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Final Report: Assessment of rate and timing of P application in corn-soybean rotations on the potential for P loss to surface waters and tile.

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OBJECTIVES 1-4
OVERVIEW AND OBJECTIVES

Phosphorus (P) is an essential nutrient in corn and soybean systems for maximizing yields and profits in Minnesota. The over-application of P fertilizer has led to the impairment of freshwater ecosystems throughout the Midwest and United States. This excess P in freshwater systems can ultimately lead to eutrophication and detrimental species population shifts in Minnesota lakes and rivers.

The majority of research conducted for P loss in agricultural systems has been focused on runoff P, or P attached to soil particles. Because P is highly reactive, it tends to bind with other substances in the soil, making soil particles the vehicle for P transport. Once the soil particle reaches a freshwater body, the P is chemically released and made available for biological use, leading the large algae blooms.

Action such as reduced tillage and buffer strips have been implemented to help reduce this P loss. However, few researchers have considered the loss of P through leaching, as it has been considered an insignificant P loss pathway (Sims et al., 1998). However, some studies have indicated otherwise, especially for soils with high initial soil test P (STP) levels (Heckrath et al., 1995; Hooda et al., 2000; McDowell and Sharpley, 2001). Additional research has indicated that soils enriched from P fertilization may be prone to P leaching to subsoils (Sims et al., 1998).

Other studies have reinforced the risk of P leaching due to soil physical properties, with preferential flow and macropores leading to large hydrologic movement in soils, in turn leading to movement of P (Djodjic et al., 1999). Soils which are poorly drained and with little changes in topography are at further risk for soluble P movement (King et al., 2015). The over-saturation of these soils pose a risk for greater subsurface movement of P, especially for P movement to tile drains.

Limited research has been conducted on the threat of P leaching from agricultural land, and less is known on how to quantify the potential losses. To help mitigate P pollution, research was completed to identify the risk of P leaching loss to the environment from agricultural soils with the following objectives:

1. Evaluate how rate and timing of P application in a 2-year corn-soybean rotation affects the soluble and bio-available P loss of surface soils for contrasting soils.
2. Study the impact of phosphorus fertilizer management on the enrichment/depletion of soil P from soil depths greater than 6” from the soil surface using traditional soil test methods.

3. Determine the effect of P fertilizer application on the potential for P leaching in contrasting soils.
4. Study the impacts of long-term P management on the amount of P that can be sorbed to surface (0-6”) and sub-surface soils (6-12”).

METHODS

Site Description

This study included six locations throughout the state of Minnesota ranging in soil texture from sandy loam to clay loam with various physical and chemical properties (Table 1). Locations were part of a long term phosphorus study under consistent P management since 2010 (Sims et al., 2014). For the initial study evaluating influence of timing, soil type, and volume; sixteen plots were selected at each location to represent soils previously classified as Low (L), Medium (M), High (H), and Very High (VH) in P concentration using the Olsen P agronomic soil test. Classification of soils by soil test P (STP) levels was completed according to University of Minnesota Extension guidelines. Exact soil test values for cores collected within each plot are summarized in Table 2 (Kaiser, 2010). For the study evaluating influence of fertilizer source and volume, two-three of the initial six sites were selected to represent varying soil textures.

Sampling

At leach location, intact soil columns were collected from plots categorized as low (L), medium (M), high (H), and very high (VH) STP. A tractor operated hydraulic soil probe was used to drive PVC pipe (3.81 cm in diameter) to a depth of 15 cm to collect the intact columns. Columns were beveled on the bottom edge to help prevent compaction as the PVC forced into the ground. The complete sets of columns were capped at each end and stored in cold rooms at 4°C. Eight soil cores were collected from the top 0-15 cm of the soil surface within 30 cm radius of where PVC cores were sampled and composited. Samples were dried at 40°C, ground to pass through a 2 mm sieve, and analyzed for chemical and physical properties.

Soil Sample Analysis

Samples were analyzed for pH [1:1 soil/water (Peters et al., 2015)], Bray-P1 and Olsen P extractable P (Frank et al., 2015) following recommended procedures for the North-Central Region of the USA. Bulk density was determined using the core method (Blake and Hartge, 1986) and water holding capacity at 33 kPa was determined for soils using the volumetric method (Tan, 1996). Soil textural class was determined with particle size analysis using the hydrometer method (Bouyoucos, 1962). Soil water extractable P (WEP) was measured according to methods by Pote et al. (1999) and Bio-Available P was measured using methods according to Chardon (2000). Concentration of P for both WEP and bio-available P (BAP) content was determined using Ascorbic Acid colorimetric method (Murphy and Riley, 1962) and were measured at 882nm with a Biotek Epoch microplate spectrophotometer (Biotek, Winooski, VT). Calcium carbonate equivalency (CCE) was determined using the modified pressure calcimeter method (Sherrod et al., 2002). Soils were analyzed for iron (Fe), aluminum (Al), manganese (Mn), and calcium (Ca) content following the citrate-bicarbonate-dithionite (CBD) method (Mehra, 1958; Mehra and Jackson, 1960), and element concentration was determined by inductively coupled plasma optimal emission spectroscopy (ICP-OES) analysis. Procedures from

McKeague and Day (1966) were used to determine iron, aluminum, and manganese content from acid ammonium oxalate extraction with ICP-OES analysis. Phosphorus sorption was measured for all composite soils measured using an adapted multi-point procedure from Pagliari (2016). From the P concentration, the P sorption index (PSI) was determined for the 75 ppm and 100 ppm treatment and degree of P saturation (DPS) was calculated using four methods.

a
$$\mathrm{DPS}_{\mathrm{STP1}} = \frac{\mathrm{STP}}{\mathrm{PSI}}(100)$$

b
$$\mathrm{DPS}_{\mathrm{STP2}} = \frac{\mathrm{STP}}{(\mathrm{STP}+\mathrm{PSI})}(100)$$

c
$$\mathrm{DPS}_{\mathrm{ox}} = \frac{\mathrm{P}_{\mathrm{ox}}}{(\mathrm{Al}_{\mathrm{ox}}+\mathrm{Fe}_{\mathrm{ox}})}(100)$$

d
$$\mathrm{DPS}_{\mathrm{CBD}} = \frac{\mathrm{P}_{CBD}}{(\mathrm{Al}_{\mathrm{CBD}}+\mathrm{Fe}_{\mathrm{CBD}})}(100)$$

Abbreviations: CBD, citrate-bicarbonate-dithionite; DPS, degree of P saturation; OX, oxalate; PSI, P sorption index; STP, soil test P;

Leaching Procedure

Sixteen columns were leached at one time which allowed for four replications of the four STP classifications for a single soil to be leached at one time. Vacuum pressure was applied to ensure consistency in leaching across the set of 16 columns and to ensure all gravitational water was drained from the columns. Pressure applied to the column was between 50 to 100 kPa (0.5 – 1.0 bar), slightly higher than field capacity (33 kPa).

The amount of water leached was standardized to each soil based on the soils available water holding capacity at 33 kPa (Table 1). Each column was leached at 10 times field capacity to ensure a leaching event would occur. Before leaching was carried out, four sets of soil columns received a fertilizer treatment of 100 kg P ha^{-1} (11.38 mg P column^{-1}) as a solution of KH_2PO_4 in deionized water. The P rate applied was high representing around 2x P removal for crops was used to ensure a greater potential for P movement. Treatments were administered with a calibrated electronic pipet to ensure accuracy and uniform soil contact across experimental units. The fifth set of columns acted as a control with no fertilizer treatment to evaluate influence of initial STP level alone. Treated columns were leached with deionized water 0 day, 1 day, 3 days, or 7 days after fertilizer application. The 0 day timing was undisturbed for approximately 2 hours after fertilization and before leaching. These treatment timings are denoted as ‘leach times.’

The volume intensity study was set up using the same procedure outline above except leaching volumes were kept constant across soils receiving one of the three volumes for leaching treatments: 200 mL, 400 mL, or 600 mL of deionized water. The experiment evaluating P fertilizer sources consisted of similar leaching methods with the same timing treatments. Four P sources were evaluated using the same rate in the previous study of 100 kg P ha^{-1} and the same liquid treatment as one of the P sources: 1) Dry reagent grade potassium dihydrogen phosphate (KH_2PO_4) powder; 2) KH_2PO_4 in solution with DI water; 3) homogenized liquid dairy manure; 4) KH_2PO_4 as a solution with DI and AVAIL (0.5%). Avail contains a maleic–itaconic copolymer which has a cation exchange capacity and is marketed to increase P availability by sorbing elements like Ca which bind with P.

Manure for the study was collected from a University dairy research collaborator and analyzed for P concentration prior to the study. Manure was 13.85 percent dry matter with a P content of 0.269 g P ha^{-1}. Before application to columns, manure was homogenized and weight was used to determine amount to apply to columns. Similar to the former study, an electronic pipet was used to administer the liquid treatments. After the appropriate amount of time had passed (0, 1, 3, 7 days), columns were leached at a consistent leaching volume, 200 mL, for both sites.

Leachate collected was weighed and recorded to determine P load and analyzed for WEP and DRP. A portion of the leachate was filtered through Whatman 42 filter paper (2.5 um pore size) and analyzed colorimetrically by methods used for soil sample P determination (Chardon, 1979; Pote et al., 1996). A second subsample of the leachate was filtered through a 0.45-micron filter and analyzed for dissolved reactive P (DRP) using the same colorimetric methods.

Phosphorus leaching loss was quantified as: P concentration (mg P L^{-1}), total P leached per column (P load), P load normalized based on the dry weight of soil in each column (P loss per unit soil), percent P fertilizer loss per column.

The P quantification method is of great importance in this study, as the P concentration represents a subsample, and P load represents total P loss; these two estimates are not equated.

Statistical Analysis

Statistical analyses for these experiments were conducted in R (R Development Core Team, 2018). The volume, timing, and source studies were analyzed as split-split plot designs, and split plot by location. The influence of STP was analyzed as a randomized complete block design. The factors for the experiments included two to three of the following: timing, STP level, soil type, source, and volume intensity. Statistical analysis for these experiments included ANOVA, ANCOVA, Tukey's HSD and Fischer's LSD mean separation tests; and pairwise t tests for comparison of factors. Correlation between soil sample tests and leachate P load was identified using linear regression and Pearson's Correlation. Predictive linear models for P leaching concentration based on STP measurements and soil properties were assessed using validated and training data sets. Sorption parameters were determined by fitting a model using the Langmuir equation for each site and STP level. Two nonlinear exponential decay models were fit to explain the P decrease in leaching over time using both P leachate concentration and percentage of P fertilizer lost as the dependent variables

RESULTS

Variation in soil chemical properties

A summary of soil series information is given in Table 1. Sites were selected to represent major soil associations in their particular area of the state. Table 2 summarizes Soil P tests for the Bray and Olsen tests for the individual soil test levels at each location. The target build points for the soil test levels were the Low, Medium, High, and Very High classifications (Bray P1 P 5-10, 11-15, 16-20, and >20 ppm, respectively). The build points were close for all sites except for Lamberton where the soil test values were well over the expected range with the soil test for the intended Low classification actually testing in the high category and Morris where there was little difference between the High and Very High category. The soil samples were collected in close proximity to where the leaching cores were taken thus some of the variation in intended versus measured soil test values could be due to small scale variability within the plot.

Environmental soil tests were assessed to determine if they would better estimate P loss. Table 3 summarizes the impact of the different soil P classifications on water extractable P (WEP) and bio-available P (BAP). Measured WEP values were less than BAP due mainly in part to the smaller fraction of WEP in the soil. Overall, there was a general increase in both WEP and BAP as plant availability (soil test P) increased. The BAP measurements were greater on average for Lamberton which reflects the greater Bray P1 and Olsen soil test values. However, WEP at Lamberton was in the middle of all values indicating that the increase in Bray or Olsen P is not necessarily reflected in increased WEP. The lowest overall BAP and WEP values were found at Becker where there was no difference in WEP and BAP among the Low, Medium, and High soil test classifications.

Correlations among routine agronomic and WEP and BAP are summarized in Table 4. All measurements were highly correlated. The weakest correlations were between WEP and Bray and Olsen P. The BAP measures were highly correlated to both Bray and Olsen values across and within sites. The Bray P test generally results in an under extraction of available P for high pH soils which are high in carbonate. The carbonate content of the soils in the study were low and had little impact on the Bray P test. Thus, the overall correlation between the two tests was high across locations. It was surprising that WEP had the poorest correlation with the other tests. The Bray and Olsen extractions should extract from the same pool as the WEP test. However, some of the additional soil P pools may be impacted by the Bray and Olsen tests versus the WEP portion.

Effects of Soil Type and Properties and initial STP on P Leaching

Without fertilizer added, phosphorus leachate concentrations did not significantly ($P \leq 0.05$) differ among the six sites when averaged across STP classifications (Table 5). Initial level of P in the soils was the primary factor influencing the P leachate concentration, rather than other inherent soil properties. The only discrepancy between P concentration and STP ranking was at Rochester, which may be due to soil chemical properties such as Fe and Al oxide (Table 6) or Ca presence that could potentially hold soil P more securely in a leaching event. Rochester, with the greatest concentrations of Fe and Al oxides of the six soils, was likely complexing P, which in turn, lessened the concentrations of P in the column leachate. In this study, analysis across the six sites suggested P concentration was primarily driven by the initial STP levels in the soil, with some influence due to high presence of oxides in the Rochester soil.

Further analysis of initial STP levels indicated an increase in STP level; categorized as Low (L), Medium (M), High (H) and Very High (VH); led to increase in average P leaching losses as DRP and WEP. Considering total P lost as P load, only the VH initial STP level was significantly different from all other STP levels when averaged across the six sites as P Load (mg P column^{-1}) (Figure 1). The trend of P leaching losses follows an intuitive increase with the increase in initial STP. Examined individually, four sites showed significant differences in P leaching loss as P load (Table 7, Figure 2) between the L and VH plots.

Looking at P leaching losses with the OP soil test as a covariate, there was a significant effect, indicating the initial STP concentration in the soil was influencing P leachate concentrations. An increase in P leachate concentration with increasing STP levels also follows trends shown in runoff studies, with P runoff losses increasing with increasing STP concentration (Sims et al., 1998; Hooda et al., 2000; Allen et al., 2002).

With the addition of fertilizer, soil type and initial STP level significantly affected P fertilizer loss. The initial OP levels in the soil influenced P loss, with greater initial STP levels leading to greater percentages of P lost (Table 8, Figure 3). However, there was no significant differences between STP levels at individual sites (Figure 4) which was reflective in a high degree of variation among the replications for each treatment. On average across STP, Becker had the greatest P concentrations in leachate possibly due to a lesser sorption capacity of the sandy loam soil, similar to previous research findings (King et al., 2015). Clay soils have also been found to be particularly susceptible to P leaching losses due to preferential flow (Djodjic et al., 1999; Andersson et al., 2013; King et al., 2015). This was reflected in results the soils with the greatest clay content, Lamberton and Waseca (28 and 30 % clay respectively) (Table 8). The development of preferential flow pathways in the clay soils likely led to greater transport of the P fertilizer through the column, leading to higher P concentrations (Figure 5). Despite the suspect low sorption capacity of the sandy loam soil, Becker had the lowest percentage of fertilizer leached, pointing to the volume of the leaching event (Table 8).

In evaluating the potential for P fertilizer leaching, each soil's sorption capacity was calculated using the methods outlined above. Results were generally varied between the sites, and no one site showed a sorptive capacity advantage over the others. The variety of the methods for estimating sorption revealed the chemical variability of the soils. For instance, estimates for sorption using DPS_{ox} indicate Crookston has the highest potential for sorption. Estimates using DPS_{STP} suggests the opposite, as Crookston is the site with the lowest DPS_{STP} sorption potential (Table 9). The difference in these sorption estimates indicates the variation in the inherent soil properties, which should be considered in evaluation of P sorption and P leaching.

Volume Effects

While P concentration was relatively similar between locations (ns) without fertilizer application, P load showed significant differences between sites (Table 10). With a fertilizer application, volume of the leaching event was also suspected to influence P leaching loss. Soils receiving the highest leaching volumes also leached the greatest percentage of fertilizer. The sandy loam, Becker, had the highest P leachate concentration, but the lowest P load. The large disparity in P load between the sandy soil and the five additional soils led to a follow-up experiment to identify the effects of leaching intensity (volume) on the potential for P leaching.

Analyzed across all sites, P concentration showed no significant differences between the three leaching volume intensities of 200, 400, and 600 mL which correspond to rainfall events of 6.9, 13.9, and 28.4 inches, respectively. While rainfall events of these sizes are not likely the volume used was to ensure a substantial amount of water would be leached through each column. Only the P leachate concentration between sites was significantly different. This was likely due to initial STP differences between the sites. Volume intensity had the greatest influence on P load across all soil types and STP levels, similar to the results in the initial study, where leaching was driven by the amount of water leached through the column. All sites evaluated individually showed significant increases in P load with increasing volume of the leaching event (Table 10). Averaged over each STP level, P load followed the same trend, with increasing P leaching losses with increasing volume intensity.

Volume of the leaching event did not cause a significant change in P leachate concentration at either STP level, but had a significant effect on P load (Figure 6). This suggests a prediction method may be developed to estimate P load leaching losses if initial soil type, STP level, and volume of a leaching event are known.

Effects of Timing

Across all sites, leachtime was a significant factor, with P fertilizer loss and P leachate concentration decreasing over time. This relationship follows the initial hypotheses that greater amounts of time between fertilizer application and the leaching event would lead to lesser P losses, as fertilizer would have more time to sorb to the soil. Phosphorus fertilizer loss was greatest for the immediate leach (0 day) and significantly different from the 1, 3, and 7-day leachings at each site (Table 11).

Site and STP level influenced P concentration and P fertilizer loss between individual timings, though these influences often followed similar patterns (Figure 7). The immediate, 3-day, and 7-day leachtime P concentrations were significantly affected by initial STP levels, with the VH classified soils releasing greater amounts of P than the L STP soils. At all leach times, the percentage of fertilizer leached was greatest in the clay soils, Lamberton, Waseca and Crookston; and lowest for the sand soil Becker (Figure 8). The influences of soil type and STP among the individual timings followed the same trends as the averages, with clay soils leaching greater amounts consistently across the timings.

The decrease in P leaching over time suggested sorption was occurring between the leaching events. Phosphorus fertilizer leached was reduced between 37 to 63 percent from the immediate leach to the 1-day leachtime (Table 12). By the 7-day leach, the decrease in the amount leached from the immediate leach was over 70 percent for all sites, which the exception of Crookston (54 % reduction).

Timing of the onset of leaching after fertilizer application had significant effects on P leaching losses for Minnesota soils. At Lamberton, an immediate leaching event after P fertilizer application led to greater than 30 percent loss (Table 11). Seven days later, total P fertilizer loss dropped to lower than 7 percent.

Phosphorus leaching was reduced by over 70 percent for five sites of the six sites between the immediate leaching event and the leaching event occurring seven days after fertilization. The reduction in P leaching loss over a seven day period points to the soil's ability to sorb the P fertilizer. An exponential model was fit to the decrease in P fertilizer leaching across leach times to determine if there was a relationship between the timing of a leaching event and the sorption potential of the soils (Figure 9).

