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Ferric chloride amendment reduces phosphorus losses from flooded soil monoliths to overlying floodwater

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Abstract

The accumulation of phosphorus (P) in agricultural soils and subsequent losses to waterways contribute to eutrophication in surface water bodies. In agricultural lands prone to prolonged flooding during spring snowmelt, P may be released to overlying floodwater and transported to lakes downstream. Ferric chloride ($FeCl_3$) is a potential soil amendment to mitigate P losses, but its effectiveness for flooded soils with snowmelt is not well documented. Thirty-six intact soil monoliths taken from four agricultural fields in Manitoba's Red River Valley region were surface-amended with $FeCl_3$ at three rates (0, 2.5, and 5 Mg ha^{-1}) to evaluate the effectiveness of $FeCl_3$ in minimizing P losses to porewater and floodwater. Over 8 weeks of simulated snowmelt flooding, porewater, and floodwater samples taken weekly were analyzed for concentrations of dissolved reactive P (DRP), calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), and pH. Change in the redox potential was also measured weekly. With time of flooding, redox potential decreased in all soil monoliths. At early stages of flooding, the porewater pH values were significantly lower in $FeCl_3$-amended monoliths but increased with flooding time. Porewater and floodwater DRP concentrations increased in all soils when flooded, but the magnitudes varied. Amendment of $FeCl_3$ decreased the DRP concentrations from 17% to 97% in porewater and 26% to 99% in floodwater, with the effectiveness varying depending on the soil, $FeCl_3$ rate, and flooding time. Amendment of $FeCl_3$ increased porewater concentrations of Ca, Mg, Fe, and Mn. Soil amendment with $FeCl_3$ at both rates shows promise in mitigating redox-induced P losses from flooded soils.

Key words: anaerobic conditions, ferric chloride amendment, flooded soil monoliths, phosphorus release, simulated snowmelt flooding

Résumé

Le phosphore (P) qui s'accumule dans les terres cultivées puis échoue dans les cours d'eau aggrave l'eutrophisation des étendues d'eau superficielles. Dans les terres agricoles susceptibles d'être longtemps inondées au printemps, à la fonte, il arrive que le P soit libéré dans les eaux de crue et transporté en aval dans les lacs. On pourrait bonifier le sol avec du chlorure de fer ($FeCl_3$) pour réduire les pertes de P, mais on ignore quelle serait l'efficacité d'un tel amendement sur les sols inondés à la fonte. Les auteurs ont prélevé 36 blocs de sol intact sur quatre terres cultivées dans la vallée de la rivière Rouge, au Manitoba, et les ont amendés avec 0, 2,5 ou 5 Mg de $FeCl_3$ par hectare, épandu en surface, afin d'évaluer l'efficacité avec laquelle le chlorure de fer réduit les pertes de P dans l'eau interstitielle et les eaux de crue. Ils ont simulé huit semaines d'inondations printanières et échantillonné l'eau chaque semaine afin d'en établir le pH et de doser la concentration de P dissous réactif (PDR), de calcium (Ca), de magnésium (Mg), de fer (Fe) ainsi que de manganèse (Mn). La variation du potentiel d'oxydoréduction a aussi été mesurée hebdomadairement. Le potentiel d'oxydoréduction diminue avec la durée de la crue dans tous les blocs de sol. Au début de la crue, le pH de l'eau interstitielle est sensiblement plus bas dans le sol amendé avec du FeCl3, mais il augmente avec la durée de l'inondation. La concentration de PDR dans l'eau interstitielle et les eaux de crue s'accroît de façon variable dans tous les sols inondés. L'addition de $FeCl_3$ diminue la concentration de PDR respectivement de 17 à 97 % dans l'eau interstitielle et de 26 à 99 % dans les eaux de crues, en fonction de la quantité de $FeCl_3$ ajoutée et de la durée de l'inondation. Le $FeCl_3$ augmente la concentration de Ca, de Mg, de Fe et de Mn dans l'eau interstitielle. Les deux taux d'application du FeCl3 semblent prometteurs pour atténuer les pertes de P induites par l'oxydoréduction, sur les terres immergées. [Traduit par la Rédaction]

Mots-clés : conditions anaérobies, chlorure de fer, blocs de sol inondé, libération du phosphore, simulation des crues dues à la fonte

Introduction

Phosphorus (P) is a principal limiting nutrient in crop growth and is frequently supplemented to agricultural soils in the form of fertilizers or manure. However, P is also a non-point source water pollutant (Carpenter et al. 1998) when mobilized via runoff, leaching, and/or erosion from terrestrial ecosystems (Sharpley et al. 1994; Smith et al. 2015; Baker et al. 2017). Even at low concentrations, P can trigger unwarranted algal blooms in freshwater bodies downstream, such as Lake Winnipeg (Daniel et al. 1998; Schindler et al. 2012, 2016). The loss of P from soils as a result of mobilization from soils is profoundly influenced by various biochemical and hydrological processes (Heathwaite and Dils 2000; McDowell et al. 2001).

Under prolonged flooding soils become anaerobic (Young and Ross 2001), a state that results in a decrease in redox potential (Eh) in soil (Ponnamperuma 1972) inducing microbially mediated reductive dissolution of manganese (Mn) and iron (Fe) phosphates (Patrick et al. 1973; Moore and Reddy 1994; Miller et al. 2015), which can enhance mobilization of P forms usually retained in well-drained soils (Amarawansha et al. 2015; Jayarathne et al. 2016). In addition, reductive dissolution of Fe and Mn (hydr)oxides may release P adsorbed to these mineral species. As P is released to porewater in substantial amounts, it ultimately diffuses to floodwater mostly in the form of dissolved reactive P (DRP), the predominant bioavailable form of P, and the dominant form of P lost from agricultural fields (Little et al. 2007; Cade-Menun et al. 2013). Accordingly, DRP concentration in overlying floodwater often increases with time of flooding (Kumaragamage et al. 2020) and if transported from a field to a water body, may contribute to P enrichment and accelerated eutrophication (Sharpley et al. 1994). In cold climate regions, the preeminent driver of agricultural P to surface waters is snowmelt runoff (Tiessen et al. 2010; Corriveau et al. 2013; Rattan et al. 2017). Due to flat landscapes and low permeability (Bedard-Haughn 2009; Buttle et al. 2016), as well as limited water infiltration caused by frozen soils (Liu et al. 2019), most agricultural fields of the Canadian prairies are poorly drained. These conditions, in conjunction with the rapid release of water derived from melting snow, may lead to recurrent flooding that may span from a few days to several weeks in the Canadian prairies.

The application of soil amendments capable of enhancing soil P retention in agricultural fields is a management strategy that can be adopted to limit P leaching and runoff losses (Elliott et al. 2002; Yang et al. 2007; Murphy and Stevens 2010). Through chemical precipitation of phosphate as calcium (Ca) phosphates, gypsum ($CaSO_4 \cdot 2H_2O$) is effective in reducing dissolved P in runoff water (Norton 2008; Watts and Torbert 2016) and in floodwater of flooded soils under both simulated spring snowmelt and summer-flooding conditions (Dharmakeerthi et al. 2019a, b). Surface amendment of magnesium (Mg) sulfate significantly reduced DRP in porewater and floodwater under simulated snowmelt flooding, with a lower rate of 2.5 Mg ha^{-1}, showing greater effectiveness than the higher rate of 5 Mg ha^{-1} (Vitharana et al. 2021). Ferric chloride ($FeCl_3$) is an inorganic coagulant widely utilized in wastewater treatments due to its high performance in removing turbidity (Shi et al. 2004). Considering that $FeCl_3$ can precipitate with phosphate and form an insoluble salt (Adhya et al. 2015), it demonstrates a strong potential of being a soil amendment successful in mitigating P loss from soils to floodwater. Numerous studies have investigated the efficacy of $FeCl_3$ in reducing P concentrations in lake water. For instance, a laboratory study with lake sediments from Dianchi Lake in China revealed that the application of $FeCl_3$ at a rate of 10 mg g^{-1} decreased the total P concentration of the overlying water by approximately 87% (Li et al. 2020). Another study reported that the addition of 100 g m^{-2} of Fe^{3+} to Lake Groot Vogelenzang in the Netherlands reduced P release from sediments from 4 to 1.2 mg P m^{-2} day^{-1} (Boers et al. 1992). Furthermore, the bioavailability of sediment-bound P decreased from 34% to 23% after treatment. In a packed soil column study using an organic wetland soil, chemical amendment with $FeCl_3$ was more effective in reducing floodwater P concentrations than alum, Ca(OH)$_2$, CaCO$_3$, and dolomite (Ann et al. 1999). They also suggested an application rate of 1–2 kg $FeCl_3$ per kg of soil as the most effective rate to minimize P release from the soil to the overlying floodwater.

