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Effects of increasing soil pH to near-neutral using lime on phosphorus saturation index and water-extractable phosphorus

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Abstract

We studied the effects of liming to increase soil pH from acidic to near-neutral on the degree of phosphorus saturation (DPS), the P saturation index (PSI), Mehlich-3 P (P_{M3}), and water-extractable P (P_w). Soils collected from a long-term highbush blueberry experiment were incubated at 22.5 °C for 93 days after CaCO_3 amendment to increase pH values from 4.1, 4.8, and 5.5 to 6 and from 5.8 to 6.5. Liming decreased P_{M3} by 8%, 6%, 10%, and 11% with increasing initial soil pH. The P_{M3} concentrations of all the studied soils belonged to the very high class with critical DPS > 25%, which are associated with increased environmental risk of P loss with runoff. For soils with initial pH values of 5.8, P_w was 3.65 mg kg⁻¹, in line with critical DPS > 25%, but decreased to 2.74 mg kg⁻¹ with CaCO_3 addition. In contrast, soils with initial pH < 5.5 had lower P_w concentrations and CaCO_3 did not significantly decrease P_w at the end of the incubation averaging 1.02, 1.11, and 1.43 mg kg⁻¹ for initial pH 4.1, 4.8, and 5.5, respectively. The low P_w concentrations of soils with initial pH < 5.5 were in line with low PSI (5.2%–6.1%), but did not reflect DPS values > 25%. It is possible that high exchangeable aluminum (Al) (Al_{M3} > 2500 mg kg⁻¹) enhanced the fixation of phosphate ions from the soil solution, thus reducing P_w . Our results suggest that using P_{M3} as a sole indicator of environmental risk likely underestimates potential P losses compared with P_w .

Key words: degree of phosphorus saturation, liming, oxides and oxyhydroxides of aluminum and iron, phosphorus fractionation, risk of phosphorus loss

Résumé

Les auteurs ont étudié les effets du chaulage utilisé pour neutraliser le pH d'un sol acide i) sur le taux de saturation du P (TSP), l'indice de saturation du P (ISP), la teneur en P selon la technique Mehlich-3 (P_{M3}) et la teneur du P extractible à l'eau P (P_w). Des échantillons de sol venant d'une expérience de longue haleine sur le bleuët en corymbe ont été incubés pendant 93 jours à 22,5 °C après avoir été amendés avec du CaCO_3 de façon à augmenter le pH de 4,1, 4,8 ou 5,5 à 6 et de 5,8 à 6,5. Le chaulage diminue la concentration de P_{M3} de 8, 6, 10 et 11 %, selon le pH du sol de plus en plus élevé. Dans tous les sols examinés, la concentration de P_{M3} se retrouve dans la classe la plus élevée, avec un TSP supérieur à 25 %, associé à un risque plus grand de lixiviation par le ruissellement. Pour les sols dont le pH initial était de 5,8, la concentration de P_w s'établissait à 3,65 mg par kg, ce qui est cohérent avec un TSP critique de plus de 25%, mais l'addition de CaCO_3 ramène la concentration à 2,74 mg par kg. En revanche, les sols au pH inférieur à 5,5 au départ se caractérisaient par une concentration inférieure de P_w qui n'avait pas été affectée de manière significative par le CaCO_3 à la fin de la période d'incubation (concentration moyenne de 1,02, 1,11 et 1,43 mg par kg pour un pH initial de 4,1, 4,8 ou 5,5, respectivement). La faible concentration de P_w observée dans les sols dont le pH initial était inférieur à 5,5 est cohérente avec le faible ISP (de 5,2 à 6,1 %), mais pas avec un TSP inférieur à 25 %. Il se peut qu'une concentration élevée d'aluminium facilement échangeable (Al_{M3} > 2 500 mg par kg) ait accru la fixation des ions phosphate dans la solution de sol, ce qui a réduit la concentration de P_w . Ces résultats laissent croire que, contrairement à ce qui se produit quand on utilise la concentration de P_w , on sous-estime sans doute les pertes potentielles de P quand on se sert que de la concentration de P_{M3} comme indicateur des risques environnementaux. [Traduit par la Rédaction]

Mots-clés : taux de saturation du phosphore, chaulage, oxides et oxydes-hydroxydes de l'aluminium et du fer, fractionnement du phosphore, risque de perte de phosphore

Introduction

Excessive phosphorus (P) from manure and inorganic fertilizer applications to agricultural soils is the major cause of surface water eutrophication (Sharpley et al. 2015). In many parts of the world, agri-environmental indicators are used to monitor the risk of P loss in cropped soils under intensive nutrient management (Sharpley et al. 2015). The degree of P saturation (DPS) developed in the Netherlands to monitor the risk of P loss for acidic soils is defined as the ratio of the concentration of phosphate extracted by oxalate (P_{Ox}) to P sorption capacity (PSC) (Breeuwsma and Silva 1992). The PSC is derived from the concentrations of aluminum (Al) and iron (Fe) extracted by oxalate (Al_{Ox} and Fe_{Ox} ; Benjannet et al. 2018). Notably, a significant increase of P solubility at a critical saturation threshold DPS of 25% was established for acidic soils of the Netherlands (Breeuwsma and Silva 1992). The P saturation index (PSI) developed in North America is based on the ratio of P concentrations to Al and/or Fe in Mehlich-3 extracts. The PSI has been widely adopted in North America because Mehlich-3 extraction is a routine analysis in many laboratories (Khiari et al. 2000).

In several Canadian provinces where acidic soils prevail, including Quebec and the Maritimes, the PSI has been used to assess the risk of P loss for almost two decades (Khiari et al. 2000; Benjannet et al. 2018). In British Columbia (BC), the PSI was shown to be a proxy of DPS to assess the risk of P loss in agricultural soils (Messiga et al. 2020, 2021). Both DPS and PSI are related to water-extractable P (P_w) concentration and are ratios of concentrations of the same elements with different extractions (Khiari et al. 2000; Self-Davis et al. 2000). The P_w measures phosphate readily extracted in water, which, in turn, is a potential indicator of P that could be lost from soils in runoff (Khiari et al. 2000; Sims et al. 2002). The current strategies aim at relating the capacity of P loss from soils through desorption from the soil matrix using DPS and PSI as indicators of P potential to be released into the soil solution (Sims et al. 2002). The assessment of risk of P loss based on PSI and P_w with soil P tests such as Mehlich-3 P (P_{M3}) is well understood, but further work is needed to evaluate how these indicators change based on varying soil properties and agricultural practices. Soil pH is a key property that partly controls the relationships between PSI and P_w (Benjannet et al. 2018). Moreover, the PSC used to derive PSI is significantly influenced by soil pH (Penn and Camberato 2019). Previous studies reported better correlations between PSI and P_w for soils characterized by a very narrow range of soil acidity compared with soils with wide pH range (3.4–7.9; Sims et al. 2002).

A threshold PSI value of 15% above which the risk of P loss is high corresponding to 25% DPS was obtained across a range of acidic to neutral coarse-textured soils in Quebec (pH 4.6–6.7; Khiari et al. 2000). In Prince Edward Island, PSI values were 19% for soils with pH < 5.5 and 14% for soils with pH > 5.5 (Benjannet et al. 2018). Similarly, in a recent study in BC, PSI values were 18% for soils with pH < 4.7 and 10% for soils with pH > 5.5 (Messiga et al. 2021). At very low pH, P is strongly retained by Fe and Al oxyhydroxides, explaining the higher PSI thresholds, while asso-

ciation with Ca^{2+} in limed and calcareous soils is less documented (Ige et al. 2005). It is, however, expected that an increase in soil pH would introduce hydroxyl groups (OH^-) into the soil solution, which would displace P ions from oxides of Al and Fe (Hinsinger 2001). The end result of these reactions would be an increase in P release in soil solution (Penn and Camberato 2019), which could decrease PSI values.

In many agricultural regions, the excessive application of nitrogen (N) fertilizers has led to acidification of arable soils particularly in the plough layer (Messiga et al. 2013; Wang et al. 2020; Chen et al. 2021). Decreased soil pH has ripple effects on several other soil properties and processes. In acidic soils, soluble Al is increased leading to Al toxicities that inhibit plant root development (Illes et al. 2006; Barrow 2017). Studies have shown that decreased soil pH also affects ammonia (NH_3)-oxidizing bacteria and therefore the conversion of NH_3 to nitrates (Liu et al. 2014; Wang et al. 2020). In addition, decreased soil pH affects N_2O emissions (Wang et al. 2020) and represses soil phosphatase activity (Chen et al. 2021). Because acidic soil pH reduces the productivity and sustainability of many major cropping systems, liming is used to raise the pH to adequate levels. Logically, soil pH increase induced by lime has double effect of increasing the concentration of hydroxyl groups (OH^-) and desorption of Al and Fe from the exchange complex, which precipitates into Al and Fe oxyhydroxides that could also increase P sorption (Hinsinger 2001). However, the increase of P availability for root uptake as a result of increased soil pH through lime addition to near-neutral is widely reported (Haynes 1982; Lambers et al. 2008; Barrow 2017; Penn and Camberato 2019). Such increases are also attributed to decreased Al toxicity (Illes et al. 2006). While the benefits of liming are widely recognized, little is known on how increased soil pH upon liming would affect agri-environmental indicators such as PSI and P_w , P sorption characteristics, and therefore the environmental risks of P losses with runoff.

Highbush blueberries, a common cropping system in the BC Fraser Valley, are typically grown in acidic soils (pH from 4.2 to 5.5; Ponnachit and Darnell 2004). However, recent studies have shown that long-term applications of ammonia-based N fertilizers in highbush blueberries further decreased soil pH from the 4.2–5.5 range down to pH 3.8 (Messiga et al. 2018, 2021). At these low pH levels, it is expected that liming is necessary to raise soil pH to optimum levels for highbush blueberry growth and production (Bertrand et al. 1991). Given that blueberry systems in this region have high soil test P levels (van Bochove et al. 2012; Messiga et al. 2021), liming to raise soil pH before a new production cycle may shift soil pH to a range in which P is more readily desorbed, increasing P release from soil to water. A study in New Zealand showed that about 40% of the decrease in soil P upon liming resulted from net mineralization of organic P and adsorption of inorganic P extractable in 0.5 mol L^{-1} $NaHCO_3$ or NaOH (Perrott and Mansell 1989). As such, there is a need to understand how agri-environmental indicators would be affected by liming in this crop production system.

Table 1. General properties of soils with initial pH values of 4.1, 4.8, 5.5, and 5.8 collected at 0–30 cm soil depth in a long-term blueberry experiment receiving annual applications of nitrogen fertilizers (ammonium sulfate) at Agassiz RDC in British Columbia, Canada.

Initial pH _(H2O)	Treatments, ^a %	Clay, %	Silt, %	Total C, %	Total N, %	CEC, meq(+)/100 g
4.1	200	22	42	3.4	0.22	23.3
4.8	100	23	42	3.7	0.21	19.1
5.5	150	39	41	1.9	0.15	12.9
5.8	0	22	42	3.4	0.21	20.9

^aSoil was collected in plot receiving annual applications of ammonium sulfate as a percentage of the amount recommended in the British Columbia blueberry production guide to highbush blueberry (*Vaccinium corymbosum*) since 2008.

