyon and Gilbert, 1993). Coale et al. (2002) described the site and transport characteristics in the Maryland PSI to be soil erosion, soil runoff class, subsurface drainage, leaching potential, distance from edge of field to surface water, and priority of receiving water. Management and source characteristics were defined as soil test P, P fertilizer application rate and method, and organic P application rate and method.

As encompassed in the “site and transport” portion of the PSI, agricultural soils have varying qualities that may impact P retention or losses to the environment. A characteristic with great impact is soil texture, which can affect the ability of the soils to adsorb P, and can also affect the major loss pathways of P. A review of studies in northwestern Europe by Chardon and Schoumans (2007) described that sandy soils primarily lose P via subsurface pathways after excessive build-up of P, while clay soils tend to lose P incidentally due to surface erosion and preferential flow. Finer textured soils (i.e. soils with high clay content) also tend to have a greater capacity to adsorb or fix P, and can do so for many years due to the natural chemical properties in their composition (e.g. the Fe and Al content). Leytem et al. (2004) confirmed with incubation studies that high variability in P sorption properties between different soil textures and classifications exists.

The amount and form of P applied are considered “management and source” characteristics, and differences in these may cause variability in the P retention capacity of the soil. Variability can be attributed to organic matter content and other differing chemical characteristics between P sources. Shafqat and Piersynski (2013) examined

applications of P from manure from three species of monogastric animals, two ruminant animal species, and triple super phosphate fertilizer, each applied at 0, 50, and 150 mg P kg⁻¹ in six different Kansas soils. They grew corn (*Zea mays*) for seven years following the aforementioned treatments to observe P drawdown. They found that both the soil and the manure type influenced the drawdown rate, and ruminant manure treatments experienced faster drawdown than turkey litter treatments. Nichols et al. (1994) examined differences in total P concentration in runoff between poultry litter and commercial fertilizer applied at the same P application rate using simulated rainfall on tall fescue (*Festuca arundinacea* Schreber) pasture on Captina silt loam soils in Arkansas. They found total P in runoff was significantly less for the poultry litter application compared to the commercial fertilizer treatment. A review by Hart et al. (2004) summarized numerous studies that found differences in P losses to the environment due to fertilizer type, including between commercial P sources of varying solubility, in addition to examples of the variability between manure and inorganic P sources. This review also detailed how other management practices, such as the crop system, may impact P losses.

Using typical crop rotations in the Mid-Atlantic region with crop removal, a study by Kratochvil et al. (2006) showed that ASTP remained relatively constant with no additional P applications. Kratochvil et al. (2006) observed differences between forage crops (corn silage, rye haylage, and alfalfa) and grain crops (corn grain, wheat grain, and double-crop soybeans) in P removal and uptake from Maryland soils. They observed that forage crops, when harvested, were able to remove P at faster rates than grain crops, but neither cropping system had proven to significantly reduce ASTP from “high” ASTP fields to the “optimum” concentration in the three year study.

McCollum (1991), in an early study on P stability and drawdown on a Typic Umprabuult in North Carolina, noted that P-deficiency symptoms in crops were not observed for many years. They sampled 0 to 15 cm depth after crop establishment each year, so that soil mixing of the previous year's banded P applications was accomplished by routine tillage, and performed Mehlich-1 extractable P (M1P) analysis. In the first eight years of the study, which they deemed the "active phase," they found that any treatment receiving fertilizer additions of $\geq 5 \text{ g m}^{-3} \text{ P}$, including the block with the lowest initial soil test P of 22 g P m^{-3} , maintained sufficient P for corn and soybeans (*Glycine max*). In the second phase, after cessation of P applications, no differences between treatments could be observed in crop yields for many plots for more than 12 years. McCollum (1991) suggested that the timeline and results for their study might not be transferrable to other studies because of different soil, climate, and management factors. Zhang et al. (2004) conducted a study on a clay soil in the Canadian province of Quebec and found that a 4.2 kg P ha^{-1} removal by corn was required for each 1 kg P ha^{-1} reduction of M3P in the soil. They also observed an equilibrium in M3P, where with small amounts of additional fertilizer P, the M3P did not change (Zhang et al., 2004).

Multiple studies have suggested that evaluating soil P saturation is a method to more accurately determining the risk of P loss from the soil. Researchers in the Netherlands initially developed this concept, using the ammonium oxalate (AmOx) extraction to relate the molar concentration of P to the molar concentration of Fe and Al in the soil (Breeuwsma et al., 1995). Maguire and Sims (2002) later found that the Mehlich-3 extraction could be used on Mid-Atlantic soils to determine the Phosphorus Saturation Ratio (M3PSR) with information found on typical agronomic soil tests. A

laboratory incubation study using soils treated with broiler litter demonstrated a stronger positive relationship between water soluble P, a measure of P that could easily be lost to surface water, and the M3PSR, than the relationship that existed between water soluble P and the standard M3P agronomic soil analysis (Leytem and Sims 2005; Kleinman et al. 2000). Using a sampling of ten non-calcareous soils, Vadas et al. (2005) determined that P sorption saturation would likely be the best indicator of potential release of dissolved P from the soil to runoff. They observed that filterable reactive P rapidly increased at P sorption saturation values greater than 12.5%.

A component of the larger P nutrient pollution issue is the nutrient mass imbalance in the Mid-Atlantic region. Concentrated animal feeding operations, as well as the large human population in the region, are cause for a steady flow of nutrients into the area. Due to the limited amount of land to grow animal feed in comparison to the animal numbers in the region, affordability of commercial fertilizer sources, and the large scale production of commodity crops in areas such as the Midwest of the U.S., it became impractical for animal producers in areas such as the Chesapeake Bay watershed of the Mid-Atlantic U.S. to grow their entire feed supply. Many operations were considered “no land,” which meant they had poultry houses but no crop land, and needed to import 100 percent of their feed. The industry found that importing feed was less expensive and more practical, thus also importing nutrients to the region (Beegle, 2013).

A thorough understanding of the timeline of P drawdown in Maryland is important because environmental organizations and regulatory agencies are pushing for greater enforcement of nutrients lost from agricultural systems, focusing on ASTP in some instances (Copeland, 2010). Scientific knowledge of timelines in P drawdown from

soils treated with manure at different rates, under standard cropping scenarios, is necessary due to political and environmental drivers.

Materials and Methods

This study used soils collected and archived from research plots used for previous studies: a P-loading study, a corn starter fertilizer study, and a P-phytoremediation study. Kratochvil et al. (2006) described the initial study, a P-loading study, which was established at five sites in 1994. Soil samples for this study were from three of those sites, which were located on University of Maryland Research and Education Center farms near Poplar Hill (LESREC), Upper Marlboro (CMREC), and Wye Mills (WREC), MD. Descriptions of each location, soil classification, and P source can be found in Table 2.1.

Plot history and design

For the P-loading study, Kratochvil et al. (2006) established five P loading treatments at each site using a randomized complete block design. They applied manure at an equivalent total P rate of 0, 100, 200, 300, or 400 kg ha⁻¹ yr⁻¹. Initially, they replicated treatments in eight blocks at each site. Bovine dairy manure provided the P source at CMREC, while broiler litter was applied at LESREC and WREC. The same manure treatment rates were applied annually for four years, ending in 1997, accumulating a total P load of 0, 400, 800, 1,200, or 1,600 kg ha⁻¹ respectively. Hereinafter, the manure treatments will be referred to as MT-0, MT-400, MT-800, MT-1200, and MT-1600. During the build-up years (1994 to 1997), continuous grain corn was grown in all plots, without additional fertilizer beyond the manure. In 1998 the plots were left dormant (no crops or fertilizer) and then in 1999 a starter fertilizer study was

initiated using these plots. In 1999 and 2000 a banded fertilizer application ($28 \text{ kg ha}^{-1} \text{ P}_2\text{O}_5$) was made 5 cm below the surface and 5 cm adjacent to the corn row. Half of the plots received starter P treatments in 1999 and the other half of the plots received the same starter P treatment in 2000. Following the starter fertilizer study, Kratochvil et al. (2006) initiated a phytoremediation study in 2001 using the original P loading plots to evaluate soil P depletion over time. Since all plots received the same amount of P in the starter fertilizer study they resolved that the only residual differences between plots would be from the manure P treatment rates in the P loading study. The phytoremediation study imposed either a forage cropping system or a grain cropping system over the original P loading plots using a split-plot design. The forage cropping system rotated corn silage, rye (*Secale cereal* L.) haylage, and alfalfa (*Medicago sativa* L.). The grain cropping system consisted of wheat (*Triticum aestivum* L.), double-crop soybeans [*Glycine max* (L.) Merr.], and corn (Table 2.2).

Soil Analysis

Agronomic soil samples (20 cm depth) were collected annually from 2001 to 2004, and then every other year until 2012. Kratochvil et al. (2006) archived soil samples from 2001, 2004, and 2006, and we collected and archived soil samples in 2012 from the same plots. In order to confirm soil texture indicated by the soil survey (Table 2.1), a soil sample was randomly selected from a single plot in each rep for particle size analysis using a hydrometer method (Gee and Bauder, 1986). The analyses described in the following section (Table 2.3) were conducted on samples from all plots in the select years (2001, 2004, 2006, and 2012) at the three sites.

Mehlich-3

Mehlich-3 extractable P (M3P), Fe (M3Fe), and Al (M3Al) concentrations were determined on each soil sample (Mehlich, 1984). In brief, 2.50 g of soil was combined with 25 mL M3 extracting solution (0.2 N CH₃COOH + 0.25 N NH₄NO₃ + 0.015 N NH₄F + 0.013 N HNO₃ + 0.001 M EDTA) in a 100 mL snap-cap vial. The soil-solution mixture was agitated for 5 min using a reciprocating shaker with a stroke length of 4 cm set at 180 oscillations min⁻¹. Immediately upon removal from the shaker, samples were filtered through Whatman #41 filters, with the solution collected in 30 mL tubes. Each sample was analyzed within a few days at the University of Delaware on an inductively coupled plasma mass spectrometer (ICP-MS) (*Thermo Elemental: Intrepid II XSP Duo View*).

Ammonium Oxalate

Soils were analyzed for OxP, OxFe, and OxAl concentrations on an Inductively Coupled Plasma (ICP) machine (*Thermo Elemental: Intrepid II XSP Duo View*). In 50 mL screw-top centrifuge tubes, 1.000 g of soil was combined with 40 mL of 0.2 M solution of ammonium oxalate and oxalic acid extracting solution. The trays of tubes and the repipette were wrapped in aluminum foil to minimize light exposure and lights were kept off in the lab during analysis. Samples were shaken horizontally on a reciprocating shaker for two hours on low speed. The samples were then centrifuged at 2000 rpms for 15 minutes, and then filtered through Whatman #42 filter papers (Iyengar et al. 1981; McKeague et al. 1966; Pote et al. 1996). Finally, the samples were diluted 1:10 with distilled, deionized water, and submitted to the University of Delaware Soil Testing Lab where they were analyzed within two days of extraction.

Degree of Phosphorus Saturation

Studies have shown a strong relationship between M3PSR and DPS_{ox} (Nair et al. 2004; Maguire and Sims, 2002). These were calculated as follows (Nair et al. 2004; Schoumans 2000; Maguire and Sims, 2002; Breeuwsma et al. 1995):

$$DPS_{ox} = [(OxP)/\alpha(OxFe+OxAl)]$$

$$M3PSR = [(M3P)/(M3-Fe+M3-Al)]$$

A standard α of 0.5 (Breeuwsma et al. 1995) was used in this data analysis for DPS_{ox} calculation.

WEP

To determine water extractable P (WEP), 2.00 g soil was weighed and combined with 20 mL distilled, deionized water in 50 mL centrifuge tubes. These tubes were shaken for one hour horizontally on a reciprocating shaker on low speed. The tubes were centrifuged for 15 minutes at 2000 rpms, then vacuum-filtered through 0.45 μ m filters (Luscombe et al. 1979; Self-Davis et al. 2000). The orthophosphate concentration was analyzed colorimetrically on a Lachat within 24 hours of extraction.

Statistical Analysis

Statistical analyses were conducted to test for interactions between categorical variables of manure treatment ID, location, cropping system, and year. In these analyses, the replicate was treated as a random effect, and then a mixed model ANOVA with the adjustment for Tukey's test was used to test for significant differences by manure treatment level and by year for each of the dependent variables (Proc Mixed, SAS version 9.3, SAS Institute, Inc. [SAS Institute, 2011]). Each location was analyzed as a separate

study, due to interactions in treatment and crop system by location. Cropping systems had to be analyzed separately for all of the dependent variables at CMREC because significant interactions existed in crop system by treatment. The LESREC and WREC locations did not show a significant crop system interaction with treatment, so the crop systems were combined in the analyses. The points of time observed were 2001, 2004, 2006, and 2012 for each location.

Results

Mehlich-3 P (M3P)

At the LESREC location, the M3P for each manure treatment was significantly different from each other, and in the order of manure application rate, in each of the years observed (Fig. 2.2a). MT-1600 measured consistently higher in M3P than MT-1200, while MT-1200 was consistently higher than MT-800, and so on. MT-1200 did not significantly decrease between 2006 and 2012, but all other treatments demonstrated significant decrease in M3P during this timeframe. All treatments showed a significant decline over the course of this study from 2001 to 2012, though a smaller decline in M3P concentration occurred from 2006 to 2012 than from 2001 to 2006. From 2001 to 2006, treatments had 22.8 to 32.4 % decline from the 2001 concentration, while from 2006 to 2012 the treatments declined just 11.4 to 20.2% more, thus showing a decrease in the rate of decline over time.

The results at the WREC location were similar to those of LESREC (Figure 2.2b). All of the manure treatments maintained significantly different M3P concentrations from each other in 2012, except for MT-0 and MT-400, which were also not significantly different from each other in 2001 and 2006. In 2006, MT-400 and MT-800 were not

different from each other, nor were MT-1200 and MT-1600. The manure application treatment corresponded with the order of M3P concentration in each year. All manure treatments resulted in a significant decline in M3P from 2001 to 2012, but the decline from 2006 to 2012 once again took place at a slower rate than that from 2001 to 2006. In this case, a 17.1 to 38.6% decline in the M3P concentration occurred from 2001 to 2006, and a 6.3 to 31.6 % decline from 2006 to 2012.

The CMREC site exhibited greater variation than the other sites. In addition, an interaction existed between cropping system and manure treatment rate at CMREC. Therefore, manure treatment effect was analyzed separately for the grain and forage cropping systems. In the forage cropping system, soil M3P concentrations remained in order from lowest to highest relative to manure treatment rate for all years sampled; however, soil M3P concentrations were not statistically different between manure MT-0 and MT-400 or between MT-800 and MT-1200 (Figure 2.2c). MT-1600, the lowest two manure treatments (MT-0 and MT-400), and the middle two manure treatments (MT-800 and MT-1200) were significantly different from each other each year analyzed.

In the CMREC grain cropping system, MT-0 and MT-400 exhibited statistically similar soil M3P concentrations to each other in 2001 and 2012 (Fig. 2.2d). The same occurred with manure treatments MT-400 and MT-800. Also, MT-1200 and MT-1600 were not significantly different from each other in any of the years analyzed. Again, soil M3P concentrations remained in order from lowest to highest for MT-0 to MT-1600, respectively. All manure treatments significantly decreased between 2001 and 2012 for the CMREC forage cropping system except MT-0. In contrast, only MT-0 and MT-400

decreased from 2001 to 2012 for the grain crop system at CMREC, while MT-800, MT-1200, and MT-1600 did not significantly change between these years.

Mehlich-3 Phosphorus Saturation Ratio (M3PSR)

LESREC data demonstrated that all manure treatment levels had significantly different M3PSR values from each other in every year that was observed in this study (Fig. 2.3a). Manure treatment M3PSR coordinated with the manure treatment rates, with the highest P rate having the highest M3PSR through the duration of the study. The M3PSR remained fairly stable, with no significant decline between 2001 and 2006 for all manure treatments except MT-400, which declined by 1.3% from 2001 to 2006. MT-0, MT-400, and MT-800 significantly declined from 2006 to 2012, while MT-1200 and MT-1600 did not. From 2001 to 2012, all treatments except MT-1200 significantly decreased in M3PSR. A noticeable increase in M3PSR occurred between 2004 and 2006, which may be attributed to lime application.

The WREC location treatments followed a similar pattern to LESREC, with the M3PSR for all manure treatments remaining in the same order as the initial manure application rate, for each time point measured in this study (Fig. 2.3b). In 2001, MT-0 and MT-400, MT-400 and MT-800, and MT-800 and MT-1200 were not significantly different from each other, but in 2004 all treatments were significantly different from each other. Data for M3PSR in 2006 show all treatments as significantly different from each other except for MT-400 and MT-800, and MT-1200 and MT-1600. In 2012, all treatments had significantly different M3PSR from each other, with the exception of MT-0 and MT-400. For MT-800 and MT-1200, no significant change in M3PSR was observed between 2001 and 2012, but a significant decline was observed for MT-0, MT-

800, and MT-1600. No significant change was observed for any of the treatments, except MT-1600 from 2001 to 2006, and MT-400 from 2006 to 2012. A small raise, or a reduced rate of decline, of M3PSR seems to occur in 2006 across all treatments.

CMREC forage cropping system plots followed a similar trend to the other locations, with the M3PSR results following the order of the initial manure application rates (Fig. 2.3c). The figures remained in that order for all of the years observed in this study. All treatments were significantly different from each other in M3PSR, with the exception of MT-0 and MT-400 in all years of the study, MT-800 and MT-1200 in all years of the study, MT-400 and MT-800 plus MT-1200 and MT-1600 in 2001, and MT-1200 and MT-1600 in 2006. All treatments except for MT-0 significantly declined from 2001 to 2012. If observed in smaller time increments, from 2001 to 2006, only MT-400 and MT-1200 declined significantly. From 2006 to 2012, only MT-400 declined significantly. The overall decrease in M3PSR across treatments ranged from 2.1% to 13.1% and corresponded with the treatment levels, with the smallest decline coming from MT-0 and the largest from MT-1600.

For the grain blocks at CMREC, MT-1200 and MT-1600 were not significantly different from each other in M3PSR for any of the years of the study (Fig. 2.3d). MT-0 and MT-400 along with MT-400 and MT-800 were also not significantly different from each other in 2001 and 2006. Otherwise all treatments had significantly different M3PSR values in all years. The average M3PSR of all treatments remained in the order of the initial P application rate in all years of the study. MT-0 and MT-400 were the only treatments that significantly declined in M3PSR from 2001 to 2012, and only MT-0 significantly declined during the second half of that time range, from 2006 to 2012.

Ammonium Oxalate Degree of Phosphorus Saturation

At LESREC, MT-0, MT-400, and MT-800 did not have significantly different DPS_{ox} from each other in 2001, 2006, and 2012 (Fig. 2.4a). During those same years, MT-800 and MT-1200 were not different, and MT-1200 and MT-1600 were not different from each other. None of the manure treatments at LESREC increased or decreased significantly between the years examined in this study, with the exception of MT-800 between 2004 and 2012.

The WREC location exhibited slightly different results (Fig. 2.4b), with MT-400, MT-800, MT-1200, and MT-1600 converging by 2012, where they were not significantly different from each other. MT-0 was also not significantly different from MT-400 and MT-800 in 2012; however, MT-0 remained different from treatments MT-1200 and MT-1600 in terms of DPS_{ox} . MT-1200 and MT-1600 were not significantly different from each other in any of the years of this study. Convergence also occurred between the MT-0 and MT-400, MT-400 and MT-800, MT-800 and MT-1200, and MT-1200 and MT-1600 in 2001 and 2006. MT-0, MT-800, and MT-1600 significantly declined between 2001 and 2012, while MT-400 and MT-1200 did not. None of the treatments except MT-0 significantly declined from 2006 to 2012.

At the CMREC location, again variation was noticeably greater than at the other sites. The forage crop rotation manure treatments had significantly different DPS_{ox} from each other in 2012, with the exception of MT-0 & MT-400 and MT-800 & MT-1200 (Fig. 2.4c). Variation occurred from year to year in whether treatments were significantly different from each other, seemingly without pattern. In 2006, none of the manure treatments were significantly different from each other except MT-0 & MT-1600 and

MT-400 & MT-1600. For all treatments except MT-0, a significant decline in DPS_{ox} was observed between 2001 and 2012. None of the treatments, except MT-400, significantly declined from the latter half of that time range from 2006 to 2012.

The grain crop system at CMREC exhibited no difference between MT-400, MT-800, MT-1200, and MT-1600 in 2001 (Fig. 2.4d). MT-0 differed from all other treatments except MT-400 that year. By 2012, MT-0 and MT-400 were still converged, along with MT-400 and MT-800, but MT-400 became significantly less than MT-1200 and MT-1600. Similarly, MT-800 and MT-1200 had converged, and MT-1200 and MT-1600 had converged, but MT-800 was different than MT-1600 in 2012. MT-1200 and MT-1600 were not different in any of the years examined. MT-0 and MT-400 exhibited a significant decrease in DPS_{ox} between 2001 and 2012, while the other manure treatments did not. From 2006 to 2012, only MT-0 showed a decline.

Water Extractable Phosphorus (WEP)

LESREC WEP data revealed all treatments to be significantly different from one another in all years of the study, with the exception of MT-0 and MT-400 in 2004, 2006, and 2012, and MT-400 and 200 in 2006 (Fig. 2.5a). Treatments maintained the order of the initial P application rate in the WEP results. While all treatments significantly declined in WEP from 2001 to 2012 overall, none of the treatments showed significant reduction from 2006 to 2012 in WEP within that timeframe. All treatments had significantly declined from 2001 to 2006, thus indicating that WEP plateaued after that timeframe.

