Phosphorus Release from Unamended and Gypsum- or Biochar-Amended Soils under Simulated Snowmelt and Summer Flooding Conditions

R. S. Dharmakeerthi, D. Kumaragamage,* D. Goltz, and S. P. Indraratne

Abstract

Prolonged flooding changes the oxidation-reduction status of soils, often enhancing P release to overlying floodwater. We studied P release from unamended, gypsum-amended, and biochar-amended soils under simulated snowmelt flooding (previously frozen, cold flooding at +4°C) and summer flooding (unfrozen, warm flooding at +22°C) using two soils, Fyala clay (FYLCI) and Neuenberg sandy loam (NBG-SL), from Manitoba, Canada. Amended and unamended soils were packed into vessels and flooded under cold and warm temperatures in the laboratory. Pore water and floodwater samples were taken weekly for 6 wk after flooding (WAF) and thereafter biweekly for 10 WAF and analyzed for dissolved reactive P (DRP), pH, and cation concentrations. The NBG-SL showed a significantly higher DRP concentration in pore water and floodwater despite its low Olsen P content. Redox potential (Eh) decreased slowly under cold versus warm flooding; hence, redox-induced P release was substantially lower under cold flooding. Gypsum amendment significantly decreased the floodwater DRP concentrations in NBG-SL by 38 and 35% under cold and warm flooding, respectively, but had no significant effect in FYL-Cl, which had low DRP concentrations (<1.2 mg L⁻¹) throughout the flooding period. Biochar amendment significantly increased floodwater DRP concentrations by 27 to 68% in FYL-Cl under cold and warm flooding, respectively, but had no significant effect in NBG-SL. The results indicate substantially less P release under cold than under warm flooding. Gypsum was effective in reducing floodwater DRP concentrations only at high DRP concentrations; thus, the effectiveness was greater under warm than under cold flooding conditions.

Core Ideas

- Floodwater DRP concentration increased with time of flooding in amended and unamended soils.
- Increase in floodwater DRP concentration was less under simulated snowmelt than summer flooding.
- Rate of P diffusion from pore water to floodwater was less under simulated snowmelt flooding.
- Gypsum reduced floodwater DRP in one soil with DRP concentrations >1 mg L⁻¹, but not in the other.
- Woodchip biochar was ineffective in reducing P release from soils to overlying floodwater.
temperature influences P diffusion rate (Mackay and Barber, 1984), with a higher rate of P diffusion at higher temperatures. Although there is ample research documenting the enhanced P release from flooded soils under room temperature or summer-flooded conditions (Young and Ross, 2001; Amarawansha et al., 2015; Jayarathne et al., 2016), P release under cold temperature or spring snowmelt flooded conditions is poorly represented in the literature (King et al., 2015). In one study investigating the effect of temperature on P release from flooded sediments, significantly lower P release was observed at 7°C than at 35°C (Sallade and Sims, 1997).

Application of soil amendments that can increase soil P retention capacity is a management practice that can be adopted to reduce P loss from agricultural soils (Elliott et al., 2002; Yang et al., 2007; Murphy and Stevens, 2010). Gypsum application is very effective in reducing dissolved P in runoff water (Favaretto et al., 2006; Norton, 2008; Watts and Torbert, 2016), mainly through precipitation of P as Ca phosphates. Studying P dynamics in five contrasting acidic grassland soils (Murphy and Stevens, 2010), a 15 to 45% decrease in soil solution dissolved reactive P (DRP) was observed with gypsum application, with a greater reduction in high-P soils. Wallboard gypsum, a waste product from the construction and demolition industry, was found to be effective in reducing P in surface runoff from agricultural lands (Norton, 2008). In a recent study, wallboard gypsum was found to be effective in reducing flooding-induced P release from soils under simulated summer-flooded conditions in the laboratory (Dharmakeerthi et al., 2019b). In contrast, the effect of amending biochar on P release from soils was inconsistent, since biochar can act as a source as well as a sink of P due to pH changes and increased P sorption (Xu et al., 2014; DeLuca et al., 2015; Zhai et al., 2015).