Highbush blueberry systems offer a unique opportunity to study and improve our understanding of changes in soil pH upon liming on agri-environmental indicators. We hypothesize that applying calcium carbonate (CaCO₃) to decrease the acidity of low-pH soils (liming) would (i) enhance the release of phosphate ions from Al and/or Fe oxyhydroxides into the soil solution, and (ii) lower the critical PSI indicating an increased risk of P loss. The objectives of this study were to determine the effects of increasing soil pH from acidic to near-neutral using lime on (i) the DPS, the PSI, and concentrations of P_{M3} and P_w; (ii) soil P pools determined by sequential fractionation; and (iii) phosphate sorption characteristics.

Materials and methods

Long-term experimental plots

A long-term highbush blueberry experiment, established in 2008 on flat topography at 7.6 m above sea level at the Agriculture and Agri-Food Canada, Agassiz Research and Development Centre (Agassiz RDC) (49°14'N, 121°45'W), was selected for this study. The local climate is characterized as moderate oceanic with relatively cool and dry summers, and warm and rainy winters (British Columbia Agriculture and Food Climate Action Initiative 2015). Annual rainfall ranges from 1483 to 1689 mm with the peak of about 280–350 mm received in November. Average daily temperatures range between 3.4 °C in January and 18.8 °C in August (30 years average, 1981–2010, Agassiz Climate Daily Almanac-Agassiz CDA station). The soil is a loam textured soil of the Monroe series, classified as Dystric Brunisols (Canadian System of Soil Classification 1998) or Typic Dystrochrepts in the U.S. Soil Taxonomy (Soil Survey Staff 2010). The soil is moderately to well drained, shallow with a weakly developed profile. The 13-year experiment consists of annual ammonium sulfate (21-0-0) application at three rates (100%, 150%, and 200% of the annual recommendation for blueberry based on the BC blueberry production guide) applied either as broadcast or fertigation, for a total of seven treatments including a control (0%), arranged in a randomized complete block design with four replicates (Messiga et al. 2018). General physicochemical properties, shown in Table 1, include: pH, 4.1–5.8; electrical conductivity, 118–311 μs cm⁻¹; total organic carbon, 1.97%–3.74%; total N, 0.15–0.22; P_{M3}, 163–200 mg kg⁻¹; Mehlich-3 extractable Al (Al_{M3}), 2126–3218 mg kg⁻¹; and Fe (Fe_{M3}), 166–210 mg kg⁻¹.

Soil sampling

Soils were selected according to their variable pH to fit into four descriptive acidity classes (Soil Survey Division Staff 1993): (i) extremely acidic (4.1), (ii) very strongly acidic (4.8), (iii) strongly acidic (5.5), and (iv) moderately acidic (5.8). We used soil samples collected from a long-term highbush blueberry experiment with a history of ammonium-based fertilizer applications that produced a range of soil pH from extremely low to near-neutral (pH = 3.8–6.5). Three treatments of the 13-year blueberry experiment and an adjacent field with identical agri-practices were therefore selected to fit these classes: (i) broadcast N (200% for pH 4.1); (ii) fertigation N (100% for pH 4.8); (iii) control (0% N for pH 5.8); and (iv) an adjacent field under rye grass (pH 5.5). For soil sampling, after discarding the layer of sawdust mulch at the soil surface approximately 3.5 kg of soil was collected down to 30 cm depth using a shovel, and then was placed in a labeled clean 10 L bucket and mixed thoroughly. The fresh soil was sieved (<2 mm) and kept at 4 °C in the laboratory. Two 80 g soil samples taken from each bucket were air dried prior to physicochemical analyses, including pH, texture, organic matter content, cation exchange capacity (CEC), total N, total S, total C, organic P, total P, P_{M3}, Al_{M3}, Fe_{M3}, and other Mehlich-3 extractable cations including Ca (Ca_{M3}), and Mg (Mg_{M3}). The remaining soil was kept frozen at –20 °C until the beginning of the incubation experiment.

Incubation experiment

Eight combination treatments (four initial soils (pH 4.1, 4.8, 5.5, and 5.8) × two lime applications (with and without lime)) were used for this study. The lime treatment was selected to reach a target pH of 6.0 for soils initially at pH 4.1, 4.8, and 5.5, and a target pH of 6.5 for the soil initially at pH 5.8. The lime requirement (LR) was calculated using a modified procedure of Laboski and Peters (2012), which used the CaCO₃ equivalent ratio to moles of the H⁺ concentrations to be neutralized from initial pH to target pH. The LR to raise the initial pH to 6.0 was 9.0 g for pH 4.1, 4.0 g for pH 4.8, 0.7 g for pH 5.5, and 0.1 g for pH 5.8. The eight combination treatments, each replicated four times (32 experimental units in total), were (i) pH 4.1 without lime (pH4.1L0), (ii) pH 4.1 with lime (pH4.1L1), (iii) pH 4.8 without lime (pH4.8L0), (iv) pH 4.8 with lime (pH4.8L1), (v) pH 5.5 without lime (pH5.5L0), (vi) pH 5.5 with lime (pH5.5L1), (vii) pH 5.8 without lime (pH5.8L0), and (viii) pH 5.8 with lime (pH 5.8L1). For treatments without lime, 1200 g of soil was mixed in a clean bucket and 250 g was

weighed in four Mason jars per treatment. For the treatments with lime, 1200 g of soil was placed in a clean bucket, mixed with CaCO₃ (fine powder, 99.95%–100.5% dry basis, pH 8, from Sigma–Aldrich), and 250 g was weighed in four Mason jars per treatment. The 32 Mason jars were closed with parafilm into which 10 holes were punctured with a needle to allow for gas exchange. The Mason jars were arranged in a completely randomized design in a growth chamber (Convion Adaptis A1000, Winnipeg, Canada) at 22.5 °C for 93 days. The weight of each Mason jar at the start of the incubation was recorded to monitor the soil moisture content. Moisture content was maintained at 60% water-filled pore space to maximize microbial activity (Franzluebber et al. 1999). Each Mason jar was weighed every 3 days to check moisture content, and distilled water was added by a bottle-top dispenser if the moisture content decreased by more than 10%. After 30 and 44 days of incubation, 10 g subsamples were taken from each jar to monitor changes in soil pH. After 30 days of incubation, it was observed that the soils initially at pH 5.8 did not reach the target pH 6.0. An extra 20 mg of CaCO₃ was mixed with the soil in the jars for that treatment, which increased the soil pH to ~6.5.

Soil analyses

After 93 days of incubation, the soil in each Mason jar was removed and air dried for chemical analysis. Air-dried soils were analyzed for pH in distilled water (1:2 soil:solution) on a MultiLab IDS (Model 4010-3; Hendershot et al. 1993). The P_w was determined by shaking 2.0 g of air-dried soil mixed in 50 mL centrifuge tubes with 20 mL distilled water for 1 h, centrifuging the mixture at 3500 r min⁻¹ for 10 min, and filtering through Whatman Grade 42 filter paper (Self-Davis et al. 2000). Phosphorus in the extract was determined by the molybdenum blue colorimetric method (Murphy and Riley 1962). The P_{M3} , Al_{M3} , and Fe_{M3} were determined by shaking 2.5 g of air-dried soil with a 25 mL of Mehlich-3 solution (pH 2.3) for 5 min (Mehlich 1984). The P_{Ox} , Al_{Ox} , and Fe_{Ox} were determined according to Ross and Wang (1993). The concentrations of P_{M3} , Al_{M3} , Fe_{M3} , P_{Ox} , Al_{Ox} , and Fe_{Ox} were assessed with an inductively coupled plasma optical emission spectrometer (ICP-OES). Total organic P was determined by the ignition method (Saunders and Williams 1955). Total P was determined by digestion using a fluxer (M4 Fluxer, Claisse) as described by Kowalenko and Babuin (2014). Phosphorus concentrations in these digests were analyzed by an ICP-OES (ICAP 7000 series, Thermo Scientific).

Calculations of degree of P saturation and P saturation index

The DPS was calculated by using the molar ratio of P_{Ox} , Al_{Ox} , and Fe_{Ox} (Breeuwsma and Silva 1992):

$$(1) \quad DPS = \frac{P_{Ox}}{\alpha_m (Al_{Ox} + Fe_{Ox})} \times 100$$

where P_{Ox} , Al_{Ox} , and Fe_{Ox} are quantified in acid ammonium oxalate extracts (mmol kg⁻¹). The sum of Al_{Ox} and Fe_{Ox} is termed as PSC (mmol kg⁻¹). The term α_m is the maximum sorption coefficient (Breeuwsma and Silva 1992). We used

an average α_m value of 0.5 to calculate DPS (Benjannet et al. 2018).

The P saturation index was calculated using two variations, PSI₁ and PSI₂, using P_{M3} , Al_{M3} , and Fe_{M3} , as follows (Khiari et al. 2000):

$$(2) \quad PSI_1 = \frac{P_{M3}}{Al_{M3}} \times 100$$

and

$$(3) \quad PSI_2 = \frac{P_{M3}}{Al_{M3} + Fe_{M3}} \times 100$$

where P_{M3} , Al_{M3} , and Fe_{M3} are quantified in Mehlich-3 extracts (mmol kg⁻¹).

Phosphate sorption experiments

Phosphate sorption experiments were also conducted on air-dried soils (Messiga et al. 2021). In brief, solutions with a range of P concentrations were formulated in a matrix of distilled water and 100 µL of toluene (to inhibit microbial activity) for batch equilibration with the soil. Initial equilibrating solution P concentrations were 0, 10, 20, 50, 100, and 150 mg P L⁻¹ as KH₂PO₄. Sorption batches consisted of 2.0 g air-dried soil mixed in 50 mL centrifuge tubes with 30 mL of the equilibrating solution. The tubes were gently shaken end-over-end for 24 h at room temperature, centrifuged at 3500 r min⁻¹ for 10 min, and then filtered through Whatman Grade 42 filter paper. An aliquot of the supernatant solution was used to determine P in solution by ICP-OES.

Soil P fractionation

Finally, soil P fractionation was performed on the remaining air-dried soil by sequentially extracting P according to a modified method of Chang and Jackson (1958) as described by Zhang and Kovar (2009). Briefly, 0.5 g of finely ground soil (0.2 mm) was sequentially extracted by 1 mol L⁻¹ NH₄Cl (NH₄Cl-P), 0.5 mol L⁻¹ NH₄F (NH₄F-P), 0.1 mol L⁻¹ NaOH (NaOH-P), a mixture of 0.3 mol L⁻¹ sodium citrate dihydrate, Na₃C₆H₅O₇·2H₂O + 1 mol L⁻¹ NaHCO₃ for reductant-soluble P (CBD-P), and 0.25 mol L⁻¹ H₂SO₄ (H₂SO₄-P) at room temperature. For the purpose of precision, the inorganic P fractions are described by their extraction method (Barrow et al. 2020; Guppy 2021). Phosphorus concentrations in the extracts were analyzed by the molybdenum blue colorimetric method (Murphy and Riley 1962).