The efficiency of $FeCl_3$ in enhancing P retention in agricultural soils, particularly under cold flooding distinctive to spring snowmelt flooding, is poorly documented in the literature. An improved understanding of P loss reduction with $FeCl_3$ amendment under cold flooding may aid in improving management strategies to reduce P losses to waterways in the Canadian prairies. We hypothesized that soil amendment of $FeCl_3$ prior to flooding would enhance conversion of P to less-soluble forms and thereby reduce P loss from soils to overlying floodwater. To evaluate this hypothesis, we conducted a laboratory study to compare the changes in P concentrations in porewater and floodwater in intact soil monoliths with and without $FeCl_3$ amendment under simulated snowmelt flooding.

Materials and methods

Soil sampling and analysis

Intact soil monoliths were collected from four flood-prone agricultural fields situated in the Red River Valley of Manitoba (MB), Canada, in May 2019. Soils 1 and 2 were collected from uncultivated areas of two annual crop fields located near Morris, MB. The area of the field from which the monoliths were taken had not received any manure or fertilizer over the last 12 months. Soil 3 was taken from a flood-prone manured field recently seeded to corn located near La Broquerie, MB, and monoliths were extracted from between crop rows. This field received liquid swine manure in the fall of 2018 at a rate of 158 m^3 ha^{-1} where manure was injected

and incorporated. Soil 4 was taken from a flood-prone pasture field near La Broquerie, MB, that did not receive any fertilizer or manure for the past year. Soils 1 and 2 belong to the Red River Series (Gleyed Rego Black Chernozem), while Soils 3 and 4 belong to the Pine Ridge series (Eutric Brunisol) according to the Canadian system of classification (Canadian Agricultural Services Coordinating Committee 1998), with approximate U.S. soil taxonomy equivalent of Udic Boroll and Cryochrepts, respectively (Soil Survey Staff 2014). The equivalent FAO classification for the Red River and Pine Ridge series is Chernozem, and Eutric Cambisol, respectively (FAO 2006).

Approximately 8–10 soil samples (0–15 cm depth) were obtained from each site and combined to obtain a composite soil sample. A representative subsample from each soil was air-dried, sieved (2-mm mesh), and analyzed for soil pH (1:2 soil: water), electrical conductivity (1:2 soil: water), organic matter, and calcium carbonate equivalent (CCE; loss on ignition; Dean 1974), cation exchange capacity by ammonium acetate method (Sumner and Miller 1996), and soil texture (hydrometer method; Gee and Bauder 1986). Soil test P was extracted using the Olsen method (Olsen et al. 1954), and P concentrations in the extracts were determined using the molybdate blue method (Murphy and Riley 1962). Nitrate-N concentrations in 0.01 M calcium chloride extracts were determined using colorimetry after reduction by hydrazine and complexing with N-(1-naphthyl)ethylenediamine dihydrochloride (USEPA 1993).

Experimental setup and data collection

Soil monoliths had an internal diameter of 10 cm and a height of 15 cm and were collected using polyvinyl chloride (PVC) tubes (30 cm in length), each with two drilled holes (3 mm) located on opposite sides at 10 cm from the bottom (5 cm below the soil surface). To seal the bottom of the monolith, a PVC cap was glued to the PVC tube. For this experiment, three amendment treatments were used with $FeCl_3$ applied at three rates: 0 (unamended), 2.5, and 5 Mg ha^{-1}, with triplicate monoliths for each treatment. These rates were based on the 1–2 g kg^{-1} soil suggested by Ann et al. (1999) and calculated considering a 15 cm soil depth and a soil bulk density of 1.5 g m^{-3}. Twelve soil-treatment combinations (four soils and three treatments) with three replicates each resulted in a total of 36 columns.

Within each monolith, two Rhizon MOM soil solution samplers (10 cm) with an outer diameter of 1.5 mm and a 0.15 μm pore size (Rhizosphere Research Products) were installed horizontally through the drilled holes and positioned at 5 cm below the surface of the soil. The appropriate amount of $FeCl_3$ was weighed and added to the soil surface uniformly and preincubated for 2 weeks. After preincubation, soil monoliths were flooded with ultrapure water (18 MΩ cm; Millipore) to a height of 10 cm above the soil surface. An Eh probe possessing a platinum (Pt) sensor (Paleo Terra) was installed vertically to a depth of 5 cm from the surface. During incubation, the monoliths were covered with perforated Parafilm to minimize evaporation. The monoliths were incubated for 56-day in a cooler at 4 ± 1 °C to simulate spring snowmelt conditions. This selected temperature was predicated upon the average day temperatures in Manitoba during the spring snowmelt period (in late March–April). All soil columns were arranged according to a randomized complete block design.

Beginning on the day of inundation and thereafter, pore and overlying floodwater samples (20 mL) were collected periodically at weekly intervals throughout the 56-day incubation period. Porewater was extracted by applying suction using a 20 mL syringe attached to the end of the Rhizon MOM sampler. Positioning a 20 mL syringe at the center of the flooded monolith, floodwater was obtained and was immediately filtered through a 0.45 μm membrane filter. Following the collection of water samples, the monoliths were refilled to their initial water level with cold ultrapure water. Immediately after extraction, DRP concentrations in porewater and floodwater samples were analyzed with the molybdate blue color method (Murphy and Riley 1962) and absorbance was measured at 882 nm with an Ultraspec 500 pro UV–visible spectrophotometer (Biochrom). Additionally, on each sampling day, a reference electrode (Ag–AgCl saturated with KCl), which was coupled to the permanently installed Pt redox probe and a portable millivolt (mV) meter, was temporarily inserted into the soil–floodwater interface to measure the potential difference. The values were then corrected to the standard hydrogen electrode potential, since soil Eh, by definition, is measured against the standard hydrogen electrode. All water samples were analyzed for pH within 24 h of sampling using a Fisher Accumet AB15 pH meter. The overall redox status was described using pe +pH (Lindsay 1979), where pe, the electron activity, was calculated using the equation,

$$pe = \frac{Eh \times F}{2.303 \times R \times T}$$

where Eh is the redox potential in V, F is the Faraday constant (96 485 C), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K). The pore and floodwater samples were acidified with 50 μL of concentrated nitric acid and stored at +4 °C until analysis for Ca, Mg, Fe, and Mn concentrations using an AAnalyst 400 atomic emission spectrometer (PerkinElmer).

Statistical analysis

Analysis of variance (ANOVA) for Eh, porewater pH, and concentrations of DRP in the porewater and floodwater was performed for each soil separately using the Generalized Linear Mixed Models (GLIMMIX) procedure in SAS software, Version 9.4 (SAS Institute Inc., Cary, USA 2013). The $FeCl_3$ rate was considered as the fixed effect and days after flooding (DAF) as the repeated measures factor. Based on the Akaike information criterion (Littell et al. 1998), the covariance structure used in the final mixed models was compound symmetry for all parameters. The Eh, porewater pH, and porewater DRP were modeled as normal distributions, while floodwater DRP was modeled as a lognormal distribution. The Tukey multiple comparison procedure was used to compare the least square means when three or more treatment means were compared. Simple linear regression analyses were performed separately for each soil to explore relationships between DRP concentrations in porewater and floodwater. The Pearson's simple

Table 1. Chemical and physical properties of soils.

Properties	Soil 1	Soil 2	Soil 3	Soil 4
Sand (g kg^{-1})	140	160	540	540
Silt (g kg^{-1})	250	220	220	310
Clay (g kg^{-1})	610	620	240	150
pH	6.9	6.6	7.5	8.0
Electrical conductivity (dS m^{-1})	0.43	0.62	1.06	0.81
Organic matter (g kg^{-1})	66	66	74	50
Calcium carbonate equivalent (g kg^{-1})	23	48	142	147
Cation exchange capacity (cmol kg^{-1})	40.3	44.9	36.9	32.9
Olsen P (mg kg^{-1})	91.0	53.2	78.0	59.1
Nitrate N (mg kg^{-1})	22	80	100	140.0

linear correlations were established between porewater DRP, Ca, Mg, Fe, and Mn concentrations with overall redox status (pe + pH). For all statistical analyses, significance was determined at $\alpha = 0.05$.

Results and discussion

Soil properties

Soils 1 and 2 were heavy clay in texture (Table 1) with near neutral to slightly acidic pH values (6.9 and 6.6, respectively), whereas Soils 3 and 4 had loamy textures with slightly alkaline pH values (7.5 and 8.0, respectively). All soil had high organic matter content ranging from 50 to 74 g kg^{-1}; Soil 3, which had received manure, had the greatest organic matter content. Soils 1 and 2 were weakly calcareous with CCE <50 g kg^{-1}, while Soils 3 and 4 were moderately calcareous with CCE between 60 and 150 g kg^{-1} (Canada Soil Survey Committee 1978). All soils had high cation exchange capacities (32–55 cmol kg^{-1}). The Olsen P concentrations varied from 53 to 91 mg kg^{-1}, thus all soils had very high levels of soil test P (Manitoba Soil Fertility Advisory Committee 2007). Nitrate-N concentrations were very high with >100 mg kg^{-1} in Soils 3 and 4 but lower in Soils 1 and 2 (Table 1).