Enhanced P release from soils to floodwater and effective assimilation of amendments such as gypsum in reducing redox-induced P release with flooding under warm temperatures is well documented. However, very little is known on redox-induced P release from soils under cold flooding, distinctive of spring snowmelt flooding, and the effectiveness of amendments in reducing P release under these conditions. This information will be helpful in designing better management strategies to reduce redox-induced P losses from agricultural soils with spring snowmelt flooding. In the above context, we conducted a laboratory study (i) to compare the P release from flooded soils to pore water and floodwater under simulated summer and spring flood conditions, and (ii) to investigate the effect of wallboard gypsum and woodchip biochar in reducing P release from flooded soils under those conditions. We hypothesized that the release of P to pore water and floodwater is less under cold than warm flooding, and soil amendments would be less effective in reducing P release from soils to pore water and floodwater under cold than warm flooding conditions.

Materials and Methods

Soil, Biochar, and Gypsum Samples

Soils were collected from flood-prone agricultural fields in Ledwyn and Rosetown, MB, Canada, representing Fyala clay (FYL-Cl, poorly drained Rego Humic Gleysol) and Neuenberg sandy loam (NBG-SL, imperfectly drained Gleyed Carbonated

Rego Black) in September 2017. Soil samples were collected from the 0- to 0.2-m depth, passed through a 4-mm sieve, and stored at field moist contents. Recycled wallboard gypsum and woodchip biochar (produced using slow pyrolysis at ~500°C) were crushed to pass through a 1- and 4-mm sieve, respectively, before mixing with soil.

Soil and Amendment Characterization

After air drying and sieving through a 2-mm sieve, triplicate samples were analyzed for soil texture by pipette method (Gee and Bauder, 1986), pH (1:2, soil/water) using a Fisher Accuma

et al. (1986), pH (1:2, soil/water) using a Fisher Accumet AB15 pH meter, and organic matter content by loss-on-ignition method (Davies, 1974). Available P was determined by Olsen (Olsen et al., 1954) and Mehlich-3 (Mehlich, 1984) methods. Single-point P sorption capacity (P<sub>150</sub>) was determined by equilibrating soil with 150 mg P L<sup>-1</sup> solution and calculating the amount of P sorbed in milligrams per kilogram of soil using the difference between the initial and equilibrium P concentrations in the solution (Bache and Williams, 1971). Molybdate reactive P concentrations in soil and water extracts were determined by the molybdate blue color method (Murphy and Riley, 1962) measuring absorbance at 882 nm using an Ultraspex 2100 Pro ultraviolet–visible spectrophotometer (Biochrom). Degree of P saturation (DPS) in these soils was calculated using Mehlich-3 available P contents and P<sub>150</sub> as given in Eq. [1] (Ige et al., 2005; Amarawansha et al., 2016):

\[
\text{DPS} = \frac{\text{Mehlich-3 P}}{2 \times \text{P}_{150}} + \text{Mehlich-3 P} \times 100
\]  

[1]

Wallboard gypsum and biochar were crushed to pass through a 0.5-mm sieve and analyzed in triplicate for total P, Ca, Mg, Na, K, and S using inductively coupled plasma atomic emission spectroscopy (iCAP 6500, Thermo Scientific) after microwave digestion (CEM MARS 5, CEM Corporation).

Incubation Study with Simulated Flooding

Field moist soils (46.7 and 11.7% moisture in FYL-Cl and NBG-SL, respectively) were mixed either with 1% biochar (w/w) or 0.25% gypsum (w/w) and pre-incubated for 2 wk under room temperature (+22 ± 1°C). Amended and unamended soils (750 g) after pre-incubation were then packed into 1.5-L incubation vessels to a bulk density of ~1.15 Mg m<sup>-3</sup>. Amended and unamended soils were crushed to pass through a 0.5-mm sieve and analyzed in triplicate for total P, Ca, Mg, Na, K, and S using inductively coupled plasma atomic emission spectroscopy (iCAP 6500, Thermo Scientific) after microwave digestion (CEM MARS 5, CEM Corporation).

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Materials and Methods

Soil, Biochar, and Gypsum Samples

Soils were collected from flood-prone agricultural fields in Ledwyn and Rosetown, MB, Canada, representing Fyala clay (FYL-Cl, poorly drained Rego Humic Gleysol) and Neuenberg sandy loam (NBG-SL, imperfectly drained Gleyed Carbonated
without developing anaerobic conditions. After 1 wk, frozen vessels were transferred to a cold room under refrigerator conditions (+4 ± 1°C) and flooded with cold (+4°C) deionized water (Milli-Q 18 MΩ cm) to a height of 0.05 m above soil surface (cold flooding). The vessels kept at room temperature (+22 ± 1°C) were flooded similarly using deionized water at room temperature (warm flooding). Vessels were kept flooded under these conditions for 10 wk.