Sorption data fitting

Sorption data for each soil pH and lime treatments were fitted using Langmuir and Freundlich isotherms. Sorption isotherms were parameterized using SAS PROC NLIN version 9 (SAS Institute Inc. 2010). The Langmuir isotherms resulted in the best goodness of fit for all soil pH and lime treatments. The Langmuir isotherm is described as follows:

$$(4) \quad S = S_{max} \times \frac{k_a \times C}{1 + k_a \times C}$$

where S (mg P kg⁻¹) is the sorbed P onto the soil after 24 h contact, S_{max} (mg P kg⁻¹) is the P sorption maximum, k_a

(L mg P⁻¹) is the binding energy of P, and C (mg P L⁻¹) is the equilibrium P concentration in solution (Messiga et al. 2020). The goodness of fit of the sorption isotherms to experimental data was assessed by the R² and root mean square deviation (RMSD). The RMSD was calculated with the following equation:

$$(5) \quad \text{RMSD} = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (y_{\text{simulated}_i} - y_{\text{calculated}_i})^2}$$

where $y_{\text{simulated}_i}$ is the simulated value of S using the Langmuir equation and $y_{\text{calculated}_i}$ is the calculated value of S.

Statistical analyses

To statistically compare the S_{max} (not k_a because of auto-correlations) parameter between not limed and limed treatments, we calculated the following F ratio:

$$(6) \quad \text{Fratio} = \frac{[\text{rSS}_{(1+2)} - (\text{rSS}_1 + \text{rSS}_2)] / 2}{(\text{rSS}_1 + \text{rSS}_2) / (n-4)}$$

where $\text{rSS}_{(1+2)}$ is the residual sum of square of all S data obtained with one set of parameter values for the two lime treatments, and rSS_1 and rSS_2 are the residual sums of squares of the S data obtained with separate sets of parameter values for each of the two N treatments, respectively. The probability level associated with the F ratio was calculated from the F distribution with 2 and $(n-4)$ degrees of freedom: when $F = 3.20$, $P = 0.05$; when $F = 5.11$, $P = 0.01$; and when $F = 8.09$, $P = 0.001$.

Data of soil P analysis, DPS, PSI, and P fractionation were analyzed statistically using one-way Analysis of variance (ANOVA) with random effects as replicates and the eight treatments as fixed effects using SAS PROC MIXED (SAS Institute 2010). Data were first checked for assumptions of ANOVA using Shapiro–Wilk test and Q–Q plots for normality and for equal variance using residual plots and Bartlett’s tests. Differences between least square means for treatment pairs (without lime vs. with lime at each initial pH level) were tested at significance level of $P = 0.05$. Nonlinear regression techniques were applied to pH, P_{M_3} , P_w , DPS, PSI₁, and PSI₂ using NLIN procedure of SAS. The fit of the regression curves was evaluated using R² to determine how well the curve explains measured data variation. Principal component analysis (PCA) was carried out using SAS PROC PRINCOMP (SAS Institute 2010) to establish the relationships between agri-environmental indicators and chemical properties of soil and P fractions.

Results

Liming effects on soil pH, concentrations of Mehlich-3 P, and water-extractable P, and agri-environmental indicators

As projected by the LR calculations, soil pH was increased from 4.1 to 6.0, 4.8 to 6.0, 5.5 to 6.0, and 5.8 to 6.5, respectively, after 93 days of incubation with additions of CaCO₃ (Fig. 1a). The initial soil pH value did not change after 93 days

of incubation. (Fig. 1a). The concentrations of P_{M_3} ranged from 146 to 200 mg kg⁻¹ and were not significantly changed by liming (Fig. 1b). The concentrations of P_w ranged from 1.0 to 3.65 mg kg⁻¹ and were significantly affected by additions of lime only for soils with initial pH of 5.8 (Fig. 1c). The DPS, PSI₁, and PSI₂ were not affected by additions of lime for any of these soils, regardless of initial soil pH (Figs. 1d–1f). On average, the DPS values were 27%, 26%, 25%, and 27% for soils at initial soil pH of 4.1, 4.8, 5.5, and 5.8, respectively (Fig. 1d). On average, the PSI₁ values were 6.0%, 5.2%, 5.6%, and 6.1%, respectively (Fig. 1e). On average, the PSI₂ values were 5.8%, 5.0%, 5.4%, and 5.8%, respectively (Fig. 1f).

Liming effects on the relationships between concentrations of water-extractable P and agri-environmental indicators

There were two patterns of the relationships between concentrations of P_w and agri-environmental indicators at the end of incubation depending on the initial soil pH. At initial soil pH ≤ 5.5, the concentrations of P_w were related to agri-environmental indicators, P_{M_3} , DPS, PSI₁, PSI₂, PSC, and Ca_{M3}, by quadratic regressions (Figs. 2a–2f). The slopes of the quadratic regressions were positive for P_{M_3} (Fig. 2a), DPS (Fig. 2b), and PSC (Fig. 2e), but negative for PSI₁ (Fig. 2c), PSI₂ (Fig. 2d), and Ca_{M3} (Fig. 2f). In addition, the R² of the regressions were 0.25 for P_{M_3} , 0.49 for DPS, 0.22 for PSI₁, 0.23 for PSI₂, 0.23 for PSC, and 0.58 for Ca_{M3}. In contrast, at initial pH = 5.8, there was no trend in the distribution pattern of the concentrations of P_w with P_{M_3} , DPS, PSI₁, PSI₂, and PSC except the decreasing trends following additions of lime and the increased soil pH (Figs. 2a–2e). However, at initial pH = 5.8, the concentrations of P_w decreased with increasing Ca_{M3} following additions of lime (Fig. 2f).

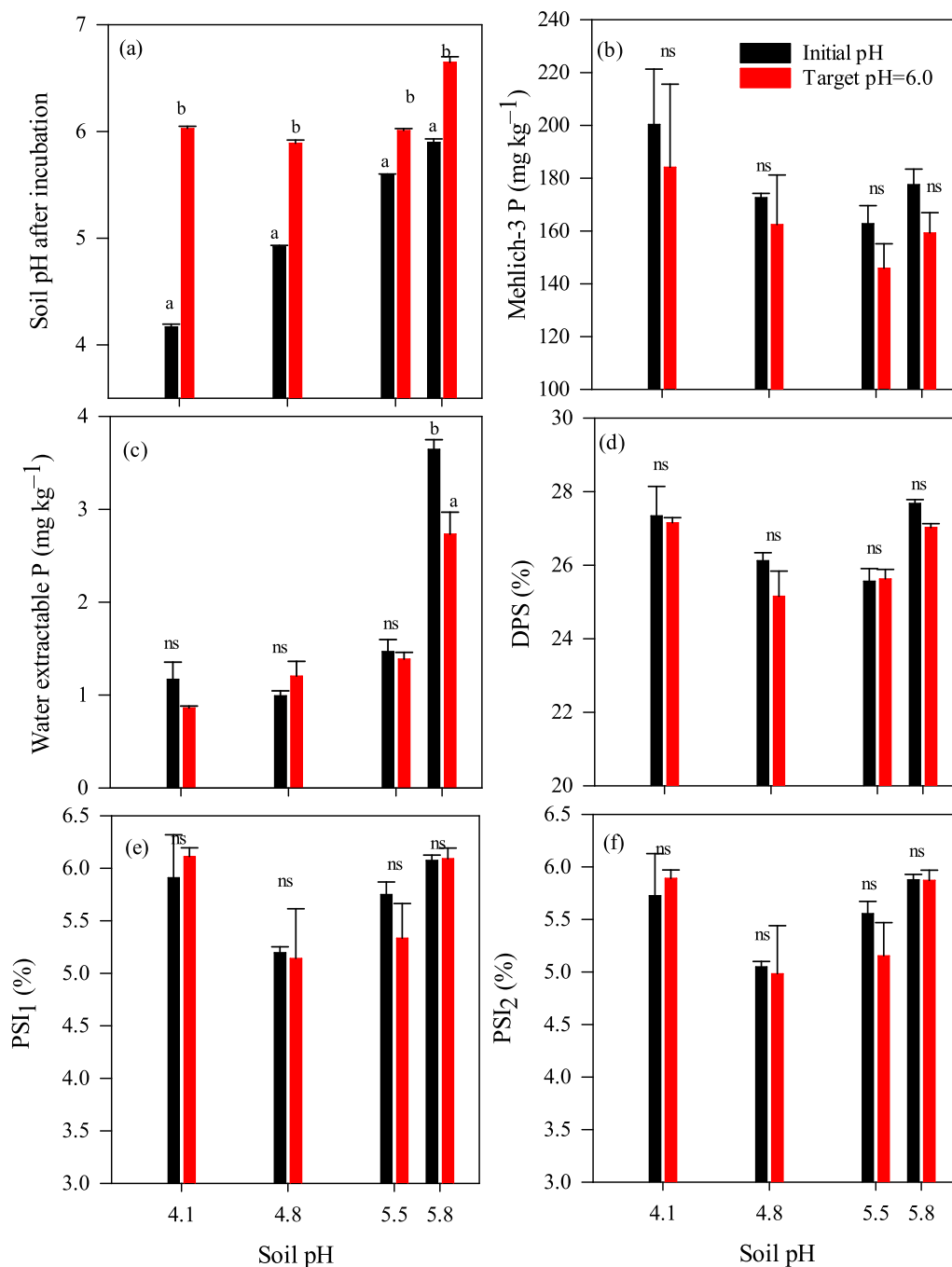
A further examination showed that the relationships among agri-environmental indicators were described by linear regressions (Figs. 3a–3d). The linear regression between PSI₁ and PSI₂ was characterized by a positive slope = 0.96 and R² = 0.99 and was not affected by liming (Fig. 3a). Similarly, the relationships between DPS and PSI₁, PSI₂, and P_{M_3} were not affected by liming and were described by linear regressions with positive slopes = 0.39 and R² = 0.52 for DPS vs. PSI₁ (Fig. 3b), positive slopes = 0.38 and R² = 0.53 for DPS vs. PSI₂ (Fig. 3c), and positive slopes = 20.5 and R² = 0.45 for DPS vs. P_{M_3} (Fig. 3d).

Liming effects on concentrations of aluminum, iron, and calcium

There was a decreasing trend of the concentrations of Al_{M3} and Fe_{M3} in soils with increasing soil pH. The addition of CaCO₃ further decreased the concentrations of Al_{M3} and Fe_{M3} by 24%, 11%, 2.3%, and 17% for initial soil pH = 4.1, 4.8, 5.5, and 5.8, respectively. The relationships between the concentrations of Al_{M3} and Fe_{M3} vs. soil pH were not affected by the addition of CaCO₃ and were described by linear regressions with negative slope = -329.61 and R² = 0.62 for Al_{M3} (Fig. 4a), and negative slope = -8.06 and R² = 0.33 for Fe_{M3} (Fig. 4b).