The WREC location WEP data demonstrated similar results, in that most treatments remained significantly different from each other and WEP concentrations for

all treatments followed the order of initial P application rate (Fig. 2.5b). MT-0 and MT-400 were not significantly different from each other in any of the years of this study. In 2001, MT-800 and MT-1200 did not significantly differ, and in 2006 MT-400 and MT-800 as well as MT-1200 and MT-1600 did not significantly differ. In 2012, MT-400 and MT-800 were also not significantly different. All treatment significantly declined in WEP from 2001 to 2012, though from 2001 to 2006, only MT-800 and MT-1600 significantly decreased, and from 2006 to 2012, MT-400 alone declined.

CMREC forage cropping system plots (Fig. 2.5c) followed the same general trend in manure treatment WEP; however, MT-0 and MT-400, and MT-800 and MT-1200 were not significantly different from each other in WEP for any of the years of the study. Additionally, MT-400 and MT-800 were not significantly different in 2001 and 2006, and MT-1200 and MT-1600 were not significantly different in 2001, 2006, and 2012. In this case, all treatments showed a significant decline from 2001 to 2006, but none declined significantly from 2006 to 2012.

The grain cropping system at CMREC (Fig. 2.5d) showed that the WEP for MT-1200 and MT-1600 was not significantly different in any of the years of the study. MT-0 and MT-400 were only different in 2001. MT-400 and MT-800 were not significantly different from each other in 2006 or 2012, and MT-800 and MT-1200 were not different in 2012. Again, all treatments showed a significant decline from 2001 to 2006, but none declined significantly from 2006 to 2012.

Discussion

Mehlich-3 P

Fifteen years without P application in any form resulted in distinct differences between all manure treatments in terms of M3P concentration. At the LESREC location, no convergence of manure treatments was observed, indicating that the M3P of the different treatments is decreasing in parallel over time. Manure applications could have changed the capability of the soil to retain P.

Karathanasis and Shumaker (2009) found that organic sources of P were sorbed at higher quantities and were retained with more energy than inorganic forms in their study on six soil clays containing hydroxy-interlayered vermiculite, two soil clays containing hydroxy-interlayered smectite, a reference gibbsite, and a reference goethite. No significant differences were noted on any of the soils examined for organic P desorption before and after an oxalate treatment, which indicated the organic P (inositol hexakisphosphate) was tightly bound to the Al- or Fe-hydroxy components in each soil. The organic P applied through the manure-P applications for this study likely behaved similarly due to the presence of Al and Fe in the soil, creating persistent differences due to the initial manure-P treatment rates after 15 years without additional P inputs.

Other characteristics of manure, such as calcium content, may have influenced the persistence of the manure rate treatment effect. Solid poultry manure without litter had an average Ca content of 40 to 45 g kg⁻¹ (4-4.5%), while general livestock manure contained 5 to 20 g kg⁻¹ (0.5-2%) on a dry matter basis in a summary of agriculturally applied beneficial by-products (Baker et al., 2000). Solid poultry manure with litter had an average Ca content of 1.77% from data including 1101 samples, according to a Manure

Summary Report by the University of Maryland Agricultural Nutrient Management Program (2003), while liquid cattle (*Bos taurus*) manure had an average of just 0.13% from 1000 samples in the same report. The Parsons et al. (2007) study of liquid dairy manure on soils in Atlantic Canada on corn, wheat, and soybean crop rotations showed over-application of Ca beyond crop demand with total P application rates of only 22 and 29 kg ha⁻¹, though yields were lower than possible for the region. With the combined manure-P application rates of 0, 400, 800, 1200, and 1600 kg ha⁻¹ in this study, Ca is very likely applied beyond crop requirements as well. Bovine dairy manure was applied to the CMREC location in this case. Excess calcium in the soil can react with P to form insoluble mineral compounds. This could contribute the manure treatment effects remaining visible in M3P in 2012 across all sites despite no further P additions for the past 15 years; the Ca-P is very stable, and more Ca would have been applied with higher manure treatment rates.

This highlights some reasons why an agronomic soil test such as M3P alone is not always the best indicator of P losses, despite a good relationship between agronomic and environmental soil tests under certain conditions (Andraski and Bundy, 2003). The decreasing rate of decline in M3P across all treatments and locations, in general, may indicate that even though M3P is elevated due to historic applications, losses of P from fields to surface water may lessen over time, though WEP provides a better measure of this.

In Maryland, ASTP is converted to the fertility index value P (FIV-P) (Coale and McGrath, 2006), a scale that allows nutrient concentrations of P, potassium (K), Ca, and magnesium (Mg) from multiple soil testing laboratories to be compared. A value of 0 to

50 indicates some degree of crop yield response to addition of P is likely, while a value over 50 indicates little to no likelihood of crop yield response to P fertilization (Coale, 2010). Only the control treatment, MT-0, was below 50 FIV-P in 2012 and would have an anticipated yield response to P fertilizer addition according to this scale.

If soil in a field measures FIV-P greater than 150, a nutrient management consultant (Code of Maryland, 2016) must use the PSI to determine if P additions are permissible on the field in question. In 2001 all of the manure treatments, aside from the control plots, at all locations and crop systems had FIV-P over 150 (Table 2.4), the level at which producers in Maryland have to run a PSI if they plan to apply P fertilizer. In 2012, MT-1200 and MT-1600 remained above the 150 FIV threshold at LESREC, WREC, and the CMREC forage cropping system, while MT-800, MT-1200, and MT-1600 were over 150 at the CMREC grain cropping system.

Mehlich-3 Phosphorus Saturation Ratio

In most cases, the M3PSR remained different between all manure treatments, and most manure treatments showed little to no significant decline in M3PSR between 2006 and 2012. At the LESREC site, all treatments remained different from each other across the duration of this study. At the other two locations, when treatments converged, they were adjacent treatments. These observations indicate that the soil at the three locations was affected for the long term by the manure treatments, and the manure applications must have caused a lasting change in the soil to allow it to hold more P, likely by adding OM, Ca, and Fe. At LESREC an overall significant decline in M3PSR occurred between 2001 and 2012 for all manure treatments except MT-1200. The WREC location only showed decline in MT-0, MT-800, and MT-1600 during the same period. CMREC

differed in results based on the crop system. The forage cropping system showed a decline in M3PSR for all manure treatments except MT-1200; however, the grain system only showed a decline in MT-0 and MT-400 from 2001 to 2012.

The decline in M3PSR seems to have occurred at a somewhat even rate across all manure treatments. The overall declines in M3PSR have been fairly small over a 15 year period. LESREC values declined from 1.6 to 4.4%, WREC values declined 3.9 to 8.9%, Forage cropping system at CMREC declined 2.2 to 13.1%, and grain cropping system at CMREC declined 2.1 to 6.4%

It is important to note that manure and any other P application was discontinued after 1997, and the first soil sample in this study was from 2001, so some reduction had likely already taken place.

Other studies in the Atlantic Coastal Plain region determined that sandy loam and sandy clay loam soils have a large capacity to sorb P (Mozaffari and Sims, 1994); however, in an incubation study on these soils, poultry litter applications decreased the P sorption capacity at three out of four sites when applied at 18 and 36 Mg ha⁻¹ (~8 and 16 tons per acre) (Mozaffari and Sims, 1996). Environmental implications of the fact that the initial manure treatments were still reflected in the M3PSR, even 15 years after application, are that the saturation of the soils by the P that was applied in manure rates likely bound to stable forms of P and reduce the amount of additional P that can be held. More of the sorption sites are filled due to this historic application. Producers with animal agriculture operations could end up with soils that remain saturated at high degrees for years after discontinuing manure application or applying at a P limiting rate.

Ammonium Oxalate Degree of Phosphorus Saturation

At all three study locations, little to no significant decline in DPS_{ox} was observed from 2006 to 2012; however, variation was observed by location as to whether the treatments declined significantly from the earliest point of this study, 2001, to 2012. An interesting difference is observed between the LESREC and WREC locations; both of these received broiler litter and are silt loam soils, yet LESREC exhibited little to no change in the DPS_{ox} between any of the years of the study, while MT-0, MT-800, and MT-1600 all significantly declined from 2001 to 2012 at the WREC location. At CMREC, where a sandy loam soil received dairy manure, the forage cropping system had significant declines in all but MT-0 for DPS_{ox} from 2001 to 2012, while the grain cropping system only had significant declines in MT-0 and MT-400. The degree that the treatments converged also seemed to vary between the study locations.

The locations were in different geographic locations and experienced variability in environmental conditions, which is why they were analyzed as separate studies. Varying crop yields and weather likely contributed to these differences in DPS_{ox} due to these factors impacting the rate of P removal.

Though well correlated in other studies (Nair et al., 2004), DPS_{ox} results were somewhat different than M3PSR results in the LESREC and the CMREC forage cropping system studies. LESREC did not change from 2001 to 2012 for DPS_{ox} , but did significantly decline for M3PSR. The CMREC forage cropping system study significantly declined in all but manure MT-0 for DPS_{ox} , but showed a significant decline in all but MT-1200 for M3PSR.

None of the study locations exhibited a significant decline in DPS_{ox} from 2006 to 2012, which is consistent with M3PSR results. This indicates that once the soil has been saturated to a certain degree, crop removal has little impact. Phosphorus sorption isotherms could help explain this observation by providing information on the maximum P sorption capacity of the soil, known as the S_{max} , using the Langmuir equation (Bolster and Hornberger, 2007). If the S_{max} were compared between manure treatments, researchers would be able to understand how manure applications affected the P sorption capacity of these soils and could relate this to the P saturation. Few studies exist that observe the changes in P saturation in scenarios where P has not been applied for many years after an initial build-up from manure sources.

Water Extractable Phosphorus

Across all of the studies, WEP showed decline in only a few comparisons from 2006 to 2012. Uniformly, the first date that WEP was examined was four years after the last manure application. Because of this, the period when the largest portion of WEP would have been expected was not a part of this study. Laboratory studies have shown WEP leaving the soil rapidly following fertilizer P additions for two weeks post-application, and then the P concentration in the top 1 cm correlates with the P sorption capacity of the soil (Sharpley 1982).

The importance of these data lies in the observation of long-term changes in WEP caused by historic manure applications. Sharpley et al. (2004) observed that long-term additions of manure change the P chemistry of the surface soil (0-5cm). In their study, it was observed that inorganic P comprised a larger percentage of the total P in manure-treated soils than soils treated with commercial fertilizer. Also, a shift was observed in P

form from Al- and Fe- complexes to Ca- mineral forms. This could lead to overestimation of the amount of soluble P and the environmental impact if the risk is based solely on M3P soil tests for these manured soils. While this result was for a more shallow section of soil compared to the 20 cm agronomic sample that was collected for this study, it offers another explanation for the plateaued WEP compared to the still relatively high M3P. Several other studies (Pote et al., 2006; Wang et al., 2010) noted that WEP in the soil was highly correlated to dissolved reactive P in runoff, and was therefore a good indicator of environmental risk.

CMREC generally had higher WEP concentrations, though this observation is not based on statistical comparison to other locations. This could have to do with differences in soil texture; CMREC has a sandy loam soil, while the other two locations have silty loam soils. Alternatively, this may be due to manure type. Poultry litter, which was applied to the LESREC and WREC locations, is higher in Ca than dairy manure, which was applied to the CMREC location (Table 2.1). Higher Ca in soils tends to hold P in less soluble forms.

Water extractable P has been described as an acceptable measure of readily available P for many crops. Loneragen and Asher (1967) found plant species in their study, including flatweed, barrel medic, capeweed, bromegrass, lupins, erodium, clover, and silver grass (only common names included in article), generally needed $\sim 0.16 \mu\text{g mL}^{-1}$ P in solution to sustain growth, though some plant species needed up to $0.77 \mu\text{g mL}^{-1}$. Clover, for example, peaked in P consumption at $0.16 \mu\text{g mL}^{-1}$ and decreased consumption at the $0.77 \mu\text{g mL}^{-1}$ rate. Later, Luscomb et al. (1979) observed this on grassland soils. Fox (1981) found that corn required 0.05 mg kg^{-1} P in solution for 95% of

maximum yield potential on one Hawaiian soil (Hali), while it required 0.06 mg kg⁻¹ P in solution on another Hawaiian soil (Wahiawa). Soybeans required 0.2 mg kg⁻¹ P in solution when grown in both of these Hawaiian soils to achieve 95% yield potential. Blume et al. (2010), as described by Wuenscher et al. (2015), found that soil P in solution should be between 0.3 and 0.8 µg mL⁻¹ for ideal crop yields.

If 0.3 µg mL⁻¹ P in solution is used as a minimum for adequate crop growth, 2012 WEP concentrations for all sites and crop treatments indicate that plots that received MT-800, MT-1200, and MT-1600 all have sufficient P in solution for crop growth (Table 2.4). At the CMREC site with the grain cropping system, MT-400 also falls above this threshold. If the lower 0.16 µg mL⁻¹ is used as the minimum requirement, WREC MT-400 and CMREC forage crop system MT-400 are added to this list. According to an overview of P-fertilizer recommendations across Europe (Jordan-Meille et al. 2012) the Netherlands and Switzerland use WEP as a standard soil test. The amount of P that is considered “Medium” in Switzerland for wheat on a loamy soil with a pH of 6.5 is 2-3 mg kg⁻¹, while in the Netherlands, the same scenario would consider 11 to 20 mg P₂O₅ L⁻¹ “medium.” According to Swiss parameters, at LESREC and WREC locations, MT-800, MT-1200, and MT-1600 would all still have adequate WEP in 2012, while manure treatments MT-400, MT-800, MT-1200, and MT-1600 would have adequate WEP for CMREC forage and grain cropping systems. The Netherlands result is difficult to compare because the method was done on a volume basis and the density of the soil is unknown.

Conclusions

The results of this study confirmed that M3P exhibits a slow decline despite ceasing further P applications after historic manure application. The data do not allow for predictions of the rate of P loss into the future; however, these results should be considered as law makers consider observing ASTP as a means of evaluating success of regulations on producers who have fields with historic manure application. In this study, fields receiving the highest two manure treatment rates remained greater than the 150 FIV-P threshold for limitations on P application in Maryland, 15 years after cessation of P application. Additionally, P saturation remained fairly constant, posing concerns for further application of P to sites with historic manure application. This could present challenges to producers with animal operations in finding solutions to handle their animal waste in an environmentally friendly way without incurring a significant expense.

Producers have expressed concern that despite high ASTP, the P may be held in forms that are not available to crops because there has been a significant amount of time since readily available P sources have been added to the soil. The results of WEP in relation to M3P indicate that there is sufficient P in solution for many crop species when M3P is in the range where P applications may be limited by the PSI or other tools. Further research has been done on these plots; change in M3P and crop removal of P over a 15 year period were summarized by Fiorellino et al. (2017). In addition to this research, exploration of the impact of the manure treatments on P adsorption isotherms would provide insight about the long term changes in the ability of the soil to hold P based on historic manure treatments.

Figures and Tables

Table 2.1. Descriptions of the soils and P source for the three research locations (adapted from Kratochvil et al., 2006)

Site	Location	Map Unit	Soil Classification	P source
Lower Eastern Shore Research and Education Center (LESREC)	38°37' N, 76°44' W	Mattapex silt loam	Fine-silty, mixed, active, mesic Aquic Hapludults	Broiler Litter
Wye Research and Education Center (WREC)	38°59' N, 76°09' W	Nassawango silt loam	Fine-silty, mixed, semiactive, mesic Typic Hapludults	Broiler Litter
Central Maryland Research and Education Center (CMREC)	38°49' N, 76°45' W	Donlonton fine sandy loam	Fine-loamy, glauconitic, mesic Aquic Hapludults	Dairy Manure

Year	CMREC		LESREC		WREC	
	Forage	Grain	Forage	Grain	Forage	Grain
2001	Corn Silage	Wheat/ Double Crop Soybeans	Rye haylage; corn silage	Corn	Wheat (grain); alfalfa planted after wheat harvest	Corn
2002	Rye haylage; corn silage	Corn	Rye haylage; corn silage	Wheat/ Double Crop Soybeans	Alfalfa	Wheat/ Double Crop Soybeans
2003	Rye haylage; corn silage	Wheat/ Double Crop Soybeans	Rye haylage; corn silage	Corn	Alfalfa	Corn
2004	Rye haylage; corn silage	Corn	Rye haylage; corn silage	Wheat/ Double Crop Soybeans	Alfalfa (one cutting); corn silage	Wheat/ Double Crop Soybeans
2005	Alfalfa	Wheat/ Double Crop Soybeans	Rye haylage; corn silage	Corn	Rye haylage; corn silage	Corn
2006	Alfalfa	Corn	Rye haylage; corn silage	Wheat/ Double Crop Soybeans	Rye haylage; corn silage	Wheat/ Double Crop Soybeans
2007	Alfalfa	Wheat/ Double Crop Soybeans	Rye haylage; corn silage	Corn	Rye haylage; corn silage	Corn
2008	Alfalfa (one cutting); corn silage	Wheat/ Double Crop Soybeans	Rye haylage; corn silage	Wheat/ Double Crop Soybeans	Alfalfa	Wheat/ Double Crop Soybeans
2009	Rye haylage; corn silage	Corn	Rye haylage; corn silage	Corn	Alfalfa	Corn
2010	Rye haylage; corn silage	Wheat/ Double Crop Soybeans	Rye haylage; corn silage	Wheat/ Double Crop Soybeans	Alfalfa	Wheat/ Double Crop Soybeans
2011	Rye haylage; Alfalfa (two cuttings)	Corn	Rye haylage; corn silage	Corn	Alfalfa (one cutting); corn silage	Corn
2012	Alfalfa	Wheat/ Double Crop Soybeans	Rye haylage; corn silage	Wheat/ Double Crop Soybeans	Rye haylage; corn silage	Wheat/ Double Crop Soybeans
2013	Alfalfa	Corn	Rye haylage; corn silage	Corn	Rye haylage; corn silage	Corn

Table 2.3: Description of analyses used in this study that measure extractable phosphorus (P) in the soil, with the P fractions that are extracted by each analysis derived from McCray et al. (2012) and Wuenscher et al. (2015)

Soil P Analysis Method	Agronomic or Environmental	Fractions of Phosphorus contained
Mehlich-3 (Mehlich, 1984)	Agronomic	Labile P, Fe-Al-bound P, humic-fulvic-bound P, Ca-Mg-bound P
Ammonium Oxalate (Iyengar et al. 1981; McKeague et al. 1966; Pote et al. 1996)	Agronomic	Labile P, Fe-Al-bound P, humic-fulvic-bound P, Ca-Mg-bound P, residual P
Water (Luscombe et al. 1979; Self-Davis et al. 2000)	Environmental	Labile P (little contribution from other fractions)

Table 2.4: Mean concentration of P, Fe, and Al (mg kg⁻¹) from the analyses used in this study for the Lower Eastern Shore Research and Education Center (LESREC), The Wye Research and Education Center (WREC), and the Central Maryland Research and Education Center (CMREC)

Manure treatment	Water Extractable P		Mehlich-3 P		Mehlich-3 Al		Mehlich-3 Fe		Ammonium Oxalate P		Ammonium Oxalate Al		Ammonium Oxalate Fe	
	2001	2012	2001	2012	2001	2012	2001	2012	2001	2012	2001	2012	2001	2012
Total P (mg kg⁻¹)														
LESREC														
0	1.16	0.25	73.76	36.62	1137.91	813.30	108.69	54.60	253.22	222.18	2074.8	1710.6	955.56	888.90
400	4.14	1.02	146.10	69.10	1132.19	819.51	112.13	60.35	350.97	216.33	2360.7	1288.7	982.90	833.50
800	8.96	3.07	233.22	125.00	1136.89	834.57	126.76	69.41	508.26	285.30	2549.0	1797.1	1052.51	805.67
1200	15.63	6.19	299.61	196.02	1124.41	847.09	133.82	80.27	626.32	411.49	2456.0	1602.7	980.05	826.54
1600	20.62	9.23	368.38	237.91	1148.85	860.04	144.50	87.37	772.96	461.93	2181.1	1577.2	1035.83	889.23
WREC														
0	3.88	0.69	120.66	51.70	935.15	698.49	143.20	79.69	307.63	149.64	1330.0	887.4	988.86	883.25
400	5.57	1.81	165.34	84.90	964.59	717.76	148.79	90.01	371.02	243.76	1392.6	945.3	988.89	902.19
800	12.57	4.11	255.31	127.13	966.94	707.85	167.25	96.05	510.53	264.93	1482.2	868.0	1026.89	1027.21
1200	16.09	7.69	285.29	177.83	950.36	712.58	170.30	109.47	535.08	431.79	1388.6	1101.9	976.45	1122.96
1600	24.15	10.43	413.55	227.58	976.13	739.24	189.53	118.10	714.18	363.64	1392.8	887.1	1004.53	1074.30
CMREC														
Forage														
0	3.92	1.92	115.20	59.92	681.03	450.86	434.78	244.62	397.16	238.27	956.8	584.2	2563.77	1706.61
400	8.39	2.77	182.81	78.42	655.69	519.03	503.56	258.69	361.53	300.75	907.8	715.7	2086.48	1886.48
800	17.27	6.12	277.14	137.55	623.17	445.29	555.55	362.60	505.60	408.96	687.6	592.3	1865.32	1756.02
1200	22.86	7.64	337.08	167.12	688.13	525.16	506.28	345.14	602.17	555.13	865.9	788.5	2262.48	2178.81
1600	32.31	10.13	415.28	211.36	597.97	462.49	603.10	423.15	821.18	607.14	723.0	622.8	2224.89	1997.91
Grain														
0	2.82	0.81	86.47	39.56	709.62	482.23	418.18	193.79	318.32	194.58	989.3	662.2	2520.10	1793.23
400	10.61	4.33	188.4	102.45	658.64	479.72	462.89	344.21	491.45	317.21	842.2	580.64	2334.93	1861.16
800	19.74	8.70	270.15	164.12	609.88	462.08	518.23	353.30	620.37	477.53	833.5	650.4	2310.85	1901.13
1200	34.09	13.94	415.85	241.62	619.63	428.34	579.25	408.25	813.41	592.02	821.6	617.4	2336.45	1911.83
1600	39.74	15.85	453.9	256.72	608.26	388.59	606.23	416.72	900.88	711.14	949.9	642	2586.00	2097.44

