

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

Authors: Nyamaizi, Sylvia, Messiga, Aimé J., Cornelis, Jean-Thomas, and Smukler, Sean M.

Source: Canadian Journal of Soil Science, 102(4) : 929-945

Published By: Canadian Science Publishing

URL: <https://doi.org/10.1139/cjss-2021-0197>

---

BioOne Complete ([complete.BioOne.org](https://complete.BioOne.org)) is a full-text database of 200 subscribed and open-access titles in the biological, ecological, and environmental sciences published by nonprofit societies, associations, museums, institutions, and presses.

Your use of this PDF, the BioOne Complete website, and all posted and associated content indicates your acceptance of BioOne's Terms of Use, available at [www.bioone.org/terms-of-use](https://www.bioone.org/terms-of-use).

Usage of BioOne Complete content is strictly limited to personal, educational, and non - commercial use. Commercial inquiries or rights and permissions requests should be directed to the individual publisher as copyright holder.

---

BioOne sees sustainable scholarly publishing as an inherently collaborative enterprise connecting authors, nonprofit publishers, academic institutions, research libraries, and research funders in the common goal of maximizing access to critical research.

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

Sylvia Nyamaizi<sup>a,b</sup>, Aimé J. Messiga<sup>a</sup>, Jean-Thomas Cornelis<sup>b</sup>, and Sean M. Smukler<sup>b</sup>

<sup>a</sup>Agassiz Research and Development Centre, Agriculture and Agri-Food Canada, 6947 Highway 7, PO Box 1000, Agassiz, BC V0M 1A0, Canada; <sup>b</sup>Faculty of Land and Food Systems, The University of British Columbia, 123-2357, Main Hall, Vancouver, BC V6T 1Z4, Canada

Corresponding author: Aimé J. Messiga (email: [aime.messiga@agr.gc.ca](mailto:aime.messiga@agr.gc.ca))

## 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  $\text{CaCO}_3$  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<sup>-1</sup>, in line with critical DPS > 25%, but decreased to 2.74 mg kg<sup>-1</sup> with  $\text{CaCO}_3$  addition. In contrast, soils with initial pH < 5.5 had lower  $P_w$  concentrations and  $\text{CaCO}_3$  did not significantly decrease  $P_w$  at the end of the incubation averaging 1.02, 1.11, and 1.43 mg kg<sup>-1</sup> 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) ( $\text{Al}_{M3}$  > 2500 mg kg<sup>-1</sup>) 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  $\text{CaCO}_3$  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  $\text{CaCO}_3$  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  $\text{CaCO}_3$  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 ( $\text{Al}_{M3}$  > 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 ne 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 <sub>(H2O)</sub>	Treatments, <sup>a</sup> %	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

<sup>a</sup>Soil 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 (CaCO<sub>3</sub>) 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  $\mu\text{S cm}^{-1}$ ; total organic carbon, 1.97%–3.74%; total N, 0.15–0.22;  $P_{M3}$ , 163–200  $\text{mg kg}^{-1}$ ; Mehlich-3 extractable Al ( $\text{Al}_{M3}$ ), 2126–3218  $\text{mg kg}^{-1}$ ; and Fe ( $\text{Fe}_{M3}$ ), 166–210  $\text{mg kg}^{-1}$ .

### 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,  $P_{M3}$ ,  $\text{Al}_{M3}$ ,  $\text{Fe}_{M3}$ , and other Mehlich-3 extractable cations including Ca ( $\text{Ca}_{M3}$ ), and Mg ( $\text{Mg}_{M3}$ ). 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)  $\times$  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 CaCO<sub>3</sub> equivalent ratio to moles of the H<sup>+</sup> 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  $\text{CaCO}_3$  (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 (Conviron 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  $\text{CaCO}_3$  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<sup>-1</sup> 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<sup>-1</sup>). The sum of  $Al_{Ox}$  and  $Fe_{Ox}$  is termed as PSC (mmol kg<sup>-1</sup>). The term  $\alpha_m$  is the maximum sorption coefficient (Breeuwsma and Silva 1992). We used

an average  $\alpha_m$  value of 0.5 to calculate DPS (Benjannet et al. 2018).

The P saturation index was calculated using two variations,  $PSI_1$  and  $PSI_2$ , 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<sup>-1</sup>).

## 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<sup>-1</sup> as  $\text{KH}_2\text{PO}_4$ . 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<sup>-1</sup> 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<sup>-1</sup>  $\text{NH}_4\text{Cl}$  ( $\text{NH}_4\text{Cl-P}$ ), 0.5 mol L<sup>-1</sup>  $\text{NH}_4\text{F}$  ( $\text{NH}_4\text{F-P}$ ), 0.1 mol L<sup>-1</sup>  $\text{NaOH}$  ( $\text{NaOH-P}$ ), a mixture of 0.3 mol L<sup>-1</sup> sodium citrate dihydrate,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$  + 1 mol L<sup>-1</sup>  $\text{NaHCO}_3$  for reductant-soluble P (CBD-P), and 0.25 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$  ( $\text{H}_2\text{SO}_4\text{-P}$ ) 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<sup>-1</sup>) is the sorbed P onto the soil after 24 h contact,  $S_{\max}$  (mg P kg<sup>-1</sup>) is the P sorption maximum,  $k_a$

(L mg P<sup>-1</sup>) is the binding energy of P, and C (mg P L<sup>-1</sup>) 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 R<sup>2</sup> 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  $S_{\text{max}}$  (not  $k_a$  because of autocorrelations) 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  $\text{rSS}_1$  and  $\text{rSS}_2$  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,  $P_{\text{M}_3}$ ,  $P_w$ , DPS, PSI<sub>1</sub>, and PSI<sub>2</sub> using NLIN procedure of SAS. The fit of the regression curves was evaluated using  $R^2$  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 CaCO<sub>3</sub> (Fig. 1a). The initial soil pH value did not change after 93 days

of incubation. (Fig. 1a). The concentrations of  $P_{\text{M}_3}$  ranged from 146 to 200 mg kg<sup>-1</sup> and were not significantly changed by liming (Fig. 1b). The concentrations of  $P_w$  ranged from 1.0 to 3.65 mg kg<sup>-1</sup> and were significantly affected by additions of lime only for soils with initial pH of 5.8 (Fig. 1c). The DPS, PSI<sub>1</sub>, and PSI<sub>2</sub> 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 PSI<sub>1</sub> values were 6.0%, 5.2%, 5.6%, and 6.1%, respectively (Fig. 1e). On average, the PSI<sub>2</sub> 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  $\leq 5.5$ , the concentrations of  $P_w$  were related to agri-environmental indicators,  $P_{\text{M}_3}$ , DPS, PSI<sub>1</sub>, PSI<sub>2</sub>, PSC, and Ca<sub>M3</sub>, by quadratic regressions (Figs. 2a–2f). The slopes of the quadratic regressions were positive for  $P_{\text{M}_3}$  (Fig. 2a), DPS (Fig. 2b), and PSC (Fig. 2e), but negative for PSI<sub>1</sub> (Fig. 2c), PSI<sub>2</sub> (Fig. 2d), and Ca<sub>M3</sub> (Fig. 2f). In addition, the  $R^2$  of the regressions were 0.25 for  $P_{\text{M}_3}$ , 0.49 for DPS, 0.22 for PSI<sub>1</sub>, 0.23 for PSI<sub>2</sub>, 0.23 for PSC, and 0.58 for Ca<sub>M3</sub>. In contrast, at initial pH = 5.8, there was no trend in the distribution pattern of the concentrations of  $P_w$  with  $P_{\text{M}_3}$ , DPS, PSI<sub>1</sub>, PSI<sub>2</sub>, 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<sub>M3</sub> following additions of lime (Fig. 2f).