Change in redox and porewater pH with flooding and FeCl$_3$ amendment

The highest Eh values in all monoliths were observed on the day of the flooding, which ranged from +207 to +480 mV depending on the soil and treatment (Fig. 1). Lower initial Eh values were observed in Soils 3 and 4 than in Soils 1 and 2. In general, Eh values of Soils 3 and 4 were below +350 mV, indicating that these soil monoliths were initially anaerobic to some extent, considering that +350 mV is the approximate Eh level signifying the onset of oxygen (O$_2$) disappearance from the soil system (Pezeshki and DeLaune 2012). Repeated-measures ANOVA of Eh revealed a significant main effect of DAF in all soils ($p < 0.001$), while the main effect of treatment, and DAF by treatment interaction, was not significant (Supplemental Table S1). The decrease in Eh (mean Eh of all three treatments) was significant by 7 DAF in Soils 1 and 3, whereas in Soils 2 and 4, the differences were significant by 21–28 DAF (Fig. 1). Irrespective of the soil and the treatment, the Eh significantly decreased over time after flooding and by 56 DAF,

all soil monoliths had Eh values between +66 and +314 mV, indicating severe to moderate anaerobic conditions. The decrease in redox potential in soils with flooding is expected since the diffusion of O$_2$ is slower across standing water than in soil, resulting in rapid O$_2$ depletion due to microbial respiration leading to anaerobic conditions (Ponnamperuma 1972). Similar decreases in Eh have been reported in other studies using flooded intact soil monoliths (Concepcion et al. 2020; Vitharana et al. 2021; Weerasekara et al. 2021).

The porewater pH in unamended soils (Soils 1, 3, and 4) on the day of flooding was slightly alkaline with a pH of around 7.4, whereas Soil 2 had an acidic porewater pH of 5.8 (Fig. 2). Repeated-measures ANOVA showed highly significant DAF by treatment interaction on the porewater pH in all soils ($p < 0.01$). In all four soils, the porewater pH on 0 DAF was significantly ($p < 0.05$) lower in FeCl$_3$-amended treatment at the 5 Mg ha^{-1} rate compared with the 0 Mg ha^{-1} rate, although the magnitudes of decrease varied between soils. The decrease in porewater pH on 0 DAF in FeCl$_3$-amended treatment at 2.5 and 5 Mg ha^{-1} rates compared with 0 Mg ha^{-1} rate was greatest in Soil 1 and was least in Soil 4. In Soil 1, the porewater pH decreased to 3.7 and 2.7 with FeCl$_3$ amendment at 2.5 and 5 Mg ha^{-1}, respectively. In contrast, the porewater pH in Soil 4 decreased to 6.2 and 5.7 on 0 DAF in FeCl$_3$-amended monoliths at 2.5 and 5 Mg ha^{-1} rates, respectively. The higher pH buffering capacity of Soil 4 to buffer pH upon addition of FeCl$_3$ is likely due to the presence of free Ca carbonate in this soil (Van Breemen and Wielemaker 1974; Bache 1984) as indicated by a high CCE value, whereas Soil 1, which had the lowest CCE value, showed a dramatic drop in pH with the addition of FeCl$_3$. A similar trend was observed with floodwater pH (data not shown).

The decrease in pH in soils with an FeCl$_3$-amendment has been previously reported (Ann et al. 1999; Guo et al. 2016) and is attributed to the dissolution of FeCl$_3$ and subsequent hydrolysis of Fe^{3+}, yielding Fe hydroxides with an accompanying release of protons. The decrease in pH with FeCl$_3$ however, was transient under the flooded environment in this study. Over time of flooding, the porewater pH of FeCl$_3$-amended treatments increased, whereas in unamended treatment porewater pH slightly decreased or remained relatively stable. Thus, by the 56 DAF, the differences in porewater pH between treatments with different FeCl$_3$ rates were slight.

Porewater and floodwater DRP concentration changes with flooding

Porewater and floodwater DRP concentrations varied widely depending on the soil, FeCl$_3$-amendment rate, and time or DAF (Fig. 3; Supplemental Table S2). Mean porewater concentrations and back-transformed floodwater DRP concentrations were very low (<1.0 mg L^{-1}) in Soil 1 and 2 throughout the flooding period irrespective of the amendment treatment (Fig. 3). In contrast, Soil 3, taken from a recently manured field, had higher DRP concentrations than the other three soils which averaged 8.6 mg L^{-1} in porewater and 5.2 mg L^{-1} in floodwater. The DRP concentrations in Soil 4 were intermediate between Soils 1 (or 2) and Soil 3, with both porewater and floodwater DRP concentrations <1 mg L^{-1} up

Fig. 1. Variation in soil redox potential (Eh) with days of simulated snowmelt flooding in Soils 1, 2, 3, and 4. Values are the pooled means of three treatments (unamended and FeCl$_3$-amended at 2.5 and 5 Mg ha^{-1} rates). Values sharing the same letter within each soil are not significantly different at $p < 0.05$. [Colour online.]
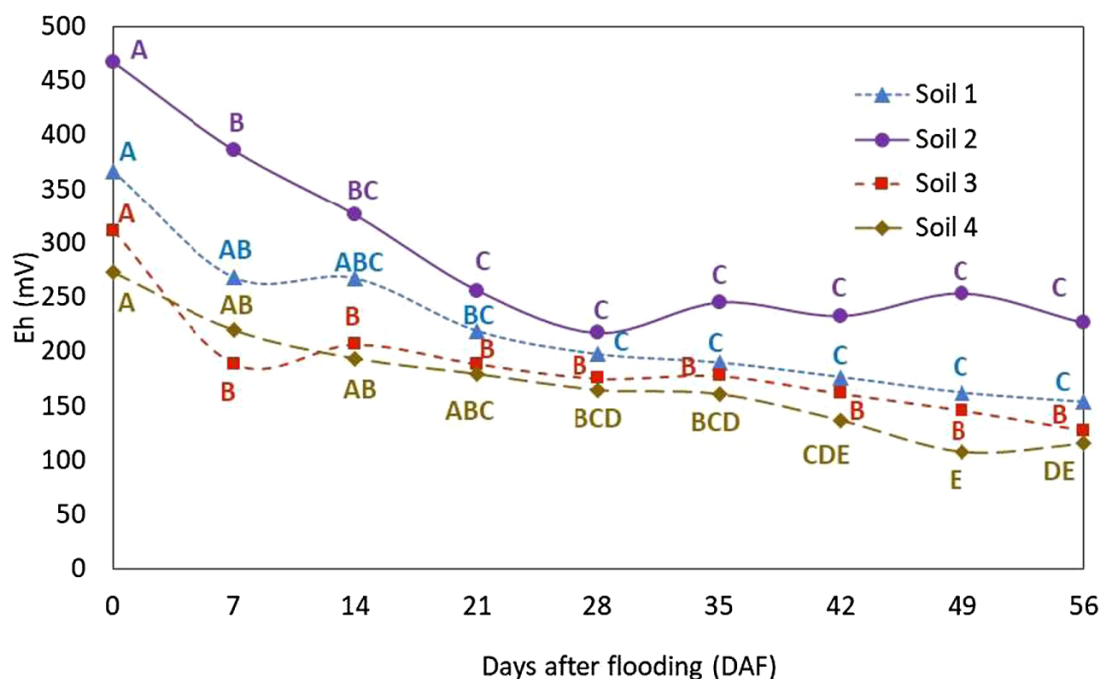
to 21 DAF, which then increased with the time after flooding to >3 mg L^{-1} by 56 DAF. The 10-fold higher porewater DRP concentration for Soil 3 compared with the other soils most likely results from the high proportion of water-soluble P from recently applied liquid swine manure, which is a rich source of water-soluble and labile P (Kumaragamage et al. 2011, 2012). Our results also support the findings by Smith et al. (2021) highlighting that common soil tests (such as Olsen P) performed under aerobic conditions are not suitable for predicting P release from soils that are temporarily or permanently saturated. Significantly greater porewater and floodwater DRP concentrations from flooded soils have been previously reported when liquid swine manure was applied prior to flooding than from unmanured control treatment (Amarawansha et al. 2015), as observed in this study.

