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Fertilizer-induced phosphorus dynamics in alkaline-calcareous soils as influenced by soil chemical properties

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Short title: Soil phosphorus status in fertilized alkaline soils

Abbreviations: **CEC**, Cation exchange capacity; **DPS**, Degree of phosphorus saturation; **DRP**, Dissolved reactive phosphorus; **MAP**, Monoammonium phosphate; **M3P**, Mehlich 3 extractable phosphorus; **OM**, Organic matter; **OP**, Olsen extractable phosphorus

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Abstract

For proper fertility management, the influence of soil properties on phosphorus (P) dynamics with fertilizer application should be better understood. We examined the influence of soil chemical properties on P dynamics with the application of monoammonium phosphate (MAP) to alkaline-calcareous soils from Manitoba. Non-fertilized and MAP-fertilized soils (at 30 and 60 kg P ha⁻¹) were incubated for eight weeks. At 2-week intervals, we analyzed pore water samples for dissolved reactive P (DRP) concentration, and soil samples for Olsen P (OP), and Mehlich-3 P (M3P) concentrations. Change in pore water DRP concentration with fertilizer application varied from a slight decrease (-0.02 mg L⁻¹) to a significant, large increase (3.1 mg L⁻¹), and showed a significant, negative relationship with P sorption capacity. The increase in OP and M3P with fertilizer application was influenced by the rate of P applied, initial soil test P and P sorption capacity. The estimated mean OP and M3P to maintain pore water DRP concentration at 0.2 mg L⁻¹ were 25 and 48 mg kg⁻¹, respectively. Fertilizer application at the same rate resulted in a widely varying degree of P saturation (DPS) increment depending on soil properties, indicating the importance of monitoring DPS changes for sustainable fertilizer use.

Key Words Alkaline-calcareous soils, Degree of P saturation, Fertilized soils, Pore water P, Soil test P

INTRODUCTION

Phosphorus (P) is essential for a wide range of plant metabolic functions and most importantly, carbon fixation during photosynthesis. Since P is indispensable for biochemical and physiological reactions in plant tissues, frequent fertilizer P application is essential to obtain sustainable yields where soil reserves are low. However, continuous application of synthetic fertilizer P in excess of crop removal results in a build-up of soil P (Reddy et al. 1999; Withers et al. 2001; Rubaek et al. 2013; Ringeval et al. 2014), which may initially benefit crop growth, especially in soils that are P deficient. Further accumulation of P above a critical level may lead to increased soluble P concentration in surface runoff and / or downward movement of P to ground water, posing environmental problems such as eutrophication of water resources (Heckrath et al. 1995; Chowdhury et al. 2014; Withers et al. 2014; McDowell et al. 2015). MacDonald et al. (2011) estimated that high P fertilizer application relative to crop P use resulted in P surpluses $>13 \text{ kg of P ha}^{-1}\text{y}^{-1}$ globally. Hence, proper fertilizer P management in agricultural lands is essential to realize the agronomic benefits while ensuring environmental safety.

Phosphorus added as fertilizer undergoes several chemical reactions in soil, which may influence its short-term and long-term availability to plants. It is estimated that about 80-90% of the added inorganic P fertilizer to soils becomes unavailable in the year of application as a result of adsorption and precipitation reactions (Brady and Weil 2008). In calcareous soils, P adsorption to surfaces of iron oxides and calcite particles dominate at low soil solution P concentrations, whereas at higher solution P concentrations, precipitation of Ca phosphates dominates (Castro and Torrent 1994; Samadi and Gikes 1999). As a result, bioavailability of P in calcareous soils is often low, and inferior to non-calcareous soils (Delgado and Torrent 2000).

Various soil test P measures are used to assess bioavailable P status in soils, predict crop yield responses to applied P fertilizer, monitor P buildup in soil and to predict potential P loss (Maguire et al. 2005; Kumaragamage et al. 2007; 2011). The Olsen method (Olsen et al. 1954) remains a widely used soil test method for both agronomic and environmental purposes in many parts of the world including the Canadian Prairies (Kumaragamage et al. 2007). Sánchez-Alcalá et al. (2014) observed that Olsen P (OP) concentration at a specific pore water (soil solution) P concentration could be predicted using easily measurable soil properties, which would facilitate decision-making on fertilizer P management.