Effects of P Source

The study evaluating P fertilizer sources indicated soluble P losses were due to site, P fertilizer source, and timing of the leaching event; with interactions between source and timing, and source and site. On average, P leachate concentration and the percentage of P fertilizer lost was largely affected by source (Figure 10). Dry P fertilizer leachate resulted in significantly higher P concentration than the other sources. AVAIL treated liquid fertilizer did not differ from liquid without AVAIL. Manure had nearly negligible P concentrations in comparison to the other sources and the percentage of P leached tended to be negative indicating tie-up of P by manure (Table 13). Timing of the leaching event followed similar trends as the first study, with significantly greater leaching occurring for the immediate leach, followed by the 1-day, 3-day and 7-day leach timings (Figure 11). These rankings were consistent for the percentage of P fertilizer lost when considering total P load. While the numerical values between liquid treated with and without AVAIL appeared differ there analysis indicated similar changes in P transferred over time between the two sources. Since AVAIL is meant to prevent tie-up of P with metal cations it was expected that P concentration would greater and more of the P applied would potentially be lost with AVAIL. The data from this study indicated that loss potential is the same and that AVAIL did little to protect P from binding with metals in the soil.

Leaching of P between sources were evidently different, with the manure application leading to sorption of P, and negative numbers for percent P fertilizer leached. As this number is corrected by a blank column to standardize for desorption without fertilizer applied, it indicated manure reduced the potential for P leaching in comparison to no fertilizer application. This conflicts with some of the literature indicating liquid manure application increases P leaching losses (Jiao et al., 2004; King et al., 2015). Research completed by Young et al. (2017) to identify the effect of controlled drainage found the application of manure to intact soil columns caused a significant increase in P loss as total P (TP) and soluble reactive P (SRP) in comparison to the non-treated soils. An explanation for the contrasting results of this study may be that the manure increased the sorptive capacity of the soil. Furthermore, the dry matter content of the manure may explain these discrepancies. In many studies a lagoon liquid is used as the organic fertilizer manure treatment versus a pen pack manure which was collected in this study.

In this study, a semi-solid form of manure was applied to leaching columns. Research by Kleinman et al. (2006) found the water to solids ratio greatly impacts the potential for P leaching. Using the WEP test for P on manure, Kleinman et al. (2006) found increasing WEP concentrations with increased dilution of manure solids. Furthermore, other researchers have indicated using only liquid forms of manure specifically for their solubility, as the release of solid-phase P is too time intensive, requiring decomposition and dissolution for study (Kang et al., 2011).

The type of P in leachate may also clarify the path of P leaching on manured soils. The leachate in this study was analyzed for WEP and DRP, but not Total P (TP). As this was an organic source, the amount of TP may indicate more fully the total P content of leachate (Kang et al., 2011). Further analysis and research is necessary to identify the long-term effects of manure on P leaching on these soils.

Overall, the dry fertilizer source caused the greatest amount of P leaching. Without incorporation, the dry fertilizer powder had minimal contact with soil water, likely preventing the P from dissolving and binding with the soil. The leaching event likely solubilized the P fertilizer and quickly drained it from the soil in a matter of hours. For the Becker soil, where the leaching event required no vacuum and leaching occurred though gravitational drainage, leaching was completed within hours. Across all leach times, 21 percent of the dry fertilizer was leached at Becker and 9 percent at Rochester (Table 13).

Mean P concentration and P fertilizer leached were slightly greater for leachate from the AVAIL treated soil, but not significantly different from the non-AVAIL treated liquid (Figure 10). The solubility of the AVAIL fertilizer and non-AVAIL treated liquid sources likely allowed the P to sorb with the soil before the leaching event. Both the liquid sources had significantly less P leaching loss in comparison to the dry fertilizer. Although the AVAIL is designed to prevent P sorption with the soil, it appears sorption occurred in the soils, as it did not leach nearly as freely as the dry P fertilizer source.

Selection of P fertilizer clearly influences P leaching as indicated by this preliminary study. Further research is necessary to decipher the in-depth influence of manure, and its components, and fertilizer solubility on P leaching.

Sorption related to P loss

Across all sites, P leachate concentration and P fertilizer loss estimates showed relationships with DPS_{STP1} and DPS_{STP2} using Pearson's correlation coefficients (Table 14). Concentration of P in leachate was also significantly related to the PSI_{75} sorption parameter, and P fertilizer loss was also related to DPS_{CBD}. There was no relationship between P leaching measurements for sites analyzed individually, except for Morris. Morris was the only site to show significant relationships between sorption parameters and P leaching.

The relationship between P sorption of the soil and loss of P fertilizer over time was identified by comparing model parameters for relationships. An exponential curve was fit for decreases over time for both P leachate concentration and P fertilizer loss for every plot of each site (similar to Figure 9). The two fits lead to different relationships between sorption estimates and model parameters for each site. Each exponential model estimated two parameters: 'A' described an initial starting point or intercept of the curve, and 'B' described the curve of the model and the rate at which it decreased. Parameter 'A' values were often close to the immediate leach value (0-day leachtime P loss) for the plot or average of plots.

Parameters from the exponential decay models for all sites had at least one parameter with significant relationships to sorption estimates. The 'B' parameter from the exponential models for P concentration and P fertilizer loss showed significant relationships to many of the sorption parameters, but were not related to the K value from the Langmuir sorption isotherm (Table 15). The second parameter, 'A' was significantly related to PSI_{75}, DPS_{STP1}, DPS_{STP2}, and DPS_{ox} across all sites. The relationship of 'A' to these DPS estimates are logical, as the DPS aims to describe a maximum P sorption level. As the 'B' parameter is describing the downward trend of the curve, it was expected it would be related to the K value from the Langmuir isotherm, which also describes the shape of the curve for sorption saturation.

While there were significant relationships across all soils, sorption parameters were not adequate for predicting P losses. Rather, these estimates may better describe P loss over time. More in depth study is required to assess the parameters and sorption methods for individual soils to determine relationships to the decrease in P leaching loss over time.

Relationship between soil test P and P leachate loss

Given that P leaching losses are evident through this research, a method is needed to predict P concentration and leaching event volume. Together these estimates might provide approximations for total P leachate as P load. Phosphorus concentration increased linearly with increases in STP measured by two routine agronomic, Bray P1 (BP) and Olsen P (OP) tests, and two environmental soil tests (WEP and BAP) (Figure 12). All sites individually analyzed showed significant linear relationships between the four soil tests and P leachate concentration, with the exception of Becker and Morris (Table 16). Morris, a calcareous soil, did not have a significant correlation between its P leaching concentration and the BP, a soil P test better suited for acidic soils. Becker also lacked a significant correlation between OP and P leachate concentration.

Waseca, a clay loam soil, showed weaker relationships than the other sites between P leachate and the four soil P tests, though the relationships were still significant (r $\leq$ 0.50 to 0.55). As a clay soil, Waseca may have had greater spread P leachate concentrations due to preferential flow and less consistent leaching rates in the study. The clay soil required more vacuum during leaching to acquire a consistent drip rate in comparison to the other soils. The range in values at Waseca may be due to these inconsistencies, as well as the preferential flow that has been found to be more prevalent in clay soils (Djodjic et al., 1999; King et al., 2015)

Averaged across all soils, the BAP environmental soil test showed the strongest relationship to P leaching losses, expressed as both concentration and load (r = 0.70 and 0.71 respectively). Bio-Available P has been found to correlate well with P loss in other runoff and leaching studies (Allen et al., 2002; Maguire and Sims, 2002). Of the two agronomic tests, the OP showed a stronger relationship to P leaching loss (r = 0.68) than the BP routine soil test (r = 0.58) (Table 16). This is consistent with other studies relating P leaching concentrations to the soil tests. Research completed by Hesketh and Brookes (2002) suggested the OP soil test was linearly related to tile drainage P concentrations and may serve as an indicator for P leaching losses.

When averaged by STP level within sites, P concentration showed strong significance across all four tests (Figure 13). The Olsen P had the highest correlation (r = 0.90) with P leachate, closely followed by the BAP, WEP, and BP soil tests respectively. Individually, Lamberton and Rochester had notably strong relationships between P leachate concentration and all STP measures, indicating a possible prediction method for P concentration of leachate at these sites.

The strong relationships between the STP extractions and P concentration indicated a possible method for predicting P losses with known P concentration and volume. Cross validation of the linear regression models for WEP, BAP, OP and BP resulted in MSE between 0.130 and 0.146, with the BAP having the lowest error rates and the BP having the highest error rates of the linear models (Table 17). The Random Forest approach was used to identify the potential influence of other variables, such as oxides and carbonates, on P leachate concentrations. Results from the Random Forest model indicated most important predictors were the four soil tests, leading to an analysis using the only top four factors (BAP, WEP, OP and BP soil tests). A cross validation regression between the model variables and P concentration indicated a relationship with a correlation coefficient of r = 0.19 and root mean square error (RMSE) of 0.0145 (Figure 14). The importance of variables to the model were ranked in the following order by the Random Forest analysis: BAP, BP, OP, and WEP.

The Random Forest did indicate other soil test methods were not significant predictors for P concentration in comparison to P soil tests. These data suggest that soil chemical concentrations are not significant in predicting STP concentrations. There may be influence from these chemical properties, but they do not serve as significant predictors of P concentration for estimating P leaching. The linear regression models showed stronger validation with lower RMSE and higher correlation coefficients in comparison to the Random Forest. The validation of the linear models indicated a clear relationship between STP methods and P concentration. The environmental soil test, BAP, served as the greatest predictor for P concentration across soil types with validation resulting in the lowest error rates. The OP test also performed well in validation with error rates similar to BAP and a greater correlation coefficient. The use of these soil tests to predict P concentration may be plausible, but requires further analysis and individual analysis between specific soils with larger training and validation sets.

Sorption curves for 6-12” sampling depth for low testing P plots are summarized in Figure 15. Table 18 summarizes the K values for the P sorption data for 6-12” depth soil samples. Sorption data was run for the 6-12” soil depth to determine if the sorption capacity below 6” could result in some of the P traveling with the soil water removed. Extractable soil test P for the Bray or Olsen tests are not summarized for these depths but the values tended to be much lower than the surface soils pointing to less available P at deeper depths and a greater storage capacity. The primary question for storage would be residence time and whether any P travelling with the leached water sufficiently reacting with the soil to result in sorption. If the P is travelling via preferential flow to a tile line it is unlikely that any P would be trapped at deeper soil depths even if there is a significant capacity to do so. The K values in Table 18 show some variability between he soils and between the soil test classifications within a soil. However, there is no clear increase or decrease for most soils thus the K values seem to be more random and are likely similar for the differing soil P classes which is not surprising since P enrichment is seldom encountered in most soils below the 6” depth.

Deep soil samples were collected from a separate set of long term trials to study whether extractable soil test P can be increased below the 0-6” depth. Figures 16-18 show data summarizing total P applied over nine cropping years in a corn-soybean rotation at different times. Locations were at Lamberton, Morris, and Saint Charles. Application of P had a greater impact on increase in soil test P for the 0-6” sampling depth at the three locations. Soil P at deeper depths was increased at two of the three locations for each of the 6-12 and 12-24” depths. The only site where soil P was increased at all three depths was at Lamberton (Figure 16). At Morris, only the 12-18” depth was increased (Figure 17), and the 6-12 depth soil P was increased at Saint Charles (Figure 18). It is plausible that deeper tillage may increase soil test P by mixing the soil below the 6” top soil sampling depth. However, increased soil P below 12 inches would likely be a result of P movement. Very high application rates should increase the chance for P movement by saturating the soil and P binding sites. It is likely that preferential flow will result in movement of P completely through the soil profile but the deposition of P at deeper depths would indicate a potential for some of the P moved to be absorbed. The amount of P absorbed will depend on the amount of reaction time of dissolved P in the soil water with the soil particles. The soil K values indicate the subsoil does have the capacity to sorb high levels of P but getting P to sorb can be an issue if water is moving solely by preferential flow.

DISCUSSION

This study indicated P leachate concentration remains consistent regardless of volume of the leaching event, though P load will increase with increasing leaching volume. The use of the vacuum ensured a consistent pressure on soil columns to maintain a similar water content in the soil. To some extent the vacuum helped to maintain a consistent flow rate, but gravitational soil water potential was the primary driver of leaching immediately after the leaching water was added to columns. Flow rate could be increased with vacuum pressure, but initial leaching was often driven by gravity rather than induced with added pressure. Because of the range in volumes, the columns with lower amounts of leaching water inherently leached more quickly. The maximum volume, 600 mL, required a greater amount of time across soils to fully complete leaching to the same pressure (approx. 0.5 bar). However, this higher volume did not influence the P leachate concentration. This study did not indicate flow rate was influencing P leachate concentration. On the contrary, the data suggests each soil may have an equilibrium point, where every 1 mL of water will result in the release of *x* mg of P. Identifying this equilibrium point or P leachate concentration in the soil solution could provide prediction tools for P leaching in the future.

Little research has been conducted to identify the influence of volume on P leaching losses, but studies on tile drainage connect with these results. A review of subsurface P movement concluded P loss was greatest in tile drains with elevated levels of flow (King et al., 2015), consistent with these results that the driver of P loss is total volume moving through the soil. Total P loads were found to be disproportionately higher in wet years than dry years, further emphasizing influence of volume as a principle influencer of P leaching loss (Gentry et al., 2007). Furthermore, several studies indicated tile discharge rates had no or poor relationships with P concentration (Baker et al., 1976; Madramootoo et al., 1992; Macrae et al., 2007).

From an environmental perspective, maintaining low STP levels is beneficial as it lowers the risk of P leaching. Generally, fertilizer is applied annual or biannually and there is no significant agronomic benefit to maintaining H STP fields, as L STP fields yield the same statistically with P applications (Kaiser, 2017). Current University of Minnesota guidelines recommend maintaining M STP levels. Phosphorus leaching losses were not significantly different between M and L classifications indicating there is no increased risk for P leaching when maintaining M STP soil in comparison to the L STP soil. Greater risk develops with when increasing soil P concentrations to H and especially VH STP classifications. According to this study, VH soils were at significantly higher risk for P leaching loss, as they generated significantly greater P leachate concentrations in comparison to the L and M classifications. Given that P leachate concentration increased quite rapidly in the VH STP level, and the linear relationship between P leaching and STP concentrations, further research evaluating soils with greater STP concentrations than those of this study. This may serve as a better indicator of the rate at which P leaching risk increases with higher STP concentrations.

Results of this study imply the increasing intensity and frequency of rainfall patterns in Minnesota may increase the potential for P leaching losses. Furthermore, as parts of the state utilize title drainage systems, this may elevates the risk of soluble P losses to drainage waterways, and eventually fresh water systems. The findings in this study emphasize the importance of leachate volume (intensity) in estimating total P leaching losses, and accentuate the need for additional attention to be directed towards P loss through subsurface flow.

The sharp decrease in P fertilizer leached from the immediate leach in comparison to the 7 day leach may provide producers with an indicator as to when to apply fertilizer according to weather forecasts. The evident decrease in P leaching from greater than 30% to less than 7% in a 7 day period may help farmers avoid the loss of fertilizer P due to a rain event.

Furthermore, it is often recommended that applying fertilizer before a light rainfall serves as an incorporation method for P fertilizer. Given the results, this may leads to loss, as the immediate leachtime leached the greatest amounts across all leach times and all sites. It must be noted that the volumes used in this study were quite intense, indicating that a light rainfall may not be enough to induce a severe leaching event. In this experiment 200 mL of water was applied, matching the intense rainfall events that continue to grow more frequent in Minnesota (Minnesota Pollution Control Agency, 2014).

A leaching event one day after fertilizer application led to 18 percent loss at sites textured as clay loams (Waseca and Lamberton). Timing appeared to be especially important on these clay soils, where preferential flow can quickly move soluble P from the topsoil. Furthermore, many fields in Minnesota with high clay content are tiled to allow for greater drainage, increasing the risk of P movement through established preferential pathways (King et al., 2015). According to data from this study, fields with preferential flow pathways may be at higher risk for soluble P movement if a rain event occurs within a day of fertilizer application. In Minnesota, P fertilizer is often applied pre-plant when rain events are more frequent given the time of the year. Considering this, the potential for P leaching should be evaluated when planning fertilizer applications.

Looking at leach times individually in the source study, dry fertilizer loss from the immediate leach was over 25% averaged between Rochester and Becker (data not shown). This illustrates the importance of avoiding P fertilizer applications before forecasted precipitation events. According to the University of Minnesota Extension Service, P fertilizer is recommended to be incorporated with broadcast applications on the soil surface to reduce P loss with erosion (Kaiser and Pagliari, 2018). Incorporation may also in turn help the P fertilizer granules to react with soil water and bind with soil particles. Broadcasting P fertilizer without incorporation not only raises the risk for greater P runoff losses, but also increases the risk for P leaching with a large rain event

Water quality standards issued by the EPA, now effective in Minnesota as of June 2018, provide updated P concentration thresholds for lakes and reservoirs (Revisor of Statutes, 2016). These new maximum thresholds range from 12 to 90 $\mu g\ L^{-1}$, dependent on the body of water. The concentrations in this study consider leaching from soil without fertilizer application, and leaching load values of approximately 0.15 mg P, or 150 μg P, per soil column averaged over all soils and STP levels. This load could be quite substantial considering the soil column only accounted for desorption from the top 15 cm of the soil with a 3.81 cm diameter. Considering P leaching loss at a field scale level indicates P leaching may play a significant role in P pollution.

These results are reflective of P interactions with the topsoils (15cm) of six Minnesotan soils. The fate of P beyond this top layer of soil is unknown and requires further study. This study provides insight for how P may be moving through the soil profile, but a further in depth study is required to evaluate the influence of subsoils on P leaching.

CONCLUSIONS

This study revealed that not only is P leaching loss a possibility, but likely a substantial contributor to P movement from topsoils. Highest risk soils are those with high initial STP levels; a parallel to high risk soils for P run-off. These results further indicate the importance of maintaining low P soils to prevent excess P loss from agricultural landscapes. The STP level of the soil is directly related to the P concentration in leachate, and total P loss (P load) is driven by the intensity of the leaching event, or the amount of water moving through the soil profile. Phosphorus leaching will occur to some extent with any rainfall, but more intense rainfall will cause significantly greater loss. To alleviate P leaching losses due to fertilizer application, growers may modify their fertilizer source and adjust timing more appropriately. For growers using sources with the greatest leaching potential (dry sources), incorporation may be the best management decision to avoid leaching losses. A light rainfall could allow for the dry fertilizer to solubilize and bind to the soil, but opens the possibility of loss through preferential flow pathways. Growers may reduce loss potential with precise timing of P application considering the source. A three day gap between rainfall and fertilizer application and significantly reduce P losses.

Results from this study indicate P leaching may be a legitimate source for P pollution. It is driven by soil STP levels and the intensity of the rainfall event. Loss can be further amplified by fertilizer application, indicating source and timing is crucial in P management. With further research, prediction of leaching losses may be calibrated with STP levels of soil and leaching volume to determine total potential P loss from topsoils.

TABLES AND FIGURES

OBJECTIVES 1-4

Table 1. Soil series, taxonomy, physical, and chemical properties for six study locations in Minnesota determined from composite soil samples.