In contrast, there was an increasing trend of the concentrations of Ca_{M3} in soils with increasing soil pH. The addition

Fig. 1. Effects of liming using calcium carbonate on changes in (a) soil pH, (b) Mehlich-3 P, (c) water-extractable P, (d) DPS (%), (e) PSI_1 (%), and (f) PSI_2 (%) after 93 days of incubation. Bars with different letters are statistically different at $P < 0.05$. [Colour online.]



of $CaCO_3$ further increased the concentrations of Ca_{M3} by 5.5 times, 2.4 times, 1.4 times, and 1.8 times for soils with initial pH 4.1, 4.8, 5.5, and 5.8, respectively. The relationship between the concentrations of Ca_{M3} and soil pH was not affected by the addition of $CaCO_3$ and was described by a power regression with a positive slope = 0.48 and $R^2 = 0.44$ (Fig. 4c).

There was no specific trend in the concentrations of Al_{Ox} and Fe_{Ox} with initial soil pH as observed with Al_{M3} and Fe_{M3} . On average, the concentrations of Al_{Ox} were 321, 332, 237, and 320 $mmol\ kg^{-1}$ for initial soil pH values of 4.1, 4.8, 5.5,

and 5.8, respectively, indicating no effect of soil pH or $CaCO_3$ additions (Fig. 4d). The concentrations of Fe_{Ox} were 87, 81, 59, and 83 $mmol\ kg^{-1}$ for initial soil pH values of 4.1, 4.8, 5.5, and 5.8, respectively, indicating no effect of soil pH or $CaCO_3$ additions (Fig. 4e).

Liming effects on phosphorus sorption characteristics

The experimental data of the sorption study for all soils at the end of the 93 days of incubation were best fitted by

Fig. 2. Effects of liming using calcium carbonate on the relationships between water-extractable P and (a) Mehlich-3 P, (b) degree of P saturation (DPS, %), (c) P saturation index (PSI_1 , $(P/Al)_{Mehlich-3}$ (%)), (d) P saturation index (PSI_2 , $(P/Al + Fe)_{Mehlich-3}$ (%)), (e) P sorption capacity (PSC, $mmol\ kg^{-1}$), and (f) Mehlich-3 calcium (Ca, $mg\ kg^{-1}$) after 93 days of incubation. Red and green highlighted points are for initial and target soil pH = 5.5, respectively, which were not included in the regression. [Colour online.]

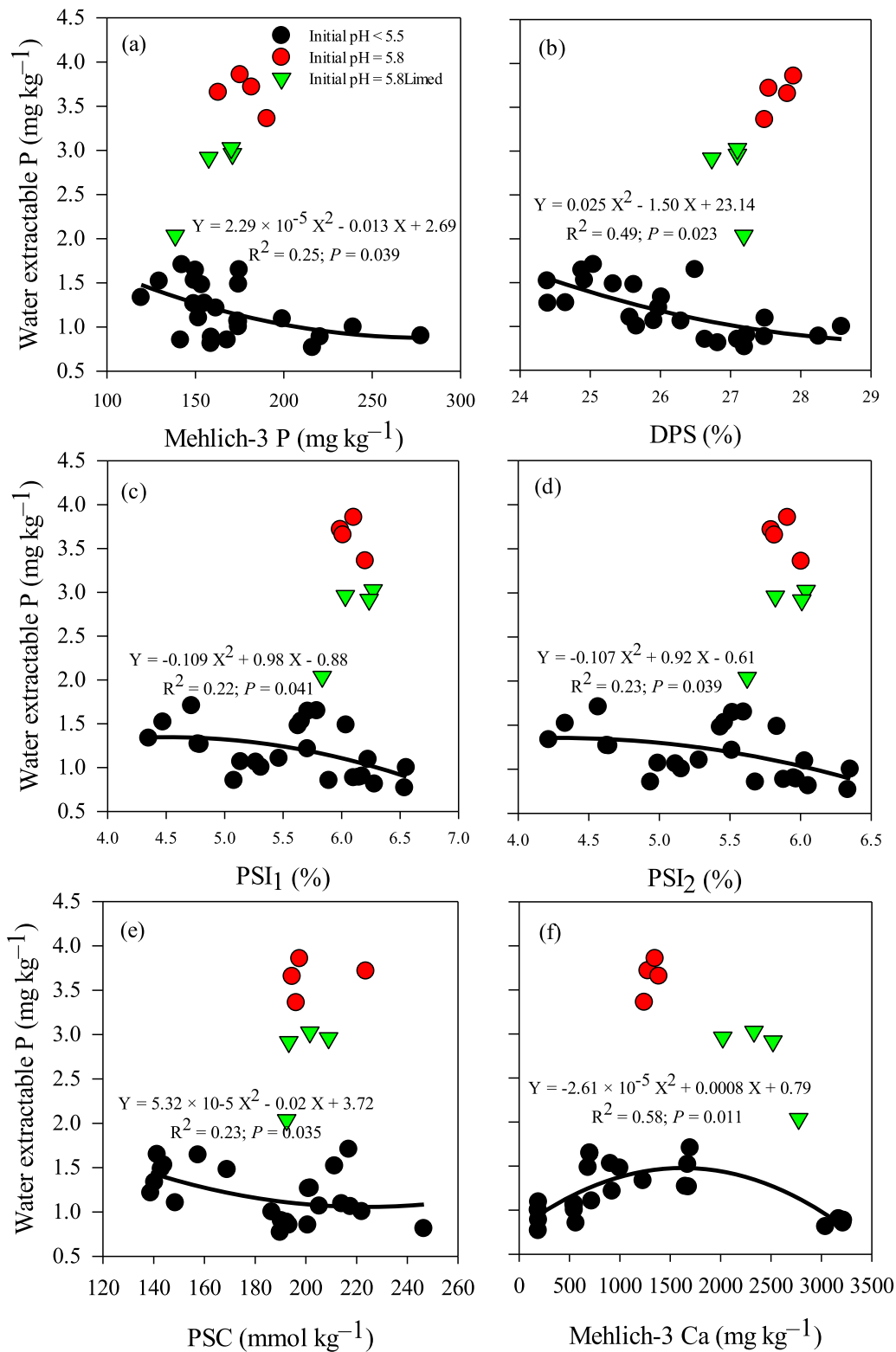
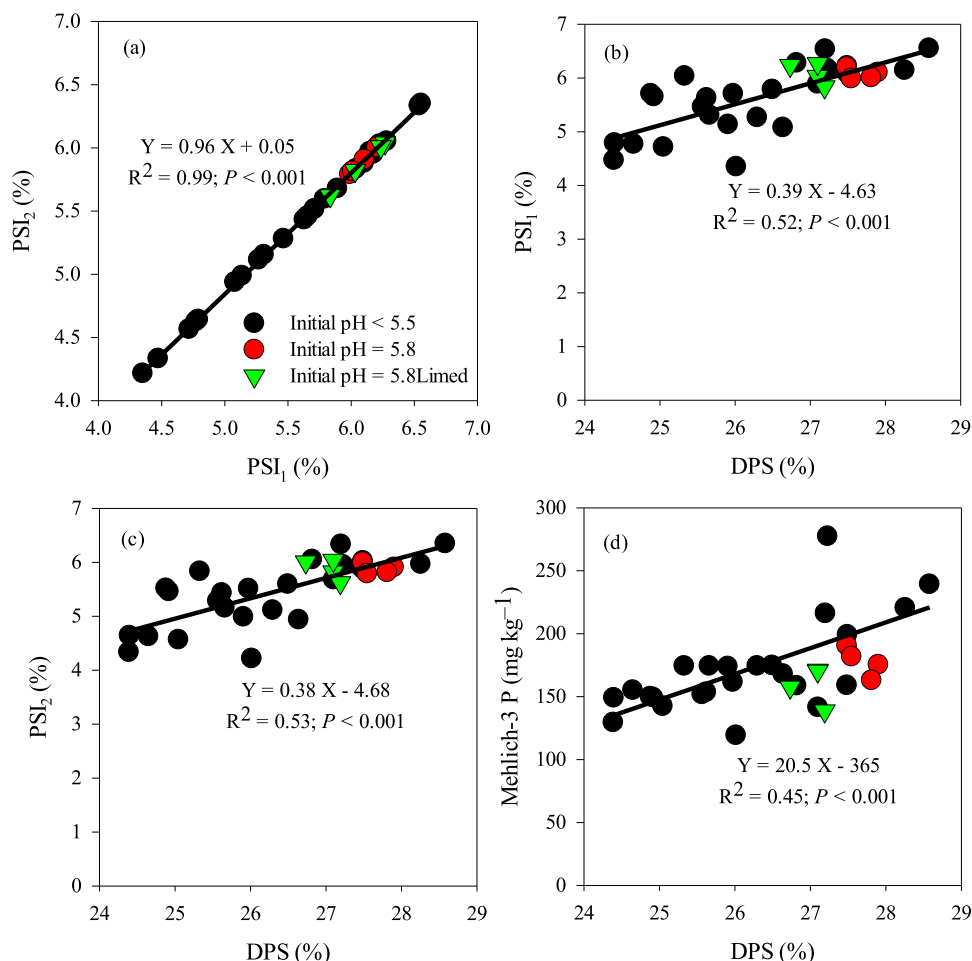


Fig. 3. Effects of liming using calcium carbonate on the relationships between (a) P saturation index (PSI_1 , $(P/Al)_{Mehlich-3}$, %) and PSI_2 ($(P/Al + Fe)_{Mehlich-3}$, %), and degree of P saturation (DPS, %) and (b) PSI_1 , (c) PSI_2 , and (d) Mehlich-3 P after 93 days of incubation. [Colour online.]



the Langmuir equation, with R^2 values 0.97 and 0.99 (Fig. 5). The S_{max} and k_a values were affected by liming only for soils with initial pH values of 4.1 and 5.8 (Figs. 5a and 5d). For soils with initial pH 4.1, the S_{max} value was $1382\ mg\ P\ kg^{-1}$ without lime but significantly decreased to $1243\ mg\ P\ kg^{-1}$ after liming (Table 2; Fig. 5d). For soils with initial pH 5.8, the S_{max} value was $1093\ mg\ P\ kg^{-1}$ without lime but significantly increased to $1114\ mg\ P\ kg^{-1}$ after liming (Table 2; Fig. 5d).

For the other soils, the S_{max} value was $1244\ mg\ P\ kg^{-1}$ without lime and $1267\ mg\ P\ kg^{-1}$ with lime with an average S_{max} value of $1254\ mg\ P\ kg^{-1}$ for initial soil pH 4.8; $745\ mg\ P\ kg^{-1}$ without lime and $795\ mg\ P\ kg^{-1}$ with lime with an average S_{max} value of $777\ mg\ P\ kg^{-1}$ for initial soil pH 5.5; and $1093\ mg\ P\ kg^{-1}$ without lime and $1114\ mg\ P\ kg^{-1}$ with lime for initial soil pH 5.8 (Figs. 5b and 5c).