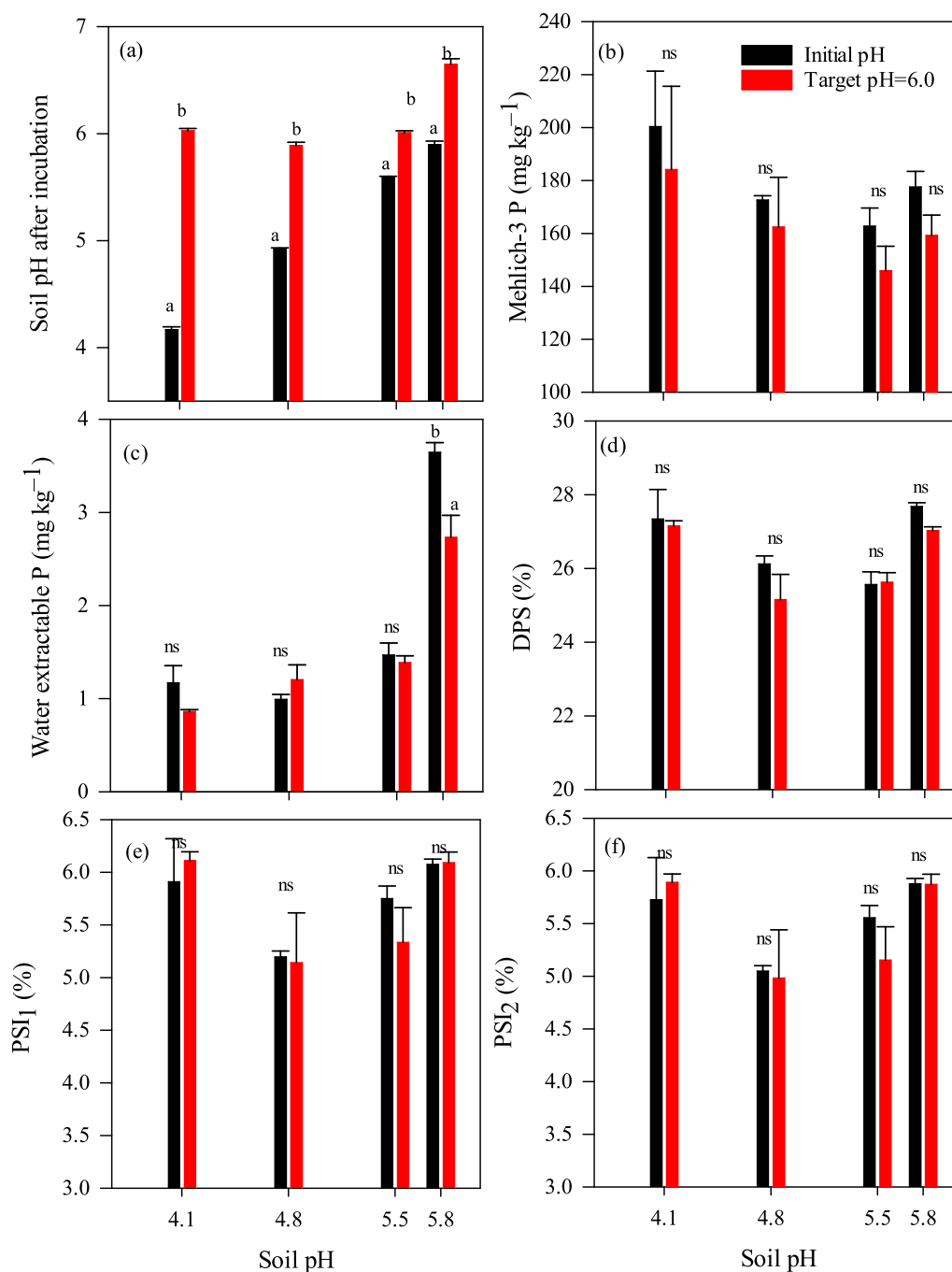
A further examination showed that the relationships among agri-environmental indicators were described by linear regressions (Figs. 3a–3d). The linear regression between PSI<sub>1</sub> and PSI<sub>2</sub> was characterized by a positive slope = 0.96 and  $R^2 = 0.99$  and was not affected by liming (Fig. 3a). Similarly, the relationships between DPS and PSI<sub>1</sub>, PSI<sub>2</sub>, and  $P_{\text{M}_3}$  were not affected by liming and were described by linear regressions with positive slopes = 0.39 and  $R^2 = 0.52$  for DPS vs. PSI<sub>1</sub> (Fig. 3b), positive slopes = 0.38 and  $R^2 = 0.53$  for DPS vs. PSI<sub>2</sub> (Fig. 3c), and positive slopes = 20.5 and  $R^2 = 0.45$  for DPS vs.  $P_{\text{M}_3}$  (Fig. 3d).

### Liming effects on concentrations of aluminum, iron, and calcium

There was a decreasing trend of the concentrations of Al<sub>M3</sub> and Fe<sub>M3</sub> in soils with increasing soil pH. The addition of CaCO<sub>3</sub> further decreased the concentrations of Al<sub>M3</sub> and Fe<sub>M3</sub> 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<sub>M3</sub> and Fe<sub>M3</sub> vs. soil pH were not affected by the addition of CaCO<sub>3</sub> and were described by linear regressions with negative slope = -329.61 and  $R^2 = 0.62$  for Al<sub>M3</sub> (Fig. 4a), and negative slope = -8.06 and  $R^2 = 0.33$  for Fe<sub>M3</sub> (Fig. 4b).

In contrast, there was an increasing trend of the concentrations of Ca<sub>M3</sub> 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).

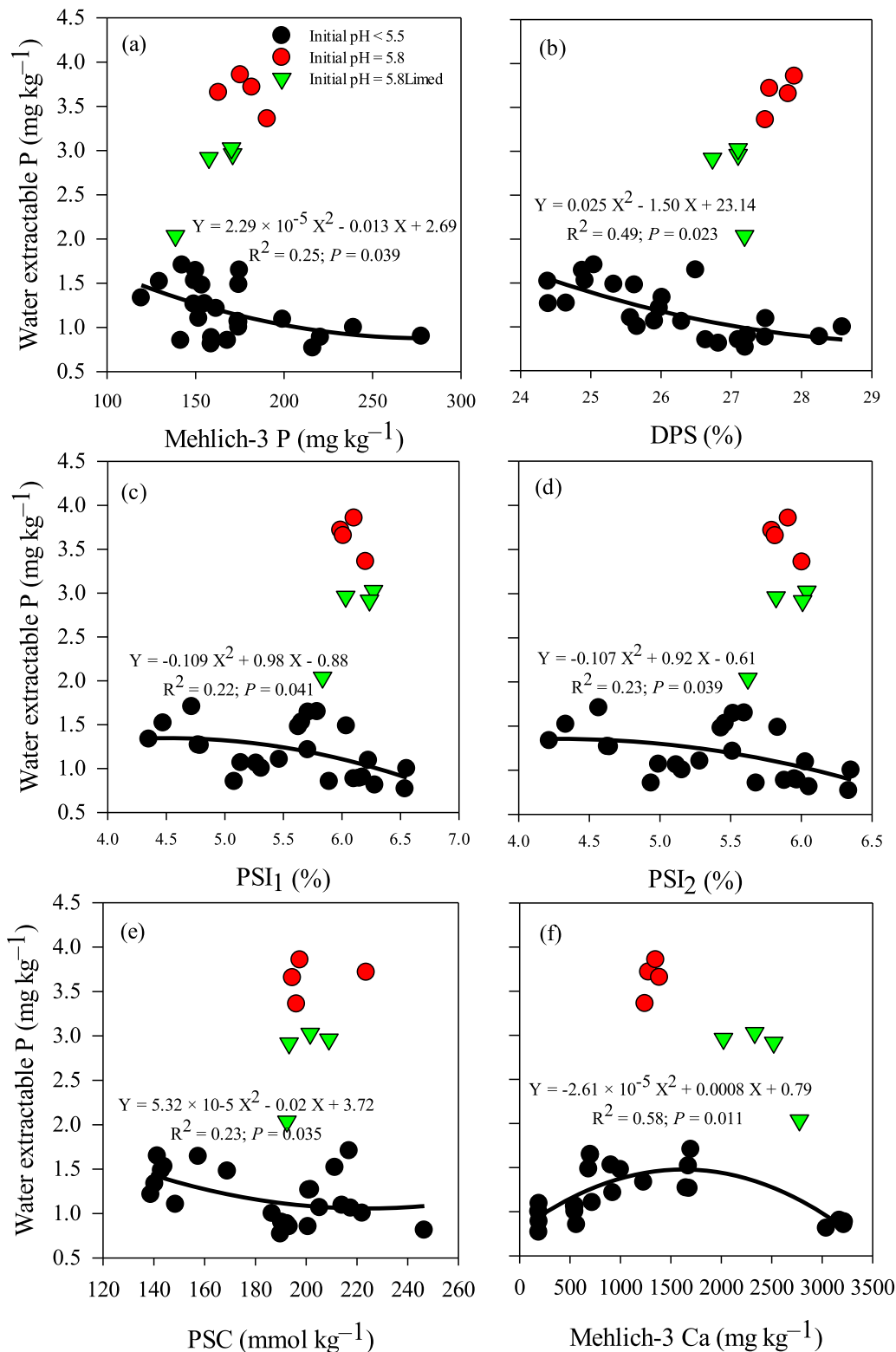
There was no specific trend in the concentrations of  $Al_{Ox}$  and  $Fe_{Ox}$  with initial soil pH as observed with  $Al_{M3}$  and  $Fe_{M3}$ . On average, the concentrations of  $Al_{Ox}$  were 321, 332, 237, and 320 mmol kg<sup>-1</sup> for initial soil pH values of 4.1, 4.8, 5.5,