	Soil					
Site	Series	Taxonomy†	Texture‡	**Bulk density**	**Field capacity**	**pH**
				g cm^{-1}	mL $column^{-1}$	
Becker*	Hubbard	En Hapludoll	S Loam	1.40	21.3	6.5
Crookston	Gunclub	Ae Calciaquoll	C Loam	1.20	46.2	7.9
Lamberton	Normania	Ca Hapludoll	C Loam	1.17	46.5	5.4
Rochester*	Mt. Carroll	Mo Haludalf	Si Loam	1.17	42.4	7.2
Morris	Dolan	Aq Calciudoll	Si Loam	1.24	40.2	7.7
Waseca*	Webster	Aq Hapludoll	C Loam	1.18	50.3	5.9

* Sampled in following year for follow-up volume study;

† Soil taxonomy abbreviations: Aquic (Aq), Mollic (Mo), Calcic (Ca), Aeric (Ae), Entic (En)

‡ Soil texture abbreviations: Sandy (S), Silt (Si), Loam (L), Clay (C), determined by hydrometer method;

Table 2. Soil Test P (STP) concentrations for six Minnesota soils according to the Bray-P1 and Olsen P agronomic soil tests.

Extractant	Becker	Crookston	Lamberton	Rochester	Morris	Waseca
STP	--------------------------- mg P kg^{-1} in soil---------------------------					
Bray-P1						
Low	6	7	17	8	5	7
Medium	11	9	22	15	12	11
High	14	18	32	20	27	21
Very High	29	30	40	36	28	32
Average	**15**	**16**	**28**	**20**	**18**	**18**
Olsen P						
Low	3	4	10	5	3	4
Medium	4	4	13	9	10	7
High	7	9	19	14	17	13
Very High	12	19	24	25	24	17
Average	**6**	**9**	**17**	**13**	**14**	**10**

Table 3. Average Olsen P, Water Extractable P (WEP), and BioAvailable P (BAP) levels for six sites in Minnesota averaged by site and Soil Test P (STP) level.

Site and STP Level	**WEP**	**BAP**
Becker	**2.11**	**4.72**
L	1.10b	1.58b
M	1.05b	3.38b
H	1.68b	4.55b
VH	4.63a	9.38a
Crookston	**6.39**	**11.77**
L	1.98b	5.10c
M	3.35b	5.93c
H	5.60b	11.83b
VH	14.65a	24.23a
Lamberton	5.01	21.54
L	3.35c	13.66d
M	3.96bc	18.35c
H	5.33b	22.66b
VH	7.42a	31.50a
Lawlers	**5.83**	**13.68**
L	2.70c	4.18d
M	3.87c	9.15c
H	6.59b	15.93b
VH	10.15a	25.47a
Morris	**5.97**	**15.22**
L	1.28d	3.62d
M	4.81c	11.67c
H	7.44b	19.49b
VH	10.36a	26.12a
Waseca	**3.52**	**11.15**
L	1.41d	4.04d
M	2.41c	7.51c
H	4.01b	14.68b
VH	6.24a	18.37a

Table 4. Simple correlation among routine and environmental soil test values by and across the studied locations.

	BRAY P1-P			**OLSEN P**		**BioP**
Site	**BioP**	**WaterP**	**OlsenP**	**BioP**	**WaterP**	**WaterP**
Becker	0.98	0.89	0.97	0.96	0.88	0.89
Crookston	0.97	0.94	0.98	0.93	0.98	0.99
Lamberton	0.93	0.95	0.97	0.95	0.94	0.92
Morris	0.81	0.77	0.80	0.99	0.93	0.95
Rochester	0.89	0.74	0.91	0.97	0.83	0.92
Waseca	0.96	0.85	0.96	0.97	0.84	0.89
All Sites	0.86	0.72	0.90	0.96	0.83	0.85

Table 5. Average P leached per unit soil, P concentration, and P Load values for soil columns from six Minnesota sites across STP classifications.

Site	Volume of Leaching Event	P Load	P Concentration	P leached per unit soil
	mL	mg P column^{-1}	mg P L^{-1}	µg P g soil^{-1}
Becker	213.1	0.05 b	0.31	0.16 c†
Morris	401.7	0.17 a	0.45	0.62 b
Crookston	462.1	0.16 a	0.40	0.65 ab
Rochester	423.8	0.14 a	0.37	0.70 ab
Waseca	503.5	0.19 a	0.40	0.84 ab
Lamberton	465.2	0.18 a	0.44	0.90 a

†Letters indicate significant difference of P leaching between sites according to Tukey's HSD test at $P \leq 0.05$. Values within columns without letters are not significantly different at $P \leq 0.05$.

Table 6. Soil chemical concentrations for Fe, Al, Mn, Ca, and Carbonates listed as percentages, for six Minnesota soils determined from composite soil samples.

Site	Fe_{ox}†	Al_{ox}	Mn_{ox}	Fe_{CBD}‡	Al_{CBD}	Mn_{CBD}	Ca	CCE§
	-- $g\ kg^{-1}$	-------------------------------------						
Becker	1.86 d	1.13 cd	0.58 cd	4.23 d	0.86 b	0.44 cd	1.35 c	3.12 bc
Crookston	0.81 e	1.07 d	0.39 c	2.29 e	0.69 b	0.34 d	10.69 a	47.41 a
Lamberton	4.02 a	1.33 bc	0.76 bc	9.00 b	1.26 a	0.61 b	3.26 bc	1.28 c
Rochester	4.54 a	1.62 a	0.97 ab	10.52 a	1.25 a	0.83 a	4.79 b	3.71 bc
Morris	2.60 c	1.42 ab	0.68 c	5.31 cd	0.84 b	0.54 bc	8.24 a	17.01 b
Waseca	3.45 b	1.52 ab	1.02 a	5.89 c	1.13 a	0.60 b	4.04 bc	2.43 c

†Letters indicate significant differences between sites for each chemical concentration according to Tukey's HSD test. Numbers within columns followed by the same letter are not significantly different at $P \leq 0.05$.

† Soil extraction abbreviation: Ammonium-oxalate extraction (ox),

‡ Soil extraction abbreviation: Citrate-bicarbonate dithionite extraction (CBD)

§ CCE: Calcium Carbonate Equivalent

Table 7. Average P leached (P load) across four soil test phosphorus levels for soil columns from six sites in Minnesota.

Site	Low	Medium	High	V. High
	------------------------------- $mg\ P\ column^{-1}$	-------------------------------		
Becker	0.05	0.06	0.04	0.07
Crookston*	0.13 b†	0.11 b	0.15 ab	0.25 a
Lamberton	0.11	0.16	0.19	0.26
Rochester	0.09	0.11	0.14	0.22
Morris*	0.09 b	0.12 b	0.17 ab	0.29 a
Waseca	0.18	0.14	0.19	0.24

†Letters indicate significant differences between STP levels for each site according to Tukey's HSD test. Numbers within rows without letters are not significantly different at $P \leq 0.05$.

Table 8. Average P leaching losses across four soil test phosphorus levels and leaching times (timing between leaching event and fertilization) for soil columns from six sites in Minnesota.

Site	Soil Olsen P Values	Volume of Leaching Event	P Load	P Concentration	P Fertilizer leached
	mg P kg^{-1}	mL	mg P column^{-1}	mg P L^{-1}	%
Becker	6	213.1‡	0.91 c†	5.13 a	7.6 c
Crookston	9	462.1	1.72 ab	4.06 ab	13.7 ab
Lamberton	17	465.2	2.19 a	5.06 a	16.6 a
Morris	14	401.7	1.55 b	4.24 ab	12.2 b
Rochester	13	423.8	1.42 b	3.63 b	11.2 bc
Waseca	10	503.5	2.10 a	4.48 ab	16.9 a

†Letters indicate significant differences between sites levels for each site according to Tukey's HSD test. Numbers within columns followed by the same letter are not significantly different at $P \leq 0.05$.

‡Volume (V) of the leaching event was determined from field capacity (FC) measurements. V = FC x 10

Table 9. Phosphorus Sorption Estimates for six Minnesotan soils determined from composite soil samples.

Site	PSI_{75}	PSI_{100}	DPS_{OX}	DPS_{STP1}	DPS_{STP2}	DPS_{CBD}
Becker	202.6 b	274.5 b	10.5 b	0.02 b	0.02 b	1.9 a
Crookston	253.0 ab	309.6 ab	19.6 a	0.02 b	0.02 b	1.5 a
Lamberton	246.6 ab	302.8 ab	6.2 c	0.06 a	0.05 a	1.0 a
Morris	297.7 a	341.9 ab	9.8 b	0.04 b	0.03 ab	0.9 a
Rochester	315.4 a	386.6 a	6.1 c	0.03 b	0.03 b	1.4 a
Waseca	281.4 ab	404.9 a	6.1 c	0.03 b	0.03 b	1.5 a

†Letters indicate significant differences between sites for each sorption estimate according to Tukey's HSD test. Numbers within columns followed by the same letter are not significantly different at $P \leq 0.05$.

Table 10. Average P leached as P concentration and average P load (mg P column-1) for each leaching volume for soil columns from three Minnesota soils over two soil test phosphorus levels.

Volume	200	400	600	200	400	600
Site	P concentration			P load		
	------------ mg P L^{-1} ------------			------------ mg P $column^{-1}$ ------------		
Becker	0.12	0.10	0.12	0.02 b†	0.04 b	0.07 a
Rochester	0.08	0.07	0.07	0.01 b	0.02 ab	0.03 a
Waseca	0.07	0.06	0.08	0.01 b	0.01 b	0.04 a

†Letters indicate significant differences between leaching volumes for each site according to Tukey's HSD test. Numbers within rows without letters are not significantly different from one another at $P \leq 0.05$.

Table 11. Differences in phosphorus (P) leachate concentration and leached P fertilizer by leachtime (days between fertilization and a leaching event) for six sites in Minnesota.

Site	P Concentration				P Fertilizer leached			
	Day of Leaching Event after Fertilization							
	0	*1*	*3*	*7*	*0*	*1*	*3*	*7*
	-------------- mg P L^{-1} --------------				----------------- % -----------------			
Lamberton*	9.61 a†	5.44 b	2.78 c	2.42 c	33.6 a	17.8 b	8.6 c	6.4 c
Waseca*	7.91 a	4.76 b	3.07 c	2.19 c	30.3 a	18.0 b	11.7 c	7.5 c
Morris*	8.31 a	4.44 b	2.35 bc	1.88 c	24.7 a	13.2 b	6.2 bc	4.6 c
Rochester*	7.00 a	3.32 b	2.68 b	1.59 c	22.3 a	10.0 b	8.5 b	4.2 c
Crookston*	6.31 a	4.0 b	3.04 b	2.9 b	22.0 a	13.3 b	10.1 b	9.4 b
Becker*	10.71 a	4.0 b	6.54 b	2.27 b	16.21a	5.57 b	5.42 b	2.99 b

†Letters indicate significant differences between levels and timings for each site according to Tukey's HSD test. Numbers within rows followed by the different letters are significantly different at $P \leq 0.05$.

*Indicates a significant difference within rows for a specific site

Table 12. Reduction in P fertilizer losses from the immediate leach expressed as a percentage.

	Percent Decrease in P loss from immediate leach (0 day)		
Days between P Fertilization and Leaching	*1 Day*	*3 Days*	*7 Days*
Site		%	
Lamberton	43	71	75
Waseca	40	61	72
Morris	47	71	77
Rochester	52	61	77
Crookston	37	51	54
Becker	63	40	79

Table 13. Phosphorus leaching estimates according to Source and the time of the leaching event after fertilization for two sites in Minnesota.

Site	Becker		Rochester	
	P concentration	P Fertilizer Leached	P concentration	P Fertilizer Leached
Days between P Fertilization and Leaching	--- mg P L^{-1} ---	----- % -----	--- mg P L^{-1} ---	----- % -----
0	11.18 a	16.7 a	9.26 a	8.9 a
1	8.32 b	12.4 b	4.25 b	-0.3 b
3	4.27 c	6.2 c	2.12 c	-0.7 b
7	3.84 c	5.6 c	2.06 c	-1.6 b
Source				
Dry	13.92 a	20.7 a	10.54 a	9.4 a
Liquid + AVAIL	7.52 b	11.2 b	4.03 b	0.5 b
Liquid	7.07 b	10.5 b	2.97 b	0.3 b
Manure	0.09 c	0.14 c	0.16 c	-3.9 b

†Letters indicate significant differences between sources or timings for each site according to Tukey’s HSD test. Numbers within columns followed by different letters are significantly different at $P \leq 0.05$.

Table 14. Relationship among soil sorption estimates and P leaching quantifications, P concentration and P fertilizer loss. Values obtained from soil samples and leaching columns across six sites in Minnesota.

	PSI$_{75}$	PSI$_{100}$	DPS$_{\text{STP1}}$	DPS$_{\text{STP2}}$	DPS$_{\text{OX}}$	DPS$_{\text{CBD}}$	P CONCENTRATION
	------------------------ correlation coefficients ------------------------						
PSI$_{100}$	0.71*						
DPS$_{\text{STP1}}$	-0.38*	-0.27*					
DPS$_{\text{STP2}}$	-0.35*	-0.26*	1*				
DPS$_{\text{ox}}$	-0.18*	-0.21*	0.07	0.04			
DPS$_{\text{CBD}}$	-0.16*	-0.38*	-0.16*	-0.18*	0.27*		
P CONCENTRATION	-0.16*	-0.07	0.13*	0.13*	-0.01	-0.08	
P FERTILIZER LOSS	-0.04	0.03	0.13*	0.13*	-0.03	-0.11*	0.89*

*Indicates significant correlation coefficient at $P \leq 0.05$ and n= 384

Table 15. Relationship among soil sorption estimates and parameters A and B from exponential models derived to describe decreases in P leaching losses over time. Values obtained from soil samples and leaching columns across six sites in Minnesota.

	Q$_{\text{MAX}}$	PSI$_{75}$	PSI$_{100}$	DPS$_{\text{STP1}}$	DPS$_{\text{STP2}}$	DPS$_{\text{OX}}$	DPS$_{\text{CBD}}$	A$_{\text{PPM}}$	B$_{\text{PPM}}$	A$_{\text{LOSS}}$
	---------------------------- correlation coefficients ----------------------------									
PSI$_{75}$	0.55*									
PSI$_{100}$	0.76*	0.71*								
DPS$_{\text{STP1}}$	-0.22*	-0.38*	-0.27*							
DPS$_{\text{STP2}}$	-0.23*	-0.35*	-0.26*	1.00*						
DPS$_{\text{ox}}$	-0.11*	-0.18*	-0.21*	0.07	0.04					
DPS$_{\text{CBD}}$	0.07	-0.16*	-0.38*	-0.16*	-0.18*	0.27*				
A$_{\text{PPM}}$	0.01	-0.10*	-0.02	0.29*	0.30*	-0.13*	-0.08			
B$_{\text{PPM}}$	0.14*	0.12*	0.13*	0.07	0.06	0.06	0.05	0.56*		
A$_{\text{LOSS}}$	0.04	-0.11*	0	0.26*	0.27*	-0.14*	-0.06	0.96*	0.53*	
B$_{\text{LOSS}}$	0.12*	0.08	0.10*	0.14*	0.13*	0.10*	0.05	0.52*	0.96*	0.51*

*Indicates significant correlation coefficient at $P \leq 0.05$ and n= 384

Table 16. Relationship between four P soil tests and P leachate concentration of soil columns for six locations in Minnesota listed as Pearson's correlation coefficients.

Site	Bio-Available P	Bray-P1	Olsen P	Water Extractable P
Becker	0.54*	0.57*	0.49	0.63*
Crookston	0.74*	0.75*	0.75*	0.73*
Lamberton	0.69*	0.65*	0.64*	0.66*
Rochester	0.87*	0.65*	0.79*	0.89*
Morris	0.66*	0.42	0.67*	0.67*
Waseca	0.55*	0.53*	0.52*	0.50*

*Indicates significant correlation coefficient (r) in the relationship between P concentration (mg L^{-1}) of leachate and soil test P level (mg kg^{-1}) where $P \leq 0.05$, n=96, $r \geq 0.2$.

Table 17. Cross Validation results for a Random Forest and four Linear Regression models for predicting P leachate concentration with four soil test P (STP) methods.

Site	Mean of R^2 (Correlation Coefficient)	RMSE	Standard Deviation of Error Rate
Random Forest	0.19	0.145	0.031
Linear Regression			
Bio-Available P	0.32	0.130	0.025
Water Extractable P	0.22	0.132	0.023
Olsen P	0.34	0.131	0.031
Bray-P1	0.20	0.146	0.035

*Indicates significant correlation coefficient in the relationship between P concentration (mg kg $soil^{-1}$) of leachate and soil test P level (mg kg^{-1}) where $P < 0.05$.

Table 18. Average K value for soil sorption data from 6-12" depth samples collected from four soil test classifications at six locations in Minnesota.

