Gypsum Amendment Reduces Redox-Induced Phosphorous Release from Freshly Manured, Flooded Soils to Floodwater

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Abstract

The effectiveness of gypsum in reducing runoff P losses from soils and the mechanisms responsible are well documented; however, gypsum amendment effects in reducing redox-induced P losses from flooded soils are less researched and documented. We examined the effect of gypsum amendment on P release from freshly manured soils to pore water and floodwater with continuous flooding for 56 d in the laboratory. Three soils (Pembina, Denham, and Dencross series) collected from Manitoba, Canada, were preincubated with liquid swine manure. Each preincubated manured soil was packed into vessels with or without recycled wallboard gypsum in triplicates and flooded for 56 d, during which pore water and floodwater were sampled weekly and analyzed for pH and dissolved reactive P (DRP), Ca, Mg, Fe, and Mn concentrations. Change in soil redox potential (Eh) with flooding was also monitored. Wallboard gypsum amendment significantly decreased the pore water and surface floodwater DRP concentrations in all three soils for most days after flooding (DAF). The Dencross soil, which had Olsen P about fivefold greater than the other soils, showed the greatest magnitude decrease in DRP concentration with gypsum amendment, by 1.27 mg L^{-1} on 49 DAF and 0.99 mg L^{-1} on 21 DAF for pore water and floodwater, respectively. Gypsum amendment (i) delayed the Eh reduction with flooding beyond +200 mV, (ii) decreased pore water pH, and (iii) increased concentrations of Ca, Mg, and Mn in pore water favoring precipitation of P, all of which may have directly or indirectly reduced the P release from flooded soils to overlying floodwater.

Core Ideas

- Floodwater P concentration increased with flooding time in all soils and treatments.
- Redox-induced P release was less from gypsum-amended than unamended soils.
- Gypsum amendment reduced both pore water and floodwater P concentrations.
- Adding gypsum reduced floodwater P concentration to a maximum of 57%.
- The effectiveness of gypsum in reducing P release from flooded soils is soil dependent.

AGRICULTURAL LANDS are major contributors to P pollution of fresh water bodies resulting in eutrophication (Schindler et al., 2012; Sharpley et al., 2018). Phosphorus from agricultural lands can be transported to water bodies either as particulate P or dissolved P via different pathways, namely, soil erosion (Sharpley et al., 1994), preferential flow and tile drainage (Rickson, 2014; King et al., 2015), surface runoff (Baker et al., 2017), and leaching (Smith et al., 2015; Toor and Sims, 2015).

Dissolution of sparingly soluble P and desorption of P-bound clays are two major processes involved in the P release to soil solution. In organic-matter-rich soils, mineralization of organic P is significant (Maranguit et al., 2017) and also may contribute to an enhanced inorganic P in soil solution. In flooded soils, microbially mediated reductive dissolution of Mn- and Fe-bound phosphates and the release of occluded phosphates may occur depending on the degree of soil reduction (anaerobiosis), which may enhance P release to soil solution (Amarawansha et al., 2015; Jayarathne et al., 2016; Maranguit et al., 2017). During the early phase of flooding, when the soil still contains free O_2, dissolution of Mg and Ca phosphates is more important for P release to soil solution (Jayarathne et al., 2016).

In recent years, flooding of agricultural lands in the Canadian Prairies has become more frequent as a result of high volumes of snowmelt runoff in the spring and early summer, and major rainfall events in the summer and fall (Bedard-Haughn, 2009; Buttle et al., 2016). In areas with flat landscapes, excess water could remain for a few days to several weeks, resulting in the release of substantial quantities of P to surface runoff water, contributing to P enrichment in surface water bodies such as Lake Winnipeg (Schindler et al., 2012). Agricultural fields in the region are often amended with organic manure at very high rates to meet the N requirement, resulting in an accumulation of P. It has been shown that the addition of swine manure to slightly alkaline soils of the Canadian Prairies initially depleted the proportion of P in the labile pool (Kashem et al., 2004; Qian et al., 2004), since most of the P from manure enters into moderately labile and stable fractions (Qian and Schoenau, 2000).