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<sup>-1</sup> 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).

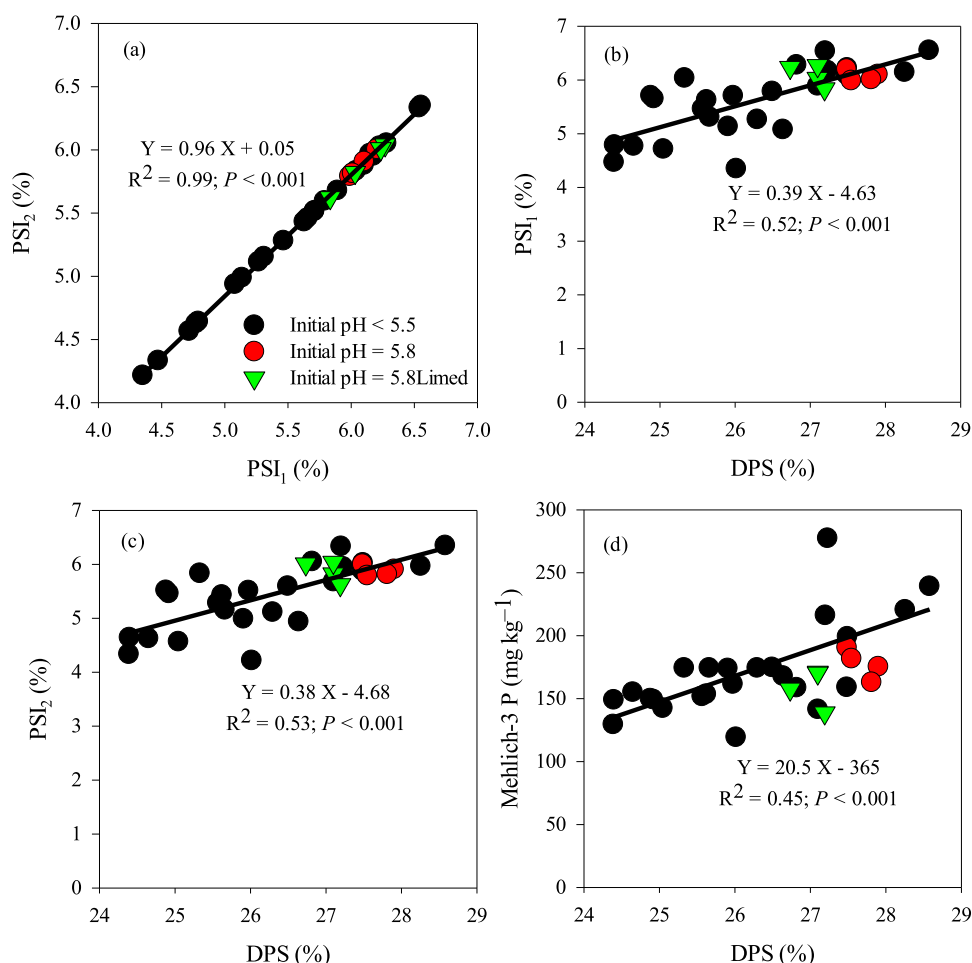
### Liming effects on phosphorus sorption characteristics

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<sup>-1</sup> without lime but significantly decreased to 1243 mg P kg<sup>-1</sup> after liming (Table 2; Fig. 5d). For soils with initial pH 5.8, the  $S_{max}$  value was 1093 mg P kg<sup>-1</sup> without lime but significantly increased to 1114 mg P kg<sup>-1</sup> after liming (Table 2; Fig. 5d).

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

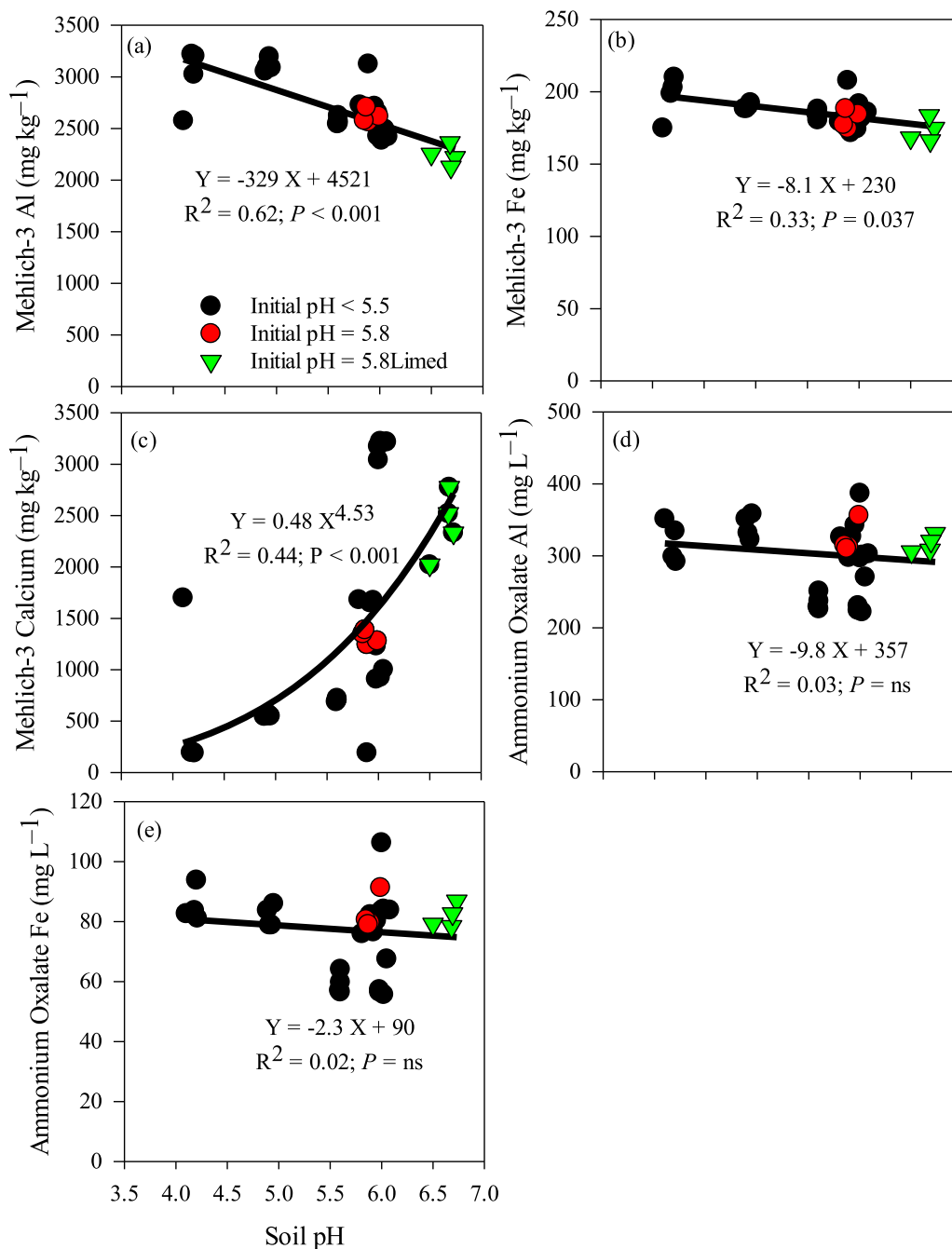
### Liming effects on phosphorus fractions, organic P, and total P