Site	Low	Medium	High	V. High
Becker	0.2015	0.0961	0.1271	0.1047
Crookston	0.0789	0.0742	0.0592	0.0665
Lamberton	0.2558	0.0823	0.0930	0.2233
Morris	0.1463	0.0989	0.1586	0.1067
Rochester	0.1554	0.1227	0.1016	0.1974
Waseca	0.0397	0.1006	0.1049	0.1464

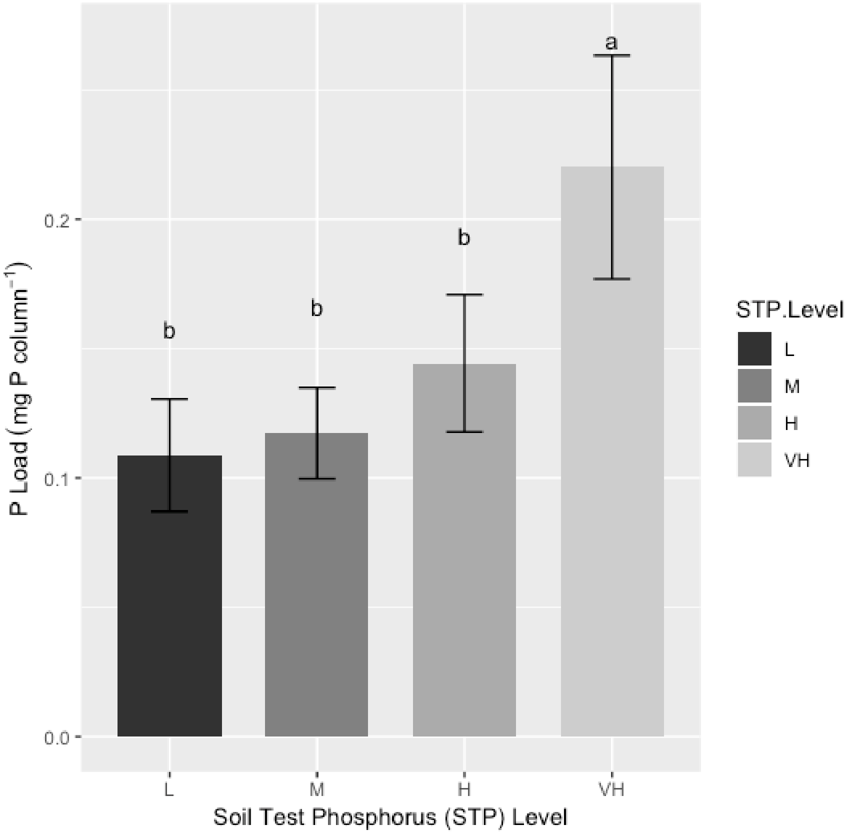

Figure 1. Leaching P loss as mg P column^{-1} by initial soil test P (STP) level averaged over six Minnesota soils. Letters represent significant differences ($P < 0.05$) in P load between STP levels according to Tukey's HSD Test. Error bars represent two standard deviations

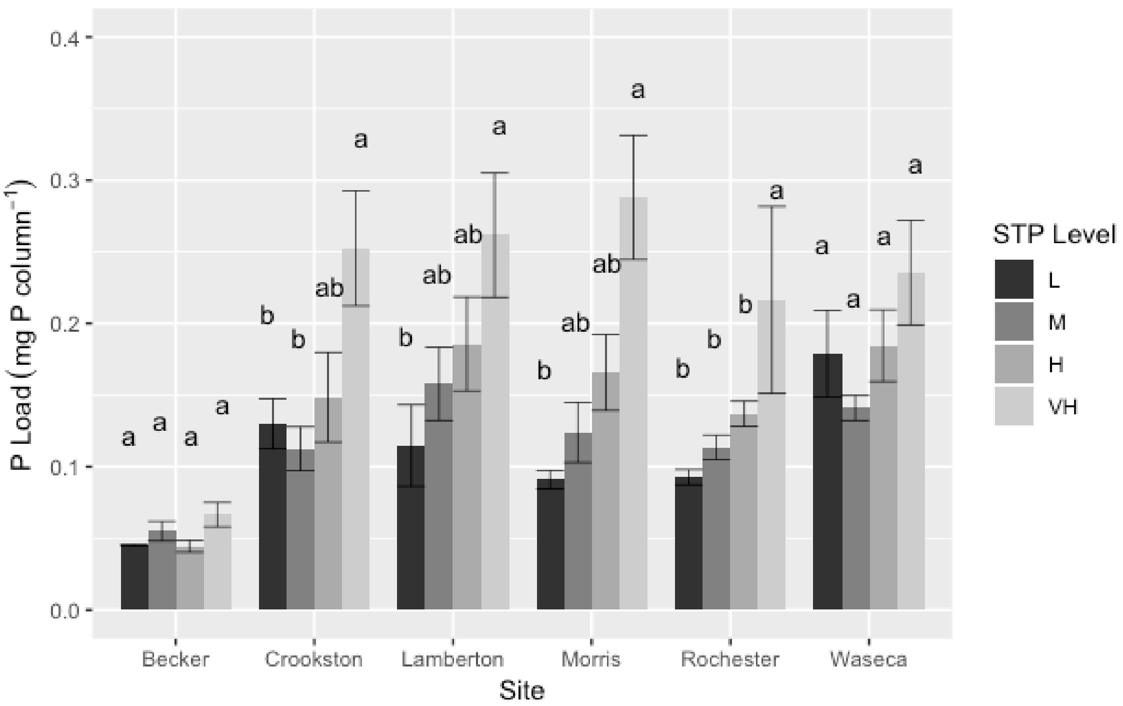

Figure 2. Phosphorus leaching means as P load (mg P column-1) for six Minnesotan soils as influenced by initial soil test P (STP) level. Error bars represent one standard deviation. Different letters represent significant differences ($P < 0.05$) within sites according to Tukey’s HSD mean separation test.

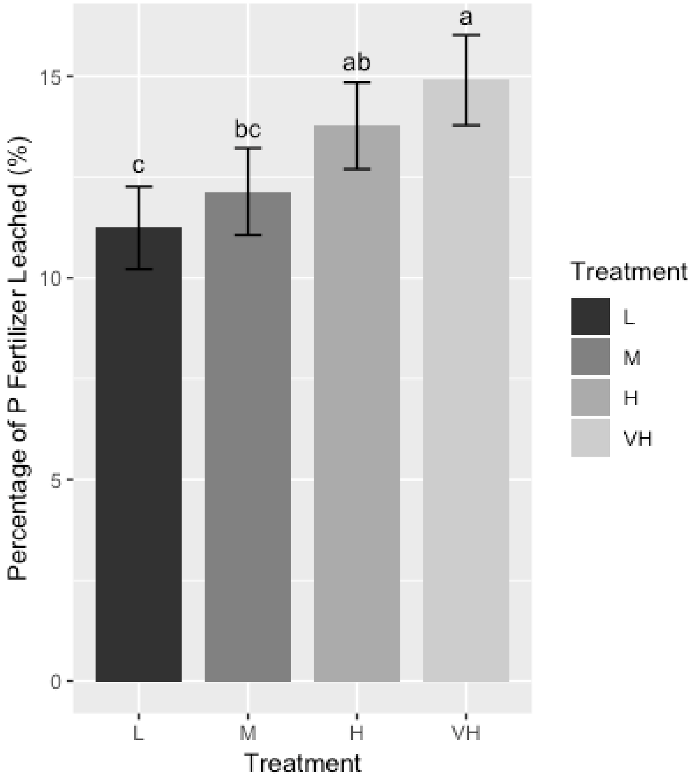

Figure 3. Average P fertilizer leached from intact soil columns across all sites and leach times (timing between fertilization and leaching event). Letters indicate significant differences between STP levels

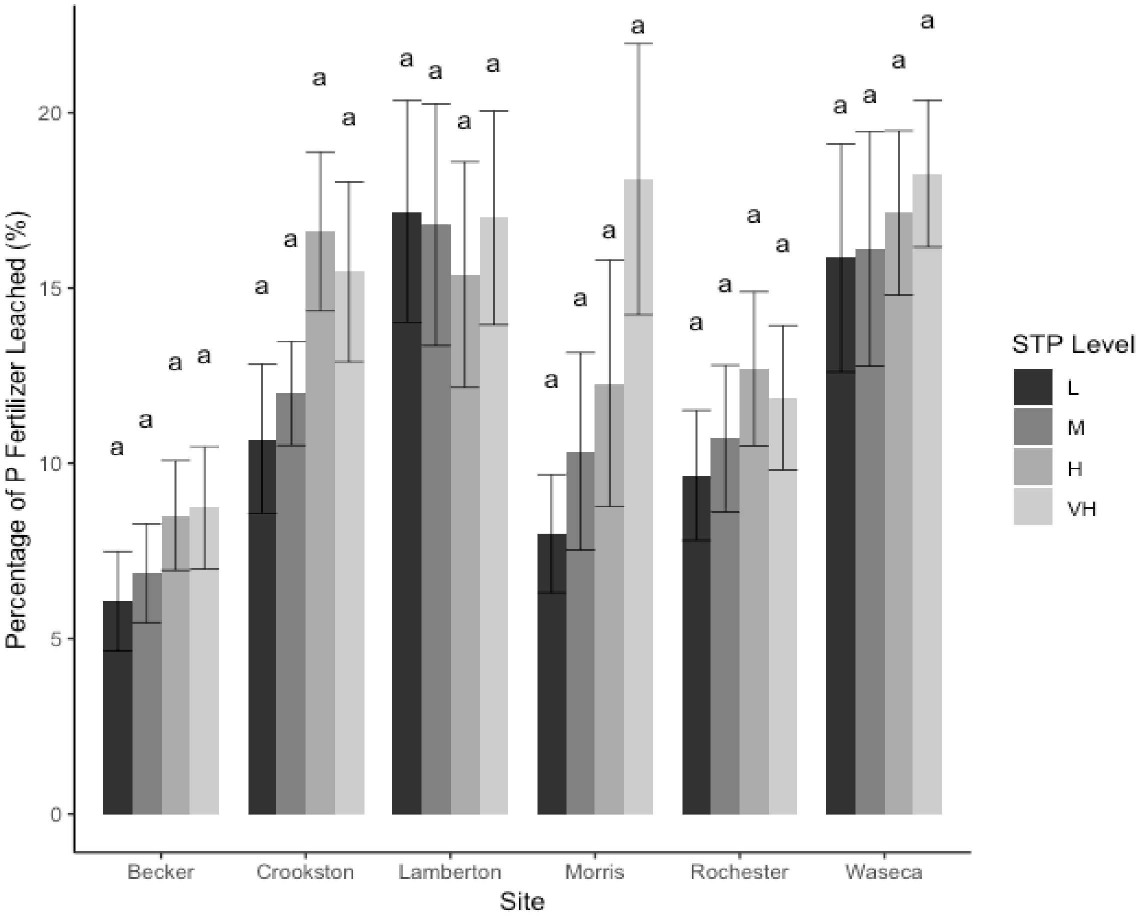

Figure 4. Average P fertilizer leached 7 days after fertilization for six sites in Minnesota categorized by four soil test P (STP) levels. Error bars represent one standard error. Different letters denote significant differences between STP levels within sites according to Tukey's HSD mean separation test.

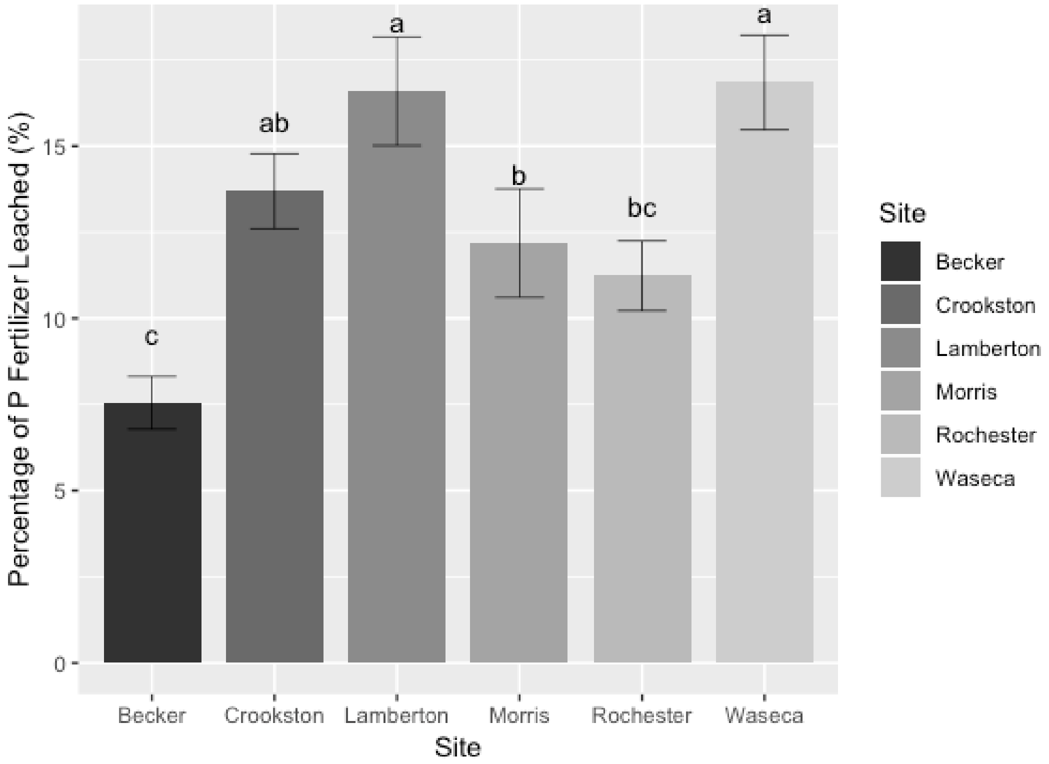

Figure 5. Average percent P fertilizer leached from intact soil columns from six sites in Minnesota. Mean average was estimated across all soil test P (STP) levels and leach times (time between fertilization and leaching event). Different letters signify significant differences between sites according to Fischer’s LSD test. Error bars are one standard deviation.

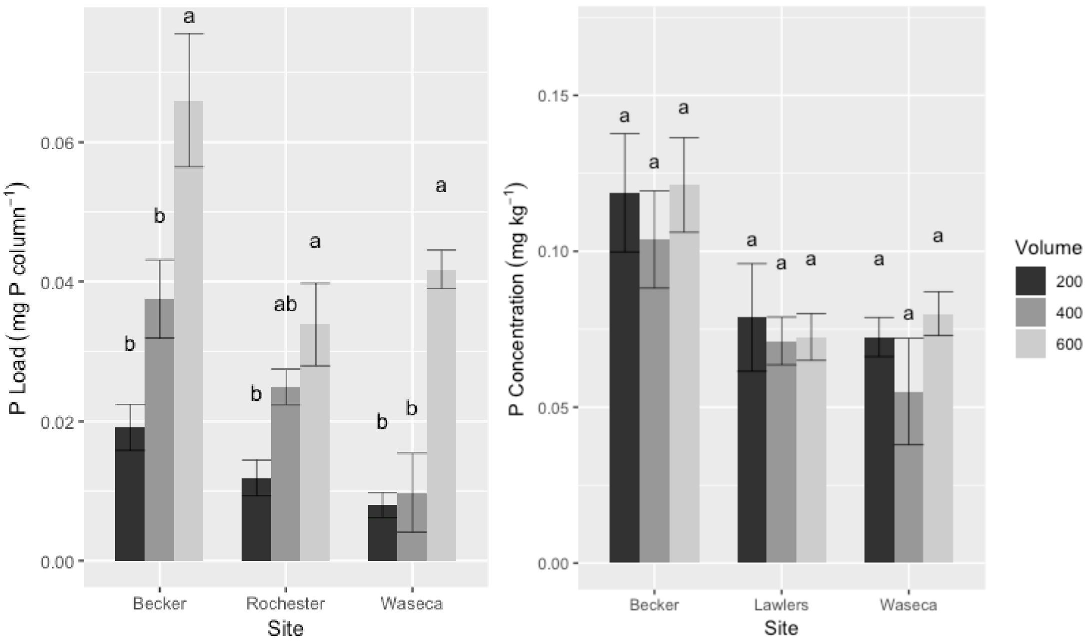

Figure 6. Phosphorus leaching losses as P load (left) and P concentration (right) averaged by site and leaching volume for three Minnesota sites. Letters indicate significantly different means within sites for the three leaching volumes ($P < 0.05$) determined with Tukey's HSD mean separation test.

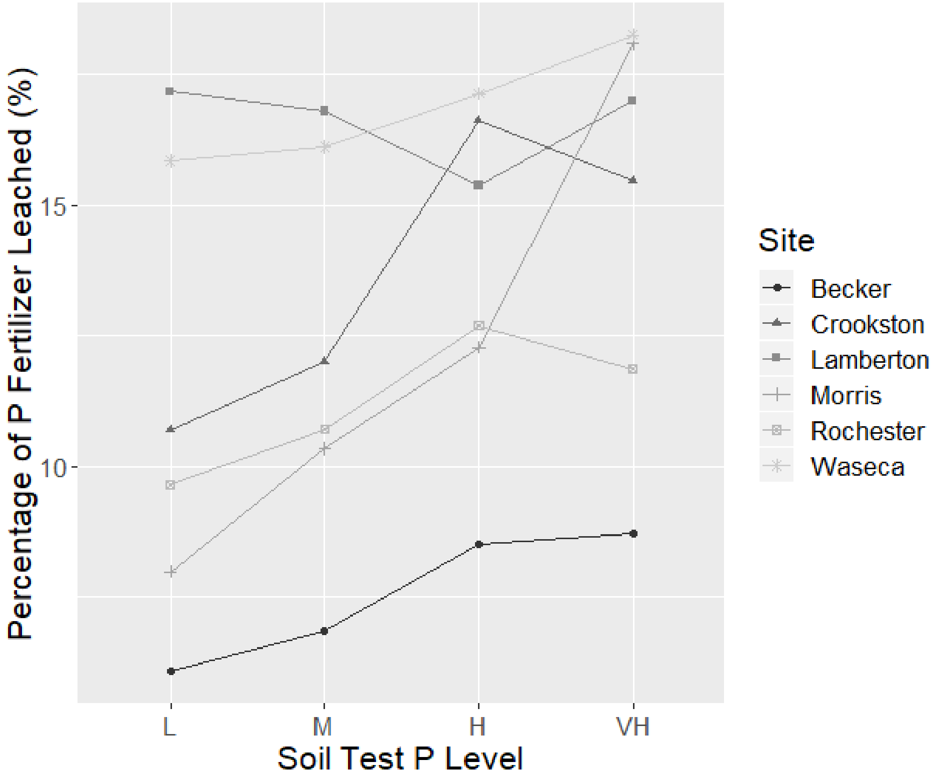

Figure 7. Percentage of P fertilizer leached across soil test P (STP) classifications for six sites in Minnesota.

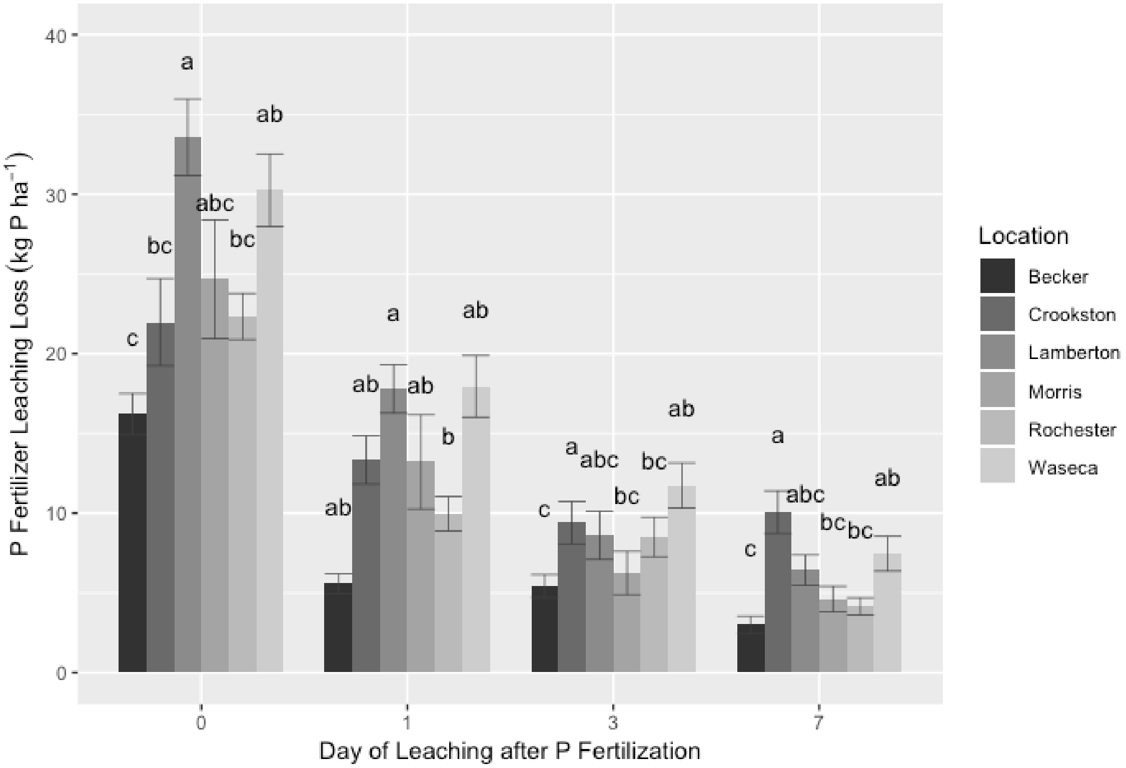

Figure 8. Fertilizer P leached (%) according to number of days between fertilization and leaching. Bars with the different letters indicate significant differences between sites within the leachtime period according to Tukey's HSD test ($P < 0.05$). Error bars are one standard deviation.