Treatments: LESREC					Cropping	System:	Replicate
1	2	3	5	4	← Grain		I
3	1	2	4	5	← Forage		
4	5	1	3	2	← Forage		II
3	2	4	1	5	← Grain		
1	2	5	3	4	← Grain		III
5	4	2	3	1	← Forage		
4	1	2	3	5	← Forage		IV
4	5	3	2	1	← Grain		

Treatments: WREC					Cropping	System:	Replicate
4	5	1	3	2	← Forage		I
1	3	2	5	4	← Grain		
5	3	2	1	4	← Grain		II
2	3	5	4	1	← Forage		
3	2	1	5	4	← Grain		III
1	5	4	2	3	← Forage		
1	3	4	2	5	← Grain		IV
5	4	2	1	3	← Forage		

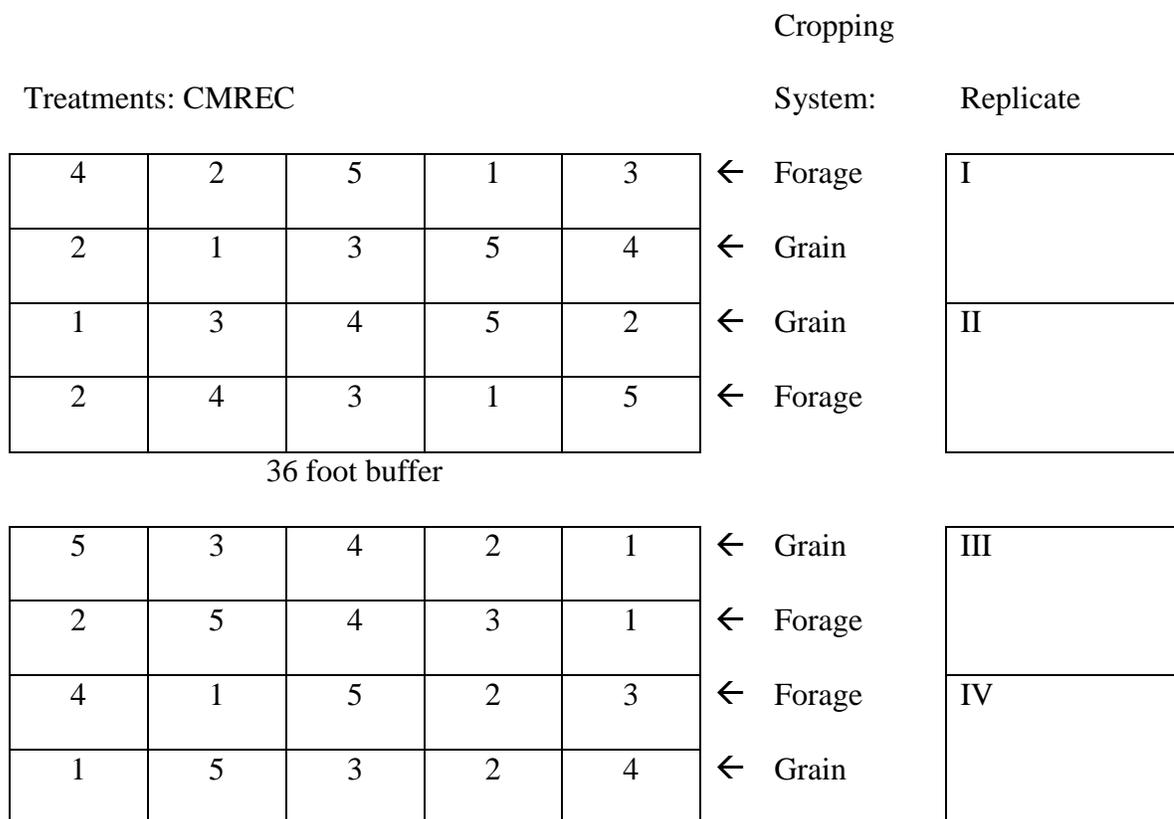


Figure 2.1: Experimental design at the three research sites. The Arabic numerals in the boxes on the left side describe the manure treatment for each plot, where 1 is 0, 2 is 100, 3 is 200, 4 is 300 and 5 is 400 kg total P ha⁻¹ y⁻¹. The cropping system was assigned in rows, as labeled using arrows. The replicate designations at each location are shown using roman numerals in the boxes on the right, but apply to the plots on the left of the diagram.

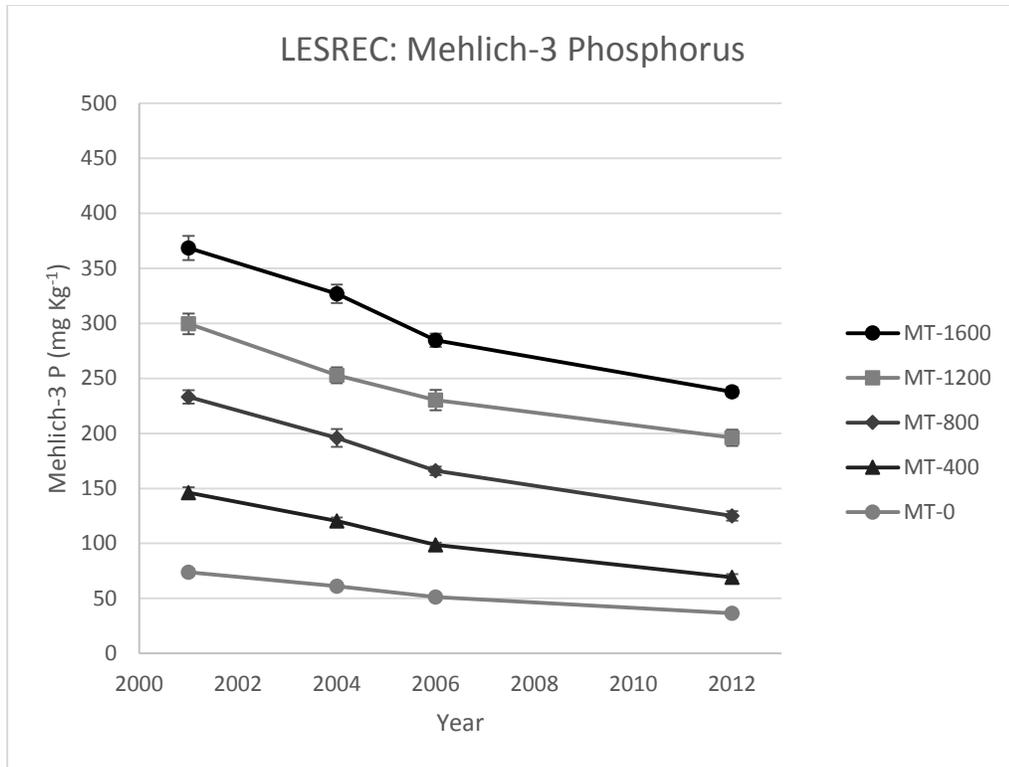


Figure 2.2a: Average Mehlich-3 phosphorus in soils by treatment and by year at LESREC. Standard error is demonstrated with error bars. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

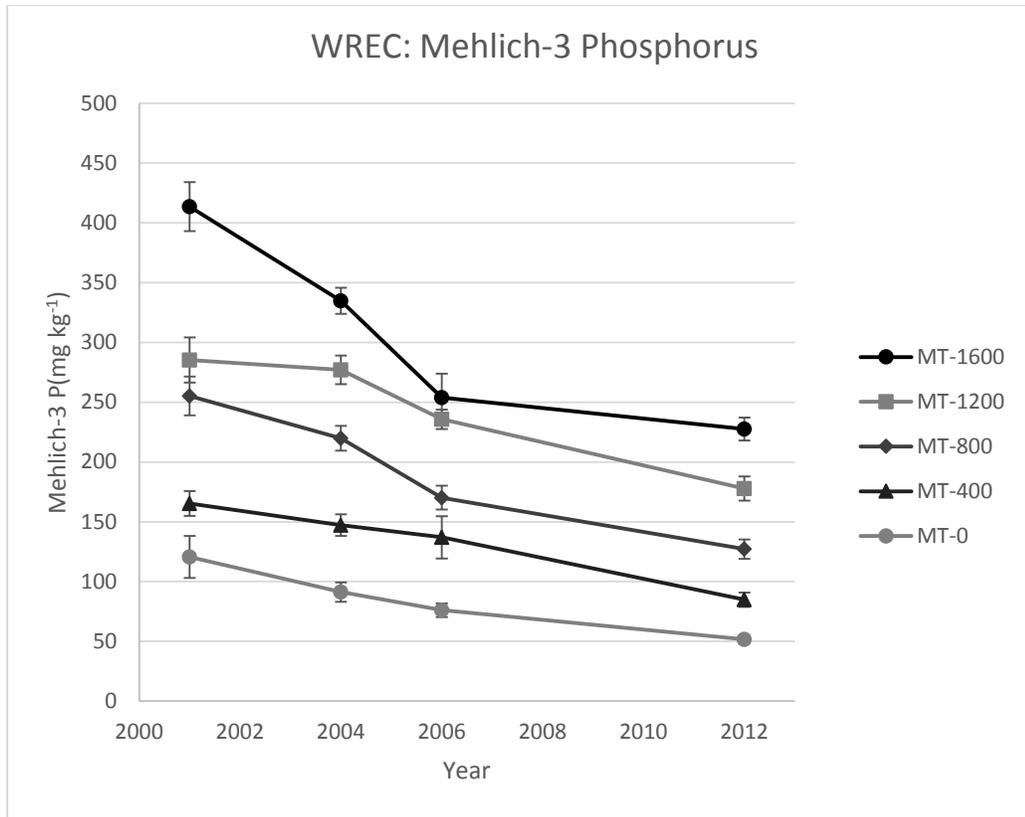


Figure 2.2b: Average Mehlich-3 phosphorus in soils by treatment and by year at WREC. Standard error is demonstrated with error bars. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

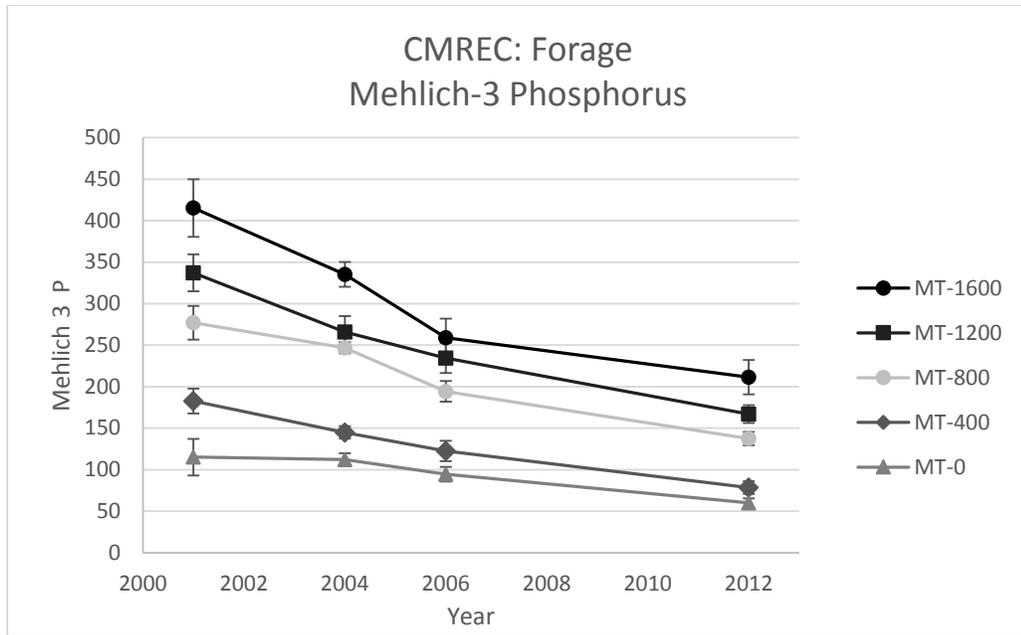


Figure 2.2c: Average Mehlich-3 phosphorus in soils by treatment and by year at CMREC for the forage cropping system. Standard error is demonstrated with error bars. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

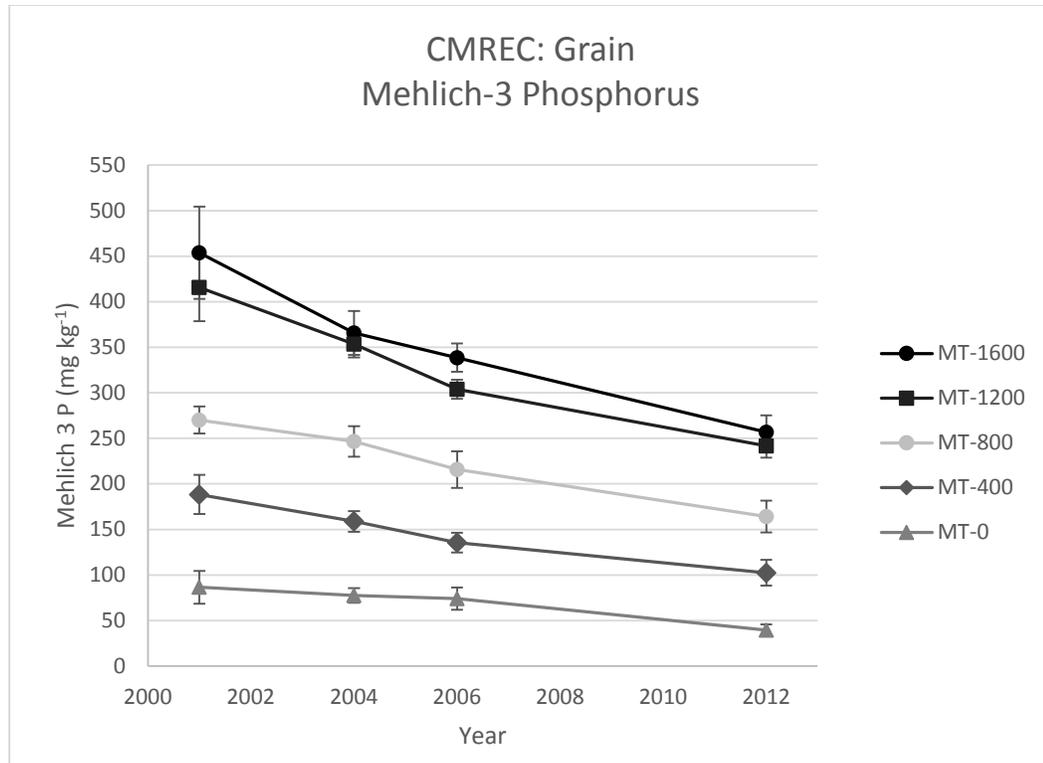


Figure 2.2d: Average Mehlich-3 phosphorus in soils by treatment and by year at CMREC for the grain cropping system. Standard error is demonstrated with error bars. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

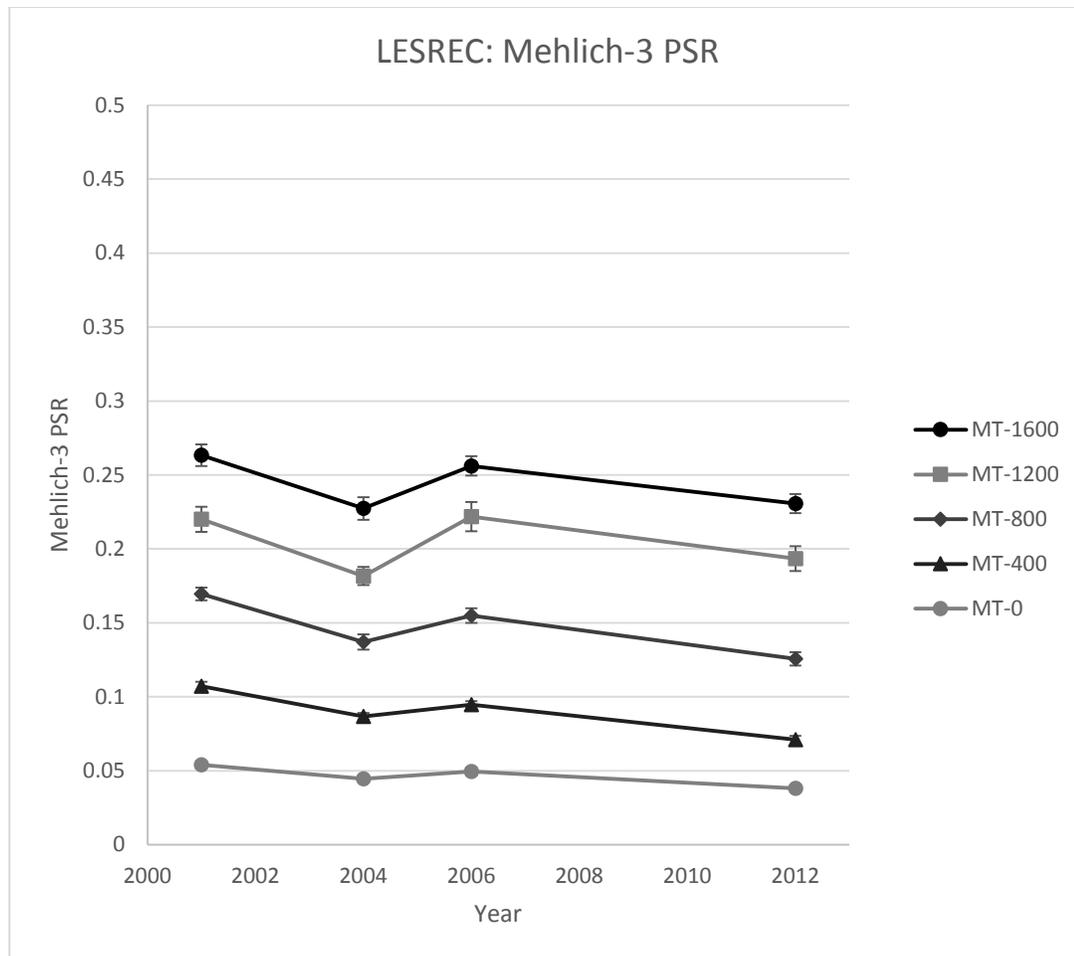


Figure 2.3a: Average Mehlich-3 phosphorus saturation ratio (M3PSR) by treatment and by year at LESREC. Standard error is demonstrated with error bars. $M3PSR = [(M3P)/(M3-Fe + M3-Al)]$, where M3P is the molar concentration of P, M3-Fe is the molar concentration of iron, and M3-Al is the molar concentration of aluminum extracted using Mehlich-3. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

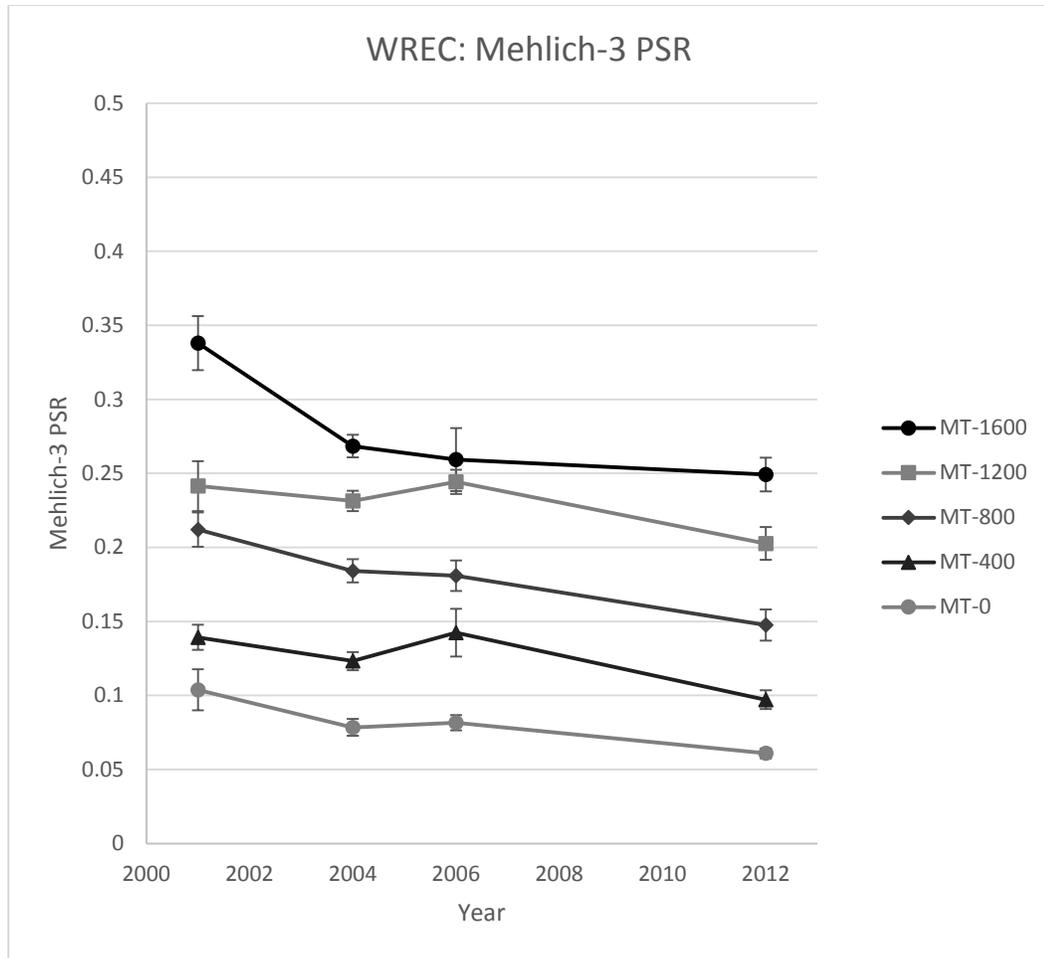


Figure 2.3b: Average Mehlich-3 phosphorus saturation ratio (M3PSR) by treatment and by year at WREC. Standard error is demonstrated with error bars. $M3PSR = [(M3P)/(M3-Fe+M3-Al)]$, where M3P is the molar concentration of P, M3-Fe is the molar concentration of iron, and M3-Al is the molar concentration of aluminum extracted using Mehlich-3. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