Porewater DRP concentrations significantly ($p < 0.05$) increased with DAF during the initial stage of flooding in all unamended soils except for Soil 3 (Fig. 3; Supplemental Table S2). Repeated-measures ANOVA of porewater DRP concentrations revealed a significant two-way interaction between FeCl$_3$ amendment and DAF in Soils 1, 2, and 4 ($p = 0.0002$, 0.0006, and <0.0001, respectively; Supplemental Table S1). In Soils 1 and 4, the porewater DRP concentrations of the unamended treatment steadily increased with DAF. Statistically, the change in DRP concentrations between 0 and 56 DAF was significant ($p < 0.05$) with 2-fold (Soil 1) and 4-fold (Soil 4) increases. The porewater DRP concentrations of the unamended treatment in slightly acidic Soil 2 increased from 0.3 mg L^{-1} on 0 DAF to 0.5 mg L^{-1} on 7 DAF, then maintained relatively stable concentrations up to 28 DAF. Thereafter, the concentrations of DRP declined between 28 and 42 DAF to

0.4 mg L^{-1}. These changes in concentrations were statistically significant ($p < 0.05$).

The increase in porewater DRP concentrations with prolonged flooding has been previously reported from soils with varying properties flooded under varying conditions, i.e., under warm temperatures simulating summer flooding (Jayarathne et al. 2016; Kumaragamage et al. 2019), as well as under cold temperatures that simulate snowmelt flooding (Kumaragamage et al. 2020; Concepcion et al. 2021; Weerasekara et al. 2021). The enhanced P release with flooding has been mainly attributed to the reductive dissolution reactions that occur under a low O$_2$ environment in flooded soils, resulting in the release of P associated with redox-sensitive cations, such as Fe and Mn (Scalenghe et al. 2010; Maranguit et al. 2017). The decrease in porewater DRP concentration, particularly in unamended Soil 2 at later stages of flooding, could be due to possible precipitation of P with other cations, as well as the transfer of P from porewater to floodwater (Amarawansha et al. 2015).

Floodwater DRP concentrations (Figs. 3e–3h), in general, were lower than porewater DRP concentrations (Figs. 3a–3d). Lower DRP concentrations in floodwater compared with porewater are expected, particularly during early stages of flooding since the soils were flooded with ultrapure water. With the development of reducing conditions with flooding, P released to porewater with reductive dissolution reactions will subsequently diffuse to floodwater, thus increasing floodwater DRP concentrations. The significant increase in floodwater DRP concentrations with DAF in unamended treatments of Soils 1 and 4 suggests an effective transfer of released P from porewater to floodwater through the soil–water inter-

Fig. 2. Variation in mean porewater pH with days of simulated snowmelt flooding of unamended and FeCl$_3$-amended (at 2.5 and 5 Mg ha^{-1} rates) monoliths from (*a*) Soil 1, (*b*) Soil 2 (*c*) Soil 3, and (*d*) Soil 4. The error bars represent the standard error of the mean. [Colour online.]
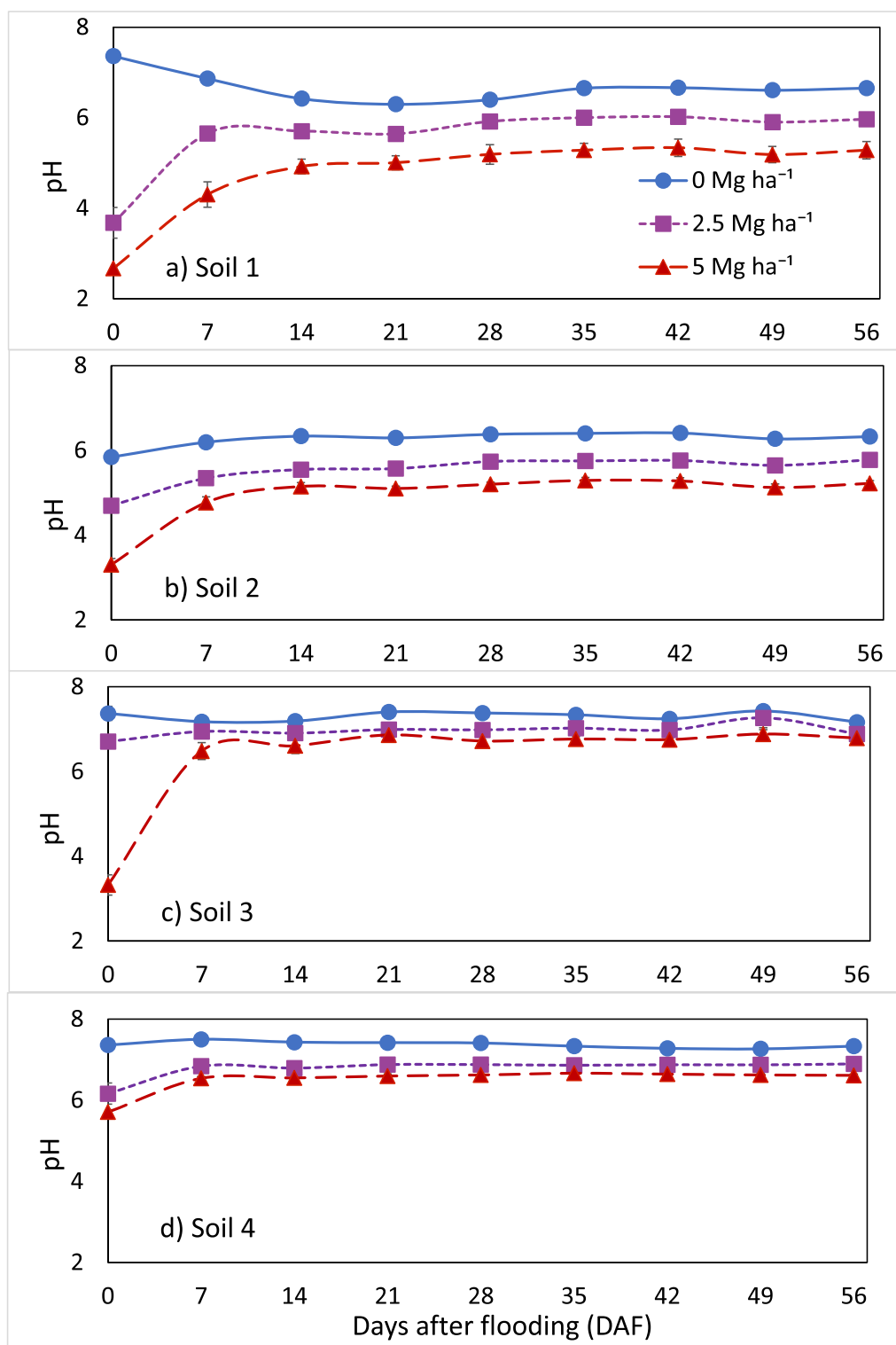
face in these two soils. Efficient transfer of P through the soil, and across the soil–water interface to floodwater, has been reported in previous studies even under simulated snowmelt conditions where intact soil monoliths were flooded under low temperatures (Concepcion et al. 2021; Vitharana et al. 2021; Weerasekara et al. 2021). Linear relationships between porewater and floodwater DRP concentrations were significant in all unamended soils (R^2 from 0.34 to 0.62; $p < 0.05$) but not when FeCl$_3$-amended, except Soil 3 at a FeCl$_3$ rate of 2.5 Mg ha^{-1} (Fig. 4).