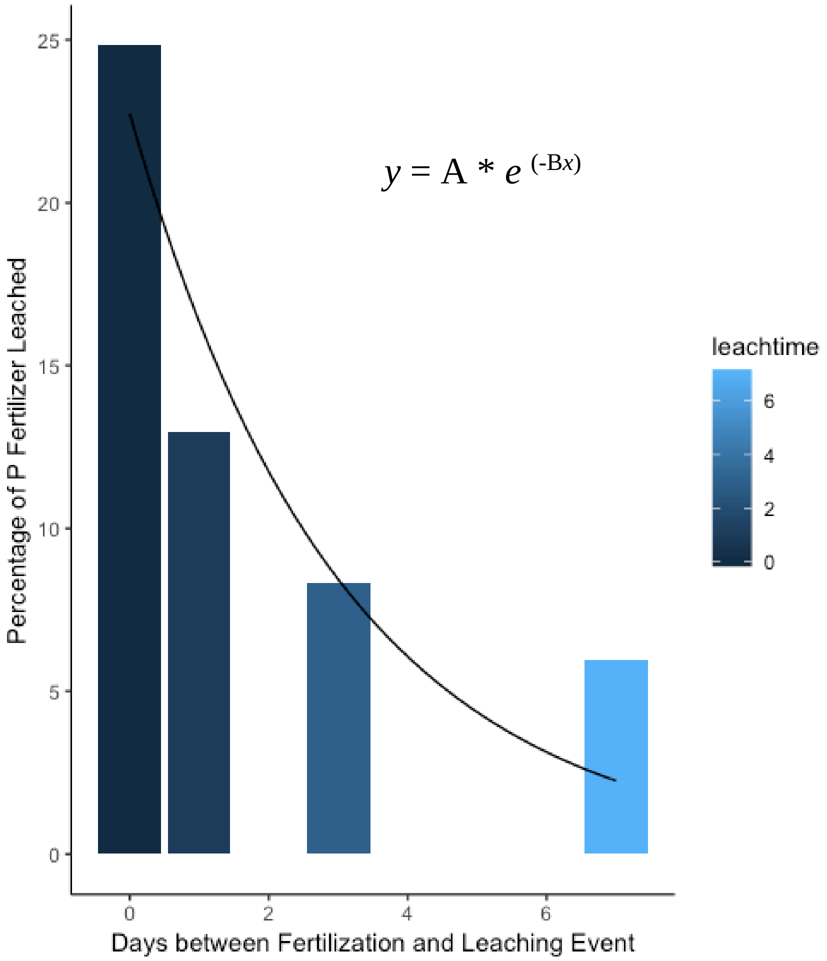

Figure 9. Decrease in Leaching of P Fertilizer over a seven-day period, fit with and exponential model. Phosphorus leaching losses are averaged over six sites and four soil test P (STP) levels.

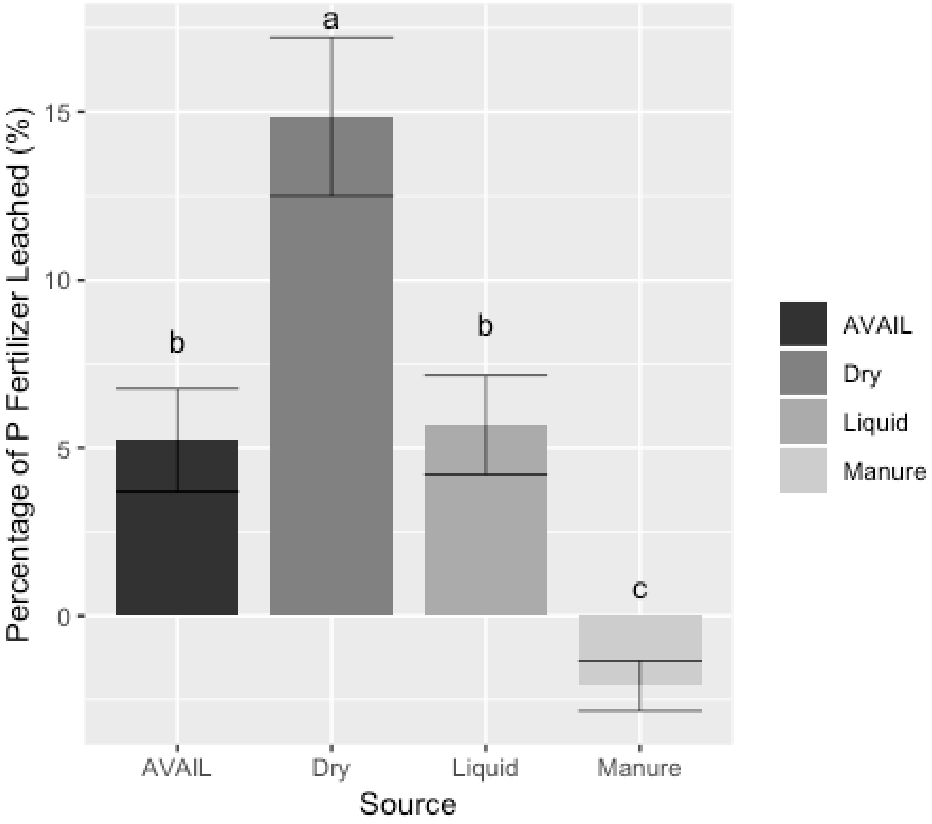

Figure 10. Effects of P fertilizer type on P leaching losses for two sites in Minnesota. Negative values implied P sorption.

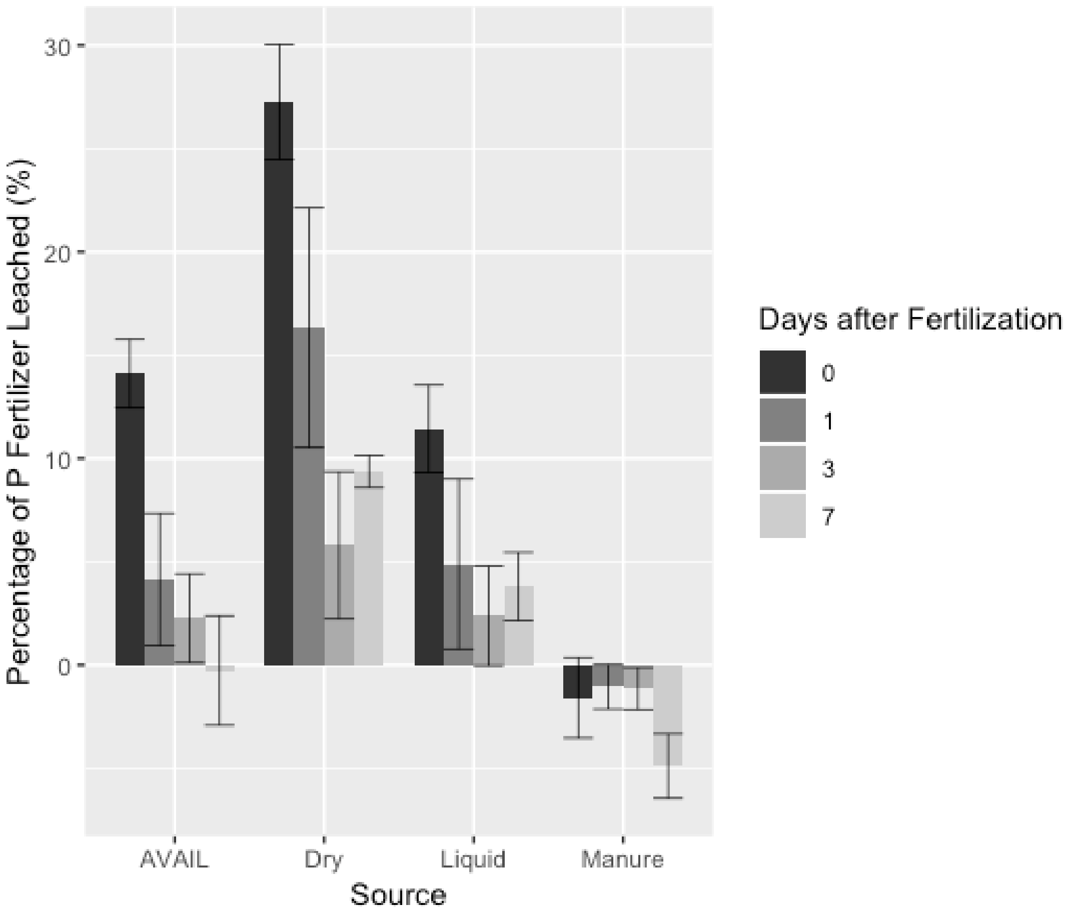

Figure 11. Effects of four P fertilizer sources on percent P fertilizer leached for four leach times (days between fertilizer application and leaching event) for two soils in Minnesota

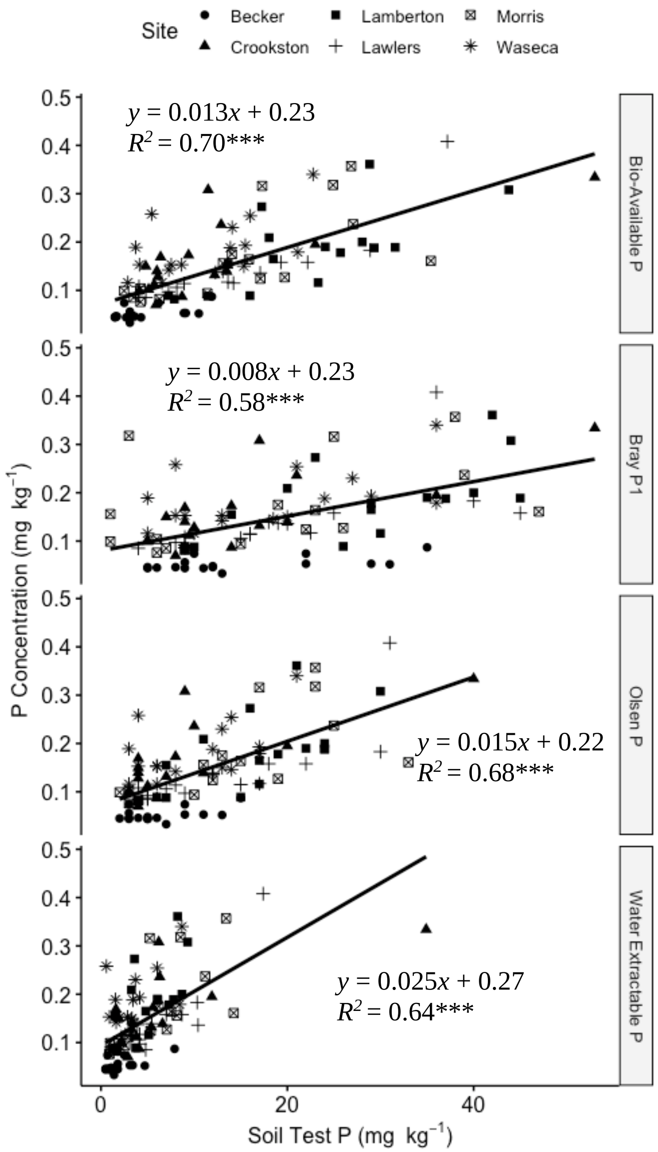

Figure 12. Relationship between soil-test P and water extractable P (WEP) from soil column leachate. A significant relationship is indicated for linear coefficients (r values) where $P < 0.05$ between soil test and P concentration of leachate.

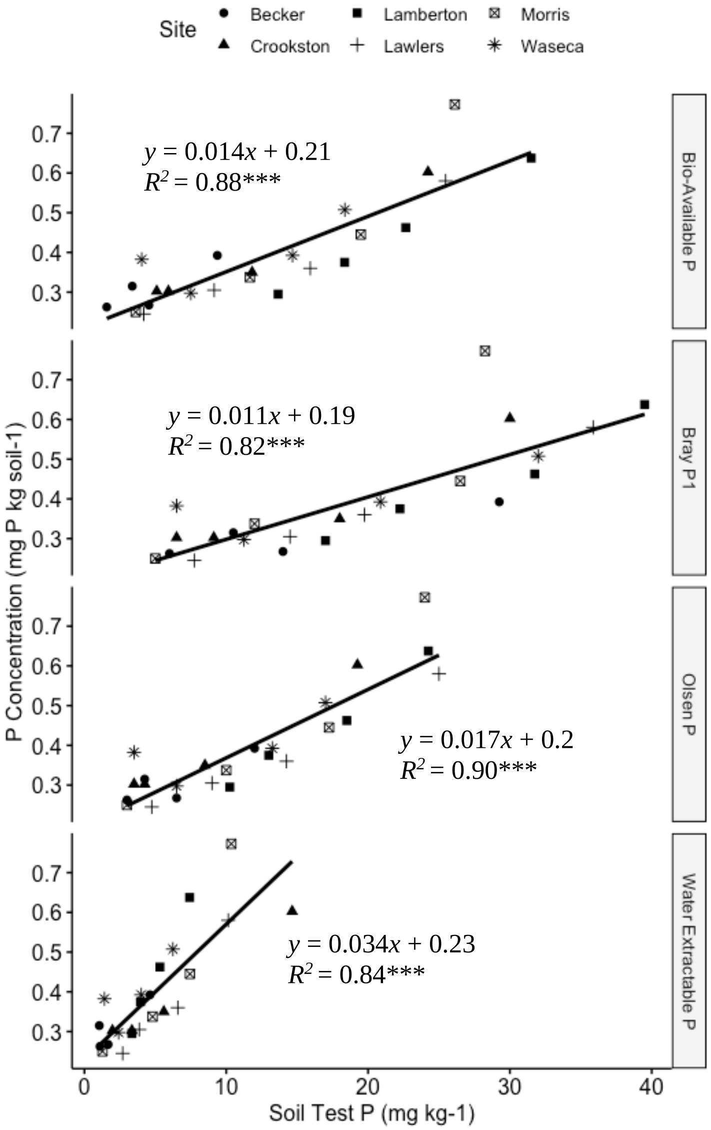

Figure 13. Relationship between soil-test P and water extractable P (WEP) from soil column leachate averaged by STP level. A significant relationship is indicated for linear coefficients (r values) where $P < 0.05$ between soil test and P concentration of leachate.

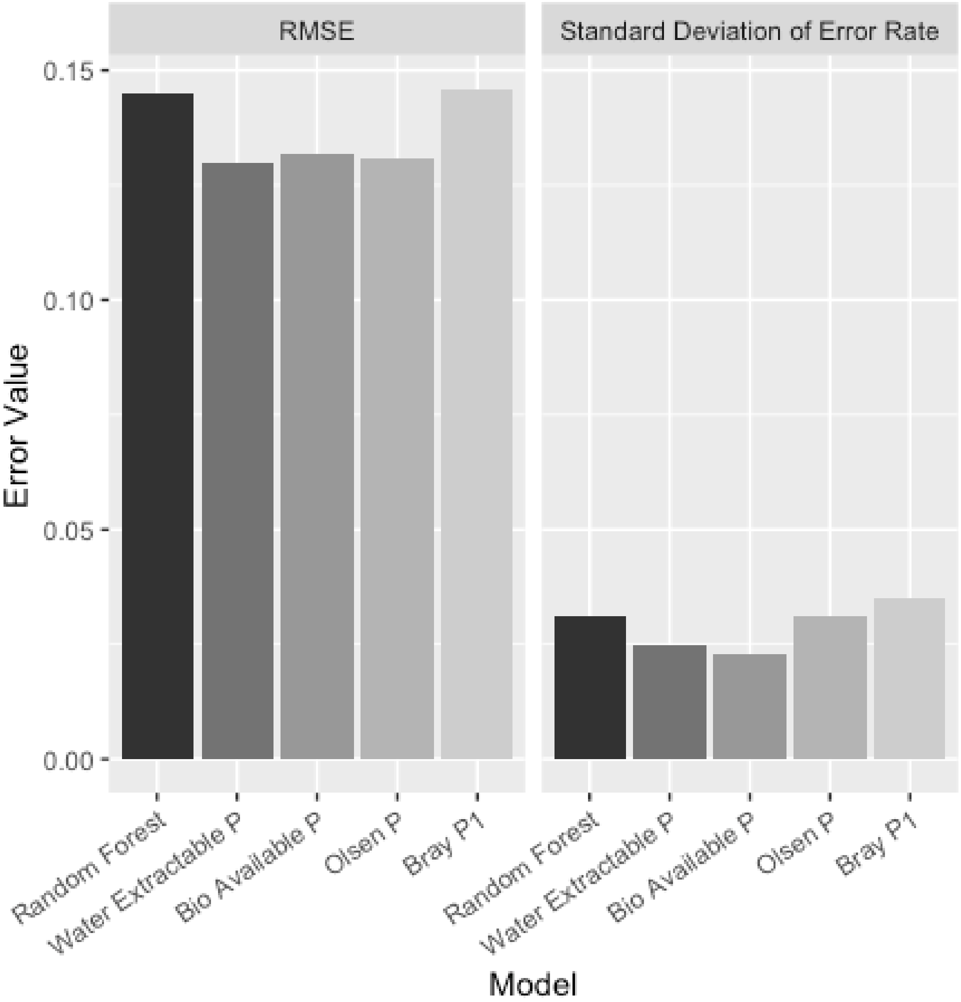

Figure 14. Error estimates for cross validation of the random forest and linear models for predicting P leaching losses from soil test phosphorus (STP) methods.