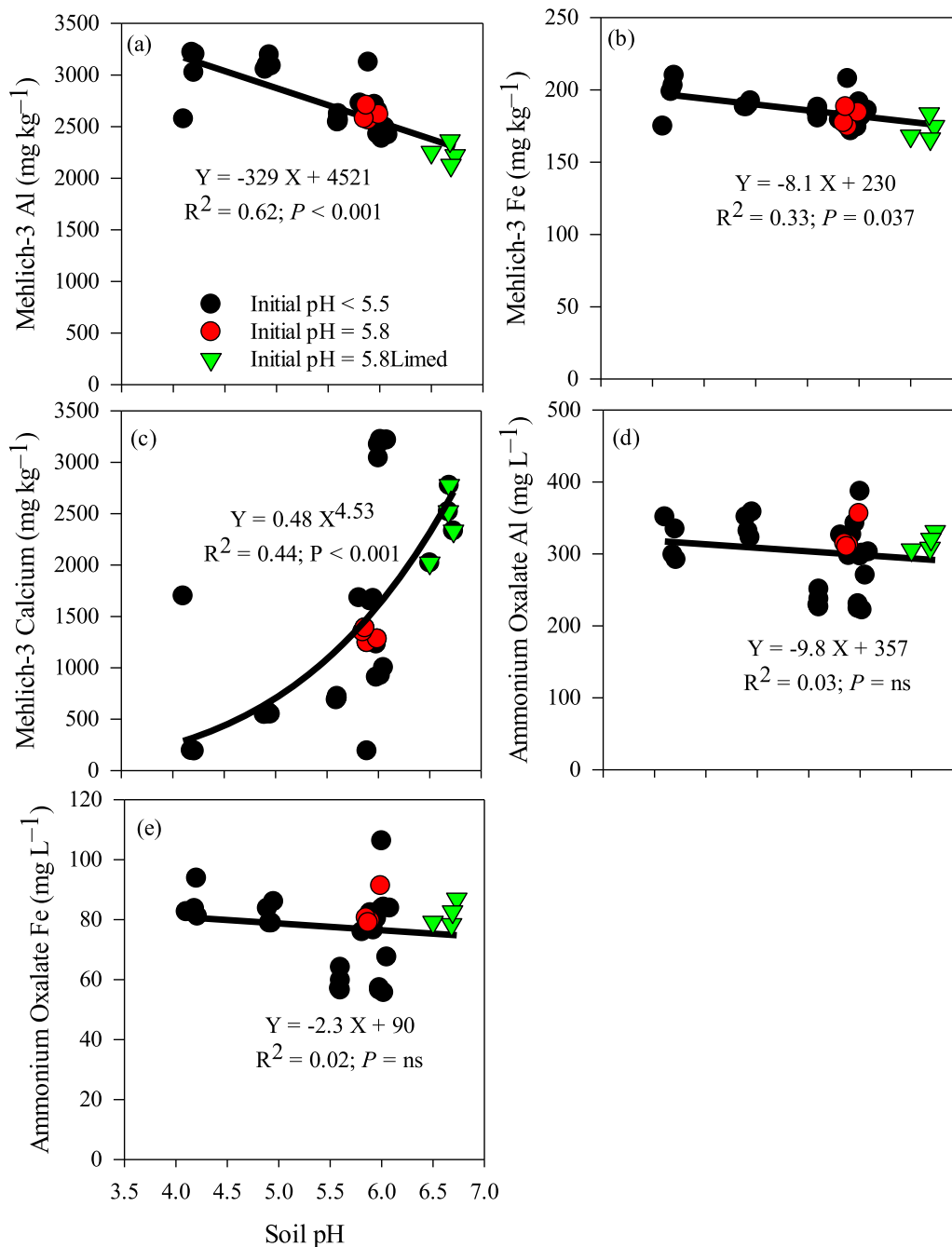
Liming effects on phosphorus fractions, organic P, and total P

At the end of the 93 days of incubation, the concentrations of NH_4Cl -P significantly decreased with addition of $CaCO_3$ for soils with initial pH 4.1 only, by 50.4% (Fig. 6a). The decreasing trends of NH_4Cl -P in soils with the other initial pH values

were not significant (Fig. 6a). The concentrations of NH_4F -P significantly decreased with addition of $CaCO_3$ for soils with initial soil pH 4.1 only, from 59 to $29\ mg\ kg^{-1}$ (Fig. 6b). The concentrations of $NaOH$ -P significantly decreased with addition of $CaCO_3$, from 324 to $247\ mg\ kg^{-1}$, for initial soil pH = 4.8 (Fig. 6c). The decreasing $NaOH$ -P trends observed with the other initial pH with addition of $CaCO_3$ were not significant. The concentrations of the reductant-soluble P fraction (CBD-P) significantly increased with addition of $CaCO_3$, from 26 to $218\ mg\ kg^{-1}$, at initial soil pH = 4.1, and significantly decreased with addition of $CaCO_3$, from 364 to $21\ mg\ kg^{-1}$ and from 103 to $23\ mg\ kg^{-1}$, at initial soil pH 5.5 and 5.8, respectively, with no significant change for soils initially at pH 4.8 (Fig. 6d). The concentrations of the H_2SO_4 -P fraction were not significantly affected by addition of $CaCO_3$ (Fig. 6e). The corresponding organic P fractions at different sequential extracts were not influenced by liming.

At the end of the 93 days of incubation, soil organic P and total P were not affected by additions of lime. On average over the two lime additions, organic P concentrations were 339 – 444 , $427\ mg\ kg^{-1}$ (Fig. 7a), while total P concentrations were 1181 – $1492\ mg\ kg^{-1}$ (Fig. 7b).

Fig. 4. Effects of liming using calcium carbonate on the relationships between soil pH and (a) Mehlich-3 aluminum, (b) Mehlich-3 iron (Fe), (c) Mehlich-3 calcium, (d) ammonium oxalate aluminum, and (e) ammonium oxalate iron after 93 days of incubation. [Colour online.]

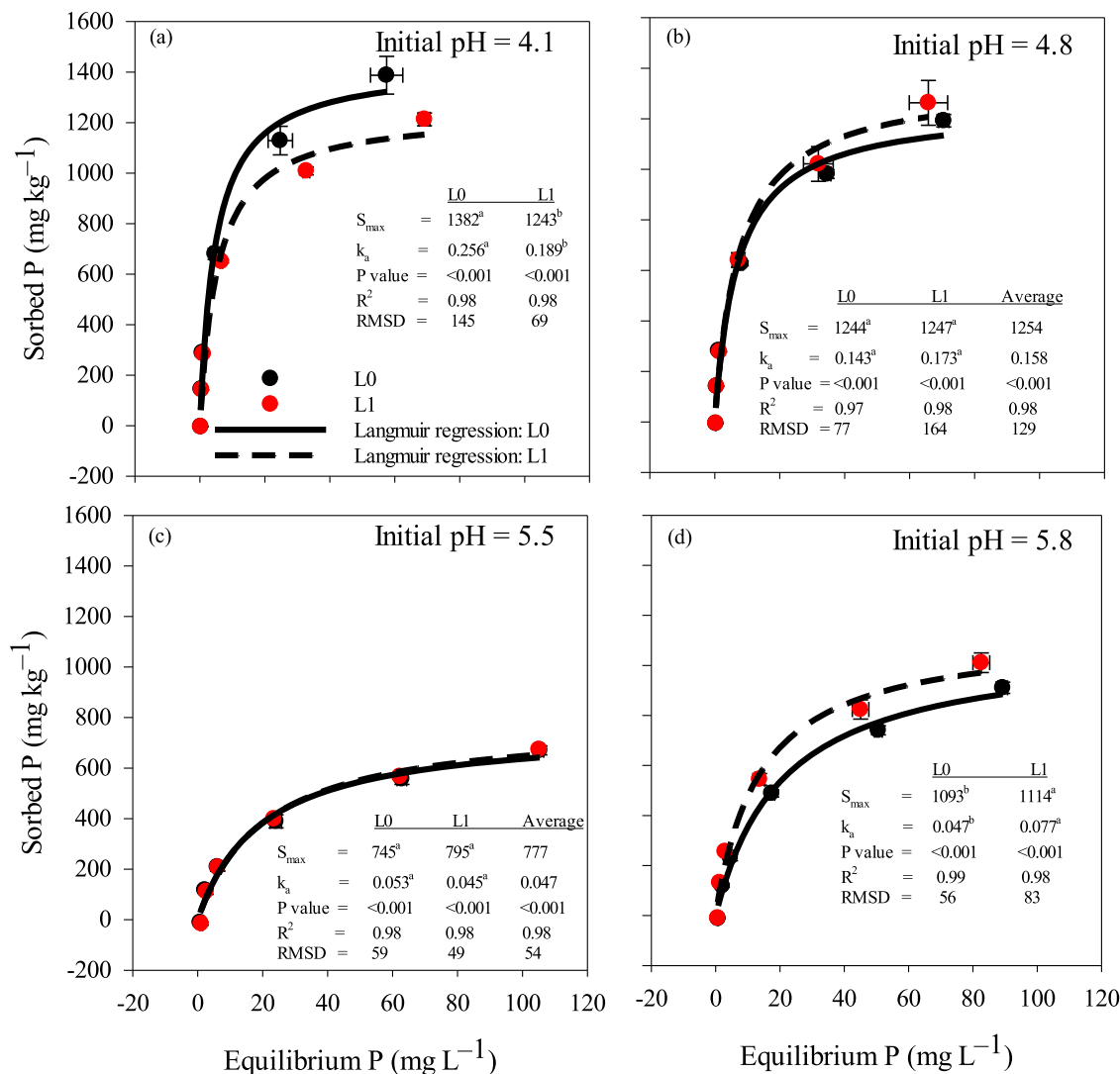


Relationships between P_w , Mehlich-3 P, agri-environmental indicators, inorganic P fractions, and chemical soil properties

The PCA showed that P_w was highly correlated to PSI_1 , PSI_2 , and $\text{Ca}_{\text{M}3}$, whereas $\text{P}_{\text{M}3}$, $\text{Al}_{\text{M}3}$, $\text{Fe}_{\text{M}3}$ inorganic P fractions and chemical soil properties were highly correlated following the addition of CaCO_3 (Fig. 8). The eight combinations of initial soil pH \times addition of CaCO_3 were separated into four groups for their effects on the studied properties, including (i) pH4.1L0 and pH4.8L0, (ii) pH4.8L1, (iii) pH5.5L0 and

pH5.5L1, and (iv) pH4.1L1, pH5.8L0, and pH5.8L1. Groups I and II positively affected $\text{NH}_4\text{Cl-P}$, $\text{Al}_{\text{M}3}$, $\text{Fe}_{\text{M}3}$, and k_a , but negatively affected P_w , PSI_1 , PSI_2 , and $\text{Ca}_{\text{M}3}$; Group III positively affected $\text{H}_2\text{SO}_4\text{-P}$ and $\text{NaHCO}_3\text{-P}$, but negatively affected DPS , Al-P , Fe-P , PSC , S_{max} , and $\text{P}_{\text{M}3}$; Group IV positively affected P_w , PSI_1 and PSI_2 , $\text{Ca}_{\text{M}3}$, and pH. Pearson's correlation among P_w , $\text{P}_{\text{M}3}$, agri-environmental indicators (PSI_1 , PSI_2 , and DPS), inorganic P fractions ($\text{NH}_4\text{Cl-P}$, $\text{NH}_4\text{F-P}$, NaOH-P , $\text{NaHCO}_3\text{-P}$, and $\text{H}_2\text{SO}_4\text{-P}$), and chemical soil properties ($\text{Al}_{\text{M}3}$, $\text{Fe}_{\text{M}3}$, $\text{Ca}_{\text{M}3}$, PSC , k_a , and S_{max}) were in line with the results of PCA (Table 3). The

Fig. 5. Effects of liming using calcium carbonate on phosphorus sorption characteristics of soils after 93 days of incubation. (a) P sorption maximum; (b) binding energy of P; (c) significant probability; (d) root means square deviation. Means followed by similar letters within the row for the same initial soil pH are not statistically different using the *F* test at the probability level of 0.05. [Colour online.]



concentrations of P_w were positively correlated with Ca_{M3} , PSI_1 , and PSI_2 . Increasing soil pH was associated with decrease in Al_{M3} , Fe_{M3} , and NH_4Cl-P more strongly at initial soil pH values of 4.1 and 4.8 (Table 3). The concentrations of H_2SO_4-P were negatively correlated with k_a and S_{max} . Remarkably, the P_w were positively associated with PSI_1 and PSI_2 than DPS (Table 3).