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A number of management strategies have been proposed to reduce the buildup of total P and soluble P in manure-amended soils (Penn and McGrath, 2014; Szogi et al., 2015; Kumaragamage and Akinremi, 2018). Soil amendment with materials containing Ca can reduce P losses from soils through conversion of soil P to less soluble forms (Callahan et al., 2002; Stout et al., 2003; Favaretto et al., 2006; Murphy and Stevens, 2010). Application of gypsum ($CaSO_4 \cdot 2H_2O$) effectively reduced P in runoff and leachate (Brauer et al., 2005; Favaretto et al., 2006; Favaretto et al., 2012), as the increased concentration of Ca^{2+} reduced the solubility of P by enhancing precipitation of insoluble Ca phosphates (Moore and Miller, 1994; Elrashidi et al., 2010).

Wallboard gypsum is a waste material from the construction and demolition industry with ∼95% of $CaSO_4 \cdot 2H_2O$ (Norton, 2008). Application of wallboard gypsum at a rate of 2.25 Mg ha^{-1} resulted in ∼50% reduction in soluble reactive P in runoff water in both manure-amended and nonamended soils (Norton, 2008). To our knowledge, the effectiveness of gypsum in reducing anaerobiosis-induced P mobilization to overlying floodwater from manure-amended flooded soils has not been investigated. We hypothesized that the application of recycled wallboard gypsum to soils prior to flooding could convert P to less soluble forms and thereby reduce the P mobility to overlying floodwater. Thus, the objectives of this study were to compare the change in P concentrations in pore and floodwater in manure-amended, flooded soils with and without wallboard gypsum amendment and to identify the reasons for changes in P release from soils using three prairie soils from Manitoba with contrasting properties.

Materials and Methods
Preincubation of Soil with Manure Amendment

Three surface soil samples (0- to 15-cm depth) were collected from Manitoba, Canada, representing the Pembina (Dark Gray Luvisol), Denham (Orthic Black), and Dencross (Gleyed Rego Black) series (Canadian Agricultural Services Coordinating Committee, 1998). All three soils collected were from flood-prone areas of Manitoba, including the Denham series consisting of moderately permeable loams over slowly permeable clayey substrate. Field-moist soils were amended with liquid swine manure with a total solid content of 4.6% and total P content of 1.1 kg 1000 L^{-1}, at the rate of 50 mg total P kg^{-1} soil (equivalent to 100 kg total P ha^{-1}) and thoroughly mixed with the soil. Manure amended soils were preincubated for 6 wk and sieved through <1-cm mesh.

Characterization of Soil and Wallboard Gypsum

Subsamples of soil prior to manure amendment were characterized, after air drying and sieving through a 2-mm sieve. Soil samples were analyzed for texture by pipette method (Gee and Bauder, 1986), and pH and electrical conductivity in soil: water suspensions (1:2 ratio) using a pH meter (Accumet AB15, Fisher Scientific Canada) and a conductivity meter (Accumet AB30, Fisher Scientific Canada), respectively. Soil organic matter and $CaCO_3$ equivalent (CCE) were determined using the loss-on-ignition method (Dean, 1974). Exchangeable cations were determined using ammonium acetate (1.0 mol L^{-1}) extraction and measuring Ca, Mg, Na, and K by inductively coupled plasma atomic emission spectroscopy (ICP–AES; iCAP 6500, Thermo Scientific).

Samples of manure amended and preincubated soils were analyzed in triplicates for available P by Olsen (Olsen et al., 1954), and Mehlich-3 (Mehlich, 1984) methods, measuring P concentrations by the molybdate blue method (Murphy and Riley, 1962) using an ultraviolet-visible spectrophotometer (Ultraspec 500, Biochrom) at 882-nm wavelength. Single-point P sorption capacity (P_{150}) was determined in triplicates by equilibrating soil with 0.001 mol L^{-1} KCl solution containing 150 mg P L^{-1}. The amount of P sorbed in milligrams per kilogram of soil was calculated using the difference between the initial and equilibrium P concentrations in the solution. Soil P fractionation analysis was performed by a modified Hedley procedure (Hedley et al., 1982). An index on degree of P saturation (DPS) in these soils was calculated using Mehlich-3 P as the intensity factor and P_{150} as the capacity factor using the following equation (Ige et al., 2005; Amarawansha et al., 2016):

$$DPS = \left[\frac{\text{Mehlich-3 P}}{(2 \times P_{150}) + \text{Mehlich-3 P}} \right] 100 \qquad [1]$$

Prior to soil amendment, wallboard gypsum was crushed to pass through a 0.5-mm sieve after removing the board attached to it. Powdered gypsum in duplicates was analyzed for total P, Ca, Mg, Na, K, and S using ICP–AES (iCAP 6500, Thermo Scientific) after microwave digestion (CEM MARS 5, CEM Corporation).