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<sup>-1</sup> (Fig. 6b). The concentrations of  $NaOH$ -P significantly decreased with addition of  $CaCO_3$ , from 324 to 247 mg kg<sup>-1</sup>, 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<sup>-1</sup>, at initial soil pH = 4.1, and significantly decreased with addition of  $CaCO_3$ , from 364 to 21 mg kg<sup>-1</sup> and from 103 to 23 mg kg<sup>-1</sup>, 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<sup>-1</sup> (Fig. 7a), while total P concentrations were 1181–1492 mg kg<sup>-1</sup> (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.]

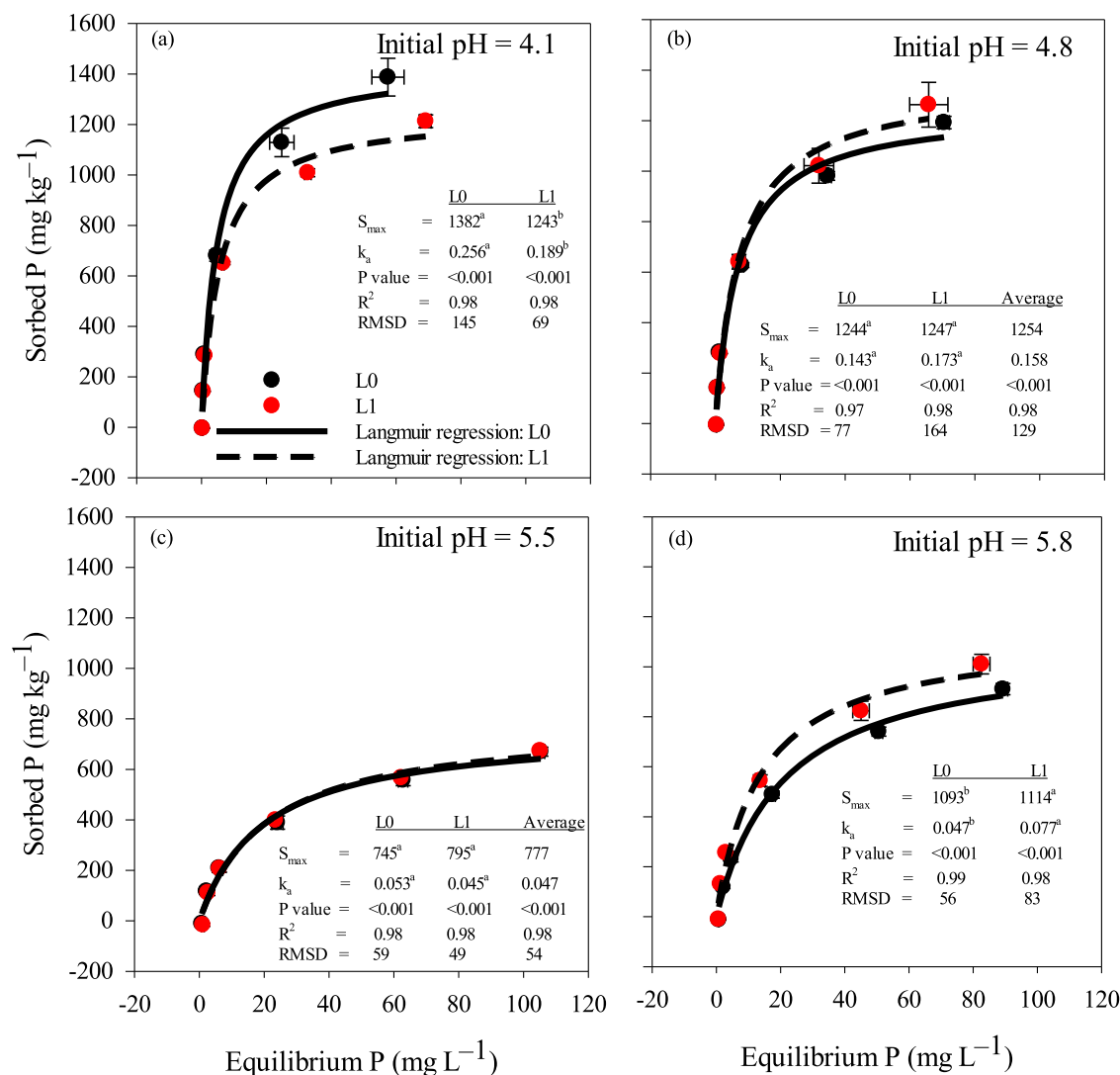


### Relationships between $P_w$ , Mehlich-3 P, agri-environmental indicators, inorganic P fractions, and chemical soil properties

The PCA showed that  $P_w$  was highly correlated to  $\text{PSI}_1$ ,  $\text{PSI}_2$ , and  $\text{Ca}_{\text{M3}}$ , whereas  $\text{P}_{\text{M3}}$ ,  $\text{Al}_{\text{M3}}$ ,  $\text{Fe}_{\text{M3}}$  inorganic P fractions and chemical soil properties were highly correlated following the addition of  $\text{CaCO}_3$  (Fig. 8). The eight combinations of initial soil pH  $\times$  addition of  $\text{CaCO}_3$  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  $\text{NH}_4\text{Cl-P}$ ,  $\text{Al}_{\text{M3}}$ ,  $\text{Fe}_{\text{M3}}$ , and  $k_a$ , but negatively affected  $P_w$ ,  $\text{PSI}_1$ ,  $\text{PSI}_2$ , and  $\text{Ca}_{\text{M3}}$ ; Group III positively affected  $\text{H}_2\text{SO}_4\text{-P}$  and  $\text{NaHCO}_3\text{-P}$ , but negatively affected DPS,  $\text{Al-P}$ ,  $\text{Fe-P}$ ,  $\text{PSC}$ ,  $S_{\text{max}}$ , and  $\text{P}_{\text{M3}}$ ; Group IV positively affected  $P_w$ ,  $\text{PSI}_1$  and  $\text{PSI}_2$ ,  $\text{Ca}_{\text{M3}}$ , and pH. Pearson's correlation among  $P_w$ ,  $\text{P}_{\text{M3}}$ , agri-environmental indicators ( $\text{PSI}_1$ ,  $\text{PSI}_2$ , and DPS), inorganic P fractions ( $\text{NH}_4\text{Cl-P}$ ,  $\text{NH}_4\text{F-P}$ ,  $\text{NaOH-P}$ ,  $\text{NaHCO}_3\text{-P}$ , and  $\text{H}_2\text{SO}_4\text{-P}$ ), and chemical soil properties ( $\text{Al}_{\text{M3}}$ ,  $\text{Fe}_{\text{M3}}$ ,  $\text{Ca}_{\text{M3}}$ ,  $\text{PSC}$ ,  $k_a$ , and  $S_{\text{max}}$ ) 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<sup>-1</sup>) 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<sup>-1</sup> (Fig. 1c), which is close to critical concentration values set at 4.0 mg kg<sup>-1</sup> across different agro-ecosystems in BC (van Bochove et al. 2012) and 3.7 mg kg<sup>-1</sup> 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 <sup>d</sup>
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

<sup>a</sup>Number of observations.

<sup>b</sup>Residual sum of squares.

<sup>c</sup>Total sum of squares.

<sup>d</sup>Not significant ( $P > 0.05$ ).