Discussion

Low soil pH and relationship between concentrations of P_{M3} , P_w , and agri-environmental indicators

The concentrations of P_{M3} across all soils (Fig. 1b) fall into the “very high” P class (above 150 mg kg⁻¹) and represented agricultural soils typically found in the BC Fraser Valley (Kowalenko et al. 2007; Reid and Schneider 2019). According

to the literature and local recommendations, these high P_{M3} concentrations are associated with increased risk of environmental impact due to P losses with runoff (Kowalenko et al. 2007; Reid and Schneider 2019). A value of DPS > 25% (Fig. 1d) is considered the critical limit above which P runoff is enhanced in acidic soils (van der Zee et al. 1987), and all the studied soils had DPS values above this critical limit. However, only soils with initial pH 5.8 had concentrations of P_w of 3.8 mg kg⁻¹ (Fig. 1c), which is close to critical concentration values set at 4.0 mg kg⁻¹ across different agro-ecosystems in BC (van Bochove et al. 2012) and 3.7 mg kg⁻¹ in silage corn and blueberry plantings (Messiga et al. 2021) in the Fraser Valley. The soils with initial pH 5.8 have not received any N fertilizers for the past 10 years (Messiga et al. 2018). The other soils with initial pH values of 4.1, 4.8, and 5.5 had concentrations of P_w below the critical level (Fig. 1c), which contrasted with their P_{M3} and DPS values, indicating significant pH effects on the solubility of P and assessment of the risk of P losses with

Table 2. Comparison of the parameters of the Langmuir equation for the four soils at their initial pH values following additions of lime after 93 days of incubation.

Treatment	n^a	rSS ^b	tSS ^c	F ratio	P value
pH1L0	24	491 842	15 181 772		<0.001
pH1L1	24	110 897	12 066 349		<0.001
pH1L0 + pH1L1	48	785 244	27 248 120		<0.001
Comparison of pH1L0 and pH1L1				6.66	0.01
pH2L0	24	134 454	11 521 535		<0.001
pH2L1	24	619 101	12 748 930		<0.001
pH2L0 + pH2L1	48	773 639	24 270 465		<0.001
Comparison of pH2L0 and pH2L1				0.37	ns ^d
pH3L0	24	78 622.8	3 444 179		<0.001
pH3L1	24	56 070.6	3 962 588		<0.001
pH3L0 + pH3L1	48	137 000	7 859 695		<0.001
Comparison of pH3L0 and pH3L1				0.37	ns
pH4L0	24	73 182.1	6 749 051		<0.001
pH4L1	24	162 736	8 360 205		<0.001
pH4L0 + pH4L1	48	337 405	15 109 256		<0.001
Comparison of pH4L0 and pH4L1				9.46	<0.001

^aNumber of observations.^bResidual sum of squares.^cTotal sum of squares.^dNot significant ($P > 0.05$).

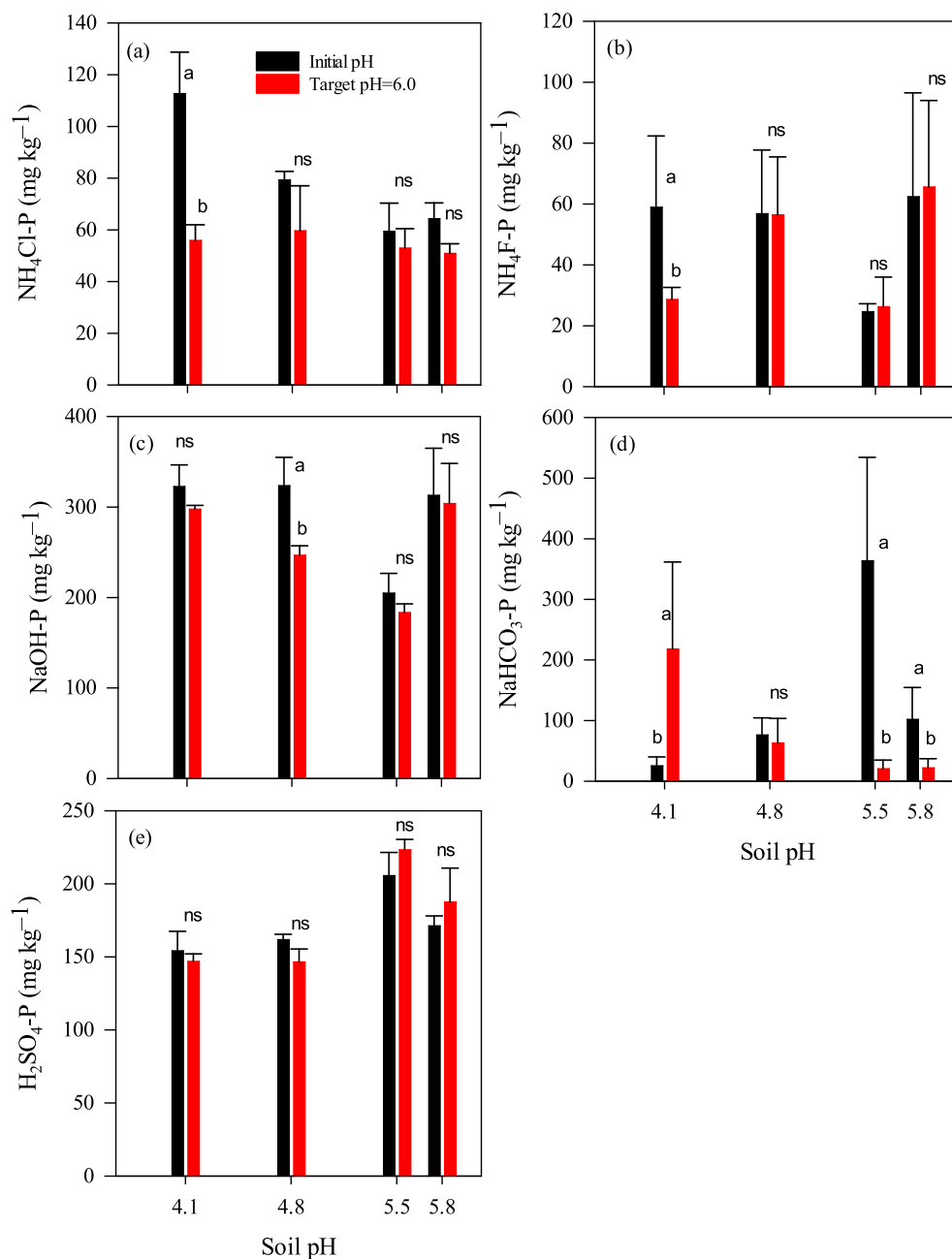
runoff. The soils with initial soil pH values of 4.1, 4.8, and 5.5 received ammonium sulfate at different rates, which resulted in the decreased soil pH and reduced changes in P_w concentration patterns compared with soils with initial pH 5.8 (Messiga et al. 2018). The significant decline with liming of P_w at pH 5.8 could be explained by the dissociation of P ions leading to speciation shifts. At pH 6.5, phosphate will occur as HPO_4^{2-} more than as H_2PO_4^- , which will increase phosphate sorption (Chang and Overby 1986; Han 2020). The mismatch between concentrations of P_{M3} , DPS, and concentrations of P_w as influenced by soil pH indicates the need to improve our understanding of the functioning of these indicators to assess the risk of P losses with runoff across the range of cropping systems and management practices found in the Fraser Valley.

The low PSI_1 and PSI_2 (Figs. 1e and 1f), which also contrasted with high concentrations of P_{M3} (150–200 mg kg⁻¹) and $\text{DPS} > 25\%$ (Figs. 1b and 1d), were in line with low P_w concentrations associated with soils at initial pH ≤ 5.5 (Fig. 1c). The discrepancy between the indicators of risk provided by DPS and PSI_1 and PSI_2 as they relate to P_w and P_{M3} of soils with initial pH ≤ 5.5 could be explained by a combination of factors inherent to the extraction solutions and the chemistry of P, Al, Fe, and Ca, and to some extent, phytates driven by soil pH. We found that the concentrations of Al_{M3} in soils with initial pH values of 4.1 and 4.8 were higher than soils with initial pH values of 5.5 and 5.8 (Table 2; Figs. 4a and 4b). On average, the concentration of Al_{M3} was 3056 mg kg⁻¹ in soils with initial pH values of 4.1 and 4.8 compared with 2594 mg kg⁻¹ in soils with initial pH values of 5.5 and 5.8 (Table 2;

Figs. 4a and 4b). The concentrations of Al_{M3} with initial soil pH ≤ 5.5 followed the same trend as P_{M3} (Fig. 1b). At these low initial pH levels, Al^{3+} cations present in the primary minerals are easily expelled in the soil solution where they form secondary minerals of Al oxides and oxyhydroxides. These secondary Al oxides and oxyhydroxides further react and precipitate with phosphate ions (Penn and Camberato 2019). In addition, the low initial pH prevailing in the soil solution increases the amount of pH-dependent charges at the edges of Al oxides and oxyhydroxides and other broken bonds of silicate minerals onto which the fixation of phosphate ions is enhanced (Penn and Camberato 2019). It is therefore possible that at low initial pH, the combination of high concentrations of Al oxyhydroxides provides large surface area for adsorption sites and large pH-dependent charges enhance the retention of phosphate ions in the soil solution, thus reducing the concentration of P_w . Furthermore, the opposite trends between the concentrations of P_w and P_{M3} and Al_{M3} indicate that phosphate ions retained at the surfaces of Al oxides and oxyhydroxides are not soluble in water and therefore are not accounted for by the colorimetric blue methods used in their assessment (Murphy and Riley 1962; Self-Davis et al. 2000; Messiga et al. 2021).