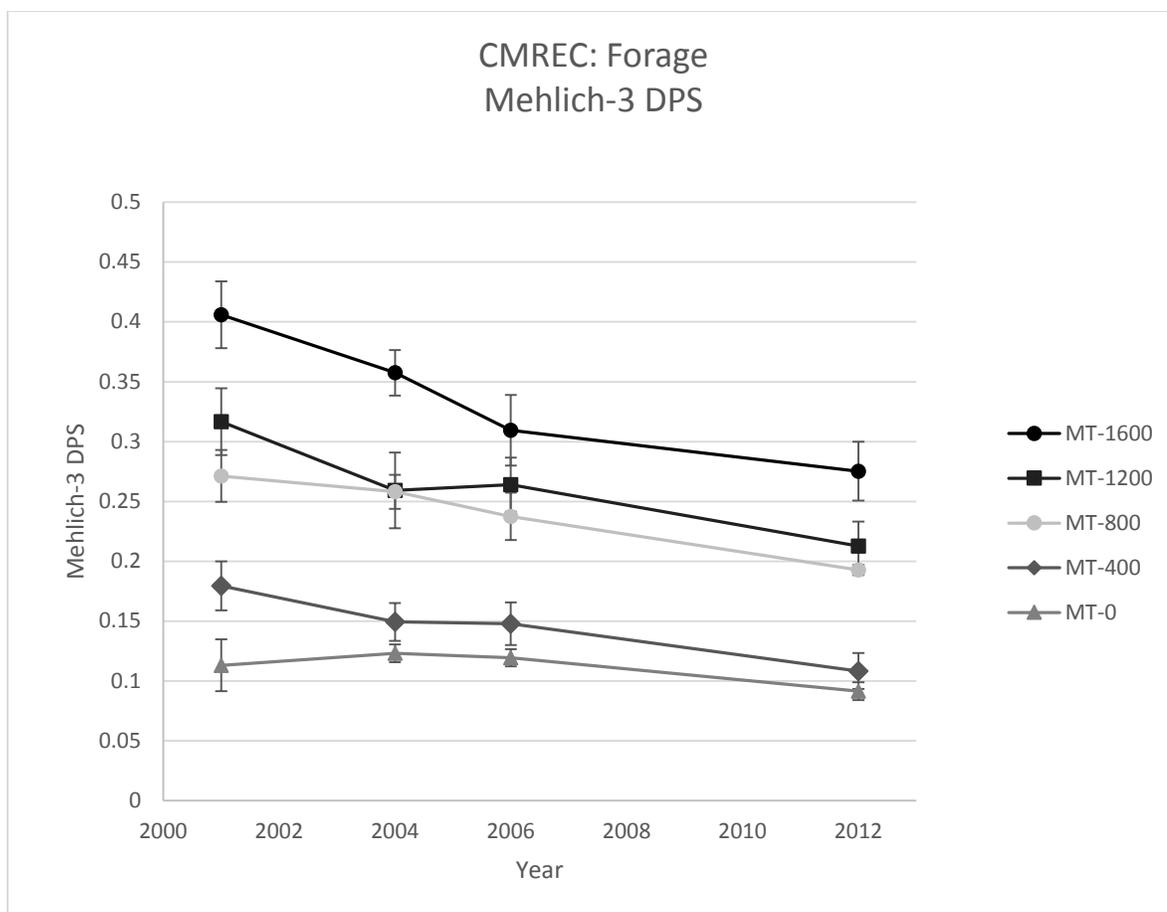


Figure 2.3c: Average Mehlich-3 phosphorus saturation ratio (M3PSR) by treatment and by year at CMREC for the forage cropping system. Standard error is demonstrated with error bars. $M3PSR = [(M3P)/(M3-Fe+M3-Al)]$, where M3P is the molar concentration of P, M3-Fe is the molar concentration of iron, and M3-Al is the molar concentration of aluminum extracted using Mehlich-3. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

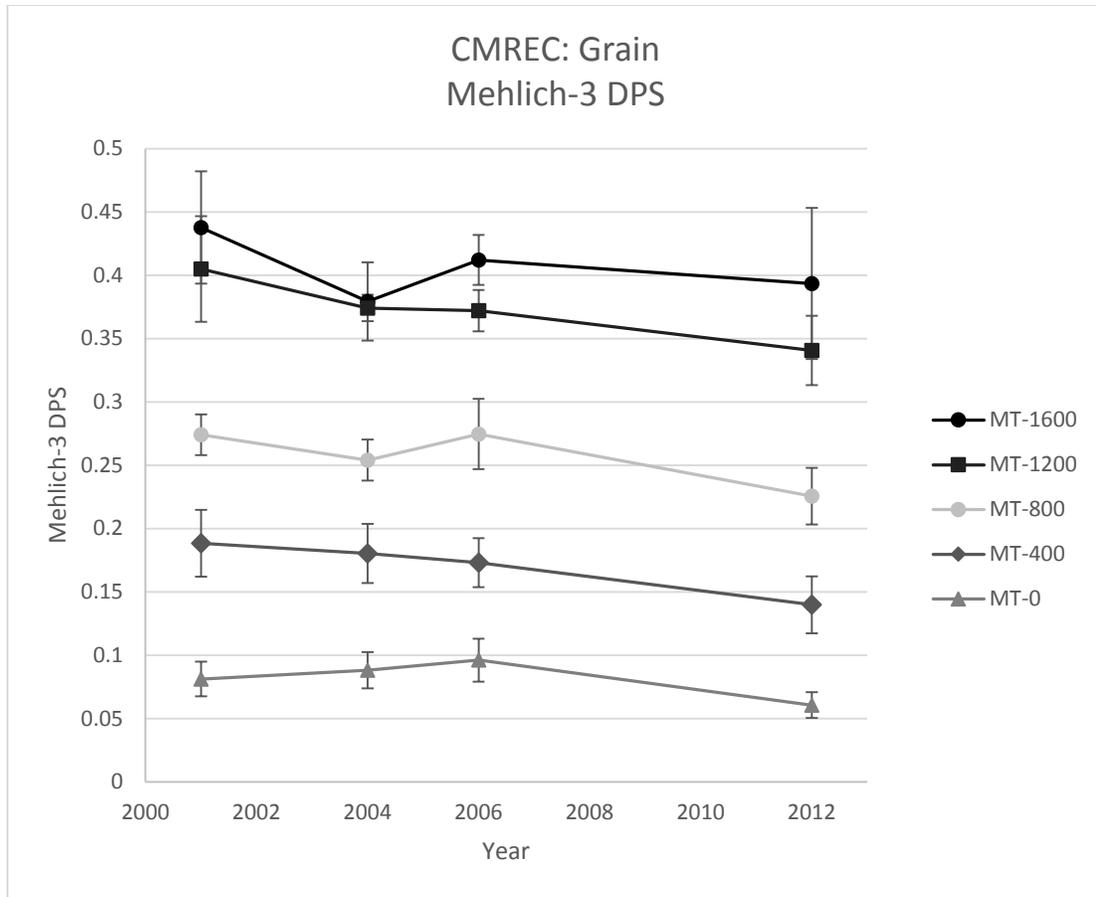


Figure 2.3d: Average Mehlich-3 phosphorus saturation ratio (M3PSR) by treatment and by year at CMREC for the grain cropping system. Standard error is demonstrated with error bars. $M3PSR = [(M3P)/(M3-Fe+M3-Al)]$, where M3P is the molar concentration of P, M3-Fe is the molar concentration of iron, and M3-Al is the molar concentration of aluminum extracted using Mehlich-3. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

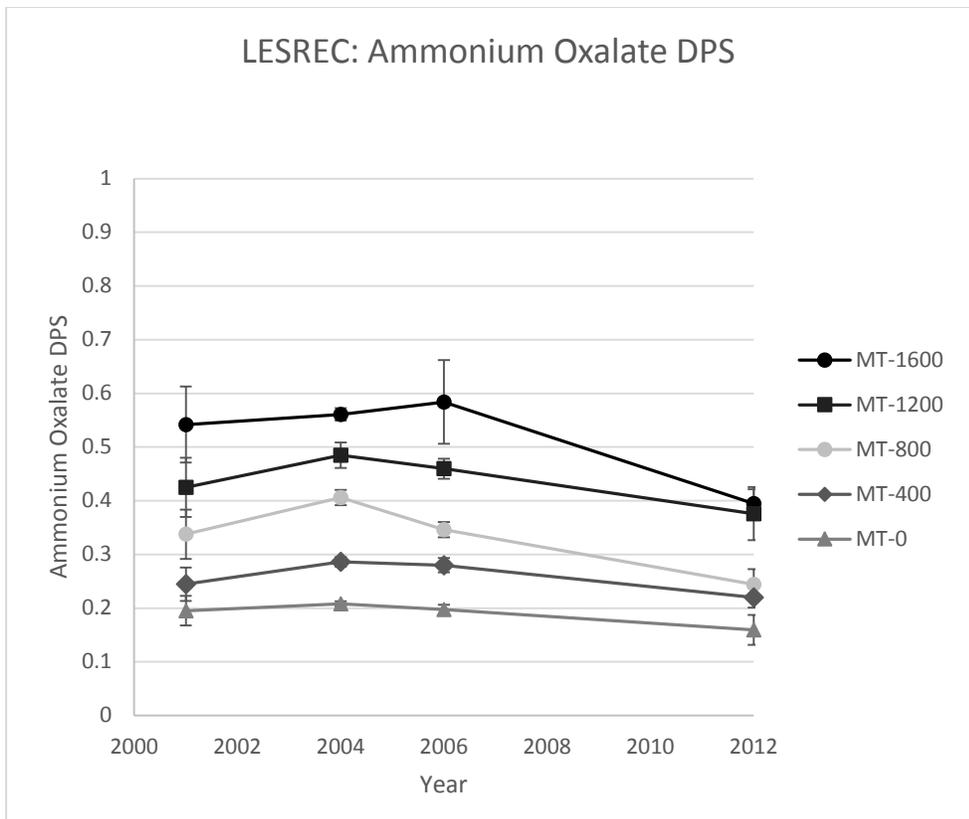


Figure 2.4a: Average ammonium oxalate degree of phosphorus saturation (DPS_{ox}) by treatment and by year at LESREC. Standard error is demonstrated with error bars. $DPS_{ox} = [(OxP)/\alpha(OxFe+OxAl)]$, where OxP is the molar concentration of P, OxFe is the molar concentration of iron, and OxAl is the molar concentration of aluminum extracted using ammonium oxalate. An α value of 0.5 was used for this study. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

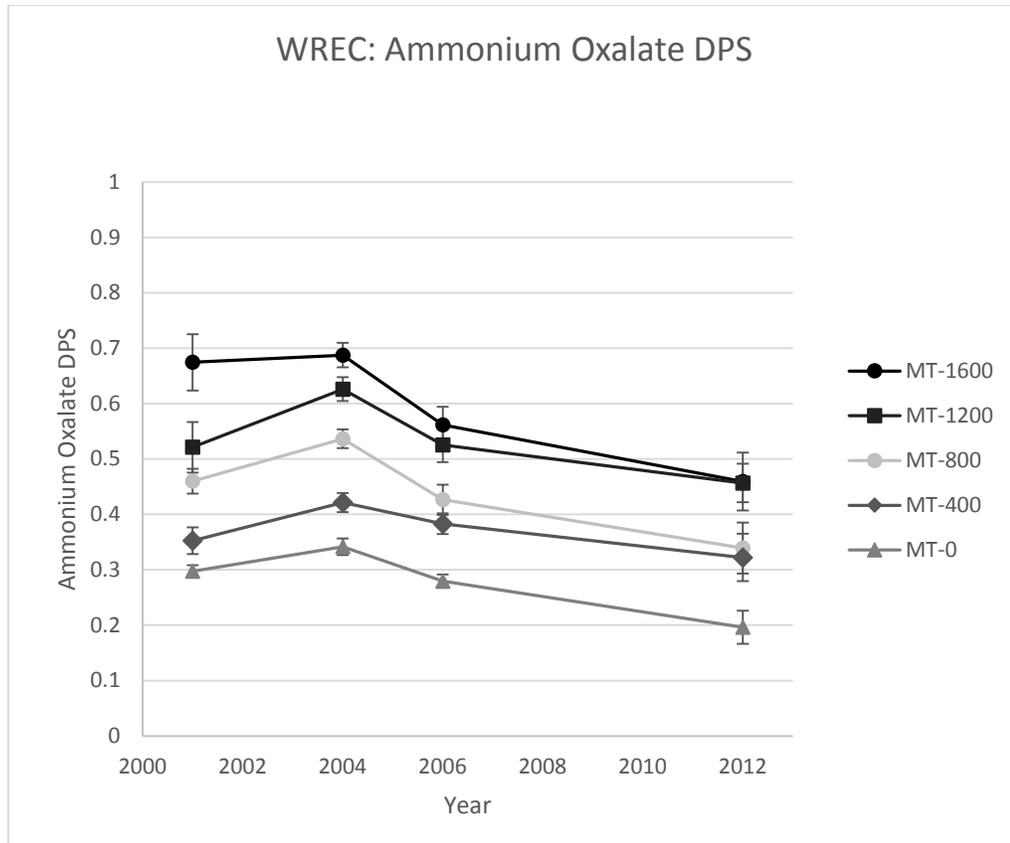


Figure 2.4b: Average ammonium oxalate degree of phosphorus saturation (DPS_{ox}) by treatment and by year at WREC. Standard error is demonstrated with error bars. $DPS_{ox} = [(OxP)/\alpha(OxFe+OxAl)]$, where OxP is the molar concentration of P, OxFe is the molar concentration of iron, and OxAl is the molar concentration of aluminum extracted using ammonium oxalate. An α value of 0.5 was used for this study. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

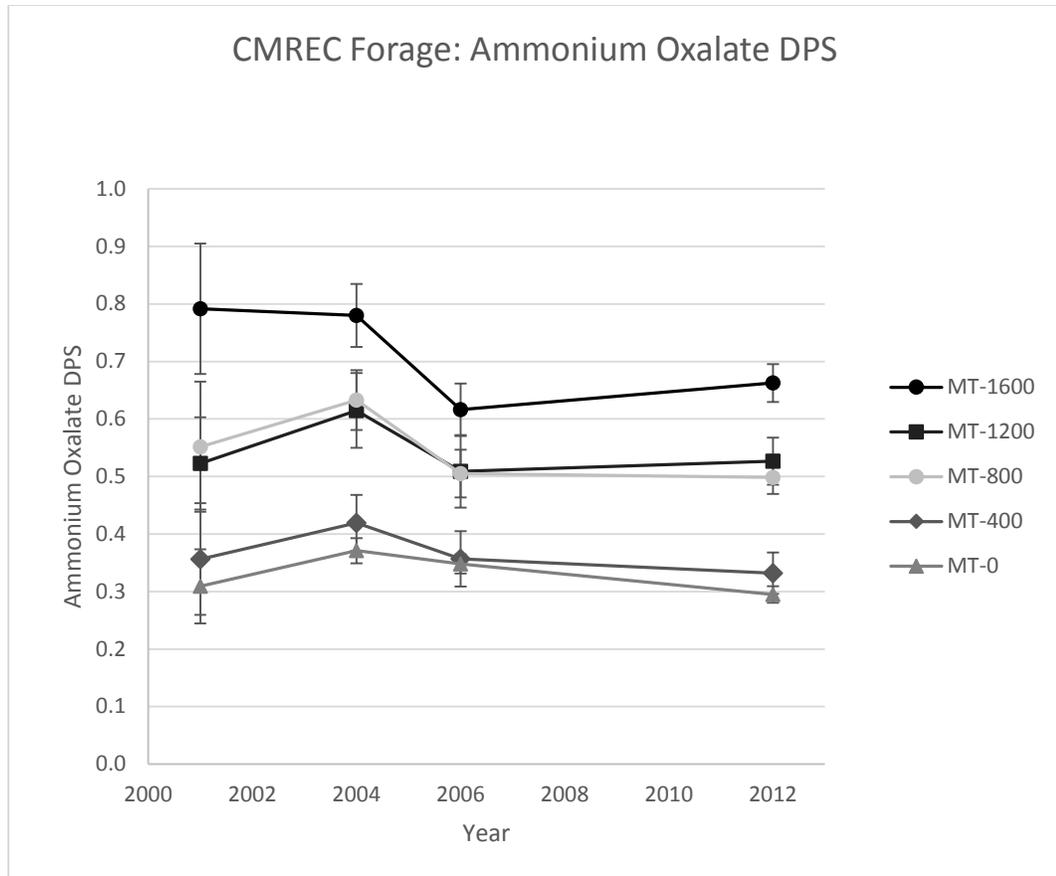


Figure 2.4c: Average ammonium oxalate degree of phosphorus saturation (DPS_{ox}) by treatment and by year at CMREC for the forage cropping system. Standard error is demonstrated with error bars. $DPS_{ox} = [(OxP)/\alpha(OxFe+OxAl)]$, where OxP is the molar concentration of P, OxFe is the molar concentration of iron, and OxAl is the molar concentration of aluminum extracted using ammonium oxalate. An α value of 0.5 was used for this study. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

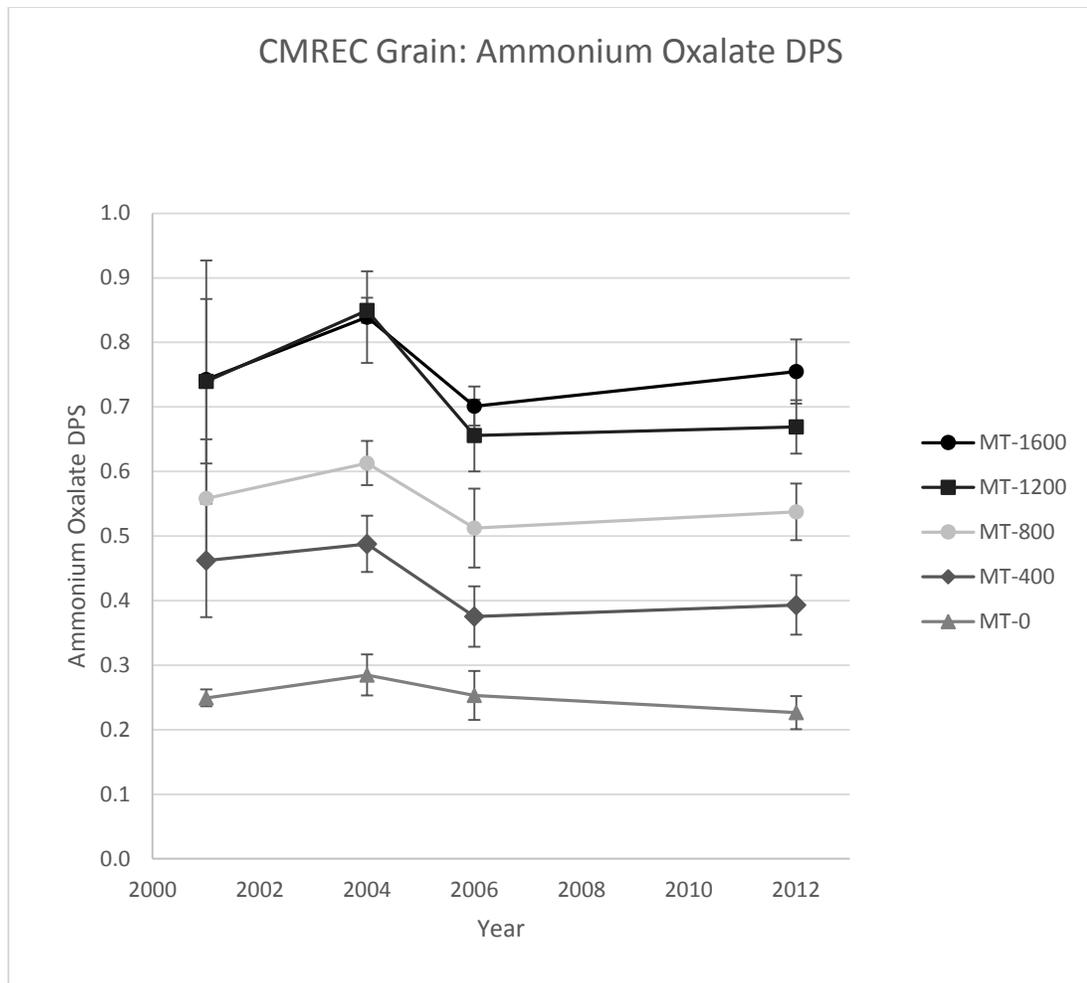


Figure 2.4d: Average ammonium oxalate degree of phosphorus saturation (DPS_{ox}) by treatment and by year at CMREC for the grain cropping system. Standard error is demonstrated with error bars. $DPS_{ox} = [(OxP)/\alpha(OxFe+OxAl)]$, where OxP is the molar concentration of P, OxFe is the molar concentration of iron, and OxAl is the molar concentration of aluminum extracted using ammonium oxalate. An α value of 0.5 was used for this study. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