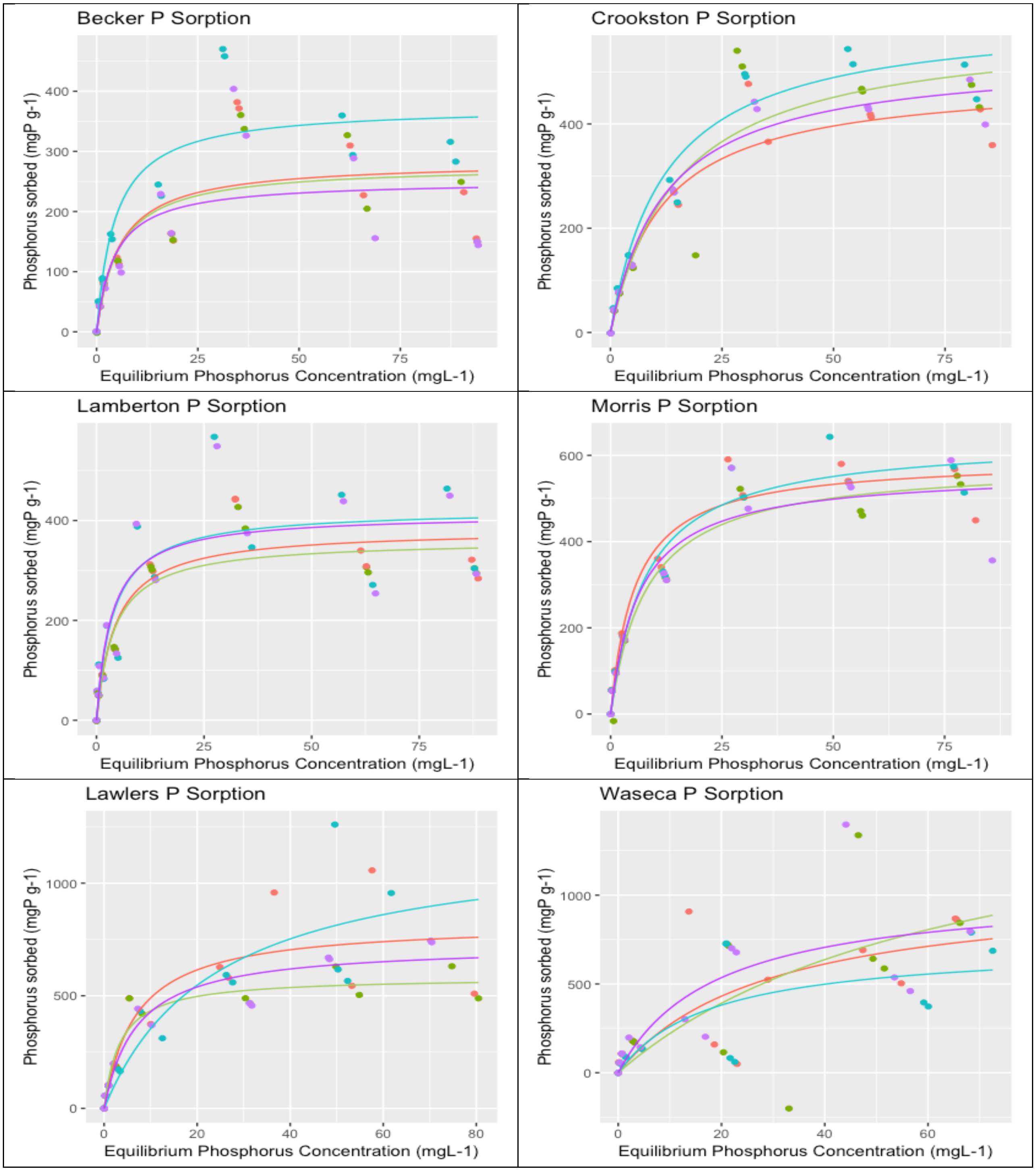

Figure 15. Summary of soil sorption data for 6-12” depth samples for low soil test P plots collected at six locations in Minnesota.

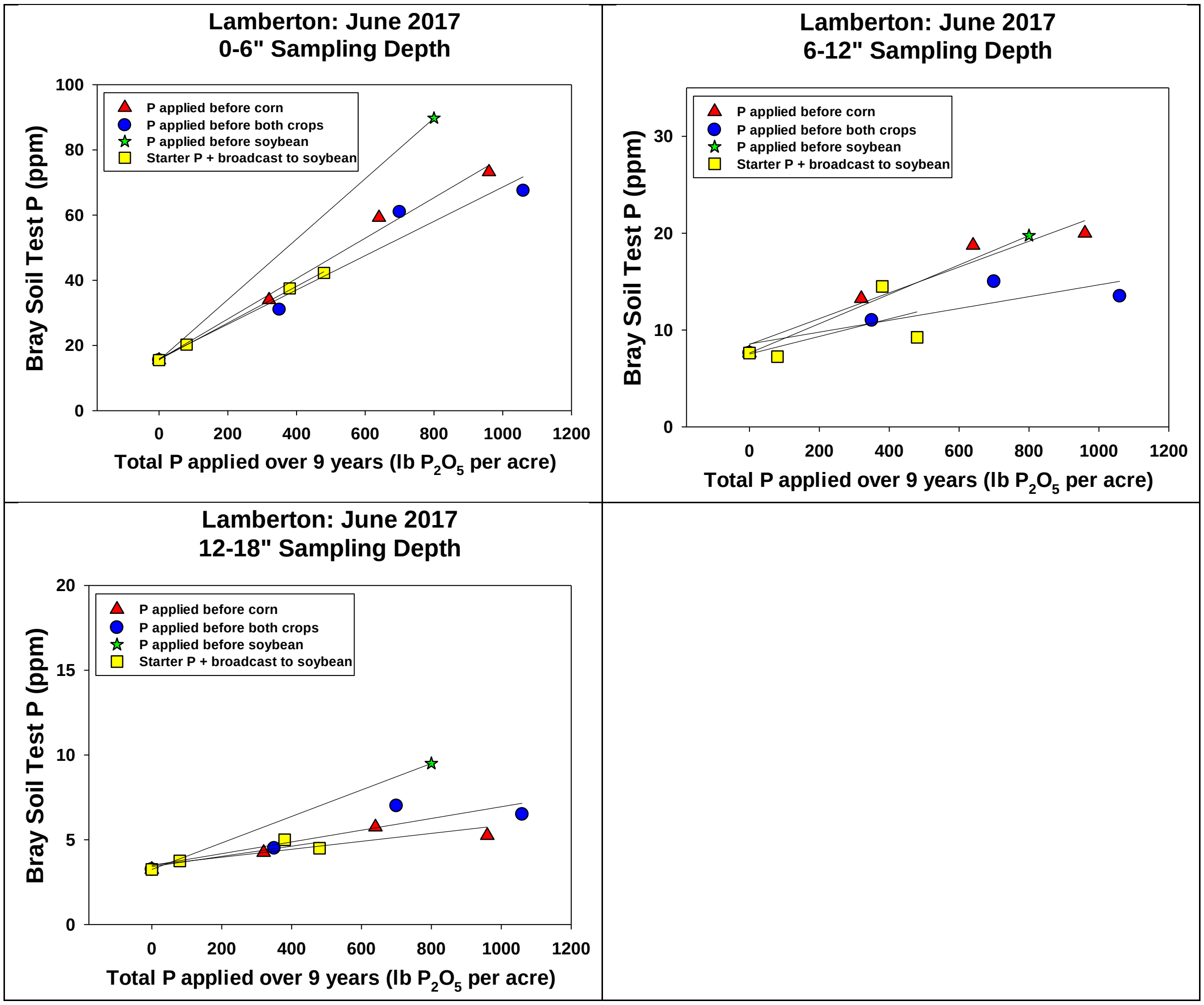

Figure 16. Summary of soil test values based on P fertilizer timing as affected by total rate of P applied over nine cropping years at three sampling depths from the P study at Lamberton. Regression lines are presented when the analysis indicated significant difference between treatments for a specific sampling depth.

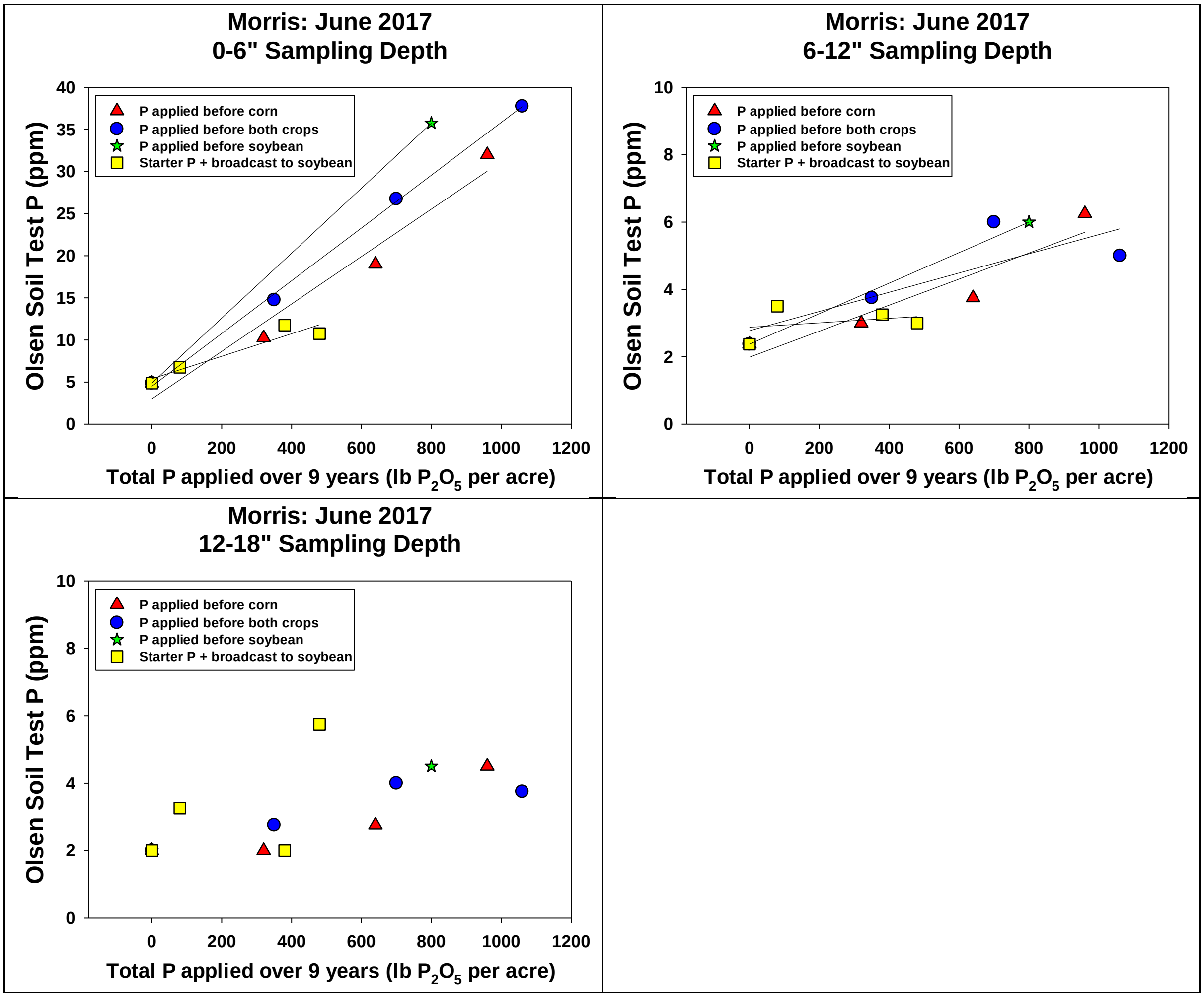

Figure 17. Summary of soil test values based on P fertilizer timing as affected by total rate of P applied over nine cropping years at three sampling depths from the P study at Morris. Regression lines are presented when the analysis indicated significant difference between treatments for a specific sampling depth.

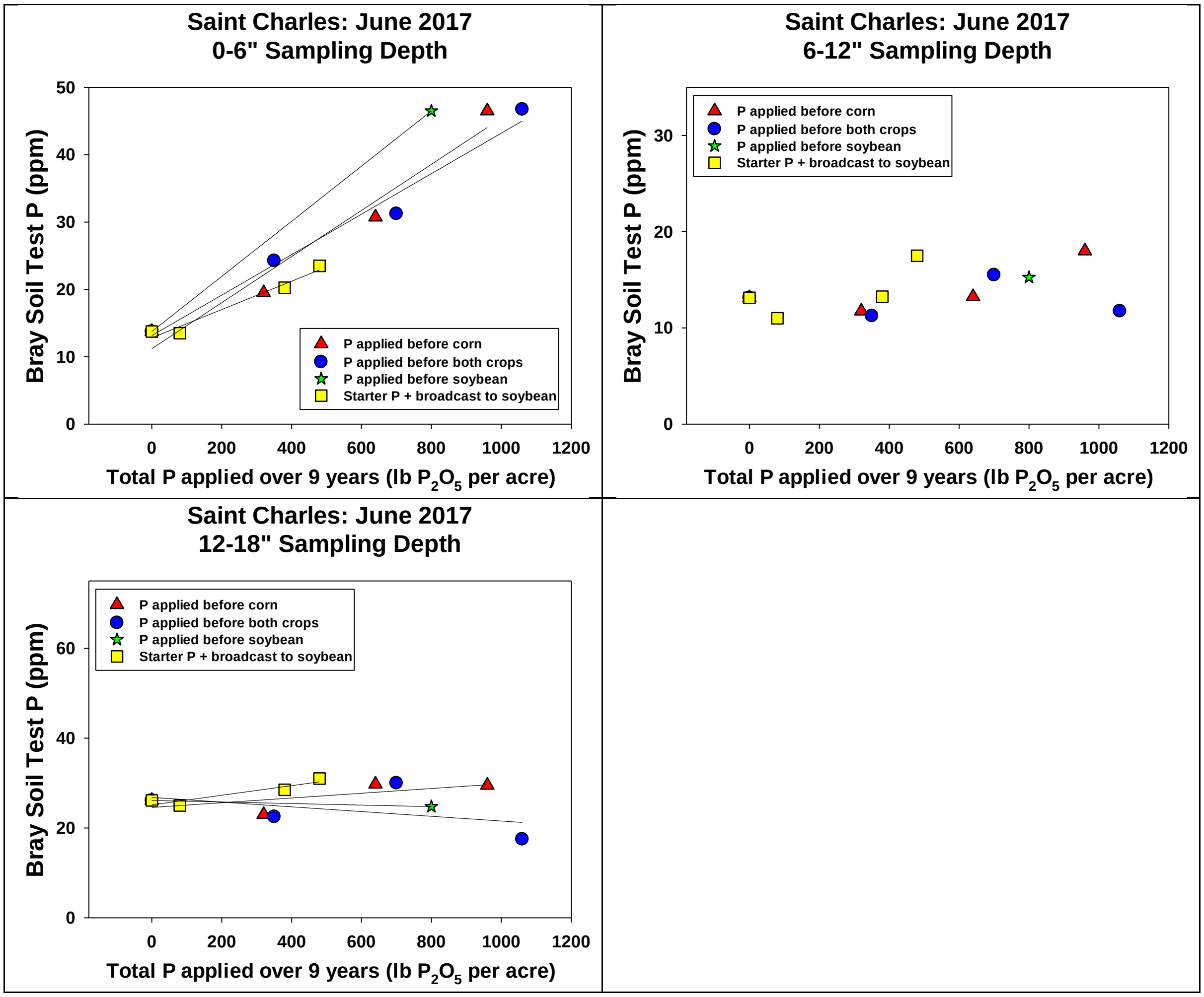

Figure 18. Summary of soil test values based on P fertilizer timing as affected by total rate of P applied over nine cropping years at three sampling depths from the P study at Saint Charles. Regression lines are presented when the analysis indicated significant difference between treatments for a specific sampling depth.

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OBJECTIVE 5 Correlate the Haney H3A soil extract to corn and soybean response to P.

REPRINTED FROM:
PREDICTION OF CORN AND SOYBEAN GRAIN YIELD RESPONSE TO P IN MINNESOTA USING THE HANEY H3A AND MEHLICH-III TESTS

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ABSTRACT

Minnesota soils are highly variable in P availability due to the wide range of chemical properties. Currently, two soil tests are used to measure soil P in Minnesota, the Bray-P1 for pH<7.4 and the Olsen P for pH≥7.4. The purpose of this study was to correlate crop response in corn and soybean rotations to the Bray-P1, Olsen, Mehlich-III, and Haney H3A extractions and to determine critical concentrations for each extraction method. Soil P tests were also correlated with one another to determine their viability for use in Minnesota soils. This study was conducted at nine field locations throughout the state from 2010 to 2014 with strip trails of 0 or 200 lb P_2O_5 ac^{-1} replicated three to four times within each field. Soil samples (0-6 inch depth) and grain harvest measurements were collected every forty feet along each strip. Critical values for the Bray-P1, Mehlich-III and Haney H3A (colorimetric) were similar near 12 ppm and slightly higher than the Olsen P extraction (9 ppm). All soil tests were strongly correlated when soil pH was <7.4 and less correlated when pH≥7.4, in particular the Haney H3A and Bray-P1 were poorly correlated to the Olsen P on high pH soils. Free carbonates in the soil were affecting the amount of P extracted by the acid soil extractants. All soil tests utilized could be correlated to crop response but calibration is necessary to make the tests useful. The Olsen P soil test is still preferred over acid extractants when soil pH is 7.4 or greater.

INTRODUCTION

Application of phosphorus (P) fertilizer is an integral management strategy for corn and soybean growers in the state of Minnesota. The state's recommendations for P application are determined by crop yield response to P over varying soil test P levels (Kaiser et al., 2011). In Minnesota, two soil tests are used to measure soil test P. The Bray-P1 is suggested for use in soils with a pH<7.4 and the Olsen P is suggested for soils with a pH≥7.4 Soils throughout the state vary greatly in chemical properties, parent materials, and pH. The abundance of basic calcareous soils on the western side of Minnesota increases potential for P fixation and requires a soil P test extractant not liable to neutralization. The high amount of calcium carbonates in these soils can neutralize acid extractants in soil P tests such as the Bray P1, Mehlich 3, and Haney

H3A (Haney et al, 2010) leading to inaccurate representations of soil test P. Calcareous soils are commonly derived from the glacial till parent material of Des Moines Lobe till and can be found in South Dakota, Minnesota, and Iowa.

All soil test P methods can measure orthophosphate colorimetrically using a colorizer solution and spectrophotometer. The Mehlich-III and Haney H3A extractants can also be analyzed with an Inductively Coupled Plasma (ICP) spectrophotometer. ICP analysis performs a number of extractions concurrently determining the concentration of several elements including both orthophosphate and organic phosphorus. The detection of both inorganic and organic forms of P often results in higher readings of soil P with the ICP method compared to colorimetric testing. The digression between these two testing methods must be considered when interpreting soil P test results.

The Mehlich-III test has grown in popularity throughout out the United States since it can be used to extract multiple elements at one time. The Haney H3A has gained attention as well for its ability to estimate soil health. However, in Minnesota the ambiguity of these tests due to potential extractant neutralization requires further testing for correlation to crop yield and explicit soil tests such as the Bray-P1 and Olsen P. Such correlations will provide information on the viability of the Mehlich-III and Haney H3A for P recommendations in Minnesota.

The goal of this study is to develop accurate prediction tools for corn and soybean yields in response to P fertilizer using the Bray P-1, Olsen P, Haney H3A and Mehlich-III soil tests. The objectives of this study are: 1) Correlate the Haney H3A, Mehlich-III, Bray-P1, and Olsen P soil test amongst themselves at varying pH levels; 2) Determine critical values (estimated at 95% of maximum yield) for each soil test; 3) Determine effect of calcium carbonates on soil P test methods and their usability.

MATERIALS AND METHODS

Table 1. Soil series information, planted crop at each location, and initial potassium soil test data from phosphorus studies conducted from 2010 to 2014. Soil test data was collected in the spring and represent a field average for the 2 acre study areas.

			Soil Test[†]			Soil Series	
Location	Year	Crop	K	CCE	pH	Major	Minor
			ppm	%			
Blomkest	2010	Corn	190	12.4	8.2	Harps-Okaboji	Canisteo-Seaforth
Foxhome	2010	Soybean	136	3.4	8.2	Elmville	Wyndmere
Lamberton	2010	Corn	143	0.0	6.1	Ves-Storden	--
New Richland	2010	Corn	279	5.4	4.9	Canisteo-Glencoe	Glencoe
Rochester	2010	Corn	158	0.4	7.5	Port Byron	Mt. Carroll
Grand Meadow	2011	Soybean	139	0.0	7.2	Clyde	Protavin
Stewart	2011	Soybean	187	0.8	7.1	Canisteo-Glencoe	Crippin
Staples	2012	Corn	100	0.1	7.2	Verndale	--
New Richland	2013	Corn	216	1.7	7.0	Canisteo-Glencoe	Crippin-Nicollet
Rochester	2014	Soybean	140	0.4	7.0	Mt. Carroll	Oronoco

† K, Soil test potassium (K-ammonium acetate); CCE, calcium carbonate equivalency.