Our results also indicate that Mehlich-3 solution extracts more Al and P at low pH compared with high pH (Figs. 4a and 4b). This is explained by high Al on the cation exchange complex at low pH and the increased Ca onto negatively charged reacting surfaces at high pH that facilitate phosphate adsorption (Barrow 2017). At low pH, the acidity of Mehlich-3 solution promotes the dissolution of Al

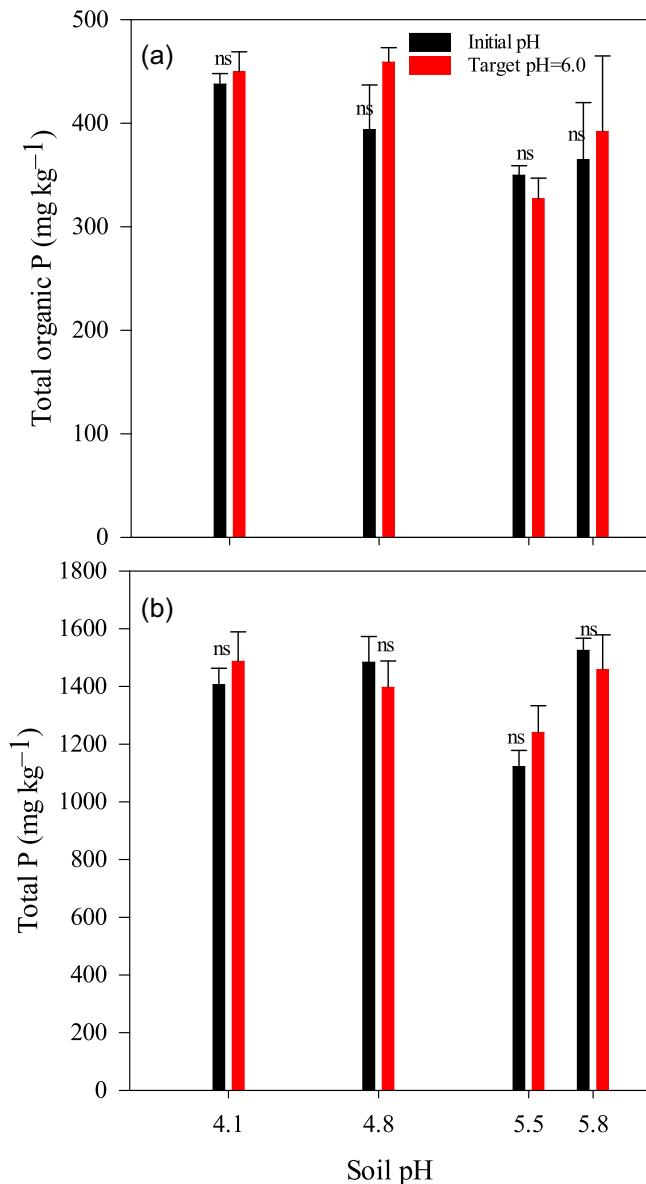
Fig. 6. Effects of liming with calcium carbonate and 93 days of incubation on changes in molybdate-reactive P pools determined by sequential fractionation. (a) Ammonium chloride-extractable P ($\text{NH}_4\text{Cl-P}$), (b) ammonium fluoride-extractable P ($\text{NH}_4\text{F-P}$), (c) sodium hydroxide-extractable phosphorus (NaOH-P), (d) reductant-soluble P (CBD-P), and (e) acid-extractable P ($\text{H}_2\text{SO}_4\text{-P}$). Bars with different letters are statistically different at $P < 0.05$. [Colour online.]



oxides and oxyhydroxides such as gibbsite, thus increasing the concentration of $\text{Al}_{\text{M}3}$ (Penn et al. 2018). The affinity of F^- with Al further increases the concentration of $\text{Al}_{\text{M}3}$ by complexing additional Al oxides and oxyhydroxides resulting into the formation of AlF_3 that is detected upon analysis of the Mehlich-3 extract by ICP (Mehlich 1984). These increased concentrations of $\text{Al}_{\text{M}3}$ associated with low soil pH and Mehlich-3 solution decrease the values of PSI_1 and PSI_2 (Figs. 1e and 1f) relative to $P_{\text{M}3}$ and DPS values (Figs. 1b and 1d; Figs. 3b–3d).

The concentrations of Al_{Ox} did not vary with initial soil pH (Fig. 4d) compared with $\text{Al}_{\text{M}3}$, indicating a more stable reaction of the ammonium oxalate extracting solution on Al and Fe over the range of acidic pH (Van der Zee et al. 1987). The oxalate extraction dissolves amorphous Al and Fe at the surfaces of which P is retained and not the crystalline Al and Fe (McKeague and Day 1966). These amorphous Al and Fe are made up mainly of Al and Fe hydroxides originating from pedogenesis and weathering processes (McKeague and Day 1966). Our results therefore

Fig. 7. Effects of liming using calcium carbonate and 93 days of incubation on (a) soil organic P and (b) total soil P. Bars with different letters are statistically different at $P < 0.05$. [Colour online.]



confirm that at low soil pH as those observed in our study, Mehlich-3 extraction tends to overestimate the concentrations of Al_{M3} , which may result into significant decrease in PSI values.

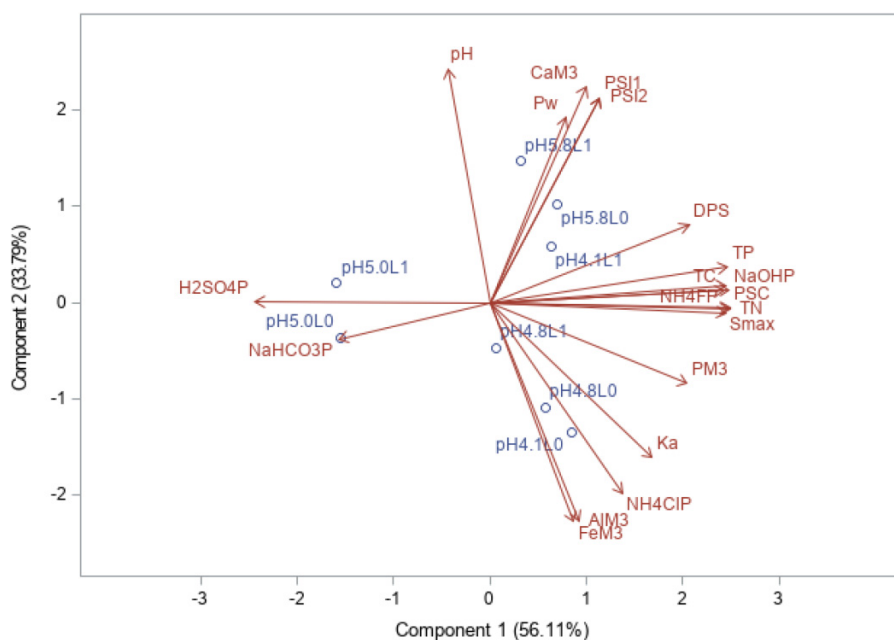
The literature also shows that Al and Fe bound phytates could be dissolved by Mehlich-3 extracting solution particularly at low-pH conditions (Penn et al. 2018). However, we did not find significant changes in total organic P or total P among soils with varying initial soil pH to support the role of phytates in the studied soils (Figs. 7a and 7b). In addition, we did not observe any changes in P sorption characteristics of the soils, which may be ascribed to compounds other than Ca added with lime (Figs. 5a and 5d). At the pH conditions prevailing in our soils, the acidity of Mehlich-3 solution had little effect on Fe because Fe oxides and oxyhydroxide minerals such as goethite and hematite remain partly insoluble.

This is also well demonstrated by the 1:1 regression between PSI_1 and PSI_2 (Fig. 3a) and similar relations between DPS vs. PSI_1 and DPS vs. PSI_2 (Figs. 3b and 3c). Similar observations were made on a range of soils in the Fraser Valley with Fe having minor effect on PSI (Messiga et al. 2021). The minor role of Fe could also be associated with the pedogenesis of the soil as Dystric Brunisols (Canadian System of Soil Classification 1998) or Typic Dystrocherepts (Soil Survey Staff 2010), which are moderately developed with the absence of appreciable quantities of Fe sesquioxides within the solum (Smith et al. 2011). The high concentrations of Al_{M3} and P_{M3} at low initial soil pH are therefore driven by the solubility of Al oxides and oxyhydroxides and further enhanced by the acidity of Mehlich-3 extracting solution (Tran et al. 1990).

Increasing soil pH and changes in agri-environmental indicators

The concentrations of Al_{M3} significantly reduced with addition of $CaCO_3$ (Fig. 4a). Liming can increase OH^- ions that increase precipitation of $Al(OH)_3$ (Haynes 1982; Penn and Camberto 2019). The Ca derived from $CaCO_3$ added to the soil decreased Al_{M3} concentrations, which is consistent with the neutralizing power of CO_3^{2-} towards the acidic component (HNO_3 and CH_3COOH) of Mehlich-3 extraction (Zhang and Kovar 2009). In addition, the added Ca further reacted with fluoride (F^-) used in the Mehlich-3 solution, which likely fixed some phosphates from the solution leading to decreased P_{M3} concentrations in limed soils (Penn et al. 2018). It is interesting to observe that the addition of $CaCO_3$ with its neutralizing power on the acidic component in Mehlich-3 extraction, which decreased Al_{M3} , did not affect the concentrations of Al_{Ox} (Figs. 4a, 4b, 4d, and 4e). This result further supports the more specific reaction of the ammonium oxalate extracting solution on Al and Fe over the range of acidic pH (Van der Zee et al. 1987). One objective of this study was to understand how in soils with initial low pH, the release of phosphate ions previously retained onto Al oxides and oxyhydroxides surfaces into the soil solution would change upon increase in soil pH induced by addition of lime. We had expected that decreased Al_{M3} upon liming would result in high P_{M3} and P_w concentrations and thus increased PSI values and risk of P losses by runoff. Our results showed that PSI values did not significantly change with increased soil pH from low to near-neutral following applications of $CaCO_3$. Therefore, the decreased concentrations of Al_{M3} were not translated into increased PSI values and then potential risk of P losses (Figs. 1e and 1f). The lack of PSI change observed in our study could be primarily due to re-association of P with Ca added with $CaCO_3$ (Fig. 4c). The increase in the concentration of Ca_{M3} with addition of $CaCO_3$ was described by a power regression indicating a more than proportional increase of Ca_{M3} with increasing soil pH (Fig. 4c). The P sorption data showed that the effect of Ca was influenced by the initial soil pH and thus the LR or amount of $CaCO_3$ needed to reach the target pH. We found that the addition of $CaCO_3$ affected the sorption characteristics of soils at initial pH values of 4.1 and 5.8 (Figs. 5a and 5d) but not at initial pH values of 4.8 and 5.5 (Figs. 5b and 5c). A comparison of the parameters of the Langmuir equations describing the sorption data of the soils at the respective ini-