Pore and floodwater samples (20 mL) were drawn periodically at weekly intervals from 0 to 6 wk after flooding (WAF) and at 2-wk intervals thereafter up to 10 WAF. Pore water was collected from the Rhizon samplers by applying a vacuum, and floodwater was drawn using a 20-mL syringe. Floodwater samples were immediately filtered through a 0.45-μm membrane filter. After collection of water samples, vessels were refilled to the initial water level using deionized water at either cold or room temperatures, depending on the simulated flooding condition.

Pore and floodwater samples were immediately analyzed for their DRP concentrations using the molybdate blue color (Murphy and Riley, 1962). Pore and floodwater samples were analyzed for pH within 24 h of sampling using a Fisher Accumet AB15 pH meter. Pore and floodwater samples collected at every 2 WAF were acidified and stored at +4°C until analysis for Ca, Mg, Fe and Mn concentrations using a flame atomic absorption spectroscopy (AAnalyst 400, PerkinElmer).

The soil Eh (in mV) was measured weekly up to 6 WAF and thereafter biweekly up to 10 WAF with the permanently installed Pt electrode and a Ag–AgCl reference electrode. All Eh readings were acquired with a high impedance volt meter and corrected to the standard hydrogen electrode potential by adding the potential of the reference electrode at +4 and +22°C for soils kept under cold and warm conditions, respectively.

### Statistical Analysis

Repeated-measures ANOVA was conducted on temporally measured parameters using WAF as the “within subject” effect and the flooding temperature (cold or warm), amendment treatment (unamended, gypsum-amended, and biochar-amended), and soil (FYL-CI and NBG-SL) as “fixed” effects. When singularity of the data was significant, the Greenhouse–Geisser correction was used to test the significance. Since four-way interaction was highly significant for all parameters analyzed, subsequent ANOVAs were conducted for each soil separately (Quinn and Keough, 2002). Prior to ANOVA, normality of the residuals of the measured parameters was tested using Shapiro–Wilk’s W statistic. Concentrations of Fe in pore and surface water samples and Mn in surface water samples were not normally distributed (W < 0.9), because they were undetectable at early stages of flooding and were detected only at very late stages of the incubation. Since none of the transformations (log, inverse, arc-sine) could improve the W statistic, ANOVA was not conducted on these three parameters.

To understand the relationships between concentrations of DRP and different cations in pore water and floodwater at different stages of flooding, multiple regression analysis was conducted with pooled data (soil, amendment, and flooding temperature) for a given WAF. The Ca, Mg, Mn, and Fe concentrations in water were regressed against DRP in a stepwise procedure. When a multicollinearity among independent variables were observed (variance inflation factor > 3), the least contributory variable for R² was removed and then the regression analysis was conducted again. All statistical analyses were conducted using IBM SPSS Statistics 19.0 software (IBM Corporation, 2017).

### Results

#### Characteristics of Soil, Gypsum, and Biochar

The two soils used had contrasting properties (Table 1). The FYL-CI had a clay texture (564 g kg⁻¹ clay), slightly alkaline pH (7.56), and very high organic matter content (86.0 g kg⁻¹). In contrast, the NBG-SL soil had a sandy loam texture (148 mg kg⁻¹ clay), acidic pH (5.95), and very low organic matter content (17.5 g kg⁻¹). The degree of P saturation was 6.3 and 17.6% in the clay and sandy loam, respectively.

The recycled wallboard gypsum had mean Ca, S, and Mg concentrations of 215, 171, and 10 g kg⁻¹, respectively, with a comparatively low concentration of P (0.3 g kg⁻¹). The woodchip biochar had 723 g kg⁻¹ of organic C, slightly alkaline pH (7.53), and a total P content of 0.14 g kg⁻¹. Biochar also contained significant concentrations of cations, particularly K, Ca, and Fe (Table 1).