Fig. 3. Variation in mean dissolved reactive P (DRP) concentrations in (*a*–*d*) porewater and (*e*–*h*) floodwater with days of simulated snowmelt flooding of unamended and FeCl$_3$-amended (at 2.5 and 5 Mg ha^{-1} rates) monoliths from Soil 1, Soil 2, Soil 3, and Soil 4. Treatment means were pooled when treatment × days after flooding interaction was not significant in panels *c* and *f*. The error bars represent the standard error of the mean. [Colour online.]
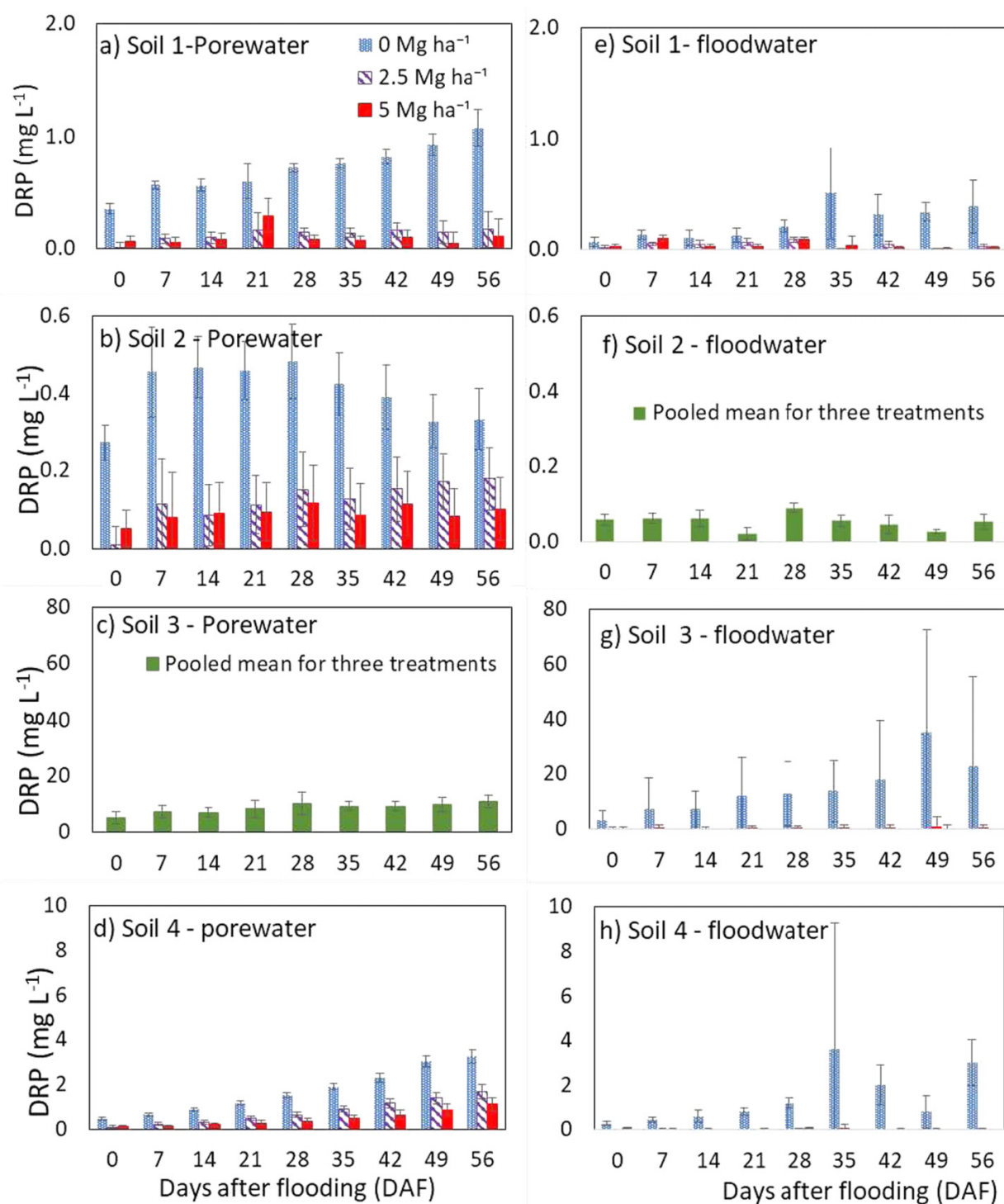
The porewater DRP concentrations in the FeCl$_3$-amended treatments were significantly lower than in the corresponding unamended treatments throughout the flooding period for Soil 1 and 4, and up to 35 DAF in Soil 2 (Supplemental Table S2). The magnitude of a decrease in DRP concentration with FeCl$_3$ depended on the soil, DAF, and the rate of FeCl$_3$. For porewater, the % decrease in FeCl$_3$-amended treatments (2.5 or 5 Mg ha^{-1}) in relation to unamended treatment ranged from 17% to 97% with a median of 77% depending on the soil and DAF. The differences in DRP concentrations among treat-

Fig. 4. Relationships between porewater and floodwater dissolved reactive P (DRP) concentrations during simulated snowmelt flooding of (*A*) unamended and (*B*) FeCl$_3$-amended (at 2.5 and 5 Mg ha^{-1} rates) monoliths from Soil 1, Soil 2, Soil 3, and Soil 4. Note: values on the *x* and *y* axes are not in the same range for all soils. [Colour online.]
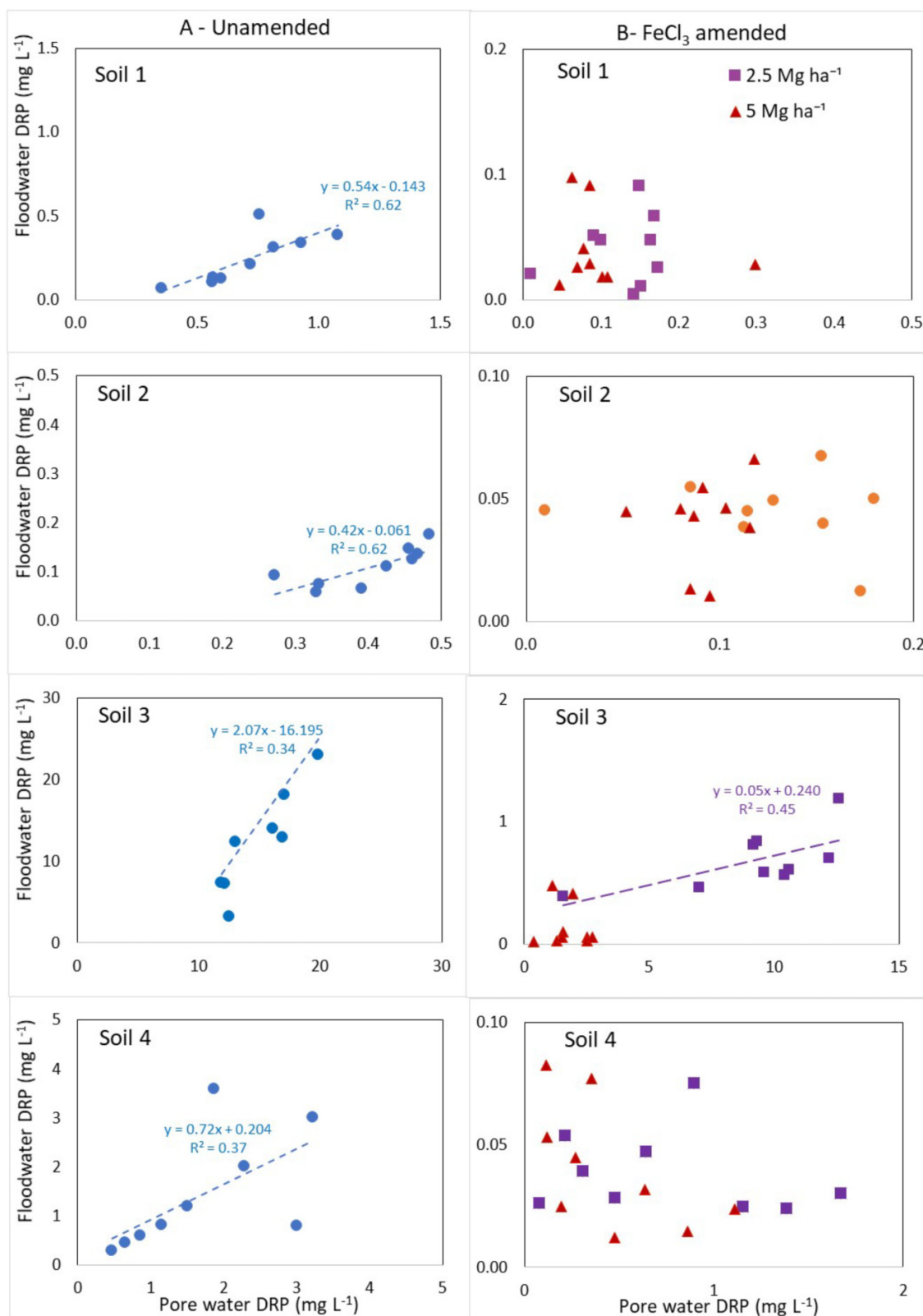
Table 2. Correlation coefficients for the linear relationships between pe + pH with dissolved reactive P (DRP), Ca, Mg, Fe, and Mn concentrations in porewater ($n = 9$).

Soil	FeCl$_3$ rate (Mg ha^{-1})	Correlation coefficients				
		DRP	Ca	Mg	Fe	Mn
1	0	−0.90***	0.05 NS	−0.55 NS	0.14 NS	−0.87**
	2.5	−0.62*	0.61*	0.87**	0.15 NS	0.21 NS
	5	0.17 NS	0.66*	0.16 NS	−0.12 NS	−0.01 NS
2	0	0.04 NS	0.00 NS	0.15 NS	−0.54 NS	−0.73*
	2.5	−0.81**	0.10 NS	0.88**	0.54 NS	0.64*
	5	−0.35 NS	0.58*	0.81**	0.26 NS	−0.19 NS
3	0	−0.78**	−0.24 NS	0.72*	−0.48 NS	−0.93***
	2.5	−0.67*	−0.80**	−0.13 NS	0.91***	0.81**
	5	−0.15 NS	0.68*	0.73*	−0.39 NS	0.02 NS
4	0	−0.93***	−0.78**	−0.52 NS	−0.89***	−0.89***
	2.5	−0.92***	0.12 NS	0.89***	0.19 NS	−0.19 NS
	5	−0.80**	0.57*	0.92***	0.67*	0.62*

Note: NS, not significant. *, **, and *** after the correlation coefficient value denote significance at 0.05. 0.01, and 0.001 probability.

ments were much larger in floodwater than porewater in all soils except for Soil 2, and the % decrease varied from 26% to 99% with a median of 91%. In a packed soil column study using an organic soil from a constructed wetland, Ann et al. (1999) also reported that floodwater DRP concentration increased during the first 8 weeks of incubation from 150 to 700 mg P L^{-1} in the unamended treatment, while FeCl$_3$ treatment even at the lowest rate they used (1.8 g kg^{-1}, a rate similar to the higher rate used in the current study) reduced DRP concentrations to <50 μg P L^{-1}. Using lake sediments from Dianchi Lake in China, Li et al. (2020) observed that the application of FeCl$_3$ at a much higher rate of 10 mg g^{-1} (5–10-fold greater than the rate used in the current study) decreased the total P concentration of the overlying water by approximately 87%. In the current study, floodwater DRP concentrations with FeCl$_3$ at 2.5 and 5 Mg ha^{-1} rates were extremely low in Soils 3 and 4, with often below-detectable concentrations, which could be the reason for a lack of a significant relationship between floodwater and porewater DRP concentrations in FeCl$_3$-amended treatments (Fig. 4).