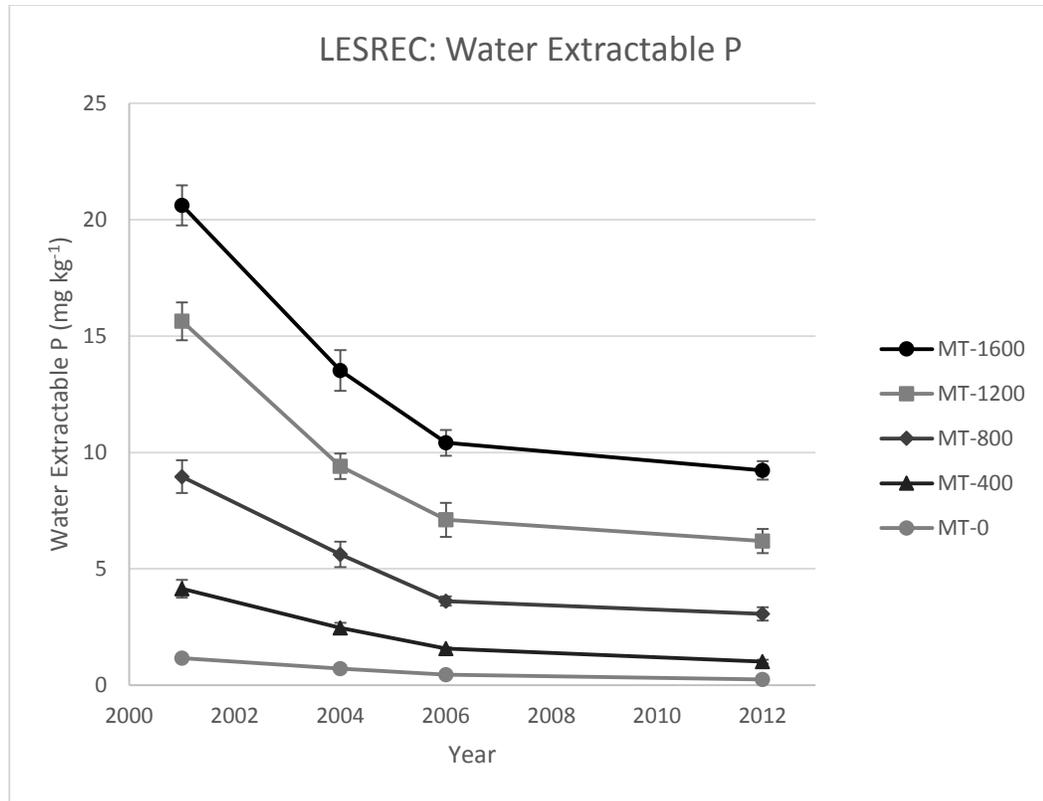


Figure 2.5a: Average water extractable phosphorus in soils by treatment and by year at LESREC. Standard error is demonstrated with error bars. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

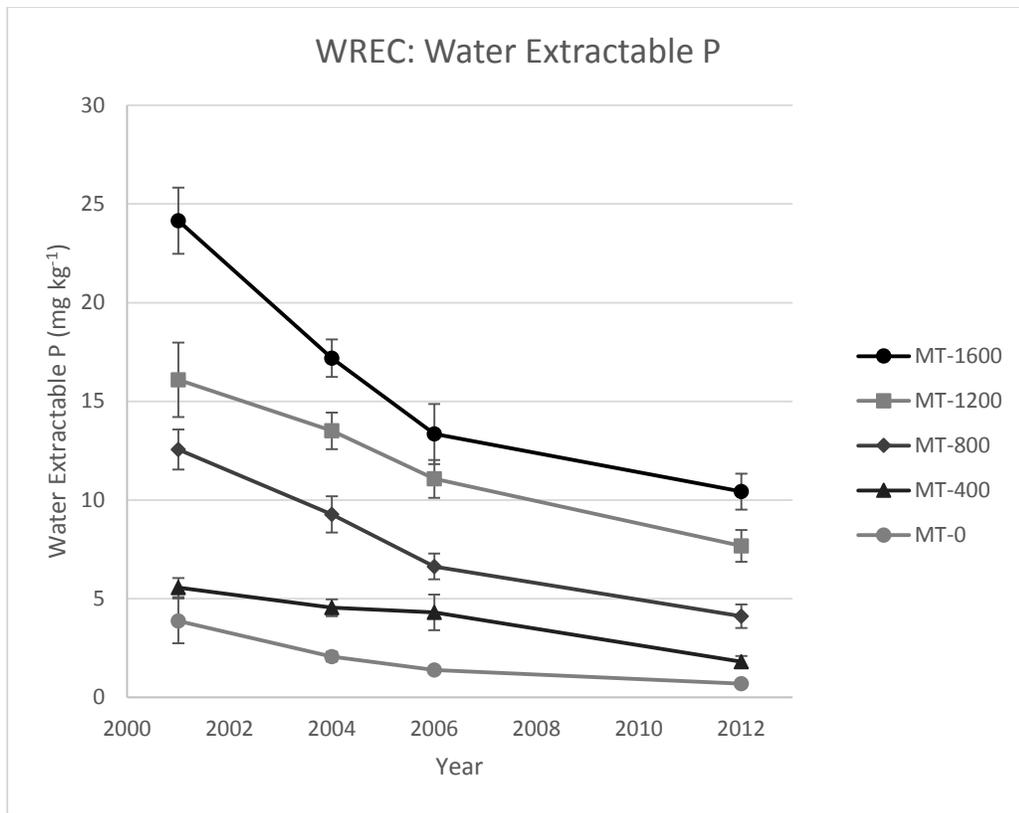


Figure 2.5b: Average water extractable phosphorus in soils by treatment and by year at WREC. Standard error is demonstrated with error bars. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

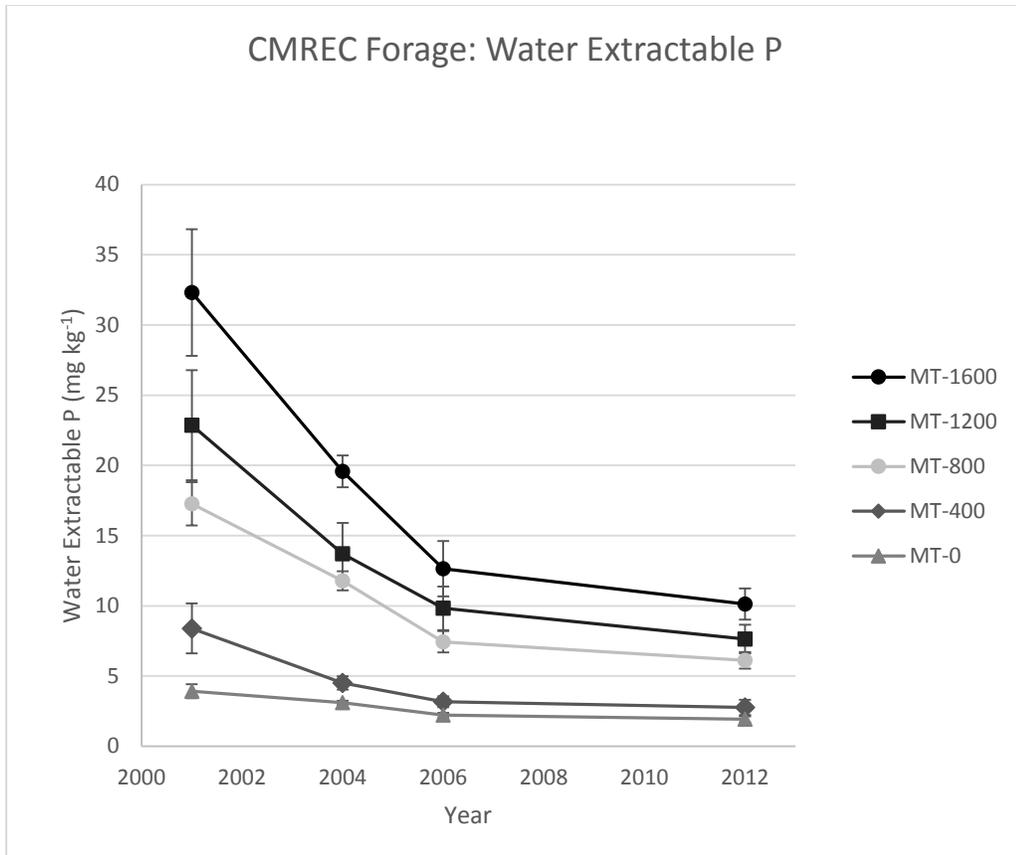


Figure 2.5c: Average water extractable phosphorus in soils by treatment and by year at CMREC for the forage cropping system. Standard error is demonstrated with error bars. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

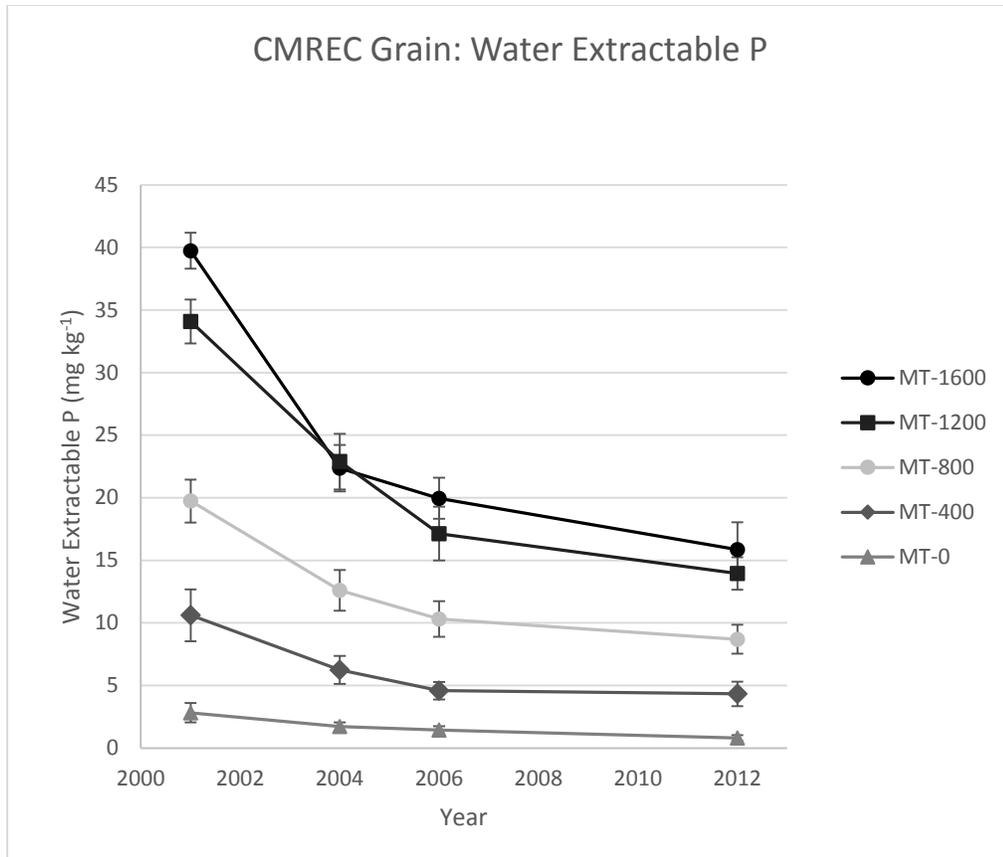


Figure 2.5d: Average water extractable phosphorus in soils by treatment and by year at CMREC for the grain cropping system. Standard error is demonstrated with error bars. Manure treatments were 0, 400, 800, 1,200, or 1,600 kg P ha⁻¹ applied in total over the initial four years of the study from 1994 to 1997 (MT-0, MT-400, MT-800, MT-1200, and MT-1600).

Chapter 3: Changes in Soil Phosphorus across Maryland Fields: Before and After Nutrient Management Planning

Emileigh Rosso Lucas

Abstract

Rationale: Data on soil test phosphorus (P) from fields across Maryland pre- and post-mandatory nutrient management planning are necessary to understand the impact of the related laws.

Objectives: This study was conducted to observe changes in agronomic soil test P and P saturation pre- and post- mandatory nutrient management planning to inform decisions regarding nutrient pollution in the Chesapeake Bay watershed and to understand the impact of regulations so far.

Methods: Researchers compared Mehlich-3 P (M3P) and ammonium oxalate-Fe (OxFe) and -Al (OxAl) data from 50 fields, sampled in 1994-1995 for a different study, with corresponding data from the same 50 fields, which were resampled in 2012. These field sites were distributed across the state of Maryland, were under varied management practices, and were sampled at 0-20 cm depth.

Results: Field sites showed a general increase in M3P across the state post-mandatory nutrient management planning. No field sites remained in the “low” agronomic category for soil test P in 2012.

Conclusions: Results show a general increase in P concentration of Maryland agricultural fields, despite implementation of mandatory nutrient management planning. This increase makes sense, as fields should move out of the below-optimum P concentrations with better management, and the regulations were not designed to draw down P from high-P soils.

Introduction

Phosphorus (P) is an essential plant nutrient required to optimize crop production; however, when present in excess of crop needs, P can accumulate in the environment and ultimately enter the surface water. In aquatic ecosystems that are less impacted by humans, P is generally present in small enough quantities that it is a limiting nutrient for algae growth in comparison to nitrogen (N). Human activities, including agriculture, within a watershed are known to contribute to larger concentrations of P to water bodies

than would occur naturally, therefore causing high primary production of algae. The algae then die and decompose, depleting oxygen in the water and killing fish and shellfish in a process called eutrophication (Correll 1998). The algal blooms also block sunlight from reaching submerged aquatic vegetation (SAV), which is an essential habitat for many Chesapeake Bay species. Eutrophication and deterioration of Chesapeake Bay water quality became a concern as Chesapeake Bay Program findings indicated declining conditions in the living resources and water quality of the Chesapeake Bay (USEPA 1983). In response to these findings, the US Environmental Protection Agency (EPA) along with the Chesapeake Bay states, which included Maryland, the District of Columbia, the Commonwealths of Pennsylvania and Virginia, agreed to work together to protect the resources of the Chesapeake Bay by signing the Chesapeake Bay Agreement in 1983. In this agreement, a plan was put in place to establish a Chesapeake Executive Council that would oversee the implementation of plans to protect and improve the water quality and living resources of the Bay. In 1987, the states and the Chesapeake Bay Commission reconvened and further outlined goals for the Chesapeake Bay watershed based on research that had taken place since their last agreement. All parties signed an updated agreement, which included such goals as: restoring and protecting living resources, reducing point and non-point pollution, managing the adverse effects of the growing human population, educating and engaging the public on the Chesapeake Bay and why it needs to be protected, and enhancing the management strategies of the Chesapeake Bay system. The issue received further attention as part of the Clean Water Action Plan, when Vice president Al Gore requested that the USEPA develop nutrient water-quality criteria for N and P loading to water bodies on a regional basis by 2000,

and then use this scientifically derived criteria to adopt as water-quality standards by 2003 (USGS 1999). Outbreaks of a toxic dinoflagellate, *Pfiesteria piscicida*, in several bodies of water in the Chesapeake Bay watershed in 1997 were believed to be a result of excess nutrient loading, and allegedly caused health problems in both humans and fish. This issue acted as an additional catalyst to drive legislation on nutrient pollution in the region, as it stirred much public debate and media coverage (Magnien 2001).

Phosphorus is relatively immobile in the soil: typically held strongly by aluminum (Al) and iron (Fe) mineral complexes in acidic soils, and calcium (Ca) in alkaline soils; however, it is well established that application of P beyond crop requirement for many years can lead to saturation of P sorption sites. At high soil P saturation, P is much more likely to desorb and be transported to surface water. Globally, P deficiency is a severe problem in crop production, but in areas with intensive, concentrated livestock production there is a net P surplus relative to crop removal. In the United States, the past several decades have shown a shift in animal production toward livestock concentration in high-production areas, resulting in problems disposing of animal manure, where the quantity of manure often exceeds the capacity of the land on the farm (Kellogg et al., 2000).

On a regional scale, P has been imported in grain and feed to support the poultry industry on Maryland's Eastern Shore. Before the Chesapeake Bay restoration effort, manure was viewed as a waste product, so the initial intent of nutrient management plans was to make farmers aware of the nutrient value of manure and to advise them on how to apply it to meet their N needs (Staver and Brinsfield, 2001). On Maryland's Eastern Shore, P was not considered an environmental concern due to its relative immobility in

soil systems, and therefore poultry manure was applied to meet the crop's N requirement, resulting P application exceeding P removal (Cabrera and Sims, 2000).

In response to water quality concerns, and particularly the perceived nutrient contribution of agriculture to the Chesapeake Bay, The Maryland Water Quality Improvement Act (WQIA) was passed in 1998. The WQIA mandated that farmers had until 2002 to develop and follow official nutrient management plans considering both N and P. The act generally dictated that farmers could not apply commercial N or P beyond rates recommended by the University of Maryland (UMD). Farmers using manure as a nutrient source were required to have a nutrient management plan developed that included a PSI for all fields that exceeded M3P of 142 mg kg^{-1} to determine if further P application would be allowed (Code of Maryland, 2000). Additionally, the PSI had to be run to determine P-risk for starter P and crop removal rates of commercial fertilizer P on soils above M3P of 142 mg kg^{-1} . This M3P value corresponds to the Fertility Index Value phosphorus (FIV-P) of 150, at which Maryland regulations determine P-applications may be limited (Table 3.1). Since P loss is not strictly controlled by soil P concentrations or P application rate the regulations allowed for P application beyond crop requirement. These regulations were designed to minimize nutrient losses of N and P to the Chesapeake Bay from farmland in the watershed, but were not designed to decrease soil P concentrations.

The PSI was developed by the University of Maryland as an educational tool that would prevent loss of P from high risk fields to the watershed (Coale and McGrath 2006). The initial Phosphorus Index was developed in 1993 to identify "critical source areas" where P loss potential was high, due to P source and transport potential, and guide management in those areas (Lemunyon and Gilbert, 1993). A PSI that was specific to

Maryland conditions was introduced beginning in 1994. The PSI was divided into two parts, A and B (Table 3.2), and was used to calculate a P-loss rating on a field-by-field basis (Table 3.3). Depending upon the P-loss rating score, P application may be restricted. Farmers could apply P, at least to expected crop removal rates, up to and including a rating of “high” (Coale, 2005).

Although Maryland is a highly regulated state in regards to agricultural nutrient management, minimal data are available on the actual impact of these regulations on soil P concentrations or P losses to the environment. Some policy-shapers feel that if the agricultural community were following the current laws, a decrease should be observed in soil P concentrations. They have therefore sought to obtain soil testing data from nutrient management plans (Hotten, J., The Court of Special Appeals of Maryland, 2013).

Agronomic soil test P (ASTP) may not provide accurate indications of environmental risk under certain field conditions, and the regulations were not designed to draw down ASTP for most fields. Schroeder et al. (2004) found that even across the same Cecil soil series in Georgia, variability in specific sites changed the relationship between ASTP and P in surface runoff. While M3P has been shown to correlate reasonably well to P concentrations in runoff under certain conditions, the accuracy of these predictions may be varied based on the pools of P in the soil and the soil conditions. For example, McDowell and Sharpley (2001) found that M3P strongly correlated with dissolved P in runoff from sites that had not recently received manure in a central Pennsylvania watershed. This relationship was not observed on recently manured sites in the same watershed. When a P index was used to predict surface runoff P on these same

eleven fields, site vulnerability to P loss was accurately predicted for both recently manured and non-recently manured fields.

Degree of phosphorus saturation (DPS) may be a reliable way to predict the relationship between ASTP and the potential for P loss. Ammonium oxalate and Mehlich-3 may be used to calculate a degree of phosphorus saturation (DPS_{ox}) or a phosphorus saturation ratio (M3PSR), respectively, which would define the maximum amount of P that could adsorb to Fe and Al binding sites in the soil. Soils with high M3PSR, when fertilized, have a greater flux in water-soluble P than soils with a lower initial M3PSR (Bond 2006).

Rainfall simulation studies measure P losses from the soil surface using dissolved reactive-P (DRP) as an indicator of P losses to the environment. One of the strongest predictors of DRP is DPS_{ox} (Schroeder et al., 2004). Maguire and Sims (2002) found similar results in studies on five acidic soils where rapid change points in P leachate, where the P concentration rapidly increased, were clearly identifiable using both DPS_{ox} and M3PSR. The M3PSR could be calculated using information that many farmers are already required to obtain for their Nutrient Management Plan, as the Mehlich-3 extraction is used by many soil testing labs that service the mid-Atlantic.

Mandatory nutrient management plans were required to be in place by 2002. Many people question whether these regulations have had an impact on ASTP. This study takes into account a non-controlled (experimentally), but widespread sampling of Maryland agricultural soils, with data pre- and post- nutrient management planning. While causation cannot be implied from these data, an important snapshot of where Maryland fields stand in regards to P content under current regulations compared to the

same fields prior to the regulations is presented here. Therefore, the objective of this study was to determine the changes in Maryland agricultural soils, before and after regulations requiring nutrient management planning, on soil test P, Fe and Al in the different regions of Maryland.