The efficiency of added mineral P fertilizer in increasing soil test P levels is greatly influenced by the P sorption capacity of soils (Haden et al. 2007; Kumaragamage et al. 2011). Haden et al. (2007) observed that the amount of P required to raise Mehlich-3 extractable P (M3P) concentrations by 1 mg kg^{-1} was positively and linearly related to extractable Al in soils, suggesting the need to account for the higher P sorption capacity of soils inherently high in extractable Al. Zhan et al. (2015) observed positive P balances with P application, and an increase in the OP concentration under a P surplus; however the increase in the soil OP caused by each 100 kg ha^{-1} P balance was influenced by the soil properties, including P activity coefficient (percentage of OP to total P), soil organic matter and pH.

The degree of P saturation (DPS) is usually calculated as the ratio of soil test P to the P sorption capacity of soil (Sharpley 1995; Ige et al. 2005). The DPS has been shown to be closely related to the vulnerability of P loss from soils than soil test P alone (Sharpley 1995; Sharpley et al. 1996; Zhou 2001; Amarawansa et al. 2016) since it takes into account the ability of soils to retain P as well as soil test P. Monitoring the changes in different soil test P and DPS can provide in-depth information on P dynamics needed for better management of inorganic fertilizers.

This study was undertaken to investigate the influence of soil chemical properties on P dynamics with the application of monoammonium phosphate (MAP) to alkaline-calcareous soils from Manitoba with varying soil properties. We hypothesized that the absolute change in pore water P concentration and soil test P with the application of the same rate of P fertilizers would be influenced by soil properties. The specific objectives were to: (1) evaluate the periodic changes of pore water P, OP, M3P, and DPS in non-fertilized and monoammonium phosphate-fertilized soils at two different rates of P application and (2) to examine the influence of soil chemical properties on pore water P concentration, soil test P, DPS and their interrelationships.

MATERIALS AND METHODS

Soil collection and analysis

Agricultural soils with varying soil properties were collected from different locations in Manitoba, representing seven major soil series; namely, Almasippi, Lakeland, Long Plain, Newdale, Niverville, Reinland and Scanterbury (Table1). Most soils were black chernozems with the exception of Scanterbury heavy clay (vertisol) and Long Plain sandy loam (Regosol). Bulk soil samples (0-15 cm layer) obtained from agricultural fields were air-dried, screened (<2 mm), and stored at room temperature.

Soil characterization

Soils were analyzed in duplicate for basic properties. Particle size analysis was conducted using the pipette method (Gee and Bauder 1986). Soil pH was determined in 1:2 soil-water suspensions using a Fisher Accumet AB15 pH meter (Fisher Scientific Canada Ltd.). Organic matter (OM) content was determined by the loss-on ignition method (Davies 1974).

Soil samples (triplicate) were analyzed for OP and M3P. To determine OP, 1.0 g of soil mixed with 0.25 g of P-free charcoal were shaken for 30 min with 20 mL of 0.5 M NaHCO₃ solution at pH of 8.5 and then filtered through Whatman No. 40 filter paper (Olsen et al. 1954). To determine M3P, 2.5 g of soil with 25 mL of Mehlich-3 extractant (0.2 N CH₃COOH + 0.25 N NH₄NO₃ + 0.015 N NH₄F + 0.013 N HNO₃ + 0.001 M EDTA at a pH of ~ 2.5) were shaken for 5 min in a reciprocal shaker and then filtered through Whatman No. 40 filter paper (Mehlich 1984). Phosphorus concentration in Olsen and Mehlich-3 extracts were determined using molybdate blue method (Murphy and Riley 1962). Mehlich 3 extractable Ca, Mg, Al, Fe and Mn were determined by inductively coupled plasma atomic - emission spectroscopy (ICP-AES). Exchangeable Ca, Mg, K, and Na concentrations were determined in 1 M ammonium acetate extracts using inductively coupled plasma atomic - emission spectroscopy (ICP-AES; Thermo I CAP 6500 Duo). The sum of exchangeable basic and acidic cations was used as the cation exchange capacity (CEC) of the soil.

Single point P sorption capacity (P₁₅₀) was determined in triplicate using a P concentration of 150 mg P L⁻¹ at a soil: solution ratio of 1:10 (Ige et al., 2005). Two grams of air dried, sieved (<2 mm) soils were equilibrated with 20 mL of solution containing 150 mg P L⁻¹ by shaking the suspension in an end-to-end shaker at room temperature for 24 h. The samples were filtered through Whatman No. 1 filter paper and the P concentration of the filtrate was determined using the molybdate blue method (Murphy and Riley 1962). Phosphorus sorption capacity, P₁₅₀, was calculated using the initial and equilibrium P concentrations and expressed in mg P adsorbed per kg soil. The DPS was calculated using the following formula:

$$\text{DPS \%} = \frac{\text{OP}}{\text{P}_{150}} \times 100$$

Incubation Study

An incubation experiment was conducted in a completely randomized design with a factorial combination of seven soils and three fertility treatments with three replicates. The treatments were, non-fertilized control (T1), two rates of P as mono ammonium phosphate (MAP), 30 (T2) and 60 (T3) kg P ha⁻¹. Air-dry soil (approximately 500 g) was mixed with MAP at 20 (T2) and 40 (T3) mg P kg⁻¹ soil which provided 30 and 60 kg of P per hectare, respectively, considering a bulk density of 1.0 g cm⁻³ and a rooting depth of 15 cm. Treated soils of each replicate were mixed, moistened to field capacity and were packed into 1.5-L incubation vessels with a 10-cm diameter. Soils were packed to a depth of 8 cm and a bulk density of 1.0 ± 0.2 g cm⁻³ for clay and clay loam soils and 1.1 ± 0.2 g cm⁻³ for loamy sands and sandy loams. During packing, a Rhizon flex soil solution sampler with an outer diameter of 2.5 mm and 0.15 µm pore size (Rhizosphere Research Products, Wageningen, Netherlands) was installed at 5 cm depth. The vessels were covered with perforated parafilm (Fisher Scientific) to allow gas exchange between the soil and the atmosphere and incubated for a period of eight weeks at 20±3 °C. Soil moisture was maintained at field capacity by weighing the soil-filled vessels weekly and adding reverse osmosis water as required. Approximately 10-g of surface soil samples (0-5 cm depth) were taken using a spatula at 2, 4, 6 and 8 weeks of incubation. Pore water samples (20-mL) were also extracted from Rhizon flex soil solution samplers installed at 5-cm depth at 2, 4, 6 and 8 weeks of incubation and immediately analyzed for dissolved reactive P (DRP) concentration by the molybdate blue method. Soil samples from the treated and check treatments collected at 2, 4, 6 and 8 weeks of incubation were air-dried, ground, sieved (2-mm) and analyzed for OP, and M3P.

Statistical analysis

A three-way analysis of variance (ANOVA) was performed for pore water DRP, OP, and M3P concentrations, and DPS using the MIXED procedure in SAS version 9.3 (SAS institute 2011) considering soil series and treatment as fixed effects and time (days after treatment) as

repeated measure factor. Normality of data was tested using the Shapiro-Wilk statistic ($W < 0.9$) from PROC UNIVARIATE. The LS means statement with DIFF option was used to compare least square mean differences using the Tukey-Kramer method. Regression analysis was conducted to obtain linear relationships between changes in pore water DRP concentration with fertilizer application and P_{150} . The best-fit model for the relationships between pore water DRP concentration and OP/M3P were obtained through curve fitting using IBM SPSS Statistics, Version 19 (SPSS Inc., IBM Company, Chicago, USA). For all statistical analysis, significance was determined at $P < 0.05$.

RESULTS AND DISCUSSION

Soil Characteristics

Soils used in the study varied widely in soil properties. The textural classes of studied soils varied from loamy sand to clay (Table 1). All soils were alkaline with a pH range of 7.39 to 8.24. This pH range is quite expected since most agricultural soils in Manitoba are typically developed on calcareous parent materials. The OM content varied from 23 to 97 g kg⁻¹ with an average of 36 g kg⁻¹. The CEC of the soils varied widely from 22.0 to 51.4 cmol kg⁻¹. The OP ranged between 12.6 and 65.7 mg kg⁻¹, depicting that soils' agronomic P level is low to moderate according to the Manitoba Soil Fertility Guide (Manitoba Agriculture, Food and Rural Initiative 2007). The P_{150} varied from 133 to 663 mg kg⁻¹, with the lowest in the Reinland loamy sand, and the greatest in the Scanterbury heavy clay. The reason for the large variation in P_{150} among soils can be attributed to the large variation in physical and chemical properties of the studied soils. Previous studies have shown P sorption capacity of soils is closely related to soil properties, which included clay content (Freese et al. 1992; Ige et al. 2005), pH (Barrow, 1984), sand content (Yuan and Lucas 1982), organic C (Daly et al. 2001), Fe and Al oxides (Toor et al. 1997; Freese et al. 1992), exchangeable Ca and Mg (Ige

et al. 2005), and carbonate content (Bertrand et al. 2003). In alkaline Manitoba soils, P retention is greatly influenced by the exchangeable Ca and Mg concentrations and soil texture (Ige et al. 2005). Soils used in this study had high exchangeable Ca and Mg concentrations and moderate to low exchangeable Fe, Mn and Al concentrations (Table 2) and thus, exchangeable Ca and Mg concentrations would play a more dominant role in P sorption reactions in these soils.