#### Change in Dissolved Reactive P Concentrations in Pore Water and Floodwater with Flooding Time

The DRP concentrations in pore water and floodwater varied with the soil, amendment treatment, and flooding temperature (Dharmakeerthi et al., 2019a). For a given soil, the three-way interaction among flooding temperature, amendment treatment, and flooding time was highly significant (p < 0.001) for both pore water and floodwater DRP concentrations (Supplemental Table S1).

The pore water DRP concentrations in the unamended sandy loam were significantly greater than in the clay soil, with the exception of the last 2 wk of flooding (Fig. 1a and 1b). In the sandy loam, pore water DRP concentration in all treatments increased with flooding time up to ~4 WAF and thereafter remained relatively stable or decreased. In contrast, pore water DRP concentrations in the clay soil steadily increased with flooding time under warm conditions, with a greater rate of increase after ~6 WAF. This effect, however, was not observed under cold conditions, and DRP concentrations remained relatively stable throughout the flooding period.

In both soils, floodwater DRP concentrations at 0 WAF were negligible, but steadily increased with WAF (Fig. 1c and 1d). The magnitude of increase, however, varied, with a greater increase in the sandy loam than in the clay. Floodwater DRP concentrations increased to >3.5 mg L⁻¹ by the end of the flooding period (10 WAF) in the unamended sandy loam under warm conditions, whereas in the clay, the DRP concentration increased to ~1.2 mg L⁻¹ under same conditions. The magnitude of increase in DRP was greater under warm than cold flooding for a given soil and amendment treatment. By the end of the flooding period (10 WAF), the DRP concentrations were about twofold greater under warm than cold condition for a given soil and amendment treatment (Fig. 1).

The effect of amendment treatments on DRP concentrations in the two soils was inconsistent. In the sandy loam, irrespective of incubation temperature, gypsum application significantly decreased the DRP concentration in both pore
water and floodwater compared with those in unamended and biochar-amended treatments. This effect was observed throughout the flooding period, with the exception of pore water at 10 WAF, and the differences were often statistically significant. By the end of the flooding period, floodwater DRP concentrations in gypsum-amended sandy loam were 39 and 45% less than in the unamended treatment under cold and warm conditions, respectively. However, in the clay soil, pore water and floodwater DRP concentrations were greater in gypsum-amended than unamended treatments except for the pore water DRP concentrations during the last 5 wk of flooding under warm conditions (Fig. 1), and the differences were often significant ($p < 0.05$).

In the clay soil, biochar amendment significantly increased the DRP concentrations in both pore water and floodwater, with the only exception of floodwater DRP under cold conditions, where the increases became statistically significant only at 6 WAF (Fig. 1d). At 10 WAF, the floodwater DRP concentrations in the biochar-amended clay were 27 and 68% greater than in unamended clay under cold and warm conditions, respectively. In contrast, biochar amendment to sandy loam had no significant effect on pore water and floodwater DRP concentrations during the early stages of flooding, whereas the concentrations were often less than in the unamended treatment at later stages of flooding. Significantly lower DRP concentrations in biochar amended than unamended sandy loam were observed for pore water at 10 WAF under warm conditions (Fig. 1a), and for floodwater after 6 WAF under both cold and warm conditions (Fig. 1c). The floodwater DRP concentration at 10 WAF in the biochar-amended sandy loam was lower than corresponding concentrations in unamended treatment by 9 and 5%, under cold and warm conditions, respectively.

Table 1. Properties of the two soils, Fyala clay (FYL-Cl) and Neuenberg sandy loam (NBG-SL), and two amendments (wallboard gypsum and woodchip biochar) used in the study (means of three replicates).

<table>
<thead>
<tr>
<th>Soil</th>
<th>Property†</th>
<th>pH</th>
<th>OM</th>
<th>Olsen P</th>
<th>Mehlich-3-extractable cations</th>
<th>EC</th>
<th>Sand</th>
<th>Clay</th>
<th>P$_{150}$</th>
<th>DPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>g kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>S m$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>%</td>
</tr>
<tr>
<td>FYL-Cl</td>
<td></td>
<td>g kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>NBG-SL</td>
<td></td>
<td>g kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
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<td>mg kg$^{-1}$</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Amendment</td>
<td>pH</td>
<td>OC</td>
<td>Olsen P</td>
<td>P</td>
<td>Ca</td>
<td>Mg</td>
<td>Fe</td>
<td>Mn</td>
<td>K</td>
<td>Na</td>
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<td>Gypsum</td>
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<td>10.1</td>
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<td>Biochar</td>
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<td>1.0</td>
<td>2587</td>
<td>302</td>
<td>2366</td>
<td>430</td>
</tr>
</tbody>
</table>
|† OM, organic matter content; OC, organic carbon content; EC, electrical conductivity; P$_{150}$, single-point P sorption capacity; DPS, degree of P saturation.