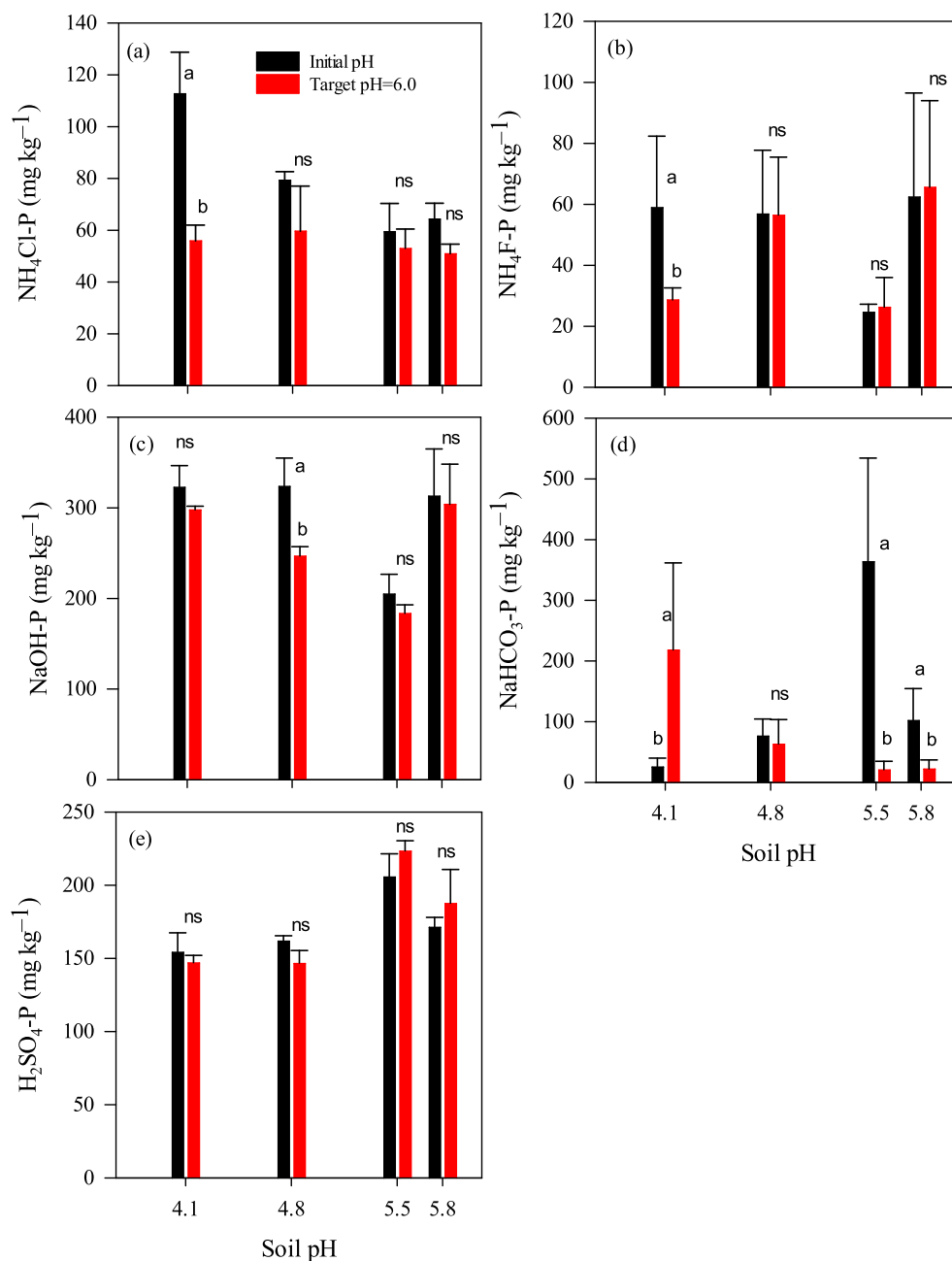
runoff. The soils with initial soil pH values of 4.1, 4.8, and 5.5 received ammonium sulfate at different rates, which resulted in the decreased soil pH and reduced changes in  $P_w$  concentration patterns compared with soils with initial pH 5.8 (Messiga et al. 2018). The significant decline with liming 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<sup>-1</sup>) and  $DPS > 25\%$  (Figs. 1b and 1d), were in line with low  $P_w$  concentrations associated with soils at initial pH  $\leq 5.5$  (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  $\leq 5.5$  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<sup>-1</sup> in soils with initial pH values of 4.1 and 4.8 compared with 2594 mg kg<sup>-1</sup> 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  $\leq 5.5$  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

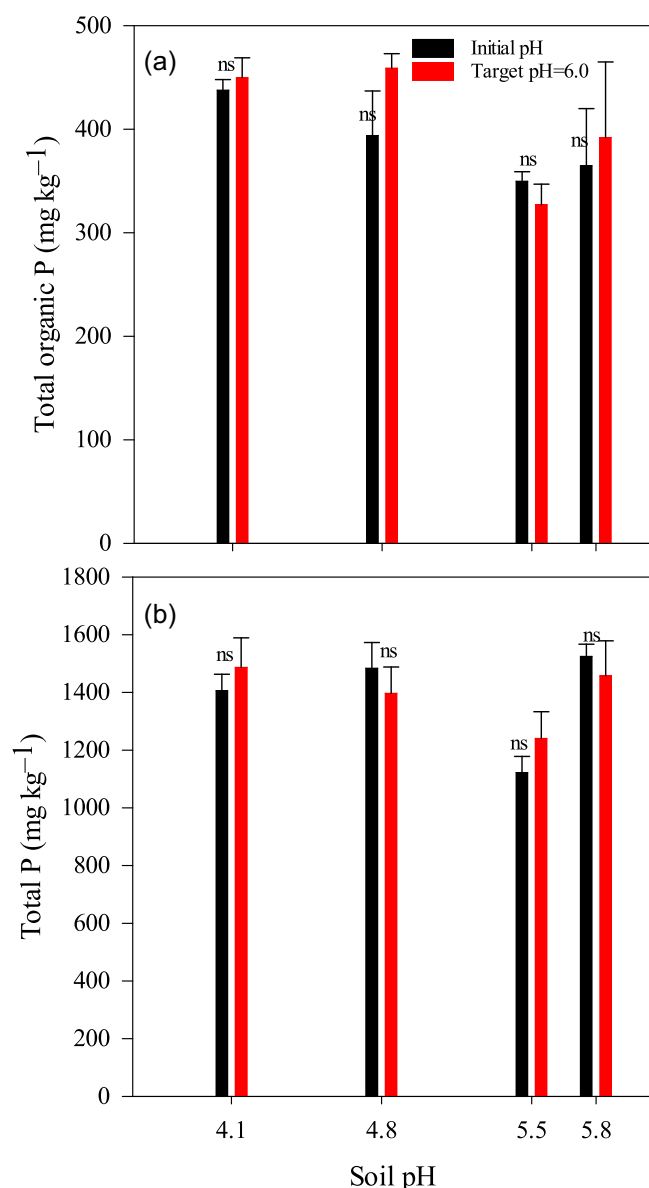
**Fig. 6.** Effects of liming with calcium carbonate and 93 days of incubation on changes in molybdate-reactive P pools determined by sequential fractionation. (a) Ammonium chloride-extractable P ( $\text{NH}_4\text{Cl-P}$ ), (b) ammonium fluoride-extractable P ( $\text{NH}_4\text{F-P}$ ), (c) sodium hydroxide-extractable phosphorus ( $\text{NaOH-P}$ ), (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  $\text{Al}_{\text{M3}}$  (Penn et al. 2018). The affinity of  $\text{F}^-$  with Al further increases the concentration of  $\text{Al}_{\text{M3}}$  by complexing additional Al oxides and oxyhydroxides resulting into the formation of  $\text{AlF}_3$  that is detected upon analysis of the Mehlich-3 extract by ICP (Mehlich 1984). These increased concentrations of  $\text{Al}_{\text{M3}}$  associated with low soil pH and Mehlich-3 solution decrease the values of  $\text{PSI}_1$  and  $\text{PSI}_2$  (Figs. 1e and 1f) relative to  $P_{\text{M3}}$  and DPS values (Figs. 1b and 1d; Figs. 3b–3d).