Laboratory Incubation

One-half of the manure-amended, preincubated, and sieved soils were thoroughly mixed with 0.25% (w/w) wallboard gypsum, which is equivalent to 5 Mg ha^{-1}. Gypsum-amended and unamended soils were packed into 1.5-L incubation vessels to a depth of 7 cm and a wet bulk density of 1.0 Mg m^{-3}. One Rhizon flex soil solution sampler with an outer diameter of 2.5 mm and 0.15-μm pore size (Rhizosphere Research Products) was installed during soil packing at 5-cm depth from the soil surface. A redox probe with a platinum sensor (Paleo Terra) was also installed vertically in each vessel at 5-cm depth to measure the redox potential (Eh) changes during the flooding period. Vessels were flooded using deionized water (Millipore, 18 MΩ cm) to a height of 5 cm of standing water, covered with Parafilm (Fisher Scientific), and incubated at room temperature (20 ± 2°C) over a period of 8 wk. All jars (n = 18) from each soil and gypsum amendment combinations with three replicates were arranged according to a complete randomized design.

On the day of the flooding and thereafter at weekly intervals, pore water was extracted using a 20-mL syringe attached to the end of the Rhizon flex sampler, whereas floodwater was extracted using a 20-mL syringe. Pore and floodwater samples were analyzed for dissolved reactive P (DRP) concentration using the molybdate blue color method (Murphy and Riley, 1962) immediately after the extraction, and for pH within 24 h. At each day of sampling, Eh was also measured by temporarily inserting an Ag–AgCl reference electrode coupled to the permanently installed Pt electrodes. Pore and floodwater samples collected at every other week were analyzed for Ca, Mg, Fe, and Mn concentrations using a flame atomic absorption spectroscopy (AAnalyst 400, PerkinElmer). At the end of the incubation period, soils were air dried and sieved, and triplicate samples were subjected to sequential P fractionation using the modified Hedley method (Hedley et al., 1982).

Statistical Analysis

Repeated-measures analysis was conducted using soil and amendment as between-factor effects and days after flooding (DAF) as the within-factor variable. Analysis of residuals indicated that data were normally distributed according to the Shapiro–Wilks test ($W > 0.9$) and was verified using normal probability plots. When a significant sphericity in the data was observed, Greenhouse–Geisser correction was used to test the significance of the within-factor effects. Simple regression analysis was conducted separately for three soils to investigate the gypsum amendment effect on the relationship between floodwater and pore water DRP concentrations with time of flooding. All statistical analysis were conducted using the software IBM SPSS version 19 (IBM, 2010), and significance levels were considered as $p < 0.05$.

Results and Discussion
Soil and Gypsum Characteristics

The texture of the three soils varied widely (Table 1) from sandy loam (Denham series) to clay (Dencross series). All soils had high organic matter contents (75–106 g kg^{-1}) and moderate to high cation exchange capacities (21–70 cmol$_c$ kg^{-1}). The pH of the three soils varied from strongly acidic to mildly alkaline. Olsen and Mehlich-3 P concentrations in preincubated, manured soils were greatest in Dencross series (138 and 164.3 mg kg^{-1}, respectively), whereas the lowest concentrations were observed in Pembina series (38.1 and 47.3 mg kg^{-1}, respectively). Single-point P sorption capacity values were similar in the three soils (338–363 mg kg^{-1}) but resulted in a wide range of DPS from 6.1 (Pembina series) to 19.6% (Dencross series). All three soils were weakly to moderately calcareous (CCE < 150 g kg^{-1}).

Recycled wallboard gypsum had mean ($n = 3$) total Ca and S concentrations of 213 and 172 g kg^{-1}, respectively. Wallboard gypsum had relatively high concentrations of total Mg (10.1 g kg^{-1}), Fe (265.7 mg kg^{-1}), P (293.1 mg kg^{-1}), K (415.8 mg kg^{-1}), and Na (520.9 mg kg^{-1}), but a much lower concentration of total Mn (30.1 mg kg^{-1}).

Table 1. Physical and chemical properties of initial soils (means of three replicates).