Fig. 1. Change in mean dissolved reactive P (DRP) concentrations in pore water and floodwater with flooding time under simulated summer (unfrozen, warm flooding at $+22^\circ$C) and snowmelt (previously frozen, cold flooding at $+4^\circ$C) conditions in unamended, gypsum-amended, and biochar-amended Fyala clay and Neuenberg sandy loam soils. Vertical bars in each week indicate the SE ($n = 18$). Note the differences in the y axis scale in comparative figures.
Changes in Soil Redox Potential and Pore Water and Floodwater pH with Flooding

A significant ($p = 0.003$ to $<0.001$) three-way interaction among flooding temperature, amendment treatment, and flooding time was observed for soil Eh and pore water and floodwater pH (Supplemental Table S1). In general, soil Eh was largely influenced by temperature and the duration of flooding, whereas the pH changes were largely influenced by soil type and flooding duration (Fig. 2).

Soil Eh decreased after flooding in both soils, but the decrease was very slow under cold flooding. Soon after flooding, the average Eh across all treatments in the clay was $+339$ mV, whereas that in sandy loam was $+504$ mV. Even after 10 wk of flooding, the Eh in the clay and sandy loam under cold flooding decreased only down to $+211$ and $+329$ mV, respectively. In contrast, the corresponding values in the clay and sandy loam under warm flooding were $−90$ and $+103$ mV. In the flooded sandy loam under cold conditions, gypsum application significantly decreased the soil Eh compared with the other two treatments; however, application of gypsum seemed to delay the decrease in Eh below $+200$ mV in both soils (Fig. 2b). Application of biochar had no significant effect on Eh decrease with flooding in both soils under warm and cold conditions.

The pore water pH in the sandy loam increased under cold and warm flooding (Fig. 2c). In contrast, the pore water pH in the clay slightly decreased under warm flooding but remained relatively constant under cold flooding (Fig. 2d). Except for gypsum-amended clay under warm flooding, amendments had no significant influence on pore water pH changes during the flooding period. Floodwater pH in both soils increased rapidly until 2 WAF and then remained relatively stable in the clay and slightly decreased in the sandy loam (data not shown). The increase in floodwater pH was greater in clay than in sandy loam, and with warm flooding than with cold flooding in all amended and unamended soils. In general, amendments did not have a significant effect on floodwater pH, with a few exceptions under warm flooding.

Cation Concentrations in Water

A significant ($p = 0.042$ to $<0.001$) three-way interaction of flooding temperature × amendment × WAF was observed for Ca and Mg concentrations in pore water and floodwater except for pore water Mg in the sandy loam. As expected, gypsum application increased the Ca concentrations in pore water in both soils, but the pore water concentrations decreased with time while floodwater concentrations increased. In unamended soils, pore water Ca concentrations under warm flooding increased with WAF in the clay soil but decreased in the sandy loam (Supplemental Fig. S1; Dharmakeerthi et al., 2019a).

Both pore water and floodwater Ca concentrations were significantly higher under warm than cold flooding in the clay soil, but such an increase could be seen only in the floodwater of the gypsum-amended sandy loam. Biochar amendment had no significant effect on pore water and floodwater Ca concentrations when compared with unamended soils. Both pore water and floodwater Mg concentration changes with WAF in different amendment treatments showed a similar trend to that of Ca; however, the differences were slight (Supplemental Fig. S1).