Dissolved Reactive P concentration in pore water

Pore water P concentration in non-fertilized soils varied widely. The greatest pore water DRP concentration (0.59 mg L^{-1}) was observed in the non-fertilized Lakeland soil, which was about 50-fold greater than the pore water DRP concentration in the non-fertilized Scanterbury soil (0.01 mg L^{-1}), which had the lowest pore water DRP concentration (Fig. 1a). High DRP concentration in the non-fertilized Lakeland soil is to be expected since it had comparatively high available P, with OP $>65 \text{ mg kg}^{-1}$, while OP concentrations of all other soils were $<32 \text{ mg kg}^{-1}$. Scanterbury soil, which had a very high $P_{150} >650 \text{ mg kg}^{-1}$ had the lowest P concentration in solution, which is to be expected since high P fixing soils maintains a very low P concentration in solution (Nair and Reddy 2013). Since dissolved P in the pore water is the immediate source of P to plants (Mengel and Kirkby 1987), the results indicate a greater P availability in the Lakeland soil in the short-term compared to other soils, when non-fertilized. In general, a P concentration of 0.2 mg L^{-1} in pore water is considered as the optimum concentration for most crops (Beckwith 1965). Fox (1981) reported a solution P concentration ranging from as low as 0.005 mg L^{-1} to as high as 0.30 mg L^{-1} as optimum for crop growth, depending on the crop. In this study, the pore water concentrations were lower than the optimum (0.2 mg L^{-1}) in all non-fertilized soils with the exception of Lakeland soil, which had a solution P concentration of $>0.5 \text{ mg L}^{-1}$.

Fertilizer application at both rates, in general, increased the pore water DRP concentration in all soils with a few exceptions, but the differences were not always significant (Table 3; Fig. 1b and 1c). He et al. (1998) also reported that the solution P concentrations generally increased with P application rates, specially a few days after. The interactions of soil series $\times$ treatment ($P < 0.001$), soil series $\times$ time of incubation ($P < 0.01$) and treatment $\times$ time of incubation ($P < 0.01$) were highly significant. The three-way interaction of soil series $\times$ treatment $\times$ time, however, was not significant (Table 3). The magnitude of increase in pore water DRP concentration with fertilizer application depended on the rate of P application as well as the soil series.

In general, pore water DRP concentration in fertilized treatments increased with time of incubation up to about 4 weeks and then declined (Fig. 1b and 1c). In Reinland series, pore water DRP concentration was significantly greater in fertilized treatments at both rates (30 and 60 kg P ha⁻¹) compared to the non-fertilized treatment at 4 weeks of incubation, while the differences between the non-fertilized treatment and the higher rate of fertilizer (60 kg P ha⁻¹) treatment were significant ($P < 0.05$) at all times of incubation. In Newdale soil, the increase in pore water DRP concentration in fertilized treatment compared to the non-fertilized treatment was significant ($P < 0.05$) only at 4 weeks of incubation for the higher rate of fertilizer applied (60 kg P ha⁻¹, T3). In Almasippi, Lakeland, Long Plain, Niverville and Scanterbury soils, the increases in pore water DRP concentration with both rates of fertilizer treatments were not significantly different from that of the control.

Absolute change in pore water DRP concentration with MAP application varied from a slight decrease (-0.02 mg L⁻¹) to a significant, large increase (3.1 mg L⁻¹), depending on P application rate and soil properties. The greatest increase in DRP concentration was observed in the Reinland soil for the higher rate of fertilizer P application, whereas in Scanterbury soil,

application of fertilizer P resulted in a slight decrease or a slight increase in solution DRP, depending on the incubation time (Fig. 1). It is interesting to note that with the higher rate of fertilizer application, the Reinland soil which had the greatest sand content and the lowest P_{150} showed the greatest increase in pore water DRP, whereas Scanterbury soil which had the greatest clay content and P_{150} showed the least change in DRP concentration in pore water. Thus the textural differences between Reinland loamy sand and Scantebury clay may have influenced the P removal from pore water through sorption reaction once dissolution of fertilizer P occurs.