In Soils 1 and 4, the porewater DRP concentrations in FeCl$_3$-amended treatments were consistently and significantly ($p < 0.05$) lower than their unamended counterparts, while the differences between the two rates of FeCl$_3$ were significant only at certain DAFs in Soil 1 (Supplemental Table S2). In slightly acidic Soil 2, the differences in porewater DRP concentrations between unamended and FeCl$_3$-amended treatments were significant only during the early stages of flooding up to 35 DAF. The transfer of P from porewater to floodwater may have masked the effect of FeCl$_3$ amendment on porewater DRP concentrations at later stages of flooding, and, hence, DRP concentrations in porewater and floodwater were similar in magnitude in FeCl$_3$-amended treatments of this soil. This resulted in a nonsignificant main effect of treatment, as well as a nonsignificant interaction effect of

DAF × treatment in Soil 2 for floodwater DRP. In Soil 3, which had very high porewater DRP concentrations, the main effects of DAF, FeCl$_3$ amendment, as well as their interaction effect, were not significant ($p > 0.05$). A lack of significant DAF effect is likely due to the more effective diffusion of released P from porewater to floodwater, increasing floodwater DRP with a corresponding decline in porewater DRP concentration. Furthermore, this is confirmed by the higher slope of the regression relationship between floodwater and porewater DRP concentration in unamended Soil 3 compared with other soils (Fig. 4), and by the significant interaction effect of DAF by treatment for floodwater DRP concentrations while the main effect of DAF was not significant (Supplemental Table S1).

Combined effect of redox and pH on P release from FeCl$_3$-amended and unamended soil monoliths

The combined effect of changes in Eh and pH with flooding on the release of P and associated cations was evaluated using a double function parameter, pe + pH (Lindsay 1979), because both electrons and protons participate in most redox reactions involving P release. As flooding progressed, the Eh decreased significantly ($p < 0.001$) in all soils irrespective of the FeCl$_3$-amendment rate (Supplemental Table S1). Significant negative correlations were observed between pe + pH and porewater DRP concentrations in the majority of unamended soils (except in slightly acidic Soil 2), and in all soils with the lower rate of FeCl$_3$-amended treatments (Table 2), clearly implying redox-induced P release from flooded soils to porewater. This was not observed when FeCl$_3$ was amended at the 5 Mg ha^{-1} rate (except for Soil 4), despite a similar decrease in pe + pH with flooding time. In unamended treatments of all soils, correlations between porewater Mn concentrations and pe + pH were negative and significant (Table 2).

Particularly in unamended Soil 4, a highly significant negative correlation existed with porewater Fe concentration as well, further suggesting the involvement of Mn and Fe compounds in releasing P through reductive dissolution reactions, as previously documented (Maranguit et al. 2017; Wang et al. 2019; Warrinnier et al. 2020). In $FeCl_3$-amended treatments, porewater concentrations of Ca, Mg, and Mn were greater than their unamended counterparts (Supplemental Tables S3–S6), with even higher concentrations at 5 Mg ha^{-1} than at 2.5 Mg ha^{-1} rate of $FeCl_3$. The higher cation concentrations in porewater with $FeCl_3$ amendment are likely due to the cation exchange reactions that displaced exchangeable cations from soils by added Fe, and/or enhanced solubility of Ca and Mg compounds at low pH induced by $FeCl_3$. It can be speculated that the higher Ca, Mg, and Mn concentrations favored reprecipitation of released P with these cations, reducing DRP concentrations despite the prevailing anaerobic conditions favoring P release. The significant positive correlation between porewater Ca and Mg in $FeCl_3$-amended treatments with pe + pH, particularly at the higher rate of $FeCl_3$ (Table 2) is likely due to the removal of Ca and Mg from the soil solution as flooding progressed, which possibly occurred through precipitation reactions involving P and other anions. Using a thermodynamic model (SOILCHEM) to predict P speciation, Ann et al. (1999) reported that porewater in $FeCl_3$-amended soil was supersaturated with respect to $FePO_4$, strengite, $(Fe_3PO_4 \cdot 2H_2O)$ and hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$, suggesting that precipitation of these minerals decreased the DRP concentrations in floodwater.

The results of the current study show that $FeCl_3$ amendment is highly effective in reducing P loss from flooded agricultural soils; however, the agronomic impacts of $FeCl_3$ amendment are less known. Amendment with $FeCl_3$ is used to correct Fe deficiency in plants (Hagstrom 1984), with foliar sprays being more commonly used than soil applications because of greater effectiveness. High Fe loading with Fe-containing amendments such as $FeCl_3$ can lead to Fe toxicity, but such cases are relatively isolated (Heyden and Roychoudhury 2015). A study conducted by Akahane et al. (2013) with spinach reported no significant impact of $FeCl_3$ amendment on crop growth and yield.

Conclusions

Prolonged flooding enhanced P release from most soils, increasing DRP concentrations in porewater and floodwater; however, in slightly acidic Soil 2, the concentrations declined after about 35 DAF, likely due to precipitation reactions. Amendment of $FeCl_3$ at 2.5 and 5 Mg ha^{-1} rates decreased the DRP concentrations up to 97% and 99% in porewater and floodwater, respectively, with the effectiveness varying depending on the soil, $FeCl_3$ rate, and DAF. The decrease in pH with $FeCl_3$ amendment was short-lived in these highly buffered calcareous soils. While $FeCl_3$ amendment shows promise as a strategy to mitigate redox-induced P losses from flooded soils to overlying floodwater, the agronomic and environmental impacts of $FeCl_3$ amendment need to be assessed at the field scale.

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Author contributions

EV—conceptualization, validation, formal analysis, investigation, visualization, and writing the original draft.
DK—conceptualization, methodology, validation, investigation, resources, project administration, visualization, supervision, funding acquisition, writing-review, and editing.
GA—formal analysis, investigation, visualization, writing-review, and editing.
DG—Methodology, resources, visualization, supervision, writing-review, and editing.

Competing interests

The authors declare there are no competing interests.

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Supplemental material

Supplementary data are available with the article at https://doi.org/10.1139/CJSS-2021-0135. The supplemental material includes a table providing information on ANOVA results for porewater and floodwater dissolved reactive P (DRP) concentrations (Table S1), mean porewater DRP concentrations and back-transformed mean floodwater DRP concentrations in unamended and FeCl3 amended soils (Table S2). It also contains four tables providing information on variation of pe + pH values, and variation of porewater and floodwater Ca, Mg, Fe, and Mn concentrations with time after flooding in unamended and FeCl3-amended treatments of Soil 1 (Table S3), Soil 2 (Table S4), Soil 3 (Table S5), and Soil 4 (Table S6).

References

Adhya, T.K., Kumar, N., Reddy, G., Podile, A.R., Bee, H., and Samantaray, B. 2015. Microbial mobilization of soil phosphorus and sustainable P management in agricultural soils. Curr. Sci. **108**: 1280–1287.

Akahane, I., Makino, T., Maejima, Y., Kamiya, T., Takano, H., and Ibaraki, T., 2013. Remediation of cadmium-contaminated paddy soils by washing with ferric chloride (FeCl3): effect of soil washing on the cadmium concentration in soil solution and spinach. Jpn. Agric. Res. Q. **47**: 273–228. doi:10.6090/jarq.47.273.

Amarawansha, .A.G.S., Kumaragamage, D., Flaten, D., Zvomuya, F., and Tenuta, M. 2015. Phosphorus mobilization from manure-amended and unamended alkaline soils to overlying water during simulated flooding. J. Environ. Qual. **44**: 1252–1262. doi:10.2134/jeq2014.10.0457. PMID: 26437107.

Ann, Y., Reddy, K.R., and Delfino, J.J. 1999. Influence of chemical amendments on phosphorus immobilization in soils from a constructed wetland. Ecol. Eng. **14**: 157–167. doi:10.1016/S0925-8574(99)00026-9.