Concentrations of Mn and Fe in pore water and floodwater in soils flooded under cold conditions were not detectable. Even under warm conditions, a detectable concentration of Mn in

Fig. 2. Changes in mean soil redox potential (Eh, mV) and pore water pH with flooding time under simulated summer (unfrozen, warm flooding at $+22^\circ$C) and snowmelt (previously frozen, cold flooding at $+4^\circ$C) conditions in unamended, gypsum-amended, and biochar-amended Fyala clay and Neuenberg sandy loam soils. The vertical bars in each week indicate the SE ($n = 18$).
floodwater was observed only in the clay soil at 10 WAF. Soils flooded under warm conditions showed detectable Mn concentrations in pore water around 2 WAF, and Mn concentrations increased with WAF and reached a maximum concentration of \( \sim 1.0 \) and 2.5 mg L\(^{-1}\) by 8 WAF in the sandy loam and clay, respectively (Supplemental Fig. S1). In general, amendments significantly increased the pore water Mn concentrations, and the increase was greater in the gypsum treatment. Pore water Fe concentrations were detectable only under warm flooding at 4 WAF in the clay and 8 WAF in the sandy loam. Pore water Fe concentrations were significantly lower in gypsum-amended treatments, and significantly higher in biochar-amended treatments, compared with the unamended treatments (Supplemental Fig. S1).

Stepwise multiple regression analysis revealed that throughout the flooding period, pore and floodwater DRP concentrations were significantly \( (p < 0.001) \), and negatively, related to Mg concentrations (Table 2). At 0 WAF, pore water DRP concentration was positively related to Ca concentration as well. At latter stages of flooding from 6 WAF, DRP was also positively related to Mn and/or Fe concentrations in pore water, whereas in floodwater, DRP was positively related to Fe concentrations only at 10 WAF.

**Discussion**

With prolonged flooding and development of anaerobic conditions, soil P is first released to pore water, which then diffuses into surface floodwater. Consistent, and often significant, increase in floodwater DRP in amended and unamended soils under both warm and cold flooding clearly demonstrate the enhanced P release from flooded soils, as previously reported under conditions similar to the warm flooding (Amarawansha et al., 2015; Jayarathne et al., 2016; Tian et al., 2017). Pore water DRP concentrations, however, did not show a consistent increasing trend under all experimental conditions, which may be due to the diffusion of released P from pore water to floodwater, since pore water DRP concentrations were greater than in floodwater, facilitating upward diffusion. Despite lower available P contents, both pore water and floodwater DRP concentrations were significantly greater in the sandy loam than in the clay under all experimental conditions, except for the last 2 WAF. This could be due to significantly higher DPS in the sandy loam than that of the clay. Thus, our results are in line with the previous observations that the magnitude of redox-induced P release is better related to DPS than soil available P (Amarawansha et al., 2016).

**Floodwater DRP concentrations**

Pore water and floodwater DRP concentrations were substantially greater under warm than cold flooding in both soils for the respective amendment treatment, indicating the influence of temperature on flooding-induced P release. Decrease in Eh is related to the microbial activity, which is greater at high soil temperatures. Organic matter provides required C and energy for microorganisms that are active under flooded conditions. For a soil to be reduced, however, there should be adequate electron acceptors such as Fe\(^{3+}\) and Mn\(^{4+}\). Therefore, in soils containing higher organic matter and reducible cation concentrations, the Eh reduction with flooding would be more rapid at higher than at lower temperatures (Ponnampetnam, 1972). In line with this, we observed a rapid reduction in Eh with flooding in amended and unamended clay soil with warm flooding. This reduction was associated with early release of Mn (after 2 WAF) and Fe (after 4 WAF) into pore water in the clay soil, probably through reductive dissolution reactions with an associated release of P. In the sandy loam, which had low organic matter content, the decrease in Eh was much slower than in the clay even under warm flooding, and subsequent release of Mn was very slow despite having high Mehlich-3-extractable Mn content. The temporal patterns in the release of Fe and Mn coincided well with the trends observed in Eh. In the sandy loam where Eh did not decrease below +200 mV (e.g., under cold flooding), release of Mn or Fe was not observed, since microbial-mediated reduction of Mn\(^{4+}\) to Mn\(^{2+}\) occurs when Eh falls below approximately +200 mV depending on pH, whereas reduction of Fe\(^{3+}\) to Fe\(^{2+}\) occurs at even lower Eh values around +100 mV (Gotoh and Patrick, 1974; Patrick and Jugsujinda, 1992). Thus, the small increase in DRP in pore water observed at early stages of flooding in the sandy loam under cold flooding is likely related to the dissolution of P associated with Ca and Mg, as reported previously (Jayarathne et al., 2016). Our data suggest that under cold conditions, the duration of flooding should have little impact on the decrease in Eh, and thus redox-induced P release from soils.