Phosphorus studies were established beginning in 2010 through 2014 (Table 1). Studies consisted of two treatments, either no P or 200 lbs P_2O_5 broadcast in long strips within fields and incorporated prior to planting. All yes/no treatment combinations were replicated three to four times. Any additional nitrogen, K, sulfur, or zinc fertilizer was applied based on needs for the individual locations to keep these elements non-limiting when they were not specifically being studied.

Soil samples were collected prior to treatment application to a depth of six inches. Samples were collected every 40 feet from the center of each paired yes/no strip and consisted of a composite of ten cores. A total of 16 to 21 samples were taken from each strip making the total strip length 640 or 840 feet at each location. An additional 20’ was added to the end of each strip to allow space for application equipment to reach optimum speed prior to entering the research plot area. Strip width varied from 15 to 20’ wide at each location. Considering both the yes and no strips, each soil sample would represent a 30 to 40’ wide by 40’ long area (0.0275 to 0.0367 ac) within the field. This small of an area was chosen in order to limit random variability in yield between each yes/no area.

The center two rows of each 6 or 8 row strip was harvested using a research grade plot combine. Harvest samples were collected every 40’ along the strip to be representative of the soil samples collected in Spring. Corn grain yield is adjusted to 15.5% moisture content. Soybean grain yield is adjusted to 13.0%. Soil samples were dried at 65^{o}F in a force air oven and ground to pass through a 2 mm sieve. Samples were analyzed colorimetrically with the Bray-P1, Olsen P, Mehlich-III (Frank et al., 1998), and modified Haney H3A (Haney et al., 2010) methods. Phosphorus in the Mehlich-III and Haney H3A extracts were additionally determined with inductively coupled plasma spectrometry (ICP).

Statistical analysis was conducted using SAS. Critical concentrations for each soil test were determined using PROC NLIN in SAS. The critical concentration is defined as the soil test at which 95% of maximum yield was produced. Data was grouped for analysis to improve correlation between grain yield response and soil test values by averaging soil test and grain yield results from four neighboring yes/no comparisons within the field. All unique combinations of plots in a 2 x 2 arrangement were grouped for analysis. Correlation among the individual soil tests was conducted using PROC CORR and PROC REG.

RESULTS AND DISCUSSION

Soil test variability

Table 2. Summary of Soil Test P varying in location, year and testing method taken prior to fertilizer application. Summary includes average (AVG) and standard deviation (ST) of each testing method from 63-64 sampling areas within each location.

	Bray-P1		Olsen-P		M3P-C		M3P-ICP		H3A-C		H3A-ICP	
	AVG	ST	AVG	ST	AVG	ST	AVG	ST	AVG	ST	AVG	ST
	---ppm---											
Blomkest	2.9	2.2	7.1	2.7	11.3	6.3	30.1	8.8	5.7	3.1	10.0	3.6
Foxhome	4.5	3.7	4.8	2.3	13.8	6.9	31.9	7.3	8.8	4.1	12.4	4.7
G. Meadow	20.3	10.8	11.2	5.7	18.4	8.8	42.5	9.9	16.6	7.9	31.5	9.8
Lamberton	16.9	7.0	12.5	4.2	15.3	6.0	31.7	8.2	13.7	6.5	25.8	7.2
New Rich.’10	5.6	3.2	6.4	1.2	6.1	2.5	20.5	4.4	10.0	5.2	17.3	8.1
Roch. ‘10	23.0	12.3	12.1	5.4	20.0	10.6	38.0	13.0	20.2	10.2	32.8	12.5
Stewart	24.5	14.1	13.8	6.8	25.2	11.3	37.0	12.6	25.3	11.2	32.7	12.6
Staples	34.3	15.6	14.8	6.7	33.7	18.3	54.8	23.2	24.9	15.3	34.7	17.8
New Rich.’13	13.7	8.5	7.5	4.1	15.8	4.7	31.6	7.3	16.5	8.4	22.3	9.7
Roc.‘14	15.3	5.4	9.0	3.3	13.6	5.9	28.8	8.2	15.2	5.5	23.8	5.6

Average and the standard deviation of individual soil samples taken from each location are given for the Bray-P1, Olsen P, Mehlich-III colorimetric, Mehlich-III ICP, Haney H3A colorimetric, and Haney H3A ICP soil P tests in Table 2. Locations varied in average initial soil test P categories from Low to Very High according to the Bray-P1 soil test. Soil test values across the trial areas were Low to Very Low at Blomkest, Foxhome, New Richland and Stewart. According to past research there is a high probability of a large grain yield response at each of these locations from applied P fertilizer. Soil test values averaged High at Grand Meadow and Lamberton and Very High at Rochester and Staples. These locations along with Stewart had the highest variation in soil P across the trials as indicated by the larger standard deviations.

Critical P soil test values

The primary purpose of this study was to compare grain yield with and without P to determine relative grain yield and relate it to the soil test value measured from the area encompassing the yes/no comparison. This comparison was used to determine the critical soil test P level or the value at which crops do not respond to applications of fertilizer P. Routine phosphorus soil tests do not measure the all pools of P within the soil depth sampled, thus values can vary between soil test methods. In addition, ICP analysis differs from colorimetric analysis in its ability to measure both organic P and inorganic P (orthophosphate). The P extraction from both soil pools results in a higher value for soil test P when using ICP analysis. Since the soil tests extract different amounts of nutrients, the critical soil test levels may be different for each test method.

Table 3. Critical soil test P levels for various soil test methods summarized by relative yield level for all corn and soybean data. The critical level is summarized for 95% of maximum grain yield.

Soil Test	Corn	Soybean
	------------------------------ppm	-------------------------------
Bray-P1	12	12
Olsen	9	8
Mehlich-III: Color	14	17
Mehlich-III: ICP	32	39
H3A: Color	12	12
H3A: ICP	22	21

Figures 1 and 2 show the correlation of relative yield (yield with no P as a percentage of yield with P) with all soil test methods: Bray-P1, Olsen P, and Mehlich-III colorimetric, Mehlich-III ICP, Haney H3A colorimetric and Haney H3A ICP for corn and soybean, respectively. Shading of the data points represent differences in soil pH for soils with pH greater than or equal to or less than 7.4. The best correlation between relative corn or soybean yield and individual soil tests was for the Bray-P1 test for both crops (R^2=0.53 for corn and 0.41 for soybean). The poorest correlation was for the Mehlich-III test (ICP and color analysis) and soybean grain yield. The poor correlation for the Mehlich-III test was due to an over extraction of P at one location with a soil high in carbonates (not shown). The R^2 values for the remaining tests were mostly between 0.3-0.4.

Utilizing individual yes/no comparisons results in a great degree of variability within the relationship between yield response and soil test value. Subtitle variation in population could result in a large variation in yield that may not be related to the treatment itself. To reduce the variation the data was analyzed using average values for a set of four adjacent yes/no comparisons. For corn, the critical soil test according to the Bray-P1 test was 12 ppm while the Olsen test was 9 ppm (Table 3). For soybean, the Bray-P1 critical level was 12 ppm and the Olsen value was 8 ppm. The current corn and soybean P guidelines for Minnesota do not state a critical P soil test level for the Bray-P1 or Olsen soil tests (Kaiser et al., 2011). However, broadcast P fertilization is not suggested when soil test above the High soil test classification for corn (15-20 ppm Bray P1 or 12-15 ppm Olsen) or above the low classification for soybean (6-10 ppm Bray-P1 or 4-7 ppm Olsen). However, this study indicates the current guidelines may be slightly overestimating the critical level for corn, and underestimating the critical level for soybean.

Critical soil test P values for the Mehlich-III and Haney H3A tested colorimetrically for corn and soybean were similar to the critical values of the Bray-P, as shown in Table 3. The critical values remained fairly similar between corn and soybean in all tests with the exception of the Mehlich-III, analyzed both colorimetrically and with ICP. The critical values when using the Mehlich-III extractant indicated a higher demand for P in soybeans than corn. Colorimetric and ICP analysis specified critical values 3 ppm and 7 ppm higher respectively for soybean than for corn. All other soil test P methods indicated no increase (Bray-P1, Haney H3A Color) or increase by 1 ppm (Olsen-P, Haney H3A-ICP) between corn and soybean critical values.

Bray-P1 and Haney H3A colorimetric resulted in the same suggested critical value for both corn and soybeans at 12 ppm. The same critical value between the two tests, Bray-P1 and Haney H3A colorimetric, may indicate similarities between the two tests as acid extractants. The Mehlich-III soil P test measured colorimetrically was also similar to the Bray-P1 with values for corn of 14 ppm and 12 ppm respectively. For soybean, the Mehlich-III showed greater divergence from the Bray-P1 with a critical value of 17 ppm in comparison to 12 ppm for the Bray-P1. ICP analysis for the Mehlich-III and the Haney H3A resulted in critical values nearly doubled compared to colorimetric analysis, as well as the Bray-P1. This may be attributed to the additional organic P also measured in ICP analysis. Compared to the Olsen P, all acid extractant tests (Bray-P1, Mehlich-III, Haney H3A) measured colorimetrically resulted in slightly higher values than those of Olsen P test which was expected. The strong similarities among the Bray-P1, Mehlich-III, and Haney H3A colorimetric critical values suggest similar interpretations and calibrations could be used for the three tests. This suggests the acid extractants access similar pools of P and all extractions should provide similar interpretations of soil P availability to corn or soybean. However, soils with a pH $\geq$ 7.4 with free carbonates may cause issues in for acid extractants and these testing methods. The Olsen P test is still suggested for use in Minnesota for soils with high pH and carbonate content.

Comparison of P extracted by soil tests

It is recommended to switch to the Olsen P test in Minnesota when soil pH is 7.4 or greater due to the effect that carbonates have on the Bray-P1 test (Kaiser et al., 2011). Comparisons of the soil test P methods were measured using the correlation coefficient for soils with a pH<7.4 and soils with a pH$\geq$7.4, as shown in Tables 4 and 5, respectively. All soil P test methods were strongly correlated for soils with a pH<7.4 (Table 4). Even though all tests were correlated at low pH, there were differences among the tests in the amount of P measured in the extractants. The Bray-P1 and Mehlich-III colorimetric tests showed strong correlation (r=0.96) suggesting that the two soil tests measure soil P similarly. This correlation indicates calibration data for the Bray-P1 soil test could be used for the Mehlich-III soil colorimetric test for soil pH below 7.4. The Mehlich-III ICP correlation between both the Bray-P1 and Mehlich-III color indicated similar relationships, r=0.90 for both. The slightly weaker relationship with ICP analysis can again be attributed to the organic P that is read in ICP testing. The Mehlich-III color and ICP also correlated to the Olsen P (r=0.90 and r=0.84, respectively). However, this relationship is not as strong as the relationship with the Bray-P1. The Mehlich-III and Haney H3A tests exhibited relationships similar to the Mehlich-III- Olsen P correlation, with correlation coefficients (r) between 0.84-0.89 (Table 4). Like the Mehlich-III, the Haney H3A showed strong correlations with the Bray-P1. The correlation coefficients for the Haney H3A colorimetric and Haney H3A ICP with the Bray were both r=0.87, with neither test showing stronger correlation to the Bray-P1. The weakest correlations for the Haney H3A were with the Olsen P, both colorimetrically and through ICP analysis. However, there is still a fairly strong relationship exhibited between the Haney H3A colorimetrically and the Olsen P (r=0.84), and the Haney H3A ICP and Olsen P (r=0.85). When the analysis type was compared between the Haney extractions (ICP and colorimetric), the relationship was evident (r=0.96). These relationships suggest the Bray P1, Mehlich-III C, Mehlich-III ICP, Haney H3A C, and Haney H3A ICP soil test methods are adequate for use in Minnesota soils with a pH<7.4 Calibration data for individual tests may be developed and put into use for Minnesota farm recommendations.

Table 4. Correlation coefficients for soil test P methods when soil pH < 7.4. Correlation values above 0.06 are significant at $P \leq 0.05$. (n=923)

	Soil Test P Method				
	M3–C	M3–ICP	H3A–ICP	H3A–C	Olsen P
Bray P	0.96	0.90	0.87	0.87	0.93
M3–C		0.90	0.87	0.87	0.90
M3–ICP			0.89	0.84	0.84
H3A–ICP				0.96	0.85
H3A-C					0.84

Table 5. Correlation coefficients for soil test P methods when soil pH ≥ 7.4. Correlation values above 0.09 are significant at $P \leq 0.05$ (n=413)

	Soil Test P Method				
	M3–C	M3–ICP	H3A–ICP	H3A–C	Olsen P
Bray P	0.41	0.54	0.88	0.86	0.58
M3–C		0.90	0.55	0.56	0.83
M3–ICP			0.67	0.67	0.83
H3A–ICP				0.98	0.67
H3A-C					0.67

Locations with a pH greater than 7.4 show inconsistent results between soil P test methods, indicating possible neutralization of the acid extractants. As shown in Figure 3, there is clear neutralization of a subset of the samples when Bray extraction is used, resulting in a poor correlation with the Olsen P (r=0.58). At field locations with pH≥7.4, correlation between the

Olsen P test and Mehlich-III extracts was evident (r =0.83). However, the correlation showed a strong grouping of data points at the tail of the trendline vector indicating some differences among soils in how the Mehlich-III test relates to the Olsen test (Figure 3). The Mehlich-III ICP analysis yielded similar results to the Mehlich-III colorimetric method. ICP analysis resulted in greater approximations of soil P and correlated to Olsen P nearly as strong as Mehlich-III colorimetric test. The Haney H3A has been growing as a popular soil testing tool for its simultaneous extractions. However, the strong acid extract is suspected to have similar issues to the Bray when used for testing in soils with high pH, which may contain free carbonates. The Haney H3A soil test method showed a weaker correlation to the Olsen P (r=0.67 (C), r=0.67 (ICP)) compared to the Mehlich-III, but a greater correlation than the Bray and the Olsen P (r=0.58). It is speculated that the Haney H3A, measured both colorimetrically and with ICP analysis, underwent a similar reaction to the other acid extractants methods and is partially neutralized when used in soils with a pH≥7.4. While the correlation between the Haney H3A and Olsen P, and Mehlich-III and Olsen P are evident, the correlation with field data does not indicate the either test is a superior to the Olsen P, the current testing method suggested for use in Minnesota for soils with a pH≥7.4.

Presence of free carbonates

Soil pH is typically used as a determining factor when deciding what test to use. Data comparing the Bray-P1 test to the Olsen P for soils with a pH greater than or equal to 7.4 show that the Bray under extracts P in some soils but not in all soils. Free carbonates in the soil likely will affect acid extractants such as with the Haney H3A, Mehlich-III and Bray-P1 tests. The difference between the amount of P extracted by the Bray-P1, Mehlich-III, and Haney H3A tests is summarized in Figure 4. Data is only included for the colorimetric tests in Figure 4. The tests analyzed by ICP always resulted in greater concentration of P in the extraction solution but were affected similarly than the colorimetric analysis (not shown). As the calcium carbonate equivalency (CCE) approaches 2.5 to 5 percent $CaCO_3$ the amount of P extracted by the Bray-P1 test was less than the Olsen P. This is atypical, as the Bray-P1 and other acid extractant tests consistently extract higher amounts of P (ppm) than the Olsen P in soils without free carbonates. A similar effect is observed with the Haney H3A colorimetric analysis (Figure 4). The Haney H3A retains its ability to extract more P than the Olsen test in soils with low carbonates, but extracts similar amounts of P as CCE approaches 5 percent and less P as the Olsen P test as CCE increases beyond 5 percent.

It was interesting that the relative difference between the amounts of P extracted by ICP decreased with increasing CCE for the Haney H3A test. This effect was not seen for the Mehlich-III extraction. Soils in this study with free carbonates tend to have lower concentrations of inorganic P. The Mehlich-III test did overestimate P availability at one location. Data can be seen from this location in Figure 4 where the difference between the Mehlich-III and Olsen P test was very high in spite of high carbonates. What is interesting is that the Mehlich-III test never extracted less P than the Olsen P similarly to the Bray-P1 test. In addition, the Haney H3A tended to extract more P than the Olsen P at higher CCE in the soil. This may indicate that the Mehlich-III and H3A tests are better buffered and may be used over a wider range of CCE than the Bray-P1 test. The Olsen test would still be recommended due to the lack of impacts of carbonates on the test.

CONCLUSIONS

If properly calibrated, the Mehlich-III and Haney H3A tests could be used to assess soil P status for corn and soybean in Minnesota. Critical values were similar for corn and soybean for the Bray-P1, Mehlich-III, and Haney H3A tests when measured colorimetrically. Analysis of soil extracts by ICP requires further calibration of the tests to account for additional P measured. All P tests are correlated for neutral to acid soils. All tests can be used equally if properly calibrated and none of the tests proved a definitive advantage for the determination of P status in the soil for corn or soybean. The presence of carbonates in high pH soils affects the extraction of P by the tests with acid extractants. The Olsen P test is suggested for high pH soils as it is less impacted by carbonates.

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OBJECTIVE 6

INTRODUCTION

Products have been marketed to increase the availability of soil P. One such product, Avail (Specialty Fertilizer Products, Leawood, KS), is composed of maleic-itaconic acid copolymer that have a cation exchange capacity that is supposed to attract and bind Ca in the soil to prevent the formation of Ca-phosphate compounds. Research in Minnesota has not shown a benefit of this product for increasing P availability in soils. In a review, Chien et al (2014) explained that the active ingredients in Avail applied at labeled rates can bind little to no effect on Ca-phosphate formation as maleic and itaconic acids cannot compete with the binding potential for Ca with phosphate. Other attempts have been made to solubilize P utilizing organic acids. Soils with high pH can contain free carbonates that can neutralize acid. At this time there is no clear evidence that any weak acids can help solubilize P and reducing the pH of the soil is not a cost effective way to increase the availability of P.

Chelates have the ability to attract and hold cations. Cations such as EDTA and DTPA have been used to hold micronutrients to increase their availability to crops and DTPA has been developed into a soil test used for determining sufficiency of micronutrients in the soil. Chelates can vary in how they bind and release cations and are affected differently based on soil pH (Aboulross et al., 1983). One chelate, o-o-EDDHA (o-o represents the ortho-ortho isomer of the chelate), has been shown to be more stable across soil pH levels and the ortho-ortho isomer can protect the cation bound more completely than other chelate sources. The ortho-ortho isomer of EDDHA is currently being marketed for use in supplying Fe to soybean grown on soils prone to iron deficiency chlorosis. The EDDHA chelate without a bound cation has been studied in field trials in Minnesota. The EDDHA chelate increased early plant growth and early P uptake in corn at two locations. We would like to follow up some of the preliminary field findings to determine if the o-o-EDDHA chelate could be used to increase P availability relative to other chelate sources.

OBJECTIVE:

(6) Determine if chelates could be utilized to increase P availability to crops.