Property	Pembina series	Denham series	Dencross series
Clay (g kg^{-1})	255	154	449
Sand (g kg^{-1})	339	703	215
pH	6.2	5.1	7.7
Organic matter (g kg^{-1})	92.7	74.5	106.1
Cation exchange capacity (cmol$_c$ kg^{-1})	70.3	21.1	56.3
CaCO$_3$ equivalent (g kg^{-1})	26	22	103
Exchangeable Ca (mg kg^{-1})	3769	2010	7062
Exchangeable Mg (mg kg^{-1})	501	386	1176
Exchangeable Mn (mg kg^{-1})	115	56	110
Exchangeable Fe (mg kg^{-1})	122	209	48
Exchangeable Al (mg kg^{-1})	1160	1425	887
Olsen P (mg kg^{-1})†	38.1	49.2	138.0
Mehlich-3 P (mg kg^{-1})†	47.3	71.2	164.3
P sorption capacity (mg kg^{-1})†	363	341	338
Degree of P saturation (%)†	6.1	9.5	19.6

† Measured in manure-amended and preincubated soils.

Changes in Dissolved Reactive Phosphorus Concentrations in Pore Water and Floodwater with Time of Flooding

During flooding and development of anaerobic conditions, P would be initially released to pore water, which would then diffuse to floodwater through the oxidized soil–water interface. Both the pore and floodwater DRP concentrations were measured to evaluate the redox-induced P release and the effectiveness of P diffusion from pore water to floodwater, with and without gypsum amendment.

The three soils used in the study had contrasting properties and P status, which was reflected in their response to flooding in releasing P. For DRP concentrations in both pore and floodwater, the interaction effect of DAF × gypsum amendment × soil was significant ($p < 0.01$ and 0.001, respectively). On the day of flooding and throughout the flooding period, pore water DRP concentration was significantly greater in Dencross soil than Pembina and Denham soils, which is to be expected, since it had greater Olsen P and DPS values (>twofold) than the other soils. The DRP concentrations in pore and floodwater in Dencross soil ranged from 3.0 to 6.5 and 0.2 to 4.1 mg L^{-1}, respectively, whereas concentrations in Pembina and Denham soils ranged from 0.4 to 0.9 and 0.05 to 0.8 mg L^{-1}, respectively (Fig. 1). It has been shown that soils with greater DPS have the potential to release greater amounts of P into floodwater than soils with lower DPS (Amarawansha et al., 2016). The quantity of P release into floodwater in our study followed the same trend, with increasing amounts of P released with increasing DPS in soils.

The pore water DRP concentrations in both unamended and gypsum-amended treatments in Dencross soil increased significantly with DAF by ~1.5-fold at 42 DAF, whereas in Pembina and Denham soils, pore water DRP concentrations were more or less stable or showed a slightly decreasing trend with DAF (Fig. 1a). Similar variability among soils in their response to flooding on pore water DRP concentrations has been previously observed (Amarawansha et al., 2015; Jayarathne et al., 2016) and was mainly attributed to the textural variability and initial soil P status. The decrease in DRP concentration in pore water in Pembina and Denham soil could be possibly due to the readsorption and/or coprecipitation of P with the released cations (Shober and Sims, 2009; Amarawansha et al., 2015; Jeke and Zvomuya, 2018).