When fertilizer was applied at 60 kg ha^{-1} , pore water DRP concentration increased above the optimum concentration for crop growth (0.2 mg L^{-1}) in all soils except Scanterbury soil (Fig. 1c). In Newdale and Niverville soils, fertilizer application at the lower rate of 30 kg P ha^{-1} was adequate to raise the solution P concentration above the optimum level (Fig. 1b), whereas Lakeland soil had above optimum solution P concentration even when non-fertilized (Fig. 1a). Our results are in agreement with findings by previous researchers that the amount of fertilizer P required to achieve the optimum solution P concentration varied among the soils based on the native P content and soil properties, in particular, P sorption capacity of soils (Anjembe et al. 2014; Kumar 2015).

To investigate this further, regression analysis was conducted between P_{150} in different soils, and the change in solution DRP concentrations (ΔDRP) observed between fertilized and non-fertilized treatments. For the lower rate of P (30 kg P ha^{-1}), the relationship between P_{150} and solution ΔDRP between fertilized and non-fertilized treatments was not significant. When fertilizer was applied at the higher rate (60 kg P ha^{-1}), the change in pore water DRP concentration showed a highly significant negative relationship with P_{150} (Fig. 2) at all time periods. The slope of the regression equation decreased with incubation time,

indicating that the effect of P_{150} in regulating pore water P concentration is larger soon after fertilizer application and became weaker with time. The results confirm that for soils with high P sorption capacity, higher rates of fertilizer are needed to bring the pore water DRP concentration to the optimum level as compared to soils with low P sorption capacity.

Changes of Olsen P and Mehlich 3 over the incubation period

Application of fertilizers increased both the OP and M3P in most soils as expected, and is consistent with previous findings with different P extraction methods (Kashem et al 2004; Chang et al. 2005; Jiao et al. 2007; Goh et al. 2013). The OP values ranged from 4.2 mg kg⁻¹ in non-fertilized Almasippi soil at 2 weeks of incubation to 67.2 mg kg⁻¹ in fertilized (30 kg P ha⁻¹) Lakeland soil at 4 weeks of incubation (data not shown).

Three-way interaction of soil series × treatment × incubation time was significant ($P < 0.05$) for OP (Table 3). Irrespective of treatments, OP was significantly greater ($P < 0.05$) in Lakeland than other soil series (Fig. 3). In general, application of P fertilizer increased OP in soils, but the magnitude of increase varied among soils, the rate of P applied and the time of incubation. After 2 weeks of incubation, both rates of P fertilizer treatments showed greater OP than control treatment in all soil series except Lakeland series; however, the differences were significant ($P < 0.05$) only between the non-fertilized and the higher rate of fertilizer (60 kg P ha⁻¹) treatments. After four weeks of incubation, the differences between non-fertilized and higher rate of P treatments were smaller, and were significant only in Almasippi, Newdale, Niverville, and Reinland soils. After eight weeks of incubation, only Almasippi, Long Plain and Reinland soils showed significantly greater OP in the higher rate of fertilizer treatment compared to the control treatment. Lakeland soil, which had initially very high OP (Table 1), behaved differently from all other soils; in this soil, application of fertilizer P at both rates did not result in a significant increase in OP at any time (Fig. 3).

The M3P values varied from 13.5 mg kg^{-1} in non-fertilized Almasippi soil to 124.1 mg kg^{-1} in fertilized (30 kg P ha^{-1}) Lakeland soil at 2 week of incubation (Data not shown). Hence, the magnitude of M3P was comparatively higher than the OP as previously reported (Kashem et al. 2004; Kumaragamage et al 2007) because of the use of strong chemical extractant in M3P compared to OP extraction. Thus, M3P method, which uses a strong extractant than the OP method may have extracted P forms that are not extractable by Olsen method during the early stages of incubation, with a relatively stable M3P thereafter giving no significant change in M3P with further time of incubation. The interaction effect of soil series $\times$ treatment was highly significant ($P < 0.01$) for M3P (Table 3).

Pooled means across time periods showed that in all soil series with the exception of Lakeland series, application of fertilizers at both rates increased M3P as with OP, but the differences were significant only between the higher rate of fertilizer treatment (60 kg P ha^{-1}) and the control treatment (Table 3). The Lakeland soil, which had the greatest M3P of $>100 \text{ mg kg}^{-1}$ when non-fertilized, behaved differently from the other soils and did not show a significant increase in M3P at either fertilizer application rate. Our results with alkaline-calcareous soils confirm that the changes in soil test P with application of inorganic P fertilizers depend on the rate of P applied, inherent soil properties as well as the initial P contents, as previously reported for acidic and neutral soils amended with both inorganic and organic P sources (Griffin et al. 2003; Haden et al. 2007; Shober and Sims 2007; Zhan et al 2015).