The concentrations of  $\text{Al}_{\text{Ox}}$  did not vary with initial soil pH (Fig. 4d) compared with  $\text{Al}_{\text{M3}}$ , 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.

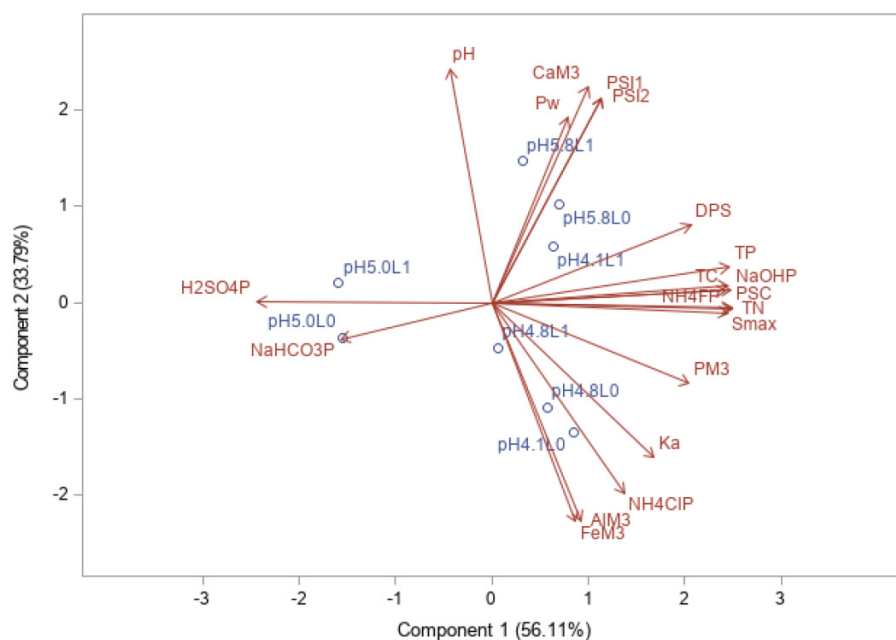
The literature also shows that Al and Fe bound phytates could be dissolved by Mehlich-3 extracting solution particularly at low-pH conditions (Penn et al. 2018). However, we did not find significant changes in total organic P or total P among soils with varying initial soil pH to support the role of 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 Dystroxerepts (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<sup>-1</sup>), TN (total nitrogen, %),  $P_w$  (water-extractable phosphorus, mg kg<sup>-1</sup>),  $P_{M3}$  (Mehlich-3 extractable phosphorus, mg kg<sup>-1</sup>), DPS (degree of phosphorus saturation, %), PSC (phosphorus sorption capacity, mmol kg<sup>-1</sup>),  $Al_{M3}$  (Mehlich-3 extractable aluminum, mg kg<sup>-1</sup>),  $Fe_{M3}$  (iron-extractable aluminum, mg kg<sup>-1</sup>),  $PSI_1$  (phosphorus saturation index,  $((P/(Al + Fe))_{Mehlich-3})$  %),  $PSI_2$  (phosphorus saturation index,  $((P/(Al + Fe))_{Mehlich-3})$  %),  $Ca_{M3}$  (Mehlich-3 extractable calcium, mg kg<sup>-1</sup>),  $NH_4Cl-P$  (ammonium chloride-extractable phosphorus, mg kg<sup>-1</sup>),  $NaOH-P$  (sodium hydroxide-extractable phosphorus, mg kg<sup>-1</sup>),  $NaHCO_3-P$  (sodium bicarbonate-extractable phosphorus, mg kg<sup>-1</sup>),  $H_2SO_4-P$  (acid-extractable phosphorus, mg kg<sup>-1</sup>);  $S_{max}$  (phosphorus sorption maximum, mg P kg<sup>-1</sup>);  $K_a$  (binding energy of phosphorus, L mg P<sup>-1</sup>) after 93 days of incubation.



tial pH upon addition of  $CaCO_3$  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  $CaCO_3$ . The low  $S_{max}$  and  $k_a$  values obtained with addition of  $CaCO_3$  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  $CaCO_3$  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  $NH_4Cl$  solution (Chang and Jackson 1958) could explain the contrast between  $NH_4Cl-P$  and concentrations of  $P_w$  with increasing initial soil pH (Figs. 1c and 6a). Gianello

and Amorim (2015) showed that  $NH_4Cl$  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  $NH_4Cl-P$  and  $NH_4F-P$  with additions of  $CaCO_3$ , 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  $NH_4F-P$  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  $NH_4Cl-P$  and  $NaOH-P$  following addition of  $CaCO_3$  for soils with initial pH 4.1 was translated into increased concentrations of  $NaHCO_3-P$  (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  $CaCO_3$ , 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  $H_2SO_4-P$  represent the sink of P accumulation from other fractions upon liming. The behavior of  $NaOH-P$  showed less significant variations with addition of  $CaCO_3$ , 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 <sub>w</sub>	P <sub>M3</sub>	DPS	PSC	Al <sub>M3</sub>	Fe <sub>M3</sub>	PSI <sub>1</sub>	PSI <sub>2</sub>	Ca <sub>M3</sub>	NH <sub>4</sub> Cl-P	NH <sub>4</sub> F-P	NaOH-P	CBD-P	H <sub>2</sub> SO <sub>4</sub> -P	S <sub>max</sub>	K <sub>a</sub>
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 <sub>w</sub>	0.434	0.085	0.296	−0.057	1.000															
P <sub>M3</sub>	−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 <sub>M3</sub>	−0.869	0.278	0.128	0.154	−0.410	0.447	−0.151	0.319	1.000											
Fe <sub>M3</sub>	−0.908	0.168	0.053	0.380	−0.624	0.756	0.089	0.258	0.776	1.000										
PSI <sub>1</sub>	0.192	0.114	0.273	0.395	0.496	0.452	0.834	NA	NA	NA	NA									
PSI <sub>2</sub>	0.166	0.122	0.279	0.402	0.496	0.473	0.843	NA	NA	NA	NA	NA								
Ca <sub>M3</sub>	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 <sub>4</sub> Cl-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 <sub>4</sub> F-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-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-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 <sub>2</sub> SO <sub>4</sub> -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 <sub>max</sub>	−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 <sub>a</sub>	−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<sub>w</sub>, water-extractable phosphorus; P<sub>M3</sub>, Mehlich-3 extractable phosphorus; DPS, degree of phosphorus saturation; PSC, phosphorus saturation capacity; Al<sub>M3</sub>, Mehlich-3 extractable aluminum; Fe<sub>M3</sub>, Mehlich-3 extractable iron; PSI<sub>1</sub>, phosphorus saturation index using aluminum alone; PSI<sub>2</sub>, phosphorus saturation index using aluminum and iron; Ca<sub>M3</sub>, Mehlich-3 extractable calcium; NH<sub>4</sub>Cl-P, ammonium chloride-extracted phosphorus; NH<sub>4</sub>F, ammonium fluoride-extractable phosphorus; NaOH-P, hydroxide-extractable phosphorus; CBD-P, bicarbonate-extractable phosphorus; H<sub>2</sub>SO<sub>4</sub>-P, acid-extractable phosphorus; S<sub>max</sub>, phosphorus sorption maximum; K<sub>a</sub>, 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<sup>-1</sup> 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.

## Acknowledgements

AJM thanks Agriculture and Agri-Food Canada for funding this work through an A-Base program (Project ID: J-002266—Solutions for carryover of legacy P in the Fraser Valley and Hullcar Valley). We thank Dr. Barbara Cade-Menun (Swift Current RDC) for her inputs and comments that helped improve the quality of the manuscript. We also thank Jessica Stoeckli

and Dean Babuin from the Agassiz RDC research support unit for their assistance with analyses using ICP.