Bache, B.W. 1984. The role of calcium in buffering soils. Plant Cell Environ. **7**(6): 391–395. doi:10.1111/j.1365-3040.1984.tb01428.x.

Baker, D.B., Johnson, L.T., Confesor, R.B., and Crumrine, J.P. 2017. Vertical stratification of soil phosphorus as a concern for dissolved phosphorus runoff in the Lake Erie basin. J. Environ. Qual. **46**: 1287–1295. doi:10.2134/jeq2016.09.0337. PMID: 29293833.

Bedard-Haughn, A. 2009. Managing excess water in Canadian Prairie soils: a review. Can. J. Soil Sci. **89**: 157–168. doi:10.4141/CJSS07071.

Boers, P., Does, J.V.D., Quaak, M., Vlugt, J.V.D., and Walker, P.J.H. 1992. Fixation of phosphorus in lake sediments using iron(III) chloride: experiences, expectations. Hydrobiologia. **233**: 211–212. doi:10.1007/BF00016109.

Buttle, J.M., Allen, D.M., Caissie, D., Davison, B., Hayashi, M. Peters, D.L., et al. 2016. Flood processes in Canada: regional and special aspects. Can. Water Resour. J. **41**: 7–30. doi:10.1080/07011784.2015.1131629.

Cade-Menun, B.J., Bell, G., Baker-Ismail, S., Fouli, Y., Hodder, K. McMartin, D.W., et al. 2013. Nutrient loss from Saskatchewan cropland and pasture in spring snowmelt runoff. Can. J. Soil Sci. **93**: 445–458. doi:10.4141/cjss2012-042.

Canadian Agricultural Services Coordinating Committee. 1998. The Canadian system of soil classification. No. 93. Soil Classification Working Group, Natl. Res. Counc. Canada, Agric. Agri-Food Canada, Res. Branch, NRC Research Press, Canada.

Canada Soil Survey Committee. 1978. The Canada Soil Information System (CanSIS): Manual for describing soils in the field. Land Resource Research Institute, Central Experimental Farm, Agriculture Canada.

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., and Smith, V.H. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl. **8**: 559–568. doi:10.1890/1051-0761(1998)008[0559:NPOSWW]2.0.CO;2.

Concepcion, A., Kumaragamage, D., Gregory, C., Goltz, D., Indraratne, S., and Amarawansha, G. 2020. Temperature and freezing effects on phosphorus release from soils to overlying floodwater under flooded-anaerobic conditions. J. Environ. Qual. **49**(3): 700–711. doi:10.1002/jeq2.20062. PMID: 33016390.

Concepcion, A., Kumaragamage, D., Akinremi, W., Dharmakeerthi, S., Goltz, D., and Indraratne, S. 2021. Phosphorus release from intact soil monoliths of manure-amended fields under simulated snowmelt flooding. J. Environ. Qual. **50**(1): 252–263. doi:10.1002/jeq2.20179. PMID: 33241863.

Corriveau, J., Chambers, P.A., and Culp, J.M. 2013. Seasonal variation in nutrient export along streams in the northern Great Plains. Water Air Soil Pollut. **224**: 1594–1609. doi:10.1007/s11270-013-1594-1.

Daniel, T.C., Sharpley, A.N., and Lemunyon, J.L. 1998. Agricultural phosphorus and eutrophication: a symposium overview. J. Environ. Qual. **27**: 251–257. doi:10.2134/jeq1998.00472425002700020002x.

Dean, W.E. 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition; comparison with other methods. J. Sediment. Res. **44**(1): 242–248. doi:10.1306/74D729D2-2B21-11D7-8648000102C1865D.

Dharmakeerthi, R.S., Kumaragamage, D., Goltz, D., and Indraratne, S.P. 2019a. Phosphorus release from unamended and gypsum- or biochar-amended soils under simulated snowmelt and summer flooding conditions. J. Environ. Qual. **48**: 822–830. doi:10.2134/jeq2019.02.0091. PMID: 31589686.

Dharmakeerthi, R.S., Kumaragamage, D., Indraratne, S.P., and Goltz, D. 2019b. Gypsum amendment reduces redox-induced phosphorous release from freshly manured, flooded soils to floodwater. J. Environ. Qual. **48**: 127–135. doi:10.2134/jeq2018.08.0308.

Elliott, H.A., O'Connor, G.A., and Brinton, S. 2002. Phosphorus leaching from biosolids-amended sandy soils. J. Environ. Qual. **31**: 681–689. doi:10.2134/jeq2002.6810. PMID: 11931462.

FAO. 2006. World Reference Base for Soil Resources, by ISSS-ISRIC-FAO. World Soil Resources Reports No. 103, FAO, Rome. 2006.

Gee, G.W., and Bauder, J.W. 1986. Particle-size analysis. *In* Methods of soil analysis. Part 1. Agronomy monograph 9. 2nd edition. *Edited by* A. Klute. SSSA and ASA, Madison, WI, USA. pp . 383–411.

Guo, X., Wei, Z., Wu, Q., Li, C., Qian, T., and Zheng, W. 2016. Effect of soil washing with only chelators or combining with ferric chloride on soil heavy metal removal and phytoavailability: field experiments. Chemosphere. **147**: 412–419. doi:10.1016/j.chemosphere.2015.12.087. PMID: 26774307.

Hagstrom, G.R. 1984. Current management practices for correcting iron deficiency in plants with emphasis on soil management. J. Pl. Nutr. **7**: 23–46. doi:10.1080/01904168409363173.

Heathwaite, A.L., and Dils, R.M. 2000. Characterising phosphorus loss in surface and subsurface hydrological pathways. Sci. Total Environ. **251–252**: 523–538. doi:10.1016/S0048-9697(00)00393-4. PMID: 10847182.

Heyden, B.P.V.D., and Roychoudhury, A.N. 2015. Application, chemical interaction and fate of iron minerals in polluted sediment and soils. Curr. Pollut. Rep. **1**: 265–279. doi:10.1007/s40726-015-0020-2.

Jayarathne, P.D.K.D., Kumaragamage, D., Indraratne, S., Flaten, D., and Goltz, D. 2016. Phosphorus release to floodwater from calcareous surface soils and their corresponding subsurface soils under anaerobic conditions. J. Environ. Qual. **45**: 1375–1384. doi:10.2134/jeq2015.11.0547. PMID: 27380087.

Kumaragamage, D., Flaten, D., Akinremi, O.O., Sawka, C., and Zvomuya, F. 2011. Soil test phosphorus changes and phosphorus runoff losses in incubated soils treated with livestock manures and synthetic fertilizer. Can. J. Soil Sci. **91**(3): 375–384. doi:10.4141/cjss10004.

Kumaragamage, D., Flaten, D. N., Akinremi, O.O., Sawka, C.A., Ige, D., and Zvomuya, F. 2012. Impact of manure phosphorus fractions on phosphorus loss from manured soils after incubation. J. Environ. Qual. **41**(3): 845–854. doi: 10.2134/jeq2011.0415. PMID: 22565266.

Kumaragamage, D., Amarawansha, G.S., Indraratne, S. P., Jayarathne, K., Flaten, D.N., and Zvomuya, F., 2019. Degree of phosphorus saturation as a predictor of redox-induced phosphorus release from flooded soils to floodwater. J. Environ. Qual. **48**(6): 1817–1825. doi:10.2134/jeq2019.04.0154.

Kumaragamage, D., Concepcion, A., Gregory, C., Goltz, D., Indraratne, S., and Amarawansha, G. 2020. Temperature and freezing effects on phosphorus release from soils to overlying floodwater under flooded-anaerobic conditions. J. Environ. Qual. **49**: 700–711. doi:10.1002/jeq2.20062. PMID: 33016390.

Li, S., Lin, Z., Liu, M., Jiang, F., Chen, J., and Yang, X., 2020. Effect of ferric chloride on phosphorus immobilization and speciation in Dianchi Lake sediments. Ecotoxicol. Environ. Saf. **197**: 110637. doi:10.1016/j.ecoenv.2020.110637. PMID: 32315789.

Lindsay, W. 1979. Chemical equilibria in soils. John Wiley Sons, New York.

Littell, R.C., Henry, P.R., and Ammerman, C.B. 1998. Statistical analysis of repeated measures data using SAS procedures. J. Anim. Sci. **76**: 1216–1231. doi: 10.2527/1998.7641216x. PMID: 9581947.

Little, J.L., Nolan, S.C., Casson, J.P., and Olson, B.M. 2007. Relationships between soil and runoff phosphorus in small Alberta watersheds. J. Environ. Qual. **36**: 1289–1300. doi:10.2134/jeq2006.0502. PMID: 17636290.