Relationships between soil test P and solution DRP concentrations

We established relationships between pore water DRP concentration and soil test P for each soil at various times of incubation for the three treatments. Such relationships provide a measure of the risk of eutrophication (Heckrath et al. 1995; Maguire et al. 2005) and can be

used to predict OP at optimum solution P concentration required for crop growth, thus facilitating decision-making in fertilizer management (Sanchez-Alcalá et al. 2014).

Pore water DRP concentration showed significant relationships with OP and M3P concentrations in all soils with the exception of Scanterbury and Lakeland series (Fig. 4). The dataset for each soil (with the exception of Scanterbury and Lakeland series), consisting of pore water DRP concentrations and OP/M3P for three treatments at four incubation times ($n=12$) fitted best to a Freundlich-type power function ($y = ax^b$; Fig. 4), which is consistent with the observations of Sanchez-Alcalá et al. (2014). The fitted lines accounted for 56 to 84% of the variance in OP, and 54 to 86% of the variance in M3P. The “a” and “b” values are comparable to those observed by Sanchez-Alcalá et al. (2014) for relationships between OP and CaCl_2 extractable P (which was taken as a proxy P concentration in the soil solution) in calcareous soils. The estimated OP and M3P at a pore water DRP concentration of 0.2 mg L^{-1} (which is considered as the optimum concentration for most crops), varied from 12 – 28 for coarse-textured soils, and 27 - 62 mg kg^{-1} , fine-textured soils (Table 4).

In Scanterbury and Lakeland soils, pore water DRP concentration was poorly related to OP (R^2 of 0.10 and 0.06, respectively) or M3P (R^2 of 0.001 and 0.07, respectively). As previously discussed, the Scanterbury soil did not show an increase in pore water DRP concentration with fertilizer application, very likely due to the high clay content and high P sorption capacity. Lakeland soil on the other hand, had a very high soil test P level even when non-fertilized, and did not show an increase in pore water DRP concentration or soil test P with addition of fertilizer beyond the lower rate (30 kg ha^{-1}) of P added (Table 3). It should be noted that Lakeland soil had a very high organic matter content (>3-fold greater than other soils) with a strong tendency for microbial immobilization of added P, which may remove P from solution and extractable forms, thus not showing an increase in pore water DRP concentration or in soil test P with fertilizer P addition. The r^2 values for simple power

function relationships between pore water DRP concentration with OP and M3P obtained for all soils including Scanterbury and Lakeland soils ($n = 84$) were close to the r^2 values obtained when Scanterbury and Lakeland soils were excluded ($n = 60$). The mean OP and M3P estimated considering all soils, to maintain pore water DRP concentration at 0.2 mg L^{-1} were 25 and 48 mg kg^{-1} , respectively (Table 4). However, to evaluate the textural influence on these relationships as indicated in the present study, more investigations are needed using a large number of calcareous soils with varying textural properties.

Degree of P saturation during the incubation period

The initial DPS calculated as the ratio of OP to P_{150} varied from 3.4% in Scanterbury soil to 13.1% in Lakeland soil. The DPS change with fertilizer amendment with different times of incubation was calculated considering the change in OP assuming that the P_{150} , which is an inherent soil property, remains the same during the 8 week incubation period. In general, the application of fertilizer at both rates increased the DPS, the higher rate of 60 kg ha^{-1} increasing the DPS more than the lower rate of 30 kg ha^{-1} (Fig. 5).

The greatest change in DPS was observed in the Reinland soil, with 25.7% at the higher rate of fertilizer application at eight weeks of incubation whereas for the same rate of fertilizer application, the DPS in the Scanterbury soil was 4.8%. Thus the change in DPS was greater for soils with low P_{150} , as expected. Degree of P saturation is closely related to the vulnerability of P loss from soils since it takes into account the ability of soils to retain P as well as soil test P (Sharpley et al. 1996; Zhou 2001; Amarawansa et al. 2016). Sallade and Sims (1997) suggested an upper threshold of 40% DPS to minimize P release to overlying water bodies from ditch sediments (where DPS was calculated as biologically available P/P sorption index $\times 100$). In all soils in the present study, the DPS, even at higher rate of fertilizers, was well below this threshold. Since the same rate of fertilizer application

resulted in a widely varying DPS increment (Fig. 5), it is evident that monitoring the DPS changes in soils is important for decision making on fertilizer management.