Materials and Methods

Between 1994 and 1995 UMD researchers sampled 72 paired fields at 36 farms located in 19 of Maryland's 23 counties. In the original study, fields were selected based on farmer willingness to participate and to represent the range of agricultural conditions in Maryland. At each farm one field with no history of manure application and one with a history of manure application were sampled. In addition, four sites were sampled that only had a history of manure application. The objective of their study was to assess the relationship between WEP (used as an index for potential of total dissolved P), Mehlich-1 P (M1P), and M3P. Additional details on the original study can be found in Olear and Coale (1996). Olear and Coale (1996) performed M1P, M3P, pH, OxFe and OxAl, and soil texture-by-feel analyses on the 0 to 20 cm samples collected in 1994-1995. On 0 to 2 cm samples, they performed water extractable P (WEP) in addition to the above listed chemical extractions. An additional set of 40 to 60 cm depth samples were taken from the sites, which had Mehlich-1, Mehlich-3, pH, ammonium oxalate, citrate bicarbonate dithionite Fe and Al, and soil texture-by-feel analyses.

Under the current study we sought to locate these fields for additional sampling. The locations of the sample sites from the original study were recorded by x- and y-coordinates measured in millimeters from page corners in soil survey books. To complete

the current study each sample site was located in the soil survey books and then using visual landmarks they were located on Google Earth images and latitude and longitude were determined (Fig. 3.1). Working with local University of Maryland Extension personnel, the current land owners or managers were located and attempts were made to contact them and obtain permission to collect a second set of soil samples. Of the original 80 fields sampled, access was granted to 50 fields that had remained in agricultural production since the original samples were collected in 1994 and 1995 (Table 3.4). Soil samples were collected from 50 sites between September 2011 and January 2012.

Soil samples were taken to 20 cm depth to match the methods of Olear and Coale (1996). Fifteen to twenty cores were taken per field, ranging from one sample per 0.02 ha to 1.3 ha. Once collected, the samples were sieved using a 1 cm field sieve and thoroughly mixed by hand. The samples were stored in cloth geological sample bags, and returned to the lab within 24 hours where they were placed into a forced air oven (60°C) until dry. Samples were then ground and sieved (2 mm) and returned to the same bag until analysis. Samples were analyzed for M3P, M3Fe, M3Al, O_xP, O_xFe, O_xAl, and WEP; these were conducted according to the methods described below.

Mehlich-3 P, M3Fe, and M3Al were determined on each sample (Mehlich, 1984; Sims and Wolf, 1989) by shaking 2.50 g of soil with 25 mL M3 solution (0.2 N CH₃COOH + 0.25 N NH₄NO₃ + 0.015 N NH₄F + 0.013 N HNO₃ + 0.001 M EDTA) in a 100 mL snap-cap container. The samples were shaken for 5 min on a reciprocating shaker set to 180 oscillations min⁻¹, with a stroke length of 4 cm. Immediately upon removal from the shaker, samples were filtered through Whatman #40 filters, and the filtrate was collected in 30 mL tubes. The filtrate for each sample was analyzed the next

day by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES; *Thermo Elemental: Intrepid II XSP Duo View*) at the University of Delaware Soil Testing Laboratory (Newark, DE).

Ammonium oxalate extractable P, Fe, and Al (OxP, OxFe, and OxAl, respectively) concentrations were measured for each soil using Inductively Coupled Plasma spectroscopy (ICP) (*Thermo Elemental: Intrepid II XSP Duo View*). In 50 mL screw-top centrifuge tubes, 1.00 g of soil was combined with 40 mL of 0.2 M solution of ammonium oxalate and oxalic acid extracting solution. Trays of tubes and repipet were wrapped in aluminum foil to minimize light exposure, and lights were off in the lab. Samples were shaken horizontally on a reciprocating shaker for two hours on low speed. The samples were then centrifuged at 2000 rpm for 15 minutes, and then filtered through Whatman #42 filter papers (Iyengar et al., 1981; McKeague et al., 1966; Pote et al., 1996). The filtrate for each sample was then diluted 1:10 with distilled, deionized water, and submitted either the same day or the following day to the University of Delaware Soil Testing Lab for analysis. Analysis was within two days of extraction for all soils.

Water extractable P (WEP) was determined on all soils. In 50 mL centrifuge tubes, 2.00 g soil was weighed and combined with 20 mL distilled, deionized water. These were shaken for one hour horizontally on a reciprocating shaker on low speed. The tubes were centrifuged for 15 minutes at 2000 rpms, then vacuum-filtered through 0.45 μm filters (Luscombe et al., 1979; Self-Davis et al., 2000). Phosphate-P was determined using the molybdate blue method on a Lachat QuikChem 8500 Flow Injection Analysis System (Hach Company, Loveland, CO) by the methods of Murphy and Riley (1962).

Simple linear regression analysis was used to compare 1994 and 2012 variables (Proc Reg, SAS version 9.3, SAS Institute, Inc. [SAS Institute, 2011]), and a mixed model ANOVA with the adjustment for Tukey's test was used to compare the change in M3P for those soils starting above 142 mg kg⁻¹ in 1994 compared to below 142 mg kg⁻¹ (Proc Mixed, SAS version 9.3, SAS Institute, Inc. [SAS Institute, 2011]).

Results

Site Description

In the initial 1994 experiment, the following soil series were represented: Beltsville, Butlertown, Chester, Cookport, Duffield, Elkton, Fallsington, Glenelg, Hagerstown, Lickdale, Matapeake, Montalto, Othello, Penn, Pocomoke, Sassafra, and Woodstown. Thirty of the original 80 sites were not sampled because access was denied by the landowner, the landowner could not be contacted, or the land was no longer in agriculture. Of the 50 sites to which access was granted, original data were missing for one of these from Talbot County in the Upper Shore region (Fig. 3.6), so the data analyses used 49 samples (Table 3.4).

Trends in Mehlich-3 Phosphorus

Mehlich-3 P concentrations generally increased between 1994 and 2012. All of the 13 sites that experienced an increase of greater than 100 M3P (mg kg⁻¹) from 1994 to 2012 started in the optimum or excessive agronomic category. Generally, sites increased M3P by one agronomic category. Exceptions to this include a Piedmont region site, which was a dairy operation that moved from low to excessive. Another dairy farm in the mountain region moved from the medium range to excessive. The change in M3P was

also observed by comparing the mean and median difference between 1994 and 2012 M3P for those starting above and below the 142 mg kg⁻¹ threshold where a PSI risk assessment was required to add P-bearing materials (Fig. 3.4). The change in M3P was significantly greater for those starting above 142 mg kg⁻¹ (P=0.03) as compared to those starting below 142 mg kg⁻¹, though both groups demonstrated an overall increase. With 1994 and 2012 concentrations plotted against each other, the trend line (R²=0.70, P<0.0001) has a slope of 1.19, and a y-intercept of 40.32 (Fig. 3.2). This indicates a general increase above the 1:1 line, which would represent the trend if M3P concentrations had not changed between those years (Fig. 3.2). Additionally, when the M3P values were put into agronomic interpretive categories of low, medium, optimum, and excessive (Table 3.1), none of the fields that were in the low category in 1994 remained there in 2012. The number of fields in the excessive category increased in 2012, with the number of fields in the optimum category decreasing, as several of the fields moved from optimum to excessive (Fig. 3.3). All fields either increased or stayed in the same category, with the exception of one field in the Lower Shore region, which moved from excessive to optimum, and one field in the mountain region, which moved from optimum to medium. Out of the 49 samples, 27% exhibited an increase in M3P of greater than 100 mg kg⁻¹ (Fig. 3.5).

Degree of Phosphorus Saturation

The 1994 data consisted of M3P, OxAl, and OxFe, but not OxP, M3Al, or M3Fe. Therefore, in order to look at trends in P saturation, M3P was observed in a ratio to OxAl and OxFe, since these data exist for both 1994 and 2012, as other studies have shown that the two extraction methods are well correlated (Maguire and Sims 2002). This ratio will

be referred to as the “hybrid” DPS (DPS_{Hybrid}) A standard alpha value of 0.5 was used to multiply the sum of the molar values of OxFe and OxAl, as described by Breeuwmsa et al. (1995), and the equation can be seen here:

$$DPS_{Hybrid} = [(M3P)/\alpha(OxFe+OxAl)]$$

Thirty nine sites could be compared for the DPS_{Hybrid} analysis, as original Ox Al and Ox Fe data from 1994 were present for 45 of the sites, consisting of 11 from the Lower Shore, eight from the Mountain, 10 from Piedmont, two from Southern, and 14 from the Upper Shore (Fig. 3.6). Then, six outliers in the OxAl data had to be eliminated due to anomalous values in the 1994 data (Appendix 1). The OxFe data did not exhibit any similar abnormal values.

The OxAl and OxFe data both demonstrated a slight decline in 2012 from 1994. A linear trend below the 1:1 line was observed for both OxFe and OxAl when plotted by site (Fig. 3.8 and 3.9). The decrease is observed in the average for each element by year as well (Fig. 3.10). The main interest in the Fe and Al concentrations for this study is in the ability of these elements to bind with P in the soil, which is examined in the following section, and can determine how “saturated” the soil is with P.

An increase was observed in the DPS_{Hybrid} of the soils across the state when plotted on a site by site basis ($P < 0.0001$) (Fig. 3.11). The mean change is an increase of 12% with a standard error of 0.02. For every unit increase in 1994 DPS_{Hybrid} , the 2012 DPS_{Hybrid} is expected to be 1.14 times greater.

Region

The mean M3P was observed in 1994 and 2012 by the five regions in Maryland: Lower Shore, Mountain, Piedmont, Southern, and Upper Shore (Fig. 3.6). When observed in this way, the Lower Shore had both the highest mean M3P to begin with, at 281.1 mg kg⁻¹, and the greatest change in M3P compared to all of the other regions, increasing to 449.2 mg kg⁻¹ (Fig. 3.7) (Compared to Mountain: P=0.002, Piedmont: P=0.006, Southern: P=0.001, and Upper Shore: P=0.004). The change in mean M3P was not significantly different between any of the other regions at $\alpha=0.05$. All regions showed an overall increase, except for southern Maryland, which included samples from only three sites. The mountain region had the lowest mean M3P in 1994, at 39.7 mg kg⁻¹, and also exhibited a relatively small increase in mean M3P, only increasing to an average of 58.0 mg kg⁻¹.

These regions were dominated by soils of differing texture; the Lower Shore region samples were predominantly sandy loam, and the mountain region samples were predominantly silt loam. Of the 13 sites that increased M3P by more than 100 mg kg⁻¹ (Fig. 3.5), 8 were from the Lower Shore, 3 from the Upper Shore, and 2 were from the Piedmont. The soil texture of these sites did not offer an explanation for the differences in the change in M3P; the sites that increased by more than 100 M3P were six sandy loams, six silt loams, and one loam.

Water Extractable Phosphorus

The 1994 data were highly variable for WEP, as samples were taken at a two centimeter depth. Figure 3.12 demonstrates the variability in the large error in the 1994 two centimeter depth samples compared to the 2012 samples, which were taken to twenty

centimeters. In 1994 there appear to be no differences in the WEP of the Southern, Piedmont, and Lower Shore regions (not statistically analyzed). The Mountain and Upper Shore regions appear to have less WEP than the other regions. In 2012, WEP concentrations were markedly lower due to the increased depth of sampling. The Lower Shore exhibited the highest concentration of WEP, while the Mountain region exhibited the lowest concentration.

To further observe relationships with WEP in the regions of Maryland, data on M3P concentrations were plotted against the WEP concentrations in each year independently (Fig. 3.13a and 3.13b). This comparison was done to observe how regional characteristics (e.g. soil texture and the P source that was applied) might impact the relationship between M3P and WEP. The data did not show a relationship between WEP in the 0 to 2 cm samples collected in 1994 and the M3P for the 0 to 20 cm depth samples collected in 1994 ($R^2=0.08$), likely due to a two centimeter sampling depth for WEP, which expresses recent management in a more exaggerated way than a 0 to 20 centimeter sampling depth. The M3P samples data was based on a 0 to 20 cm depth. Some noteworthy sites included two that had relatively high WEP compared to the M3P concentration. One of the sites was in Montgomery County and was a loam in texture, with a WEP of 127 mg kg^{-1} when the M3P was 59.1 mg kg^{-1} . The other was in Allegany County, from a silt loam soil, where the WEP was 115 mg kg^{-1} with a M3P of 57.4 mg kg^{-1} . Other sites exhibited relatively lower WEP when the M3P was excessive. Of these six soils, five were sandy loams and one was a loam. They were from Worcester, Talbot, and Wicomico counties. Two Worcester County soils had M3P concentrations of 666.3 and 532.3 mg kg^{-1} with respective WEP of 62 and 35 mg kg^{-1} . The Talbot

County soils had M3P concentrations of 436.1 and 411.6 mg kg⁻¹ with WEP of 52 and 46. Finally, the Wicomico soil had a lesser but still excessive M3P of 237.7, but the WEP was 13. With the 2012 samples, a much stronger relationship was observed ($R^2=0.60$). One Frederick County sample had a relatively high M3P concentration of 311 mg kg⁻¹ with a lower WEP of 26.11 mg kg⁻¹.

The WEP was also compared to the DPS_{Hybrid} (Fig. 3.14a and 3.14b). The results from the 1994 DPS showed no relationship, most likely because the soil samples for DPS were based on 0-20 cm depth while the WEP was 0-2 cm depth, and the surface characteristics are highly variable based on management. The 2012 samples had some relationship between WEP and DPS ($R^2=0.4$); however, two sites in Frederick seemed to exhibit a lower WEP than the others with a higher DPS. The sites had DPS of 42% and 34%, with WEP of 48.7 and 26.1 mg kg⁻¹ respectively.

Discussion

Trends in Mehlich-3 Phosphorus

An overall increase in M3P in this study (Fig. 3.2) was reasonable given the design of the regulations, the persistence of P in the soil, and the influx of nutrients to the region. P binds with Fe, Al, and organic matter in the soil. Even if P was applied within the bounds of the regulations, accumulation could still occur, as crop removal would not extract all of the applied P from the soil. Also, P application was not curtailed in many situations. The nutrient mass balance issue is still at play, with more P constantly flowing into the region to supply feed to the poultry operations, and manure is not as easily transported out of the region compared to the ease of transporting nutrients in. The initial

M3P also seemed to have an impact on the amount of increase in M3P, likely due to continuation of animal agriculture in many cases and other soil P dynamics.

Along with mandatory nutrient management planning came mandatory soil testing. With increased knowledge of the P concentration in the soil, farmers were able to better manage P and address deficiencies. Therefore, the absence of fields in the “low” agronomic category in 2012 as compared to 1994 is reasonable, as producers added P to solve the deficiency (Fig. 3.2; Fig. 3.3.). Furthermore, as detailed in the regulations, when producers wish to apply P when M3P is ≥ 142 , or no P is recommended, they need to conduct a PSI determination. If the results of the PSI are a P loss rating of “low,” “medium,” or “high,” producers may still apply P to at least the crop P removal rate.

Under the PSI regulations, manure may be applied at an N-based rate with a P-loss rating of low or medium (one year N-based out of every three years). N-based poultry litter application caused increases in M1P in a study by Maguire et al. (2008). Because of this, even with farmers following regulations, sites with ASTP in the excessive range would not be expected to decline. If the P loss rating were “very high,” no P-bearing materials could be applied, and producers would be advised to make efforts to reduce ASTP; however, due to the persistence of P in the soil, remediation efforts may take an extended period of time to draw ASTP down below excessive.

Other research has demonstrated that M3P concentrations remain elevated for extended periods of time, even with crop removal. Kratochvil et al. (2006) studied cropping systems and the ability of crop removal to lower M3P. They found that forage crops, when harvested, are observed to reduce measured M3P at faster rates than grain crops, but neither had proven to significantly reduce P from “excessive” to the

“optimum” concentration over the 4 year duration of the study. Researchers in Ireland observed similar findings in fields that fell into the highest P risk category of their version of the P Index, using Morgan extractable P. In this research, the fields took anywhere from 7 to 15 years to reduce from the highest P risk category, indicating P in excess of crop needs, to the optimum, with much variability, and some fields taking over 20 years to draw down to the optimum range (Schulte et al., 2010).

In this survey of Maryland agricultural soils, M3P increased more between 1994 and 2012 in soils with higher M3P in 1994 (Fig. 3.4). Other research has found that the rate of increase in ASTP when additional P sources are added increases in relation to elevated initial ASTP. A laboratory study by Griffin et al. (2003) conducted in Maine observed this result on a sandy loam soil, which had been amended with multiple manure and mineral sources of P. Soils were treated to have “high,” “medium,” and “low” M3P, measured as 732, 471, and 150 mg kg⁻¹, respectively. Then, manure P and KH₂PO₄ were added at 0, 100, 200, 400, and 800 mg total P kg⁻¹. The KH₂PO₄ treatments demonstrated a steeper slope of CaCl₂-extractable P as P was added in higher concentrations to the soils with “high” initial M3P, than the same concentrations added to the “medium” and “low” initial P concentration soils. Haden et al. (2007) observed a greater increase in ASTP per unit of P added to a variety of noncalcareous soils in New York. The effect of initial soil characteristics, including initial ASTP, on changes in ASTP was similarly described on a variety of Italian soils in an earlier study by Indiatì and Sharpley (1997).

Additionally, many of the farms with high initial P likely had a readily available P source since before the initial sampling date. Upon examination of aerial imagery and observations while collecting the soil samples, the ten fields with the highest initial P in

the dataset were on farms involved in animal production systems and were primarily poultry operations. These producers have likely had a source of manure-P that was used as fertilizer for many years; due to the quality of the nutrient source, as well as the necessity to remove the manure from the storage area, this manure-P was applied to the surrounding fields. This P source is still available at those locations, and there are significant challenges to transporting manure away from the farm, so producers were likely to continue P applications to these fields. The locations of the top ten sites with the highest initial P concentration were all on the Delmarva Peninsula, one of the regions in the Chesapeake Bay watershed reported to have the highest manure-applied P rates (Hainly and Lopez, 1997; Taylor and Pionke, 2000).

Degree of Phosphorus Saturation

Similar to trends over time in M3P, the DPS also significantly increased across the state. This result made sense, as the P concentration is more easily changed than the properties of the soil that allow for a greater ability to hold P, particularly the presence of Al and Fe. An exception to this may be a soil amended with biosolids or another material containing high concentrations of these elements. This increase in DPS, particularly since animal manure applications have historically occurred on these field sites, is reinforced by observations of Dou et al. (2009). Manured and non-fertilized fields from ten farmers' fields in Pennsylvania were compared, though in 0 to 5 cm depth rather than the traditional 0 to 20 cm agronomic sampling depth. The DPS in the manured soils was 80 to 90 percent compared to 11 to 33 percent in untreated soils.

Region

The varying observations by region in terms of average M3P and the average change in M3P could be explained by multiple variables including the presence of a readily available P source (e.g. poultry and dairy operations) and the type crops grown in the region.

The counties with sites that exhibited the greatest change in M3P also have a relatively large amount of animal agriculture compared to other counties. The top ten greatest increases in mean M3P came from Frederick, Wicomico, Worcester, Caroline, and Somerset counties. According to NASS 2012 Census Publications for Maryland (USDA-NASS, 2014), Frederick County leads the state in cattle (*Bos taurus*) production. The county also produces the most acres of “forage-land used for all hay and haylage, grass silage, and greenchop” as well as “corn used for silage.” Additionally Somerset, Worcester, Caroline, and Wicomico counties lead the state in “broiler and other meat-type chicken (*Gallus gallus domesticus*)” production in the order listed. Somerset County produced 14,935,325 broiler and meat-type chickens according to the NASS 2012 Census of Agriculture, Wicomico produced 11,051,592, and the other listed counties were in between. Caroline County also produced the most acres of wheat and vegetables in the state, with the second most acres in corn grain production, and third in soybean production. The USDA-NASS (2014) data suggests the counties that experienced the greatest mean change in M3P between 1994 and 2012 were likely to have readily available sources of manure P and were areas of intensive agricultural production, which may explain this observed increase.

Soil texture is often dependent on region and affects soil P dynamics; however, texture was not a contributing factor to differences in the change in P for these fields. Soil texture had minimal influence on the change in M3P. The sites that exhibited greater than a 100 mg kg^{-1} M3P increase were almost evenly split between silt loam and sandy loam, despite the fact that most of these sites were on the Eastern Shore of Maryland. While a relationship between soil texture and change in M3P was not observed in this study, other research has demonstrated that soil texture has an influence on P dynamics, especially in terms of P buffering and holding capacity. Soil test P goes up less per increment of P added in well buffered soils. Additions of P move soil extractable P more in a sandy soil than a loam or clay soil. Cox (1994) studied the impact of soil texture on the increase in M3P per unit of P application on Ultisols in North Carolina and Oxisols in Brazil. He found that the increase in M3P per unit of P applied was 0.7 for soils with approximately 10 percent clay content after one year, but only 0.2 on soils with 40 to 50 percent clay.

Additions of manure may impact the ability of a soil to hold P by adding P in an organic form and by adding elements that may bond with P. Karathanasis and Shumaker (2009a and 2009b) observed that the organic form of P (inositol hexakisphosphate) was absorbed to a greater concentration than inorganic P (KH_2PO_4) in hydroxy-interlayered vermiculite clay soils, hydroxy-interlayered smectite clay soils, gibbsite, and goethite minerals. Their study also showed that the organic P was held with greater energy than the inorganic source of P.

Conclusions

This study provides a unique opportunity to observe fields before and after mandatory nutrient management planning that were managed according to the preference of each producer. The information gained from these observations provides valuable insight to the changes in Maryland agricultural soils under the regulations of the Water Quality Improvement Act (1998). The regulations at the time of the study were not written to reduce ASTP, but were designed to reduce P losses from high risk agricultural fields into the Chesapeake Bay. Under these regulations, ASTP concentrations generally increased throughout the state. The Lower Shore region had both the highest initial M3P and the greatest increase in M3P out of the five regions of Maryland, while the mountain region had the lowest average M3P. An increase of M3P can be explained by a combination of the design of the regulations, allowing for additional P applications beyond crop requirements as long as the PSI determined that the risk of P loss is low or medium, and the availability of a P source in regions with densely populated animal agriculture. Additionally, the P drawdown research in the previous chapter has demonstrated M3P remains elevated and persists over time, despite cessation of P applications and crop removal. An increase in DPS was also noted across the state.