**Floodwater DRP increased with flooding time under all experimental conditions** as a result of effective diffusion of DRP from pore water to surface water (Jayarathne et al., 2016; Dharmakeerthi et al., 2019b). The rate of increase in floodwater DRP is faster under warm than cold conditions and in the sandy loam than in the clay. The higher rate of P diffusion in soil solution at high temperatures than at low temperatures is well established (Mackay and Barber, 1984), which is evident in this study as well, with the rapid increase in floodwater DRP under warm than cold conditions due to upward diffusion of P from pore water through the soil--water interface. The P diffusion constant is generally greater in a clay soil in a sandy soil (Olsen and Watanabe, 1963), suggesting a higher rate of P flux to floodwater in the clay than in the sandy loam, contrary to what we have

### Table 2. Regression models developed for dissolved reactive P (DRP) and cation concentrations in pore water and floodwater for 0, 2, 4, 6, 8, and 10 wk after flooding (WAF).

<table>
<thead>
<tr>
<th>Water Type</th>
<th>WAF</th>
<th>DRP Equation</th>
<th>Model*†</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pore water</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 WAF</td>
<td>( \text{DRP} = 4.637^{<em><strong>} - 0.039\text{Mg}^{</strong></em>}, 0.191 + 0.008\text{Ca}^{***}, 0.338 )</td>
<td>2</td>
<td>4.002*** - 0.017\text{Mg}***, 0.0017</td>
</tr>
<tr>
<td>2 WAF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 WAF</td>
<td>( \text{DRP} = 1.507^{<em><strong>} - 0.016\text{Mg}^{</strong></em>}, 0.127 )</td>
<td>2</td>
<td>4.058*** - 0.019\text{Mg}***, 0.297</td>
</tr>
</tbody>
</table>

* ** *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.
† DRP, dissolved reactive P. Superscripts within parentheses indicates the significance level and the partial \( R^2 \) value of each coefficient in the regression model (\( n = 36 \)), ns, not significant.

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observed. However, moisture content has a greater influence on P diffusion in sandy soils than in clay soils (Mahtab et al., 1971), where under wetter conditions, diffusion rates are faster in sandy soils. Moreover, the concentration gradient of DRP between the pore water and floodwater is much higher in the sandy loam than in the clay in the current study. All these factors may explain the higher rate of P flux in the sandy loam, as previously observed in soils with contrasting textures (Dharmakeerthi et al., 2019b). This resulted in a decrease in pore water DRP concentration in the sandy loam, particularly in the unamended and biochar-amended treatments under warm conditions beyond 4 WAF. The decrease in pore water DRP concentration under the above conditions may also be due to co-precipitation of P, which needs to be further investigated. Co-precipitation may occur with released Mn, particularly during the latter part of the incubation period, and/or with Ca and Mg (Shober and Sims, 2009; Jeke and Zvomuya, 2018), since Ca and Mg concentrations decreased in the sandy loam throughout the incubation period.

Flooding-Induced P Release in Unamended, Gypsum-Amended, and Biochar-Amended Soils

Our results suggest application of gypsum to be very effective in reducing pore and floodwater DRP concentration, particularly in soils with high DRP concentrations (>1 mg L\(^{-1}\)) such as the sandy loam. Even in the clay soil, which had relatively low DRP concentrations in the unamended treatment during the early stages of flooding, gypsum application significantly reduced the pore water DRP when the concentrations exceeded ~1 mg L\(^{-1}\) (>6 WAF). However, gypsum application increased the DRP concentrations compared with the unamended treatment at the initial stages of flooding up to 5 WAF. A decrease in DRP in runoff water, pore water, or floodwater in soils amended with gypsum has been previously observed (Favaretto et al., 2006; Norton, 2008; Dharmakeerthi et al., 2019b). In most of these studies, DRP concentrations decreased with gypsum amendment only when runoff or pore water DRP concentrations in unamended soils were >1 mg L\(^{-1}\). Our previous study (Dharmakeerthi et al., 2019b), however, showed a significant decrease in pore and floodwater DRP concentrations in two acidic soils even when DRP concentrations were <1 mg L\(^{-1}\). This is likely due to precipitation of Ca phosphates with gypsum application, a reaction favored at a pH range of 6.0 to 8.5 (Olila and Reddy, 1995), which is the pH range in pore and floodwater pH in both soils for most of the incubation period. The gypsum application also delayed the decrease in Eh beyond +200 mV after flooding, as observed in a previous study using different soils (Dharmakeerthi et al., 2019b), thus reducing the P release due to reductive dissolution reactions. The reason for the delay in Eh decrease below +200 mV with gypsum application is unclear and needs to be further investigated. Results suggest that the effectiveness of gypsum in reducing DRP release to floodwater is dependent on the interactive effects of Eh changes, floodwater pH, and DRP concentrations.