Fig. 8. Correlations between water-extractable P and Mehlich-3 P agri-environmental indicators and chemical soil properties as tested by principal component analysis (PCA): pH treatment (combinations of pH and lime), pH, TC (total C, %), TP (total phosphorus, mg kg⁻¹), TN (total nitrogen, %), P_w (water-extractable phosphorus, mg kg⁻¹), P_{M3} (Mehlich-3 extractable phosphorus, mg kg⁻¹), DPS (degree of phosphorus saturation, %), PSC (phosphorus sorption capacity, mmol kg⁻¹), Al_{M3} (Mehlich-3 extractable aluminum, mg kg⁻¹), Fe_{M3} (iron-extractable aluminum, mg kg⁻¹), PSI₁ (phosphorus saturation index, ((P/Al)_{Mehlich-3}) %), PSI₂ (phosphorus saturation index, ((P/(Al + Fe))_{Mehlich-3}) %), Ca_{M3} (Mehlich-3 extractable calcium, mg kg⁻¹), NH₄Cl-P (ammonium chloride-extractable phosphorus, mg kg⁻¹), NH₄F-P (ammonium fluoride-extractable phosphorus, mg kg⁻¹), NaOH-P (sodium hydroxide-extractable phosphorus, mg kg⁻¹), NaHCO₃-P (sodium bicarbonate-extractable phosphorus, mg kg⁻¹), H₂SO₄-P (acid-extractable phosphorus, mg kg⁻¹); S_{max} (phosphorus sorption maximum, mg P kg⁻¹); K_a (binding energy of phosphorus, L mg P⁻¹) after 93 days of incubation.



tial pH upon addition of CaCO₃ showed that S_{max} and k_a values were only influenced at initial pH values of 4.1 and 5.8 (Figs. 5a and 5d).

Indeed, the S_{max} and k_a values decreased for initial pH 4.1 and increased for initial pH 5.8 upon addition of CaCO₃. The low S_{max} and K_a values obtained with addition of CaCO₃ at initial pH 4.1 shows that the reduction of Al sorption sites was not compensated by the activity of added Ca. Finally, we would also argue that the decreased concentrations of P_w after changing the initial soil pH from 4.1 to 6 are due to the amount of Ca added to the soil with CaCO₃ to reach the target pH (Fig. 4c). Indeed, less Ca was added to the soil with initial soil pH = 4.8 and 5.5 to reach the target soil pH = 6. Our results are in line with previous works on Mehlich-3 extractions and the declining Al_{M3} concentrations reported with increased soil pH (Penn et al. 2018; Messiga et al. 2021). Another important aspect of our study is the high concentration of P_w at initial soil pH 5.8 despite similar total organic and total P across the range of soils (Figs. 1a, 7a, and 7b). This is an indication of the inhibition activity of Al oxides and oxyhydroxides at high pH (Penn et al. 2018).

Increased soil pH and phosphorus fractionation

The use of NH₄Cl solution (Chang and Jackson 1958) could explain the contrast between NH₄Cl-P and concentrations of P_w with increasing initial soil pH (Figs. 1c and 6a). Gianello

and Amorim (2015) showed that NH₄Cl solution performs well at extracting Al and other cations in acidic soils indicating the contribution of some amount of P associated with Al (Figs. 6a and 6b). The decrease in the concentrations of NH₄Cl-P and NH₄F-P with additions of CaCO₃, particularly for soils with initial pH 4.1 (Fig. 5a), is consistent with the trend of P_w concentrations (Fig. 1c). The strong adsorption of F⁻ on soil colloids at pH > 5.5 explains the decrease in NH₄F-P with increasing pH, which would otherwise displace adsorbed P ions into the solution (Chang and Overby 1986). It is worth noting that the decrease in NH₄Cl-P and NaOH-P following addition of CaCO₃ for soils with initial pH 4.1 was translated into increased concentrations of NaHCO₃-P (Fig. 6d). We also found similar trends among the other P fractions and CBD-P in soils with initial pH values of 5.5 and 5.8 (Fig. 6e), although the change was not significant. These results are consistent with the role of Ca in sorption characteristics of the soil upon addition of CaCO₃, particularly S_{max} and k_a values for soils at initial pH values of 4.1 and 5.8 (Figs. 5a and 5d). It is therefore possible that the CBD-P and H₂SO₄-P represent the sink of P accumulation from other fractions upon liming. The behavior of NaOH-P showed less significant variations with addition of CaCO₃, which is consistent with the low solubility of Fe at the initial pH under consideration. This result is consistent with the small variation of Fe_{M3} and Fe_{ox} with soil pH (Figs. 4b and 4e).

Table 3. Pearson’s correlation matrix.

	pH	TC	TP	TN	P_w	P_{M3}	DPS	PSC	Al_{M3}	Fe_{M3}	PSI_1	PSI_2	Ca_{M3}	$NH_4Cl\text{-}P$	$NH_4F\text{-}P$	$NaOH\text{-}P$	$CBD\text{-}P$	$H_2SO_4\text{-}P$	S_{max}	K_a	
pH	1.000																				
TC	-0.107	1.000																			
TP	0.009	0.888	1.000																		
TN	-0.169	0.837	0.856	1.000																	
P_w	0.434	0.085	0.296	-0.057	1.000																
P_{M3}	-0.666	0.508	0.483	0.747	-0.114	1.000															
DPS	-0.093	0.425	0.654	0.649	0.499	0.668	1.000														
PSC	-0.184	0.981	0.936	0.898	0.097	0.613	0.537	1.000													
Al_{M3}	-0.869	0.278	0.128	0.154	-0.410	0.447	-0.151	0.319	1.000												
Fe_{M3}	-0.908	0.168	0.053	0.380	-0.624	0.756	0.089	0.258	0.776	1.000											
PSI_1	0.192	0.114	0.273	0.395	0.496	0.452	0.834	NA	NA	NA	NA										
PSI_2	0.166	0.122	0.279	0.402	0.496	0.473	0.843	NA	NA	NA	NA	NA									
Ca_{M3}	0.669	0.314	0.412	0.518	0.118	0.012	0.371	0.301	-0.724	-0.392	0.547	0.528	1.000								
$NH_4Cl\text{-}P$	-0.945	0.271	0.173	0.314	-0.252	0.770	0.320	0.345	0.768	0.826	0.007	0.034	-0.538	NA							
$NH_4F\text{-}P$	-0.141	0.764	0.690	0.413	0.484	0.304	0.413	0.731	0.293	-0.061	0.082	0.096	-0.089	NA	NA						
$NaOH\text{-}P$	-0.321	0.858	0.868	0.836	0.220	0.735	0.753	0.910	0.303	0.303	0.409	0.424	0.196	NA	NA	NA					
$CBD\text{-}P$	0.069	-0.387	-0.475	-0.170	-0.164	0.029	-0.170	-0.383	-0.194	0.102	0.220	0.217	0.080	NA	NA	NA	NA				
$H_2SO_4\text{-}P$	0.329	-0.857	-0.709	-0.879	0.212	-0.715	-0.322	-0.875	-0.433	-0.527	-0.070	-0.082	-0.243	NA	NA	NA	NA	NA			
S_{max}	-0.413	0.900	0.781	0.868	-0.174	0.717	0.425	0.919	0.472	0.505	0.071	0.084	0.173	0.567	0.640	0.810	-0.429	-0.920	1.000		
k_a	-0.675	0.559	0.339	0.623	-0.563	0.729	0.155	0.575	0.599	0.789	-0.077	-0.063	-0.063	0.745	0.294	.495	-0.256	-0.771	0.842	1.000	

Note: TC, total carbon; TP, total phosphorus; TN, total nitrogen; P_w , water-extractable phosphorus; P_{M3} , Mehlich-3 extractable phosphorus; DPS, degree of phosphorus saturation; PSC, phosphorus saturation capacity; Al_{M3} , Mehlich-3 extractable aluminum; Fe_{M3} , Mehlich-3 extractable iron; PSI_1 , phosphorus saturation index using aluminum alone; PSI_2 , phosphorus saturation index using aluminum and iron; Ca_{M3} , Mehlich-3 extractable calcium; $NH_4Cl\text{-}P$, ammonium chloride-extracted phosphorus; $NH_4F\text{-}P$, ammonium fluoride-extractable phosphorus; $NaOH\text{-}P$, hydroxide-extractable phosphorus; $CBD\text{-}P$, bicarbonate-extractable phosphorus; $H_2SO_4\text{-}P$, acid-extractable phosphorus; S_{max} , phosphorus sorption maximum; K_a , binding energy of P; NA, not applicable.

Relationship between P and agri-environmental indicators, chemical soil properties, and P fractions

From the PCA results, soil pH was inversely related to Al_{M3} , Fe_{M3} , and NH_4Cl-P (Fig. 8). The decrease in Al_{M3} and Fe_{M3} with increasing soil pH has several consequences, including an increase in the concentration of P_w and PSI_1 and PSI_2 . However, the close relationship between P_w and Ca_{M3} indicates that phosphate ions released by Al and Fe oxides and oxyhydroxides with increased soil pH were later re-associated with Ca. In the conditions of our study, it is difficult to state whether CBD-P and H_2SO_4-P represent transient fractions of higher solubility that would buffer the solution P following uptake by plants or transport with runoff or leaching. To the best of our knowledge, the solubility of H_2SO_4-P at target pH selected for this study is high compared with that of NH_4F-P and $NaOH-P$ (Barrow 2017). It is well known that the availability of P to plants in acidic soils increases with liming of soil (Penn and Camberato 2019). The present study shows that coprecipitation of phosphate anions with Ca^{2+} can temporarily buffer this pH-induced increase in P availability. It would be interesting to understand how other liming materials such as dolomitic lime or $MgCO_3$ with less affinity with phosphate would affect the concentration of P_w and PSI values upon changes in soil pH.

Conclusions

At the end of the incubation experiment, soil pH was successfully raised to the target values with addition of $CaCO_3$. We observed decreasing trends of P_{M3} and P_w concentrations with additions of $CaCO_3$, but the extent was only significant for P_w in soils with initial pH = 5.8 probably because extra lime was added and final soil pH reached 6.5. These results highlight the effects of pH on PSI indicators and are supported by high concentrations of Al_{M3} in the range of 3000 mg kg^{-1} at soil pH = 4.1 and 4.8. The concentrations of Al_{M3} and Fe_{M3} at all initial soil pH decreased when soil pH was increased to the target values, but the effect on P_w was not significant. Our relationship analysis highlighted a close link between P_w and Ca_{M3} , as well as opposite relationships of H_2SO_4-P and $NaHCO_3-P$ vs. NH_4F-P and $NaOH-P$ fractions. These relationships also indicate that the decreasing trend of P_w concentrations could be due to the association of phosphate ions with Ca^{2+} added by the liming, acting as a sink for P released by NH_4F-P and $NaOH-P$ fractions. The double role of liming through the increasing pH and Ca^{2+} concentration in soils should certainly deserve joint investigation when studying liming effects on P-related agri-environmental indicators.

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