Figures and Tables

Table 3.1. Descriptions of soil test interpretive categories (Coale, 1996) and the conversion to University of Delaware mg kg⁻¹ P, calculated by the methods of Coale and McGrath (2006). The University of Delaware values were used because the Mehlich-3 analyses for this study were conducted in the University of Delaware lab. The conversion of the regulatory threshold in Maryland for mandatory P-risk analysis to apply additional P is also described.			
Soil Test Interpretive Categories	Fertility Index Value Phosphorus (FIV-P)	University of Delaware mg kg⁻¹ P (Mehlich-3)	Description
Low	0-25	0-18	The nutrient concentration in the soil is inadequate for optimum growth of most crops and will very likely limit plant growth and yield. There is a high probability of a favorable economic response to additions of nutrients.
Medium	26-50	19-43	The nutrient concentration in the soil may or may not be adequate for optimum growth of most crops and plant growth and yield may or may not be limited. There is a low to moderate probability of a favorable economic response to additions of the nutrient.
Optimum	51-100	44-92	The nutrient concentration in the soil is adequate for optimum growth of most crops. There is a very low probability of a favorable economic response to additions of the nutrient.
Excessive	>100	>93	The nutrient concentration in the soil is more than adequate for optimum growth of most crops. Nutrient additions will be unprofitable and may have undesirable effects on growth of some crops. Erosion and runoff from soils that are excessive in phosphorus may have negative impacts on surface water quality.
Regulatory threshold for Phosphorus Site Index	≥150	≥142	Farmers/Operators must have a nutrient management plan in which a PSI has been conducted to apply P on a field with soil test P concentration above this value.

Table 3.2: The two portions of the Maryland Phosphorus Site Index (PSI) as described by Coale (2005), used to calculate the P loss rating on a field-by-field basis.	
Part A: Phosphorus loss potential due to site and transport characteristics	Part B: Phosphorus loss potential due to management practice and source characteristics
Characteristics	
*Soil erosion Soil runoff class Subsurface drainage Leaching potential Distance from edge of field to surface water Priority of receiving water	Soil test P P fertilizer application rate P fertilizer application method Organic P application rate Organic P application method
* <i>Erosion was calculated using the Revised Universal Soil Loss Equation (RUSLE), developed and maintained by USDA-Agricultural Research Service (ARS), USDA-Natural Resources Conservation Service (NRCS), and the University of Tennessee.</i>	

Table 3.3: Interpretation of the Maryland Phosphorus Site Index P loss Ratings (adapted from Coale, 2005)		
P Loss Rating	Rating Descriptor	Interpretation of P Loss Rating
0-50	Low	<ul style="list-style-type: none"> • Low potential for P movement from this site given current management practices and site characteristics. • There is a low probability of an adverse impact to surface waters from P losses from this site. • Nitrogen-based nutrient management planning is satisfactory for this site. • Soil P levels and P loss potential may increase in the future due to continued nitrogen-based nutrient management.
51-75	Medium	<ul style="list-style-type: none"> • Medium potential for P movement from this site given current management practices and site characteristics. • Practices should be implemented to reduce P losses by surface runoff, subsurface flow, and erosion. • Nitrogen-based nutrient management planning should be implemented no more than one year out of three. • Phosphorus-based nutrient management planning should be implemented two years out of three during which time P applications should be limited to the amount expected to be removed from the field by crop harvest or soil-test based P application

		recommendations, whichever is greater.
76-100	High	<ul style="list-style-type: none"> • High potential for P movement from this site given current management practices and site characteristics. • Phosphorus-based nutrient management planning should be used for this site. • Phosphorus applications should be limited to the amount expected to be removed from the field by crop harvest or soil-test based P application recommendations. • All practical management practices for reducing P losses by surface runoff, subsurface flow, or erosion should be implemented.
>100	Very High	<ul style="list-style-type: none"> • Very high potential for P movement from this site given current management practices and site characteristics. • No phosphorus should be applied to this site. • Active remediation techniques should be implemented in an effort to reduce the P loss potential from this site.

Table 3.4: Descriptions of the 50 field sites that were resampled in 2012			
County	Series	Series texture*	Texture by feel (1994)
Allegany	Wharton	Silt Loam	Silt Loam
Allegany	Cavode	Silt Loam	Silt Loam
Anne Arundel	Mattapex	Silt Loam	Silt Loam
Anne Arundel	Mattapex	Silt Loam	Silt Loam
Caroline	Hambrook	Sandy Loam	Sandy Loam
Caroline	Hambrook	Sandy Loam	Sandy Loam
Caroline	Hambrook	Sandy Loam	Sandy Loam
Caroline	Woodstown	Sandy Loam	Silt Loam
Carroll	Penn	Silt Loam	Silt Loam
Cecil	Matapeake	Silt Loam	Silt Loam
Cecil	Matapeake	Silt Loam	Silt Loam
Frederick	Glenelg	Loam	Silt Loam
Frederick	Duffield	Silt Loam	Silt Loam
Frederick	Duffield	Silt Loam	Silt Loam
Garrett	Lickdale	Silt Loam	Silt Loam
Garrett	Lickdale	Loam	Loam
Harford	Chester	Silt Loam	Silt Loam
Harford	Chester	Silt Loam	Silt Loam
Harford	Montalto	Silt Loam	Silt Loam
Harford	Montalto	Silt Loam	Silt Loam
Howard	Glenville	Silt Loam	Silt Loam
Howard	Glenelg	Loam	Silt Loam
Montgomery	Occoquan	Sandy Loam	Loam
Queen Anne's	Ingleside	Sandy Loam	Loam
Queen Anne's	Ingleside	Sandy Loam	Loam
Queen Anne's	Unicorn	Loam	Sandy Loam
Queen Anne's	Unicorn	Loam	Sandy Loam
Queen Anne's	Mattapex	Silt Loam	Silt Loam
Queen	Mattapex	Silt Loam	Silt Loam

Anne's			
Saint Mary's	Beltsville	Silt Loam	Silt Loam
Somerset	Ingleside	Sandy Loam	Sandy Loam
Somerset	Glassboro	Sandy Loam	Loam
Somerset	Hammonton	Loamy Sand	Sandy Loam
Talbot	Fallingston	Sandy Loam	No Data
Talbot	Ingleside	Loam	Loam
Talbot	Woodstown	Sandy Loam	Sandy Loam
Talbot	Hambrook	Sandy Loam	Sandy Loam
Talbot	Hambrook	Sandy Loam	Loam
Washington	Duffield	Silt Loam	Silt Loam
Washington	Duffield	Silt Loam	Silt Loam
Washington	Ryder	Silt Loam	Silt Loam
Washington	Hagerstown	Silty Clay Loam	Silty Clay Loam
Wicomico	Mullica	Sandy Loam	Sandy Loam
Wicomico	Berryland	Sand	Sandy Loam
Worcester	Nassawango	Silt Loam	Silt Loam
Worcester	Cedartown	Loamy Sand	Sandy Loam
Worcester	Woodstown	Sandy Loam	Sandy Loam
Worcester	Hambrook	Sandy Loam	Sandy Loam
Worcester	Matapeake	Silt Loam	Silt Loam
Worcester	Matapeake	Silt Loam	Silt Loam
*Series texture information based on the description of the dominant soil series for each field by the National Cooperative Soil Survey			

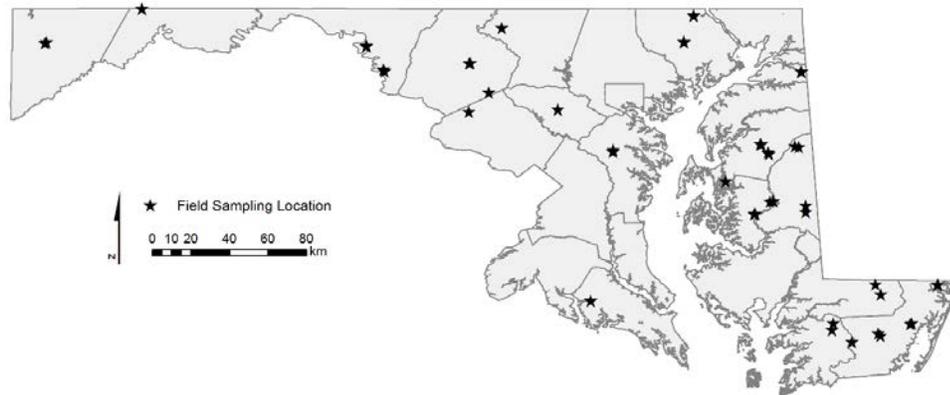


Fig. 3.1. Locations of the 50 field sites across Maryland that were resampled in 2012, out of the original 76 total field sites that were sampled in 1994. Some of the sites are overlapping at this scale, as many sites were paired fields at the same farm.

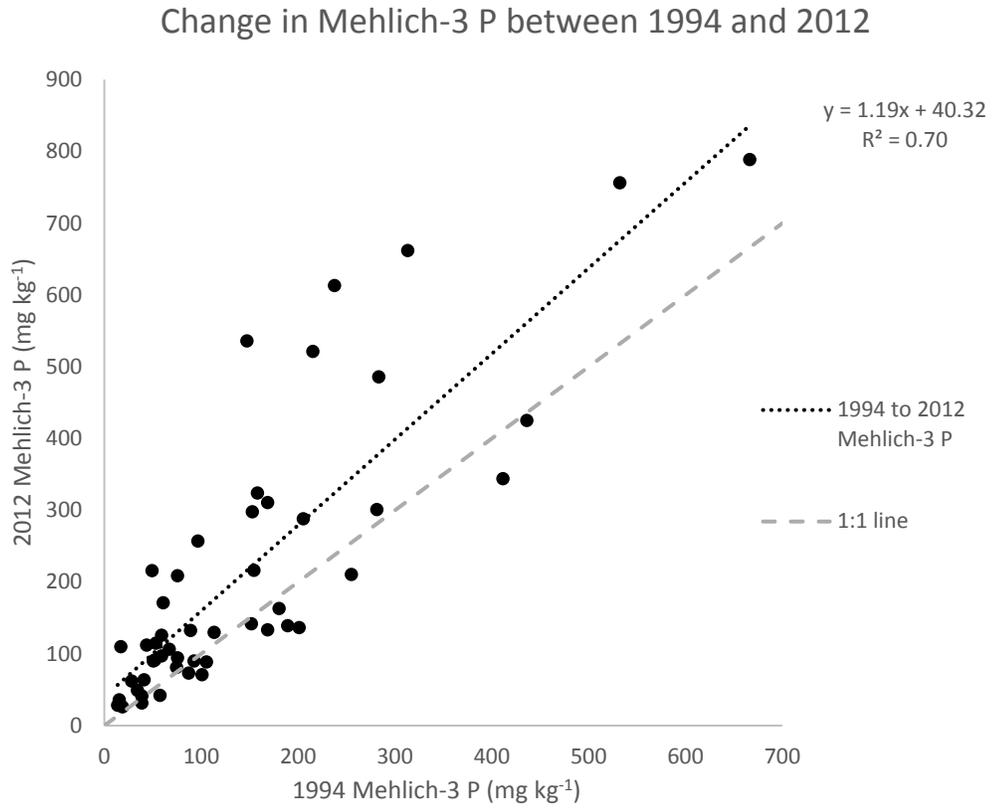


Fig. 3.2. Mehlich-3 P(M3P) analysis (mg kg⁻¹) from 1994 is regressed with 2012 M3P and compared to a 1:1 line. This demonstrates how the actual change in M3P differs from a scenario where no change in P occurred.

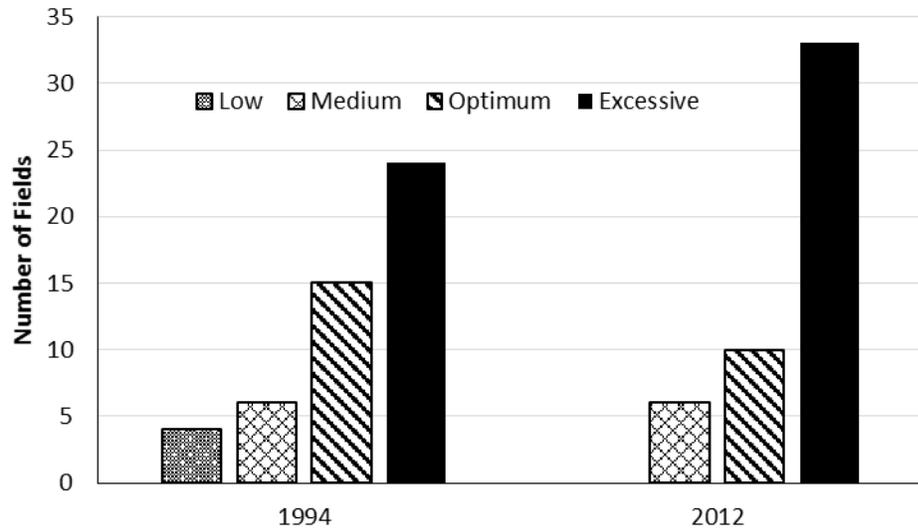


Fig. 3.3. Number of fields from 49 sites in each University of Maryland soil test interpretive category in 1994 and then in 2012. Low is 0-18 mg kg⁻¹ Mehlich-3 (M3P), medium is 19-43 mg kg⁻¹, optimum is 44-92 mg kg⁻¹, and excessive is >93 mg kg⁻¹.

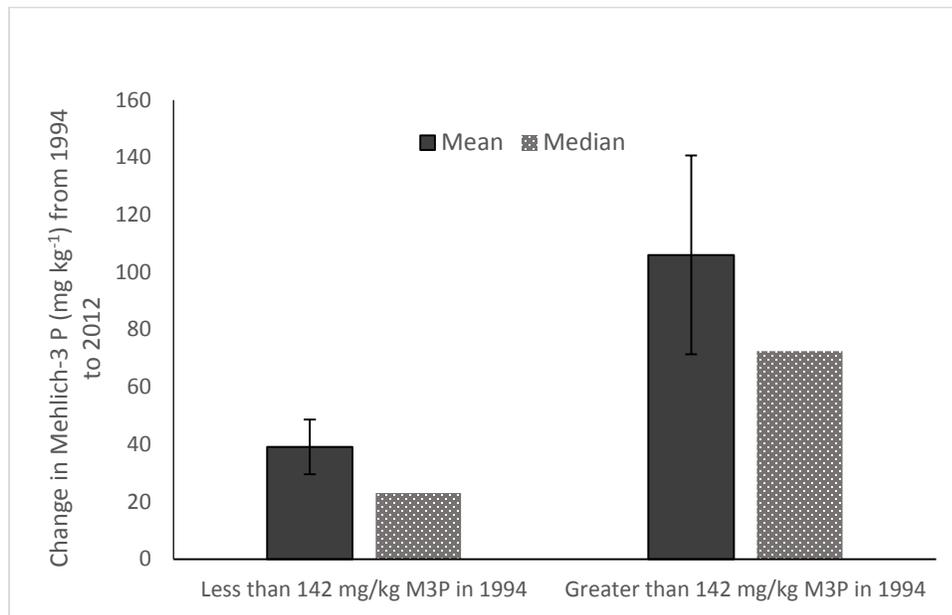


Fig. 3.4. Mean and median change in Mehlich-3 P (M3P) (mg kg⁻¹) from 1994-2012, separated by those that started with less than or greater than 142 mg kg⁻¹, the legal threshold where P additions were limited using the phosphorus site index in Maryland, which was made mandatory beginning in 2002.

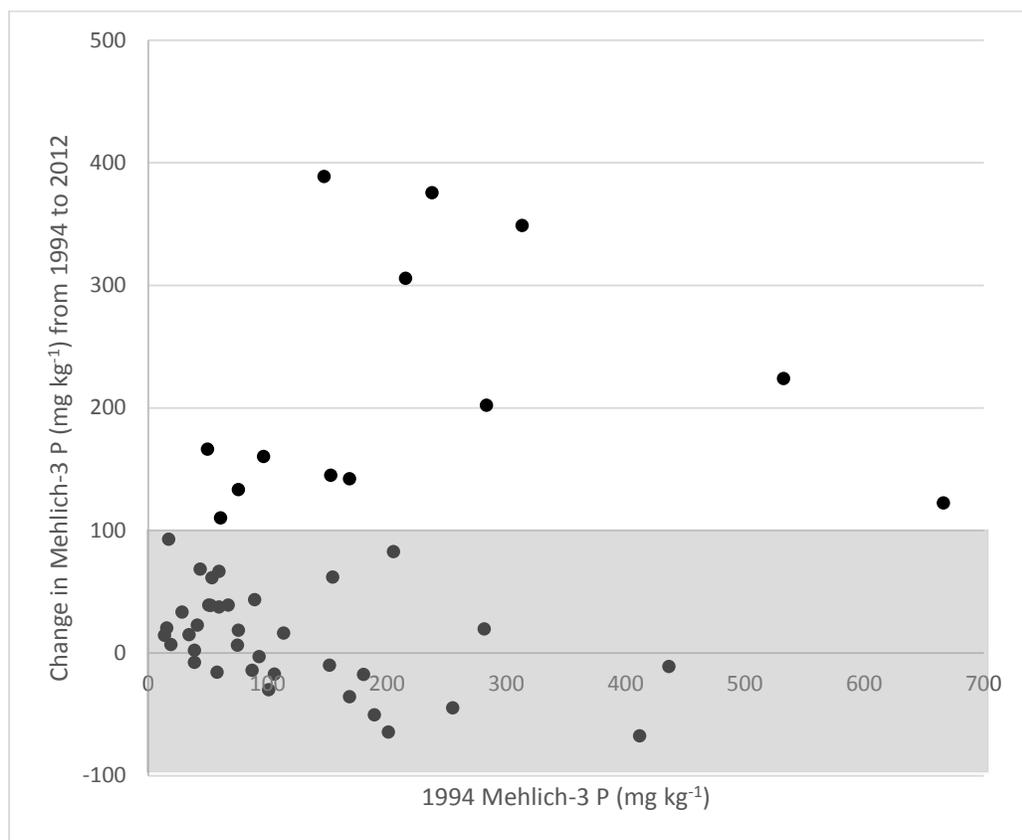


Fig. 3.5. Change in Mehlich-3 P (M3P) (mg kg⁻¹) from 1994 to 2012 at each of the 49 sites is plotted against the original 1994 M3P. The 13 points above the shaded area experienced an increase of more than 100 mg kg⁻¹ M3P.

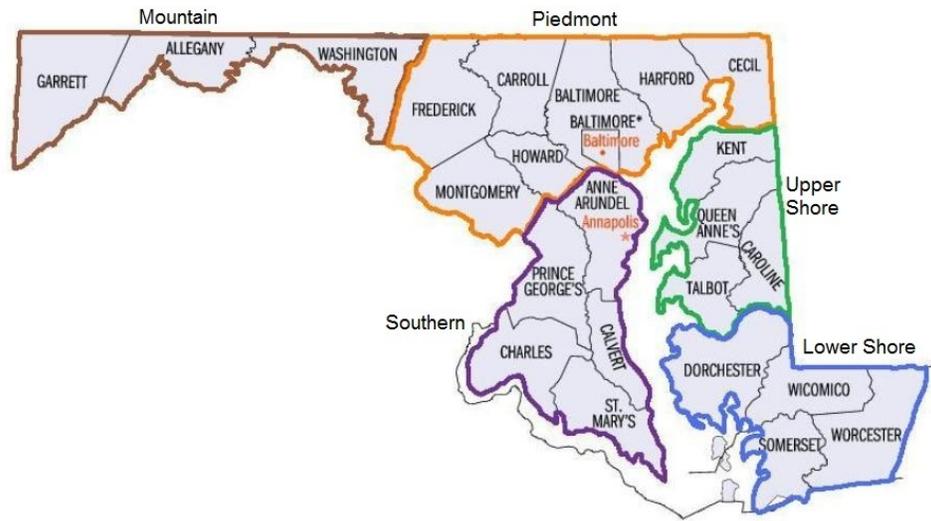


Fig. 3.6. The five regions of Maryland are outlined in thick lines. They are mountain, Piedmont, Southern, Upper Shore, and Lower Shore.

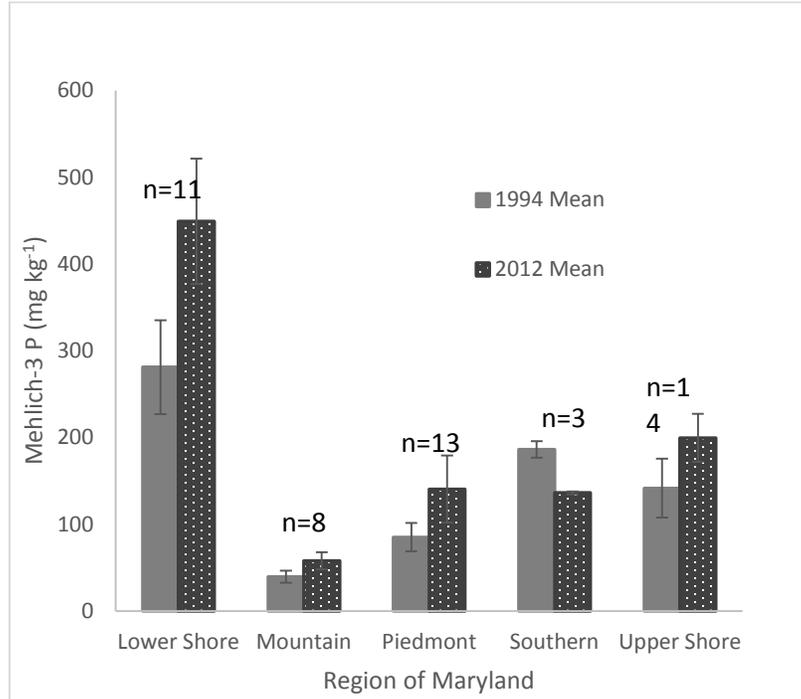


Fig. 3.7. Shift in mean Mehlich-3 P (M3P) (mg kg⁻¹) by region in Maryland from 1994 to 2012. The number of samples in each region is indicated by “n,” for a total of 49 samples across Maryland.