## Article information

### History dates

Received: 9 December 2021

Accepted: 14 May 2022

Accepted manuscript online: 2 June 2022

Version of record online: 2 November 2022

### Copyright

© 2022 Authors Cornelis and Smukler, and Agriculture and Agri-Food Canada. Copyright remains with Her Majesty the Queen in right of Canada, as represented by the Minister of Agriculture and Agri-Food Canada 2021.

## Author information

### Author contributions

S.N.: Conceptualization, Data curation, Formal analysis, Methodology, Writing – original draft, Writing - review & editing. A.J.M.: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – review & editing. J.-T.C.: Writing – review & editing. S.M.S.: Supervision, Writing – review & editing.

## References

- Barrow, N.J. 2017. Effects of pH on phosphate uptake from the soil. *Plant Soil*, **410**: 401–410. doi:[10.1007/s11104-016-3008-9](https://doi.org/10.1007/s11104-016-3008-9).
- Barrow, N.J., Sen, A., Roy, N., and Debnath, A. 2020. The soil phosphate fractionation fallacy. *Plant Soil*, **459**: 1–11. doi:[10.1007/s11104-020-04476-6](https://doi.org/10.1007/s11104-020-04476-6).
- Benjannet, R., Khiari, L., Nyiraneza, J., Thompson, B., He, J., Geng, X., and Fillmore, S. 2018. Identifying environmental phosphorus risk classes at the scale of Prince Edward Island, Canada. *Can. J. Soil Sci.* **98**(2): 317–329. doi:[10.1139/cjss-2017-0076](https://doi.org/10.1139/cjss-2017-0076).
- Bertrand, R.A., Hughes-Games, G.A., and Nikkel, D. 1991. Soil management handbook for the lower Fraser Valley. Soils and Engineering Branch, Ministry of Agriculture, Abbotsford, British Columbia.
- Breeuwsma, A., and Silva, S. 1992. Phosphorus fertilisation and environmental effects in The Netherlands and the Po region (Italy). Report No. 57. DLO. The Winand Staring Centre, Wageningen, Netherlands.
- British Columbia Agriculture and Food Climate Action Initiative. 2015. Regional Adaptation Strategies series: Fraser Valley. pp. 1–44.
- Chang, R., and Overby, J. 1986. General chemistry. Random House, New York.
- Chang, S.C., and Jackson, M.L. 1958. Soil phosphorus fractions in some representative soils. *J. Soil Sci.* **9**(1): 109–119. doi:[10.1111/j.1365-2389.1958.tb01903.x](https://doi.org/10.1111/j.1365-2389.1958.tb01903.x).
- Chen, S., Cade-Menun, B.J., Bainard, D.L., St-Luce, M., Hu, Y., and Chen, Q. 2021. The influence of long-term N and P fertilisation on soil P forms and cycling in a wheat/fallow cropping systems. *Geoderma*, **404**: 115274. doi:[10.1016/j.geoderma.2021.115274](https://doi.org/10.1016/j.geoderma.2021.115274).
- Franzluebber, A.J., Nazih, N., Stuedmann, J.A., Fuhrmann, J.J., Schomberg, H.H., and Hartel, P.G. 1999. Soil carbon and nitrogen pools under low and high endophyte infected tall fescue. *Ambio*, **63**: 1687–1694.
- Gianello, C., and Amorim, M.B. 2015. Ammonium chloride solution as an alternative laboratory procedure for exchangeable cations in