Liu, J., Baulch, H.M., Macrae, M.L., Wilson, H.F., Elliott, J.A. Bergström, L., et al. 2019. Agricultural water quality in cold climates: processes, drivers, management options, and research needs. J. Environ. Qual. **48**: 792–802. doi:10.2134/jeq2019.05.0220. PMID: 31589688.

Manitoba Soil Fertility Advisory Committee. 2007. Soil fertility guide.Manitoba Agricultural Sustainability Initiative, Winnipeg, MB.

Maranguit, D., Guillaume, T., and Kuzyakov, Y. 2017. Effects of flooding on phosphorus and iron mobilization in highly weathered soils under

different land-use types: short-term effects and mechanisms. Catena. **158**: 161–170. doi:10.1016/j.catena.2017.06.023.

McDowell, R., Sharpley, A., and Folmar, G. 2001. Phosphorus export from an agricultural watershed. J. Environ. Qual. **30**: 1587–1595. doi:10.2134/jeq2001.3051587x. PMID: 11577864.

Miller, J.J., Bremer, E., Curtis, T., and Chanasyk, D.S. 2015. An assessment of nutrient dynamics in streambank soils of the lower little bow river in southern Alberta using ion exchange membranes. Water Qual. Res. J. **52**: 196–208. doi:10.2166/wqrj.2017.007.

Moore, P.A., and Reddy, K.R. 1994. Role of Eh and pH on phosphorus geochemistry in sediments of Lake Okeechobee, Florida. J. Environ. Qual. **23**: 955–964. doi:10.2134/jeq1994.00472425002300050016x. PMID: 34872208.

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

Murphy, P.N.C., and Stevens, R.J. 2010. Lime and gypsum as source measures to decrease phosphorus loss from soils to water. Water Air Soil Pollut. **212**: 101–111. doi:10.1007/s11270-010-0325-0.

Norton, L.D. 2008. Gypsum soil amendment as a management practice in conservation tillage to improve water quality. J. Soil Water Conserv. **63**: 46A–48A. doi:10.2489/jswc.63.2.46A.

Olsen, S.R., Cole, C.V., Watanabe, F.S., and Dean, L. A. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ. 939. U. S. Government Printing Office, Washington, DC.

Patrick, W.H., Gotoh, S., and Williams, B.G. 1973. Strengite dissolution in flooded soils and sediments. Science, **179**(4073): 564–565. doi:10.1126/science.179.4073.564. PMID: 17820817.

Pezeshki, S.R., and DeLaune, R.D. 2012. Soil oxidation-reduction in wetlands and its impact on plant functioning. Biology. **1**(2): 196–221. doi:10.3390/biology1020196. PMID: 24832223.

Ponnamperuma, F.N. 1972. The chemistry of submerged soils. Adv. Agron. **24**: 29–96. doi:10.1016/S0065-2113(08)60633-1.

Rattan, K.J., Corriveau, J.C., Brua, R. B., Culp, J.M., Yates, A.G., and Chambers, P.A. 2017. Quantifying seasonal variation in total phosphorus and nitrogen from prairie streams in the Red River Basin, Manitoba, Canada. Sci. Total Environ. **575**: 649–659. doi:10.1016/j.scitotenv.2016.09.073. PMID: 27745930.

Scalenghe, R., Edwards, A.C., Barberis, E., and Marsan, Ajmone, F. 2010. The influence of pulsed redox conditions on soil phosphorus. Biogeosci. Discuss. **7**(6): 9009–9037. doi:10.5194/bgd-7-9009-2010.

Schindler, D.W., Hecky, R.E., and McCullough, G.K. 2012. The rapid eutrophication of Lake Winnipeg: greening under global change. J. Great Lakes Res. **38**: 6–13. doi:10.1016/j.jglr.2012.04.003.

Schindler, D.W., Carpenter, S.R., Chapra, S.C., Hecky, R.E., and Orihel, D.M. 2016. Reducing phosphorus to curb lake eutrophication is a success. Environ. Sci. Technol. **50**: 8923–8929. doi:10.1021/acs.est.6b02204. PMID: 27494041.

Sharpley, A.N., Chapra, S.C., Wedepohl, R., Sims, J.T., Daniel, T.C., and Reddy, K.R. 1994. Managing agricultural phosphorus for protection of surface waters: issues and options. J. Environ. Qual. **23**: 437–451. doi:10.2134/jeq1994.00472425002300030006x.

Shi, Y., Fan, M., Brown, R.C., Sung, S., and Van Leeuwen, J.H.V. 2004. Comparison of corrosivity of polymeric sulfate ferric and ferric chloride as coagulants in water treatment. Chem. Eng. Process. **43**: 955–964. doi:10.1016/j.cep.2003.09.001.

Smith, D.R., King, K.W., Johnson, L., Francesconi, W., Richards, P., and Baker, D., 2015. Surface runoff and tile drainage transport of phosphorus in the midwestern United States. J. Environ. Qual. **44**: 495–502. doi:10.2134/jeq2014.04.0176. PMID: 26023968.

Smith, G. J., McDowell, R.W., Daly, K., Ó hUallacháin, D., Condron, L.M., and Fenton, O. 2021. Estimating and modelling the risk of redox-sensitive phosphorus loss from saturated soils using different soil tests. Geoderma. **398**: 115094. doi:10.1016/j.geoderma.2021.115094.

Soil Survey Staff. 2014. Keys to soil taxonomy. 12th ed. USDA-NRCS. Washington, DC, USA.

Sumner, M.E., and Miller, W.P. 1996. Cation exchange capacity and exchange coefficients. *In* Methods of soil analysis. Part 3. Chemical methods. *Edited by* D.L. Sparks. SSSA and ASA, Madison, WI. pp. 1201–1229. doi:10.2136/sssabookser5.3.c40.

Tiessen, K.H.D., Elliott, J.A., Yarotski, J., Lobb, D.A., Flaten, D.N., and Glozier, N.E. 2010. Conventional and conservation tillage: influence on seasonal runoff, sediment, and nutrient losses in the Canadian Prairies. J. Environ. Qual. **39**: 964–980. doi:10.2134/jeq2009.0219. PMID: 20400592.

U.S. Environmental Protection Agency (USEPA). 1993. Method 353.2. Determination of nitrate-nitrite nitrogen by automated colorimetry. Environ. Monitoring Systems Lab., Office Res. Dev., U.S. Environ. Protection Agency, Cincinnati, OH, USA.

Van Breemen, N., and Wielemaker, W.G. 1974. Buffer intensities and equilibrium pH of minerals and soils: I. The contribution of minerals and aqueous carbonate to pH buffering. Soil Sci. Soc. Am. J. **38**(1): 55–60. doi:10.2136/sssaj1974.03615995003800010022x.

Vitharana, U.W., Kumaragamage, D., Balasooriya, B.L.W.K., Indraratne, S.P., and Goltz, D. 2021. Phosphorus mobilization in unamended and magnesium sulfate-amended soil monoliths under simulated snowmelt flooding. Environ. Pollut. **287**: 117619. doi:10.1016/j.envpol.2021.117619. PMID: 34426378.

Wang, J., Chen, J., Chen, Q., Yang, H., Zeng, Y., and Yu, P., 2019. Assessment on the effects of aluminum-modified clay in inactivating internal phosphorus in deep eutrophic reservoirs. Chemosphere. **215**: 657–667. doi:10.1016/j.chemosphere.2018.10.095. PMID: 30347360.

Warrinnier, R., Bossuyt, S., Resseguier, C., Cambier, P., Houot, S. Gustafsson, J.P., et al. 2020. Anaerobic respiration in the unsaturated zone of agricultural soil mobilizes phosphorus and manganese. Environ. Sci. Technol. **54**(8): 4922–4931. doi:10.1021/acs.est.9b06978. PMID: 32212656.

Watts, D.B., and Torbert, H.A. 2016. Influence of flue gas desulfurization gypsum on reducing soluble phosphorus in successive runoff events from a coastal plain bermudagrass pasture. J. Environ. Qual. **45**: 1071–1079. doi:10.2134/jeq2015.04.0203. PMID: 27136176.

Weerasekara, C., Kumaragamage, D., Akinremi, W., Indraratne, S., and Goltz, D. 2021. Phosphorus mobilization from intact soil monoliths flooded under simulated summer versus spring snowmelt with intermittent freeze–thaw conditions. J. Environ. Qual. **50**(1): 215–227. doi:10.1002/jeq2.20182. PMID: 33305377.

Yang, J., He, Z., Yang, Y., Stoffella, P., Yang, X., and Banks, D., 2007. Use of amendments to reduce leaching loss of phosphorus and other nutrients from a sandy soil in Florida. Environ. Sci. Pollut. Res. Int. **14**: 266–269. doi:10.1065/espr2007.01.378. PMID: 17668824.

Young, E.O., and Ross, D.S. 2001. Phosphate release from seasonally flooded soils. J. Environ. Qual. **30**: 91–101. doi:10.2134/jeq2001.30191x. PMID: 11215671.