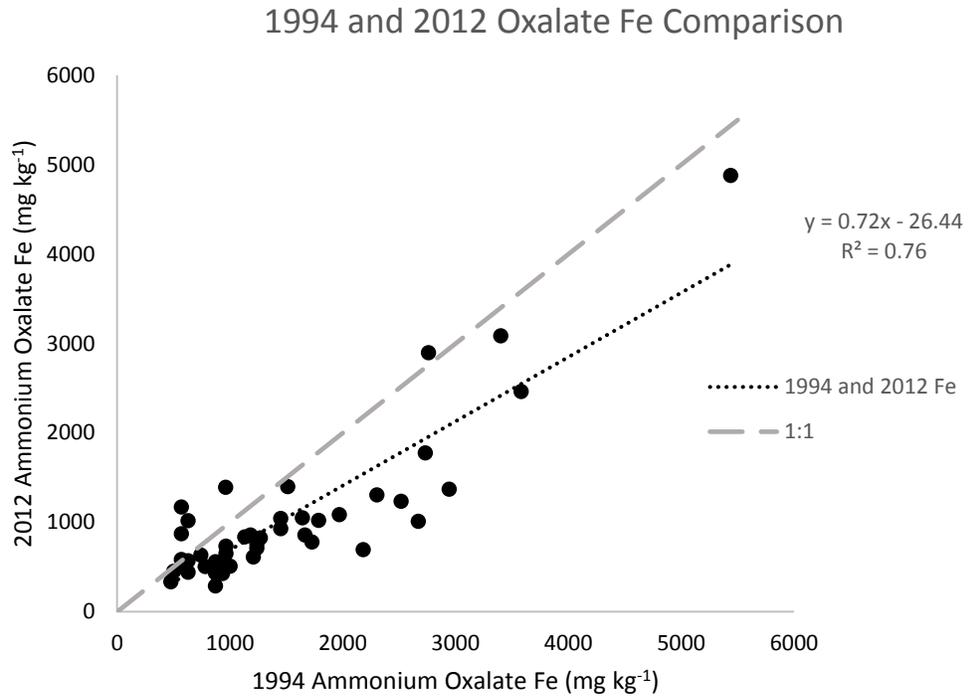


Fig. 3.8. The change in ammonium oxalate iron (mg kg^{-1}) from 1994 to 2012 for each site compared to a 1:1 line.

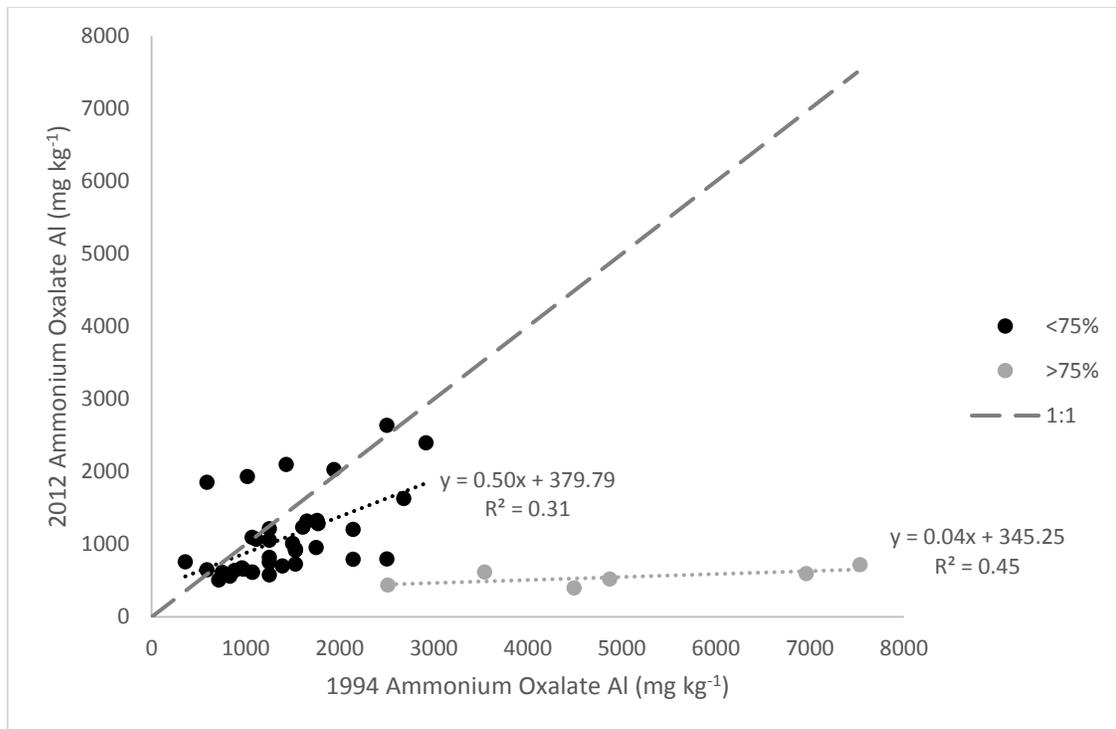


Fig. 3.9 The change in ammonium oxalate aluminum (mg kg⁻¹) from 1994 to 2012 for each site compared to a 1:1 line.

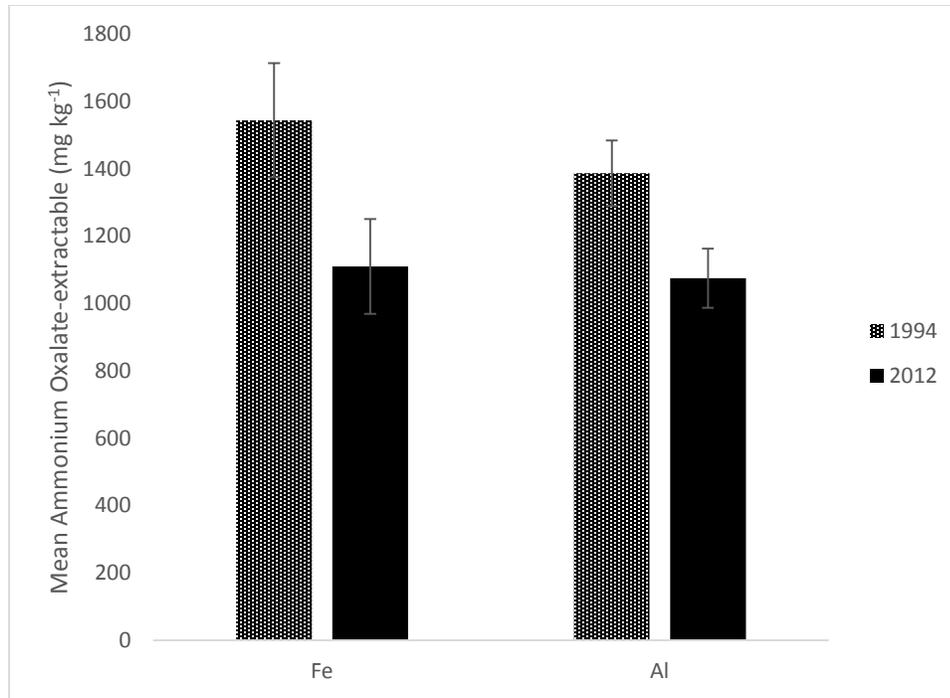


Fig. 3.10. The change in average ammonium oxalate iron and aluminum (mg kg⁻¹) from 1994 to 2012.

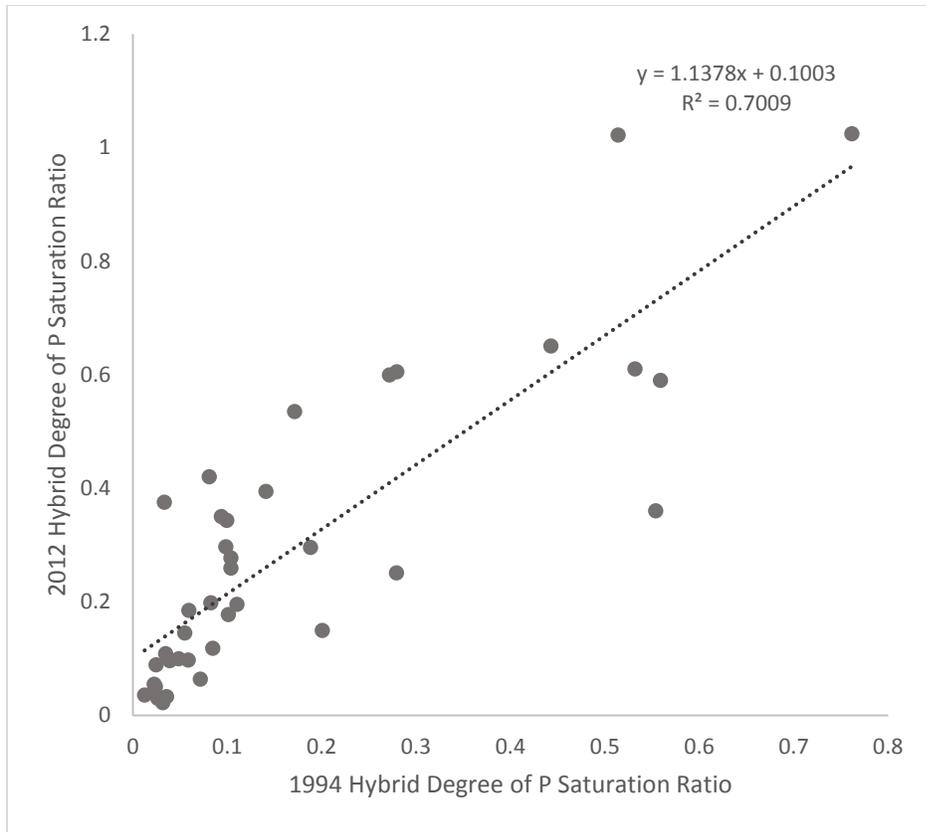


Fig. 3.11. “Hybrid” Degree of Phosphorus Saturation ($DPS_{Hybrid} = [(OxP)/\alpha(OxFe+OxAl)]$) plotted on a site by site basis.

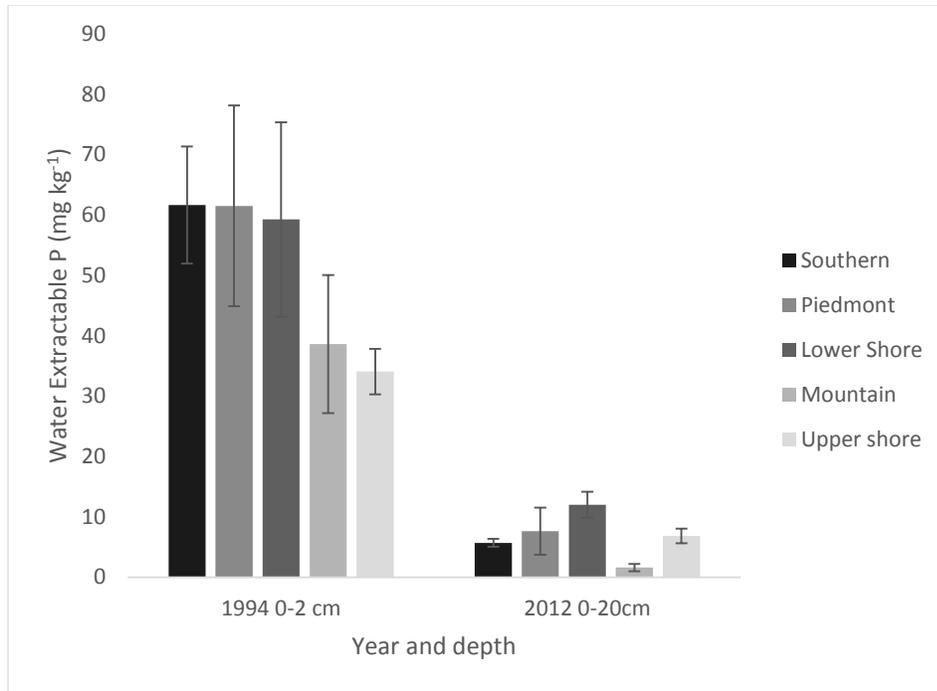


Fig. 3.12. Water extractable phosphorus (WEP) (mg kg⁻¹) in 1994 at 0 to 2 cm sampling depth, and 2012 at 0 to 20 cm observed by region. Standard error is represented by the error bars.

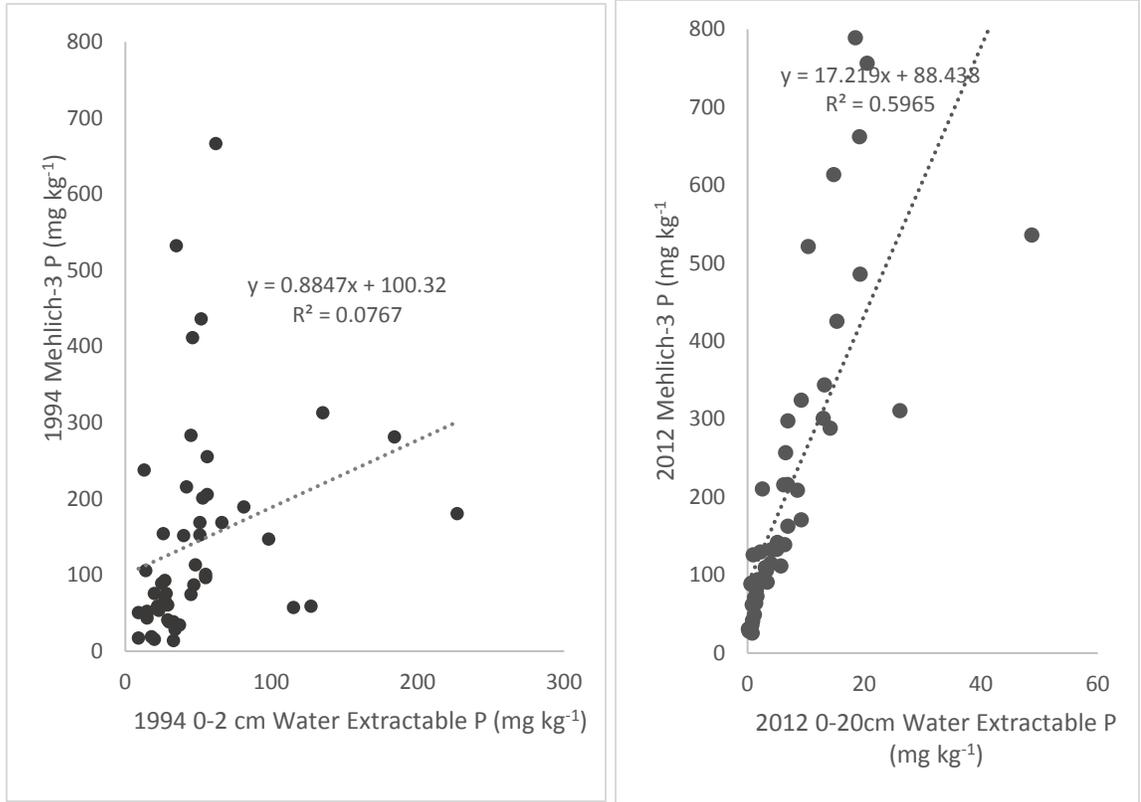


Fig. 3.13a. Mehlich-3 extractable P (M3P) (mg kg⁻¹) from 1994 sampling at 0 to 20 cm sampling depth compared to 1994 water-extractable P (WEP) (mg kg⁻¹) at 0 to 2 cm sampling depth.

Fig. 3.13b. Mehlich-3 extractable P (M3P) (mg kg⁻¹) from 2012 sampling at 0 to 20 cm sampling depth compared to 2012 water-extractable P (WEP) (mg kg⁻¹) at 0 to 20 cm sampling depth.

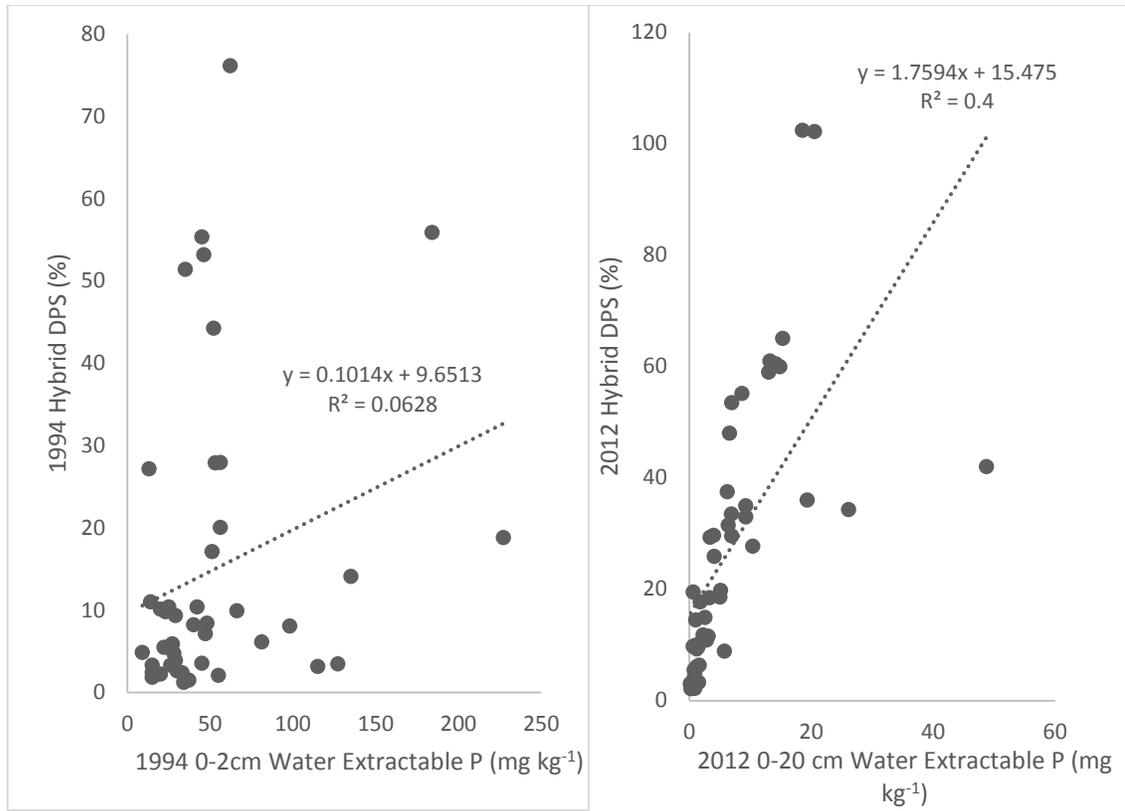


Fig. 3.14a. “Hybrid” degree of phosphorus saturation ($DPS_{Hybrid} = [(OxP)/\alpha(OxFe+OxAl)] \times 100$) from 1994 sampling at 0 to 20 cm sampling depth compared to 1994 water-extractable P (WEP) (mg kg⁻¹) at 0 to 2 cm sampling depth.
 Fig. 3.14b. “Hybrid” degree of phosphorus saturation ($DPS_{Hybrid} = [(OxP)/\alpha(OxFe+OxAl)] \times 100$) from 2012 sampling at 0 to 20 cm sampling depth compared to 2012 water-extractable P (WEP) (mg kg⁻¹) at 0 to 20 cm sampling depth.

Appendix 1: Data Refinement

Six outliers in the OxAl data had to be eliminated due to anomalous values in the 1994 data. These 6 outliers had 1994 Al concentrations of 2511, 3540, 4490, 4870, 6960, and 7530 mg kg⁻¹, with respective 2012 Al concentrations of 441, 618, 401, 523, 597, and 720 mg kg⁻¹. Shober and Sims (2007), analyzed eight soils commonly found in the mid-Atlantic, with textures including sandy loam, loamy sand, silt loam, clay loam, silty clay loam, and loam, and found a range of 285 to 1284 mg kg⁻¹ ammonium oxalate-extractable Al. Similarly, Penn and Sims (2002) analyzed Coastal Plain soils after poultry litter and biosolids amendment and found a range of ammonium oxalate-extractable Al of 493 to 1640 mg kg⁻¹. The outliers in the 1994 OxAl data were above these values reported in literature, and experienced decreases in OxAl concentration of greater than 75% by 2012. The OxFe data did not exhibit any similar abnormal values or declines. These sites were removed from the data set for observation of OxAl and OxFe trends.

The decrease in Fe and Al was unexpected. An overall decrease of these elements in the soil is unlikely, and may be explained by laboratory or sampling error. Laboratory error could be likely due to the fact that the original samples were analyzed at the University of Maryland Soil Testing Lab, and the samples taken for this study were analyzed at the University of Delaware soil testing lab. An example of a sampling error could have been that the researchers may have pushed the soil probe to slightly different depths. Potentially, some change could have occurred in the soil that make the extraction less efficient in 2012 than it was in 1994. The primary purpose of examining Fe and Al was to determine the ability of the soil to hold P, using a degree of P saturation (DPS) calculation.

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