MATERIALS AND METHODS:

Chelate testing studies were conducted using a series of greenhouse and field trials. The greenhouse studies were established in two parts. Part 1 consisted of testing six chelates applied in furrow simulating an application rate of 0.6 mol per acre. Molar mass was used to adjust the chelates based on the ability to sorb equal amounts of charge in the soil. Since the chelates differ in molar mass application at the same mass in the field would result in variations in the amount of charge which could be bound by the chelates in the soil. Five chelate sources were compared to a non-fertilized control. The chelates compared were citric and oxalic acid, DTPA, EDTA, and o-o-EDDHA. Disodium salts of DTPA and EDTA were utilized while free acid o-o-EDDHA was purchased which had to be solubilized in NaOH followed by adjusting the pH to 7.5. Chelate treatments were applied directly on the seed by opening a seed furrow in each pot and applying the liquid chelate solution with an electronic pipette. Three crops (corn, soybean, and hard red spring wheat) and three soils (Table 1) were compared in this study. Two pots were used for each treatment within each replication (four replications per treatment). Multiple seeds were planted in each pot and were thinned to 1 plant per pot for corn, 3 for soybean, and 6 for wheat.

Table 1. Site soil test levels for three soils collected in Minnesota for two chelate Greenhouse trials.

						DTPA		
Series	Texture†	P	K	pH	SOM	Cu	Fe	Zn
		-----ppm-----			-%-	-----ppm-----		
Canisteo	CL	4	320	7.4	5.8	1.9	16	2.0
Amiret	L	12	107	5.2	3.5	1.6	113	0.9
Seaton	SiL	14	125	6.6	2.9	0.9	43	1.3

† CL, clay loam; L, loam; SiL, silt loam.

P, Bray-P1; K, ammonium acetate; pH, 1:1 soil to water; SOM, soil organic matter by dry combustion; Cu, Fe, and Zn by DTPA.

Results: Greenhouse Study 1.

Table 2. Effect of chelate sources on corn plant weight and tissue nutrient concentration

		Tissue Nutrient Uptake			
Source of Variation	Plant Wgt	P	Cu	Fe	Zn
	g plant^{-1}	ug plant^{-1}			
		Soil Type			
Canisteo	0.46a	0.61	2.39a	27.3b	13.3a
Amiret	0.39b	0.53	1.54b	34.3a	10.4b
Seaton	0.44ab	0.55	1.57b	34.1a	9.3b
		Chelate Source			
None	0.43	0.54	2.02	31.2	10.8
Citric Acid	0.42	0.58	1.73	31.0	11.0
DTPA	0.44	0.57	1.88	33.7	11.7
EDDHA	0.44	0.56	1.94	32.3	11.1
EDTA	0.42	0.52	1.72	31.8	10.4
Oxalic Acid	0.45	0.59	1.71	31.5	11.0
Statistics		------------------------ *P* > F ------------------------			
Soil Type	0.07	0.23	<0.01	<0.01	<0.01
Source	0.92	0.76	0.44	0.94	0.76
Soil Type x Source	0.32	0.47	<0.01	0.69	0.55

The second greenhouse trial included only three of the five chelate sources (DTPA, EDTA, and o-o-EHHDA) applied at four rates (0, 0.2, 0.4, and 0.6 mol per acre). In contrast, each treatment by soil combination included only one pot in each of the four replications. Therefore, two corn plants were allowed to grow in each pot, 4 for soybean, and 8 for wheat to gain enough plant material for elemental analysis. Treatments were applied using an electronic pippete in a total of 10 ml of water. The same three crops and three soils were utilized in the second greenhouse trial as were used in the first study.

All plants were allowed to grow for approximately three weeks after emergence then were cut at the soil surface, bagged, dried, and weighed to determine total biomass produced. Samples where then ground and sent out for elemental analysis by ICP.

Field studies were established at two locations during 2016 and 2017. Chelate sources and application rates for the field trials used the same treatment structure as Greenhouse Study 2 except for at Lamberton in 2016 where only EDTA and EDDHA were used. All treatments were applied in-furrow by mixing the chelate with water. The chelate/water mixture was applied a 2, 4, and 6 gallons per acre. At all locations except for Becker 2016 additional treatments consisting of fertilizer P applied at 0 and 60 lb P_2O_5 per acre were included. The P treatments were main blocks and the starter treatments were superimposed across the P treatments. Early phosphorus uptake was determined by sampling 6 whole plants at the V5-V7 growth stage and mid-season P concentration was determined by sampling 10 corn leaves opposite and below the ear at the R1 growth stage (early silking). All plant samples were dried, ground, and analyzed for total P by ICP. Plant mass data was collected on the V5-V7 whole plant samples. Grain yield data was collected by harvesting 35 feet in length for both the middle two rows in each plot. Grain yield data are reported following adjustment to 15.5% harvest moisture.

Table 3. Effect of chelate sources on soybean plant weight and tissue nutrient concentration.

		Tissue Nutrient Uptake			
Source of Variation	Plant Wgt	P	Cu	Fe	Zn
	g plant^{-1}	ug plant^{-1}			
		Soil Type			
Canisteo	0.66ab	0.72a	2.72	35.7b	9.5c
Amiret	0.60b	0.55b	2.85	48.4a	12.8a
Seaton	0.71a	0.78a	2.95	45.2a	11.4b
		Chelate Source			
None	0.69	0.73	3.10	42.2	11.3
Citric Acid	0.67	0.69	2.90	40.4	11.1
DTPA	0.65	0.71	2.74	44.1	12.5
EDDHA	0.69	0.69	2.80	45.8	11.3
EDTA	0.64	0.68	2.83	41.6	11.3
Oxalic Acid	0.61	0.61	2.66	44.4	10.1
Statistics		----------------------- *P* > F -----------------------			
Soil Type	<0.01	<0.01	0.57	<0.01	<0.01
Source	0.39	0.40	0.69	0.81	0.08
Soil Type x Source	0.33	0.45	0.09	<0.01	<0.01

Corn results from Study 1 are presented in Table 2. Data in Tables 2 through 5 include copper, iron, and zinc concentrations which will not be discussed in this report. Micronutrient concentrations were measured as chelates are typically used to enhance the availability and uptake of micronutrients. There was very little response to micronutrient uptake based on chelate source so further discussion is not warranted.

Corn plant mass did vary among the soils used for the study. The Canisteo soil produced the largest plant mass while the Amiret produced the least mass. The relative growth among the soil series could not be tied to initial P concentration in the soil as the Canisteo had the lowest soil test value among the three soil types (Table 1). Early plant P uptake was not impacted by soil or chelate source indicating similar supply capacity among the soils and not increase in P availability based on chelate source.

Soybean data are summarized in Table 3. Similar to corn responses, soybean effects were common among the three soil types but did not differ among the chelate sources. Both plant mass and P uptake varied among the soils with the Canisteo soil again producing the largest plants and the greatest P uptake while having the least concentration of P. The lack of an impact of chelates again indicates little benefit among the various sources for enhancing the uptake of P in soybean.

Table 4. Effect of chelate sources on hard red spring wheat plant weight and tissue nutrient concentration.

		Tissue Nutrient Uptake			
Source of Variation	Plant Wgt	P	Cu	Fe	Zn
	g plant^{-1}	ug plant^{-1}			
		Soil Type			
Canisteo	0.93a	2.09a	8.06a	104.0a	44.9a
Amiret	0.18c	0.34c	1.50c	22.0c	6.6c
Seaton	0.52b	1.20b	3.77b	59.9b	20.0b
		Chelate Source			
None	0.61a	1.29	4.84	62.5	25.5
Citric Acid	0.61a	1.37	5.11	67.9	25.0
DTPA	0.49b	1.13	4.09	63.4	23.0
EDDHA	0.51b	1.09	4.09	57.6	21.8
EDTA	0.51b	1.16	4.31	58.4	24.2
Oxalic Acid	0.52ab	1.22	4.20	56.3	23.8
Statistics		------------------------ *P* > F ------------------------			
Soil Type	<0.01	<0.01	<0.01	<0.01	<0.01
Source	0.02	0.28	0.38	0.91	0.44
Soil Type x Source	0.01	0.65	0.22	0.32	0.31

Hard red spring wheat data are summarized in Table 4. The data showed similar strong correlation between plant mass and P uptake difference among the soil type. There was a large difference between the Amiret soil and the two other soil types. The Amiret soil had very poor wheat growth possibly due to herbicide carryover which significantly impacted the wheat plant mass and P uptake. There were difference among the chelate sources for plant mass. However, all chelate sources other than citric and oxalic acid tended to result in less plant mass compared to the control. There was a significant two way interaction for plant mass indicating a variation in the impact of source based on soil type or a variation in soil type response based on source. The treatment means for the soil type by source effect is not given in this report. However, further analysis indicated that the sources only varied for the Canisteo soil and there was no variation among the sources for the remaining two soil types.

Table 5. Effect of three soil types and three sources of chelates applied at four rates on plant mass and phosphorus uptake for corn, soybean, and hard red spring wheat collected during a greenhouse trial.

Source of Variation	Plant Weight			Plant Phosphorus Uptake		
	Corn	Soybean	Wheat	Corn	Soybean	Wheat
		g plant^{-1}			ug plant^{-1}	
Soil Type						
Canisteo	0.52a	0.41b	0.21a	0.55a	0.49b	0.48a
Amiret	0.37b	0.43b	0.08c	0.44b	0.45b	0.14c
Seaton	0.52a	0.54a	0.15b	0.57a	0.62a	0.33b
Chelate Source						
DTPA	0.47	0.46	0.14b	0.51	0.53	0.29
EDDHA	0.47	0.46	0.15ab	0.52	0.52	0.31
EDTA	0.48	0.45	0.16a	0.53	0.50	0.34
Chelate Rate (*M* acre^{-1})						
0.0	0.46b	0.44b	0.15	0.49b	0.52	0.30
0.2	0.50a	0.48a	0.15	0.55a	0.53	0.31
0.4	0.47b	0.46ab	0.15	0.52ab	0.52	0.30
0.6	0.46b	0.46ab	0.16	0.52ab	0.50	0.34
Statistics		----------------------- *P* > F -----------------------				
Soil Type	<0.001	<0.01	<0.001	<0.001	<0.001	<0.01
Source	0.75	0.68	0.05	0.54	0.44	0.24
Soil x Source	0.91	0.67	0.58	0.81	0.34	0.89
Rate	0.03	0.09	0.55	0.07	0.71	0.58
Soil x Rate	0.14	0.97	0.36	0.89	0.83	0.06
Source x Rate	0.20	0.68	0.76	0.08	0.90	0.83
SoilxSourcexRate	0.31	0.18	0.04	0.46	0.86	0.31

Study 1 showed an overall lack of impact of chelate sources for increasing plant mass and nutrient uptake. The only effect occurred for plant mass in the wheat trial where most of the chelates appeared to reduce plant mass. Due to a general lack of effect it was decided to focus on the synthetic chelate sources as they represent generally what is used in industry. The rate used in Study 1 was 0.4 mol per acre for all chelates, thus the rate structure for study 2 was based around the study 1 rate applying less and slightly more chelate rate to achieve four equally spaced rates. Table 5 summarizes plant mass and P uptake data only. Differences among treatments were primarily found among the soil types for all variables and seldom were found amount the sources. Sources did vary again for wheat where plant mass was less for DTPA versus EDTA while EDDHA did not vary from either the other two sources. Chelate rate did impact corn and soybean plant mass and corn P uptake. For both corn and soybean, plant mass was greatest when 0.2 mol per acre of all the chelates were applied while the 0.4 mol per acre rate which was also used in Study 1 did not increase plant mass over the control. This data indicates that the lack of a response to the chelate sources may have been a direct result of the rate used in study 1. There were two interactions of note, the significant three-way interaction for wheat plant mass and the soil by chelate rate interaction for corn P uptake. The three-way interaction for wheat plant mass was a result of a rate response only for EDTA only when applied to the Canisteo soil. The significant two-way interaction for corn P uptake was difficult to determine as there was indication that soil varied regardless of chelate source. It is likely that differences in P uptake among soil types were greater for certain chelates compared to others.

Results from field trials

Table 6. Soil and planting information for corn locations established in Minnesota for the 2018 Growing season

		Soil		Planting			
Year	Location	Series	Texture†	Date	Rate	Cultivar‡	Irrigated
					Seeds ac-1		
2016	Becker	Hubbard	LS	28-Apr	35,500	D49-72	Y
	Lamberton	Amiret	L	19-May	35,500	D49-72	N
2017	Becker	Hubbard	LS	10-May	35,500	C199-29	Y
	Lamberton	Webster	CL	16-May	35,500	C199-29	N

†Texture: CL, clay loam; L, loam; LS, loamy sand.
‡C, Channel; D, DeKalb.

Table 7. Site soil test levels for two Minnesota corn study locations (0-6” depth unless noted).

						DTPA		
Year	Location	P	K	pH	SOM	Cu	Fe	Zn
		-----ppm-----			-%-		-----ppm-----	
2016	Becker	25	118	5.7	1.5	0.5	33	1.8
	Lamberton	9	114	5.1	3.6	1.3	95	0.4
2017	Becker	17	70	5.6	1.8	0.6	42	1.6
	Lamberton	6	118	6.1	4.2	1.4	90	0.5

P, Bray-P1; K, ammonium acetate; pH, 1:1 soil to water; SOM, soil organic matter by dry combustion; Cu, Fe, and Zn by DTPA.

A summary of pertinent cropping management information and soil test data for the four field trials is summarized in Tables 6 and 7. Only corn was used for the field trials. Locations were targeted with low available P. However, soil test values were generally high to very high at both the Becker locations thus the P treatments were excluded at the 2016 Becker site. The 2017 Becker site was close enough to the low classification where the P treatments were included.

Irrigation water was sampled at Becker to determine the amount of total P applied with the irrigation water. The P concentration was below the detection limit for the analyzer used to determine the P concentration thus it was not possible to determine the exact amount of P applied either year. However, using the value for the detection limit the maximum amount of P potentially applied was very low and would not result in sufficient P to limit corn growth.

Table 8. Summary of irrigation totals and amount of P_2O_5, K_2O, and SO_4-S applied per year in the irrigation water at Becker, MN.

Year	Water Applied	Water Concentration P_2O_5	Water Concentration K_2O	Water Concentration SO_4-S	Applied P_2O_5	Applied K_2O	Applied SO_4-S
	-- in--	------------ppm------------			-----------lb/ac/yr----------		
2016	7.40	<0.02†	1.53	3.0	<0.03	2.55	5.0
2017	9.05	<0.02†	1.63	5.1	<0.04	3.32	10.4

† Concentration values were below the detection limit of the ICP or IC.

Table 9. Effect of chelate sources chelate rates, and P application on corn V5 whole plant phosphorus uptake at four Minnesota locations.

Source of Variation	2016 Becker	2016 Lamberton	2017 Becker	2017 Lamberton
		mg P plant^{-1}		
		Chelate Source		
DTPA	7.2	--	1.3	15.2
EDDHA	6.8	7.8	1.3	16.3
EDTA	7.7	8.0	1.3	14.8
		Chelate Rate (*M* acre^{-1})		
0.0	7.3	7.6	1.2	15.3
0.2	7.1	7.9	1.4	15.6
0.4	7.9	8.0	1.3	15.1
0.6	6.7	8.2	1.3	15.9
		P Rate (lb P_2O_5 acre^{-1})		
0	--	6.7b	0.8b	13.7b
120	--	9.1a	1.8a	17.2a
Statistics		----------------------- $P > F$ -----------------------		
P Rate	--	0.09	<0.001	0.02
Chelate Source	0.31	0.48	0.95	0.16
P Rate x Source	--	0.62	0.61	0.74
Chelate Rate	0.32	0.75	0.65	0.85
P Rate x Che. Rate	--	0.87	0.72	0.81
Source x Che. Rate	0.99	0.14	0.72	0.39
P Rate x Source x C. Rate	--	0.05	0.54	0.26

Early plant P uptake is summarized in Table 9. Early P uptake was influenced by P application at all locations which included the P application treatments. There was no impact of chelate rate or source on P uptake at any of the locations. The significant three-way interaction at Lamberton 2016 indicated that early P uptake variation when P was applied varied based on chelate source and rate. However, the variation in response based on chelate source and rate was relatively minor so the data are not shown.

Table 10. Effect of chelate sources chelate rates, and P application on corn leaf (opposite and below the ear) phosphorus concentration at four Minnesota locations.

	2016		2017	
Source of Variation	Becker	Lamberton	Becker	Lamberton
	% P			
	Chelate Source			
DTPA	0.31	--	0.30	0.27
EDDHA	0.31	0.26	0.30	0.26
EDTA	0.32	0.26	0.29	0.26
	Chelate Rate (*M* acre^{-1})			
0.0	0.32	0.27	0.30	0.25
0.2	0.32	0.27	0.30	0.27
0.4	0.30	0.25	0.29	0.26
0.6	0.32	0.25	0.29	0.27
	P Rate (lb P_2O_5 acre^{-1})			
0	--	0.25b	0.26b	0.22b
120	--	0.27a	0.34a	0.30a
Statistics	----------------------- *P* > F -----------------------			
P Rate	--	0.06	<0.001	0.01
Chelate Source	0.41	0.93	0.86	0.76
P Rate x Source	--	0.88	0.52	0.31
Chelate Rate	0.44	0.60	0.81	0.26
P Rate x Che. Rate	--	0.75	0.18	0.84
Source x Che. Rate	0.70	0.27	0.57	0.74
P Rate x Source x C. Rate	--	0.98	0.67	0.35

Mid-season leaf tissue P concentration was not affected by chelate source and rate but was impacted by P fertilizer application (Table 10). There were no significant interactions indicating a response to one variable depended on another. Corn grain yield was similarly affected by P application at the thee sites which included a P treatment (Table 11). Like plant P uptake and concentration, chelate sources and rates did not impact yield indicating a low likelihood of a benefit for additional corn P uptake from chelates increasing corn grain yield.

Table 11. Effect of chelate sources chelate rates, and P application on corn grain yield (reported at 15.5% moisture) at four Minnesota locations.

	2016		2017	
Source of Variation	Becker	Lamberton	Becker	Lamberton
		Bushels acre^{-1}		
	Chelate Source			
DTPA	217	--	253	193
EDDHA	222	186	250	194
EDTA	221	186	252	191
	Chelate Rate (*M* acre^{-1})			
0.0	223	186	250bc	193
0.2	221	177	257a	193
0.4	214	191	246c	192
0.6	222	189	254ab	193
	P Rate (lb P_2O_5 acre^{-1})			
0	--	175b	232b	181b
60	--	197a	272a	205a
Statistics	------------------------ *P* > F ------------------------			
P Rate	--	<0.001	<0.001	0.06
Chelate Source	0.65	0.96	0.69	0.57
P Rate x Source	--	0.91	0.37	0.17
Chelate Rate	0.40	0.25	0.03	0.99
P Rate x Che. Rate	--	0.81	0.14	0.66
Source x Che. Rate	0.13	0.75	0.53	0.16
P Rate x Source x C. Rate	--	0.17	0.92	0.41

CONCLUSIONS

The application of chelate fertilizer sources have shown to be of little benefit to crop production for the enhancement of the uptake of nutrients from the soil. Corn field trial data shows that application of P alone will be enough to increase yield and that data generated showing a benefit to chelates could not be replicated in Minnesota. In furrow application is an easy method to apply chelates but may not treat enough soil to increase nutrient uptake and yield of crops.