Even though prolonged flooding did not always contribute to a significant increase in pore water DRP concentration, the floodwater DRP concentrations steadily and significantly ($p < 0.05$) increased with DAF, irrespective of the soil type and amendment treatment. The increase in DRP concentration in floodwater with DAF ranged from very low initial concentrations (~0.1 mg L^{-1} at 0 DAF) to >0.3 mg L^{-1} in Pembina and Denham soils and even >3 mg L^{-1} in Dencross soil (Fig. 1b). In Pembina and Denham soils, the increase in floodwater DRP concentration relative to the zero DAF was four- to sevenfold by 56 DAF, whereas in the Dencross soil, the increase was >14-fold. The increase in floodwater DRP concentration with DAF suggests enhanced P release to pore water and effective diffusion of released P into floodwater through the oxidized surface layer. In the current study and in some previous studies (Amarawansha et al., 2015; Jayarathne et al., 2016), pore water DRP concentrations were greater than in floodwater, thus promoting upward diffusion of P from pore water to floodwater.
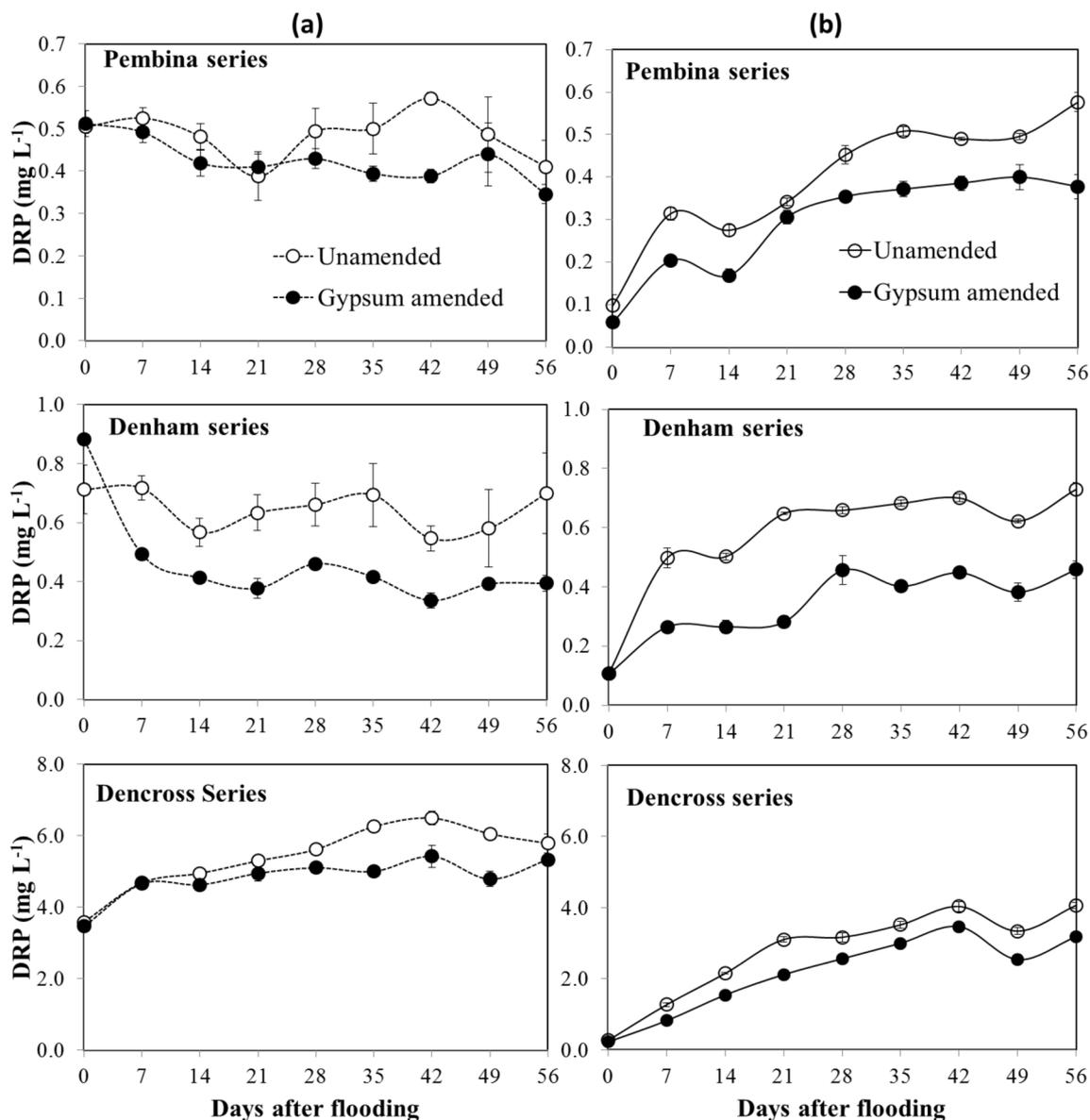
Fig. 1. The mean dissolved reactive P (DRP) concentrations in (a) pore water and (b) surface floodwater in unamended and gypsum-amended Pembina, Denham, and Dencross soils with time of flooding. Vertical error bars represent the SEM value (n = 3).

Effect of Wallboard Gypsum on Dissolved Reactive Phosphorus Concentration in Pore Water and Floodwater

The application of wallboard gypsum decreased the pore water and floodwater DRP concentrations in all three soils with the exception of pore water concentration at 21 DAF in the Pembina soil, and at 0 DAF in the Denham and Dencross soils (Fig. 1a and 1b). The decrease in DRP concentration in both pore water and floodwater with wallboard gypsum amendment was statistically significant ($p < 0.05$) for most DAFs, suggesting a reduction in P release from flooded, anaerobic soils, and/or transformation of released P to solid-state P forms. The magnitude of reduction in DRP concentration and percentage decrease with gypsum amendment varied with the soil and DAF. The maximum magnitude of reduction in pore water DRP concentration due to gypsum amendment was 0.2, 0.3, and 1.3 mg L^{-1} at 42, 56, and 49 DAF for Pembina, Denham, and Dencross soils, respectively (Fig. 