Biochar can act as a source as well as a sink for P in flooded soils. Although biochar amendment increased pore water and floodwater DRP concentrations in the clay, it only slightly decreased or had no effect on DRP concentrations over the flooding period in the sandy loam. Biochar application did not change the Ca and Mg concentrations in pore and floodwater under warm or cold condition in both soils. However, it favored the release of Mn and Fe in both soils under warm conditions, suggesting P release due to reductive dissolution reactions involving Fe and Mn. In flooded soils, biochar can help to shuttle electrons between donors and accepters, usually microorganisms and reducible cations, thus favoring reductive dissolution of P (Wisawapipat et al., 2017). Being an excellent sorbent, biochar also could sorb chelating organic acids that would otherwise bind Fe and Al in the soil solution, thus favoring co-precipitation of Fe and Mn with phosphates (DeLuca et al., 2015). This hypothesis is supported by the greater Mn concentrations in the sandy loam with a significant decrease of DRP during the latter part of incubation period under warm conditions. In addition, Ca in biochar may form precipitates with dissolved P in water (Xu et al., 2014). Our results suggest that the woodchip biochar used in this study was not effective in reducing redox-induced P release from flooded soils.

Relationship between Cation Concentrations and Dissolved Reactive P at Various Stages of Flooding

During the initial stage of flooding, the positive relationship between DRP and Ca concentrations was significant and likely due to the dissolution of Ca phosphates (Jayarathe et al., 2016). The significant, negative relationship between DRP and Mg concentrations in both pore water and floodwater throughout the flooding period was unexpected. Based on this analysis, the DRP concentration in pore water and floodwater decreases when Mg concentration increases, suggesting co-precipitation of Mg with phosphates. This needs to be further investigated. The significant, positive relationships of DRP with Mn or Fe concentrations during the latter period of flooding suggest the release of phosphates associated with Mn and Fe due to reductive dissolution, as has been previously reported (Young and Ross, 2001; Amarawansha et al., 2015; Jayarathe et al., 2016). Our results suggest that when soils were flooded for >6 wk, Mn and Fe associated P will be released into pore water, but a significant impact on floodwater is seen only at very late stages of flooding, ~10 WAF in this study.

Conclusions

Prolonged flooding enhanced P release to pore water. At cold temperatures, such as spring snowmelt conditions simulated in this study, the rate of release of DRP was much lower than under warm conditions (simulated midsummer flooding). This decrease in P release rate was mostly associated with the lower rate of reductive dissolution reactions and lower P diffusion under cold temperatures. Wallboard gypsum application was very effective in reducing surface water DRP under simulated snowmelt and summer flooding conditions, particularly when the DRP concentrations are high. The woodchip biochar tested in this study was not effective in reducing redox-induced P release from flooded soils.

Supplemental Material

The supplemental materials provide information on the ANOVA for the soil Eh, pore water and floodwater pH and concentrations of DRP, Ca and Mg during the incubation period in unamended, and gysump-
amended and biochar-amended soils under simulated spring snowmelt and summer flooding conditions (Supplemental Table S1). Changes in pore water and freshwater cation concentrations with flooding time under simulated snowmelt and summer flooding in unamended, gypsum-amended, and biochar-amended Fyala and Neuenberg soils are given in Supplemental Fig. S1.

Conflict of Interest
The authors declare no conflict of interest.

Acknowledgments
Funding for this research was provided by a National Sciences and Engineering Research Council (NSERC) Discovery Grant and a University of Winnipeg Major Grant to Darshani Kumaragamage, and a fellowship awarded by the University of Winnipeg—Queen Elizabeth Advanced Scholar Program to R.S. Dharmakeerthi. The authors acknowledge farm cooperators and colleagues in Manitoba Agriculture for their assistance in providing the soils for this study, Josh Markham for soil collection, and Chathuri Weerasekara and Carolyn Gregory for technical help.

References