Conclusions

The study investigated soil P dynamics with the application of fertilizers to alkaline-calcareous soils and investigated the relationships between soil chemical properties and changes in soil P measures. Concentrations of pore water P, OP and M3P, in general, increased with the application of fertilizers, but with varying magnitudes depending on soil properties and the rate of P application. The increase in pore water DRP was greater in soils with low P sorption capacity with the same rate of fertilizer application, indicating the need to consider the P sorption capacity in calculating P fertilizer rates to meet the crop requirements. The DPS increased with fertilizer application; however, the same rate of fertilizer application resulted in widely varying increments in DPS. Since, DPS is closely related to vulnerability of P loss from soils, our results indicate the importance of monitoring the changes in degree of P saturation in soils for making decisions regarding fertilizer management. Since this study is limited to seven alkaline-calcareous soils, evaluating P dynamics only for a short period of time of eight weeks, there is a need to investigate the influence of soil properties on P dynamics of fertilized, alkaline soils using more soils with varying properties and monitoring changes in P status for a longer period of time.

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Figure captions

Fig. 1. Pore water dissolved reactive P concentration (LS means) at different times of incubation in different soil series for (a) control (T1; 0 kg ha⁻¹), (b) monoammonium phosphate fertilized at 30 kg ha⁻¹ (T2), and (c) monoammonium phosphate fertilized at 60 kg ha⁻¹ (T3) treatments. Error bars represent the standard error of the mean.

Fig. 2. Regression relationships between dissolved reactive P concentration change (Δ DRP) with application of 60 kg P ha⁻¹ fertilizer (T3) compared to control treatment (T1), and phosphorus sorption capacity (P_{150}) of soils. R^2 -values followed by *** are significant at $P < 0.001$.

Fig. 3. Olsen P concentration (LS means) at different times of incubation in different soil series for (a) control (T1; 0 kg ha⁻¹), (b) monoammonium phosphate fertilized at 30 kg ha⁻¹ (T2), and (c) monoammonium phosphate fertilized at 60 kg ha⁻¹ (T3) treatments. Error bars represent the standard error of the mean.

Fig. 4. Relationships between pore water dissolved reactive P concentration and (a) Olsen P and (b) Mehlich 3- P. R^2 -values followed by **, and *** represent significant levels at $P < 0.01$ and $P < 0.001$, respectively.

Fig. 5. Degree of P saturation calculated as the ratio of Olsen P to P sorption capacity at different times of incubation in control (T1), monoammonium phosphate fertilized at 30 kg ha⁻¹ (T2), and monoammonium phosphate fertilized at 60 kg ha⁻¹ (T3) treatments for different soils. (a) At 2 week of incubation (b) At 4 week of incubation (c) At 6 week of incubation and (d) At 8 week of incubation. Error bars represent the standard deviation of the mean.

1 **Table 1. Physical and chemical properties of different soil series used in the study**

Soil series	Soil Order	Sand %	Clay %	Textural class	pH ^a	Organic matter ^b (g kg ⁻¹)	CEC ^{b, c} (cmol kg ⁻¹)	Olsen P ^c (mg kg ⁻¹)	P ₁₅₀ ^{a, d} (mg kg ⁻¹)
Almasippi	Mollisol	79	13	Sandy loam	8.24 (0.01) ^y	23 (1)	26.3 (0.5)	12.6 (0.3)	363.1
Lakeland	Mollisol	24	34	Clay loam	7.45 (0.01)	97 (2)	50.7 (1.1)	65.7 (0.9)	502
Long Plain	Entisol	78	11	Sandy loam	7.76 (0.01)	38 (2)	33.0 (1.2)	16.7 (0.3)	359.8
Newdale	Mollisol	35	32	Clay loam	7.39 (0.02)	39 (2)	32.9 (0.9)	23.7 (2.5)	323.1
Niverville	Mollisol	8	62	Clay	8.09 (0.01)	30 (1)	45.8 (1.4)	31.6 (0.9)	537.6
Reinland	Mollisol	84	9	Loamy sand	7.850 (0.01)	24 (1)	22.0 (0.6)	13.8 (1.3)	132.6
Scanterbury	Vertisol	5	73	Clay	7.50 (0.03)	37 (1)	51.4 (1.0)	22.7 (0.6)	663.1

2 ^a Values are means of three replicates

3 ^b Values are means of two replicates

4 ^c CEC, cation exchange capacity

5 ^d P₁₅₀- P sorption capacity

6 ^e Values in parentheses are standard deviations

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Table 2. Concentration of exchangeable Ca, Mg, Al, Fe and Mn in different soil series