- Southern Brazilian soils. *Commun. Soil Sci. Plant Anal.* **46**: 94–103. doi:[10.1080/00103624.2014.988580](https://doi.org/10.1080/00103624.2014.988580).
- Guppy, C. 2021. Is soil phosphorus fractionation as valuable as we think? *Plant Soil*, **459**: 19–21. doi:[10.1007/s11104-020-04817-5](https://doi.org/10.1007/s11104-020-04817-5).
- Han, K.N. 2020. Characteristics of precipitation of rare earth elements with various precipitants. *Minerals*, **10**: 178. doi:[10.3390/min10020178](https://doi.org/10.3390/min10020178).
- Haynes, R.J. 1982. Effects of liming on phosphate availability in acid soils. *Plant and Soil* **68**: 3 289–308. doi:[10.1007/BF02197935](https://doi.org/10.1007/BF02197935).
- Hendershot, W.H., Lalonde, H., and Duquette, M. 1993. Ion exchange and exchangeable cations. In *Soil sampling and methods of analysis*. Edited by M.R. Carter and E.G. Gregorich. Lewis Publishers, Boca Raton, FL. pp. 183–205.
- Hinsinger, P. 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant Soil*, **237**: 173–195. doi:[10.1023/A:1013351617532](https://doi.org/10.1023/A:1013351617532).
- Ige, D.V., Akinremi, O.O., and Flaten, D.N. 2005. Environmental index for estimating the risk of phosphorus loss in calcareous soils of Manitoba. *J. Environ. Qual.* **34**(6): 1944–1951. doi:[10.2134/jeq2004.0468](https://doi.org/10.2134/jeq2004.0468). PMID: [16221812](https://pubmed.ncbi.nlm.nih.gov/16221812/).
- Illés, P., Schlicht, M., Pavlovkin, J., Lichtscheidl, I., Baluska, F., and Ovecka, M. 2006. Aluminium toxicity in plants: internalization of aluminium into cells of the transition zone in Arabidopsis root apices related to changes in plasma membrane potential, endosomal behavior, and nitric oxide production. *J. Exp. Bot.* **57**: 4201–4213. doi:[10.1093/jxb/erl197](https://doi.org/10.1093/jxb/erl197). PMID: [17085753](https://pubmed.ncbi.nlm.nih.gov/17085753/).
- Khiari, L., Parent, L.E., Pellerin, A., Alimi, A.R.A., Tremblay, C., Simard, R.R., and Fortin, J. 2000. An agri-environmental phosphorus saturation index for acid coarse-textured soils. *J. Environ. Qual.* **29**(6): 1561–1567. doi:[10.2134/jeq2000.00472425002900050024x](https://doi.org/10.2134/jeq2000.00472425002900050024x).
- Kowalenko, C.G., and Babuin, D. 2014. Use of lithium metaborate to determine total phosphorus and other element concentrations in soil, plant, and related materials. *Commun. Soil Sci. Plant Anal.* **45**: 15–28. doi:[10.1080/00103624.2013.848884](https://doi.org/10.1080/00103624.2013.848884).
- Kowalenko, G.C., Schmidt, O., Kenney, E., Neilsen, D., and Poon, D. 2007. Okanagan Agricultural Soil Study 2007. A Survey Of The Chemical And Physical Properties Of Agricultural Soils Of The Okanagan And Similkameen Valleys In Relation To Agronomic And Environmental Concerns. Available online at: [https://www2.gov.bc.ca/assets/gov/farming-natural-resources-and-industry/agriculture-and-seafood/agricultural-land-and-environment/environmentalfarm\\_planning/okanagan\\_soil\\_study\\_report\\_2007.pdf](https://www2.gov.bc.ca/assets/gov/farming-natural-resources-and-industry/agriculture-and-seafood/agricultural-land-and-environment/environmentalfarm_planning/okanagan_soil_study_report_2007.pdf) [accessed on Aug 04, 2021].
- Laboski, C.A.M., and Peters, J.B. 2012. Nutrient application guidelines for field, vegetable, and fruit crops in Wisconsin: A2809. UW Extension, R-11-2012(A2809).
- Lambers, H., Raven, J.A., Shaver, G.R., and Smith, S.E. 2008. Plant nutrient-acquisition strategies change with soil age. *Tree*, **23**(2): 95–103. doi:[10.1016/j.tree.2007.10.008](https://doi.org/10.1016/j.tree.2007.10.008).
- Liu, B., Frostegård, Å., and Bakken, L. 2014. Impaired reduction of N<sub>2</sub>O to N<sub>2</sub> in acid soils is due to a posttranscriptional interference with the expression of nosZ. *mBio*, **5**: 0183–0114. doi:[10.1128/mBio.01383-14](https://doi.org/10.1128/mBio.01383-14).
- McKeague, J.A., and Day, J.H. 1966. Dithionite and oxalate extractable Fe and Al as aids in differentiating various classes of soils. *Can. J. Soil Sci.* **46**: 13–22. doi:[10.4141/cjss66-003](https://doi.org/10.4141/cjss66-003).
- Mehlich, A. 1984. A Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.* **15**(12): 1409–1416. doi:[10.1080/00103628409367568](https://doi.org/10.1080/00103628409367568).
- Messiga, A.J., Ziadi, N., Bélanger, G., and Morel, C. 2013. Soil nutrient and other major properties in grassland fertilized with nitrogen and phosphorus. *Soil Sci. Soc. Am. J.* **77**: 643–652. doi:[10.2136/sssaj2012.0178](https://doi.org/10.2136/sssaj2012.0178).
- Messiga, A.J., Haak, D., and Dorais, M. 2018. Blueberry yield and soil properties response to long-term fertigation and broadcast nitrogen. *Sci. Hortic.* **230**: 92–101. doi:[10.1016/j.scienta.2017.11.019](https://doi.org/10.1016/j.scienta.2017.11.019).
- Messiga, A.J., Lam, C., Li, Y., Kidd, S., Yu, S., and Bineng, C.S. 2020. Combined starter phosphorus and manure applications on silage corn yield and phosphorus uptake in Southern BC. *Front. Earth Sci.* **8**(101): 1–13.
- Messiga, A.J., Lam, C., and Li, Y. 2021. Phosphorus saturation index and water-extractable phosphorus in high-legacy phosphorus soils in southern British Columbia, Canada. *Can. J. Soil Sci.* **101**(3): 365–377. doi:[10.1139/cjss-2020-0129](https://doi.org/10.1139/cjss-2020-0129).
- Murphy, J., and Riley, J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta*, **27**: 31–36. doi:[10.1016/S0003-2670\(00\)88444-5](https://doi.org/10.1016/S0003-2670(00)88444-5).
- Penn, C.J., and Camberato, J.J. 2019. A critical review on soil chemical processes that control how soil pH affects phosphorus availability to plants. *Agriculture*, **9**(6): 1–18. doi:[10.3390/agriculture9060120](https://doi.org/10.3390/agriculture9060120).
- Penn, C.J., Rutter, E.B., Arnall, D.B., Camberato, J., Williams, M., and Watkins, P. 2018. A discussion on Mehlich-3 phosphorus extraction from the perspective of governing chemical reactions and phases: impact of soil pH. *Agriculture*, **8**(7): 1–20. doi:[10.3390/agriculture8070106](https://doi.org/10.3390/agriculture8070106).
- Perrott, K.W., and Mansell, G.P. 1989. Effect of fertiliser phosphorus and liming on inorganic and organic soil phosphorus fractions, New Zealand J. Agric. Res. **32**(1): 63–70. doi:[10.1080/00288233.1989.10423478](https://doi.org/10.1080/00288233.1989.10423478).
- Poonnachit, U., and Darnell, R. 2004. Effect of ammonium and nitrate on ferric chelate reductase and nitrate reductase in *Vaccinium* species. *Ann. Bot.* **93**(4): 399–405. doi:[10.1093/aob/mch053](https://doi.org/10.1093/aob/mch053). PMID: [14980973](https://pubmed.ncbi.nlm.nih.gov/14980973/).
- Reid, K., and Schneider, K.D. 2019. Phosphorus accumulation in Canadian agricultural soils over 30 yr. *Can. J. Soil Sci.* **99**(4): 520–532. doi:[10.1139/cjss-2019-0023](https://doi.org/10.1139/cjss-2019-0023).
- Ross, G.J., and Wang, C. 1993. Extractable Al, Fe, Mn, and Si. In *Soil sampling and methods of analysis*, 1st ed. Edited by M.R. Carter. Can. Soc. Soil Sci. Lewis Publishers, Boca Raton, FL. pp. 239–246.
- SAS Institute Inc. 2010. SAS user's guide: statistics. Version 9, 3rd ed. SAS Institute Inc., Cary, NC.
- Saunders, W.M., and Williams, E.G. 1955. Observations on the determination of organic phosphorus in soils. *J. Soil Sci.* **6**: 254–267. doi:[10.1111/j.1365-2389.1955.tb00849.x](https://doi.org/10.1111/j.1365-2389.1955.tb00849.x).
- Self-Davis, M.L., Moore, P.A., Jr., and Joern, B.C. 2000. Determination of water- and/or dilute salt-extractable phosphorus. In *Methods of phosphorus analysis for soils, sediments, residuals, and waters*. Edited by G.M. Pierzynski. Kansas State University, Manhattan, KS, USA. pp. 24–26.
- Sharpley, A.N., Bergström, L., Aronsson, H., Bechmann, M., Bolster, C.H., Börling, K., and Withers, P.J.A. 2015. Future agriculture with minimized phosphorus losses to waters: research needs and direction. *Ambio*, **44**(2): 163–179. doi:[10.1007/s13280-014-0612-x](https://doi.org/10.1007/s13280-014-0612-x). PMID: [25678025](https://pubmed.ncbi.nlm.nih.gov/25678025/).
- Sims, J.T., Maguire, R.O., Leytem, A.B., Gartley, K.L., and Pautler, M.C. 2002. Evaluation of Mehlich 3 as an agri-environmental soil phosphorus test for the mid-Atlantic United States of America. *Soil Sci. Soc. Am. J.* **66**(6): 2016–2032. doi:[10.2136/sssaj2002.2016](https://doi.org/10.2136/sssaj2002.2016).
- Smith, C.A.S., Webb, K.T., Kenney, E., Anderson, A., and Kroetsch, D. 2011. Brunisolic soils of Canada: genesis, distribution, and classification. *Can. J. Soil Sci.* **91**: 695–717. doi:[10.4141/cjss10058](https://doi.org/10.4141/cjss10058).
- Soil Classification Working Group. 1998. The Canadian system of soil classification, 3rd ed. Agriculture and Agri-Food Canada Publication 1646, Canada.
- Soil Survey Division Staff. 1993. Soil survey manual. USDA Handbook No. 18, US Government Printing Office, Washington, DC.
- Soil Survey Staff. 2010. Keys to soil taxonomy. 11th ed. NRCS, Washington, DC.
- Tran, T.S., Giroux, M., Guilbeault, and Audesse, P. 1990. Evaluation of Mehlich-III extractant to estimate the available P in Quebec soils. *Communications in Soil Science* **21**: 1-2 1–28. doi:[10.1080/00103629009368212](https://doi.org/10.1080/00103629009368212).
- Van Bochove, E., Theriault, G., Denault, J.T., Dechmi, F., Allaire, E.S., and Rousseau, N.R. 2012. Risk of phosphorus desorption from Canadian agricultural land: 25 year temporal trend. *J. Environ. Qual.* **41**: 1402–1412. doi:[10.2134/jeq2011.0307](https://doi.org/10.2134/jeq2011.0307). PMID: [23099931](https://pubmed.ncbi.nlm.nih.gov/23099931/).
- Van der Zee, S.E.A.T.M., Fokink, L.G.J., and Van Riemsduik, W.H., 1987. A new technique for assessment of reversibly adsorbed phosphate. *Ambio*, **59**: 599–604.
- Wang, J., Tu, X., Zhang, H., Cui, J., Ni, K. Chen, J., et al. 2020. Effects of ammonium-based nitrogen addition on soil nitrification and nitrogen gas emissions depend on fertilizer induced changes in pH in tea plantation. *Sci. Total Environ.* **747**: 141340. doi:[10.1016/j.scitotenv.2020.141340](https://doi.org/10.1016/j.scitotenv.2020.141340). PMID: [32795801](https://pubmed.ncbi.nlm.nih.gov/32795801/).
- Zhang, H., and Kovar, J.L. 2009. Fractionation of phosphorus. In *Methods of phosphorus analysis*. 2nd ed. Edited by J.L. Kovar and G.M. Pierzynski. Southern Cooperative Series Bulletin 408. Virginia Tech University, Blacksburg, VA. pp. 50–60.