Soil series	Exchangeable cations ^a (mg/kg)				
	Ca	Mg	Al	Fe	Mn
Almasippi	509 (9) ^b	144 (1)	ND ^c	5.9 (0.2)	7.5 (0.3)
Lakeland	813 (6)	175 (2)	2.8 (0.3)	13.7 (0.2)	4.1 (0.2)
Long Plain	527 (11)	79 (2)	ND	8.8 (0.2)	7.9 (0.1)
Newdale	410 (1)	94 (1)	28.0 (0.6)	7.3 (0.5)	19.9 (1.2)
Niverville	861 (11)	186 (1)	1.5 (0.1)	7.5 (0.3)	7.2 (0.3)
Reinland	358 (2)	57 (0)	22.2 (0.1)	5.8 (0.1)	14.7 (0.1)
Scanterbury	566 (31)	166 (8)	60.5 (3.4)	13.4 (1.1)	3.9 (0.3)

^a Values are means of three replicates
^b Values in parentheses are standard deviations
^c ND, Not detectable (detection limit for Al = 0.01 mg kg⁻¹ soil)

39 **Table 3. ANOVA and the LS means (pooled mean for all incubation times) of pore water dissolved reactive P concentration,**
 40 **Olsen P and Mehlich 3 P concentrations for different soil series**

Soil series		DRP concentration			Olsen P (mg kg ⁻¹) ^a			Mehlich 3 P (mg kg ⁻¹) ^a		
Soil	Almasippi	0.19			19.6			33.7		
	Lakeland	0.66			61.4			112.7		
	Long Plain	0.22			21.8			42.1		
	Newdale	0.59			26.5			46.1		
	Niverville	0.42			31.3			64.9		
	Reinland	1.15			19.7			36.9		
	Scanterbury	0.06			24.9			37.9		
		T1 ^b	T2 ^b	T3 ^b	T1	T2	T3	T1	T2	T3
Soil × Treatment	Almasippi	0.02	0.12	0.43	8.4	20.4	30.1	16.9 <i>b</i>	33.9 <i>ab</i>	50.2 <i>a</i>
	Lakeland	0.59	0.69	0.69	58.2	64.4	61.7	107.5 <i>a</i>	124.4 <i>a</i>	106.2 <i>a</i>
	Long Plain	0.03	0.05	0.60	12.9	21.1	31.4	28.1 <i>b</i>	42.3 <i>ab</i>	56.0 <i>a</i>
	Newdale	0.06	0.59	1.13	16.5	26.8	36.2	32.7 <i>b</i>	46.8 <i>ab</i>	58.9 <i>a</i>
	Niverville	0.06	0.52	0.69	22.3	30.3	41.2	53.7 <i>b</i>	64.8 <i>ab</i>	76.3 <i>a</i>
	Reinland	0.06	1.02	2.37	8.6	18.3	32.3	20.9 <i>b</i>	35.0 <i>ab</i>	54.6 <i>a</i>
	Scanterbury	0.02	0.11	0.04	16.5	25.9	32.4	26.7 <i>b</i>	36.1 <i>ab</i>	51.0 <i>a</i>
ANOVA	EFFECT	P < F			P < F			P < F		
	Soil series	<0.001			<0.001			<0.001		
	Treatment	<0.001			<0.001			<0.001		
	Time	<0.001			<0.001			0.860		
	Soil x Treatment	<0.001			0.012			0.004		
	Soil × time	0.001			0.026			0.052		
	Treatment × time	0.004			0.548			0.766		
	Soil × Treatment × time	0.258			0.027			0.689		

41 Note: LS means within the same row sharing a lowercased italic letter differ significantly different at $P \leq 0.05$ level.

42 ^a Mean comparison shown only when the interaction is not significant.

43 ^b T1- 0 kg P ha⁻¹; T2 - 30 kg of P ha⁻¹; T3 - 60 kg of P ha⁻¹

Table 4. Estimated Olsen P (OP) and Mehlich 3 P (M3P) concentration in soil at a pore water dissolved reactive phosphorus (DRP) concentration of 0.2 mg L⁻¹ using power function relationships

Soil ^a	Soil test P at a dissolved reactive P concentration of 0.02 mg L ⁻¹	
	Olsen P	Mehlich 3 P
Almasippi	21	36
Reinland	13	27
Niverville	28	62
Newdale	23	42
Long Plain	24	46
All soils	25	48
All soils excluding Scanterbury and Lakeland	21	42

^a Not calculated for Scanterbury and Lakeland soils separately, since the relationships between DRP and OP or M3P were not significant ($P > 0.05$) for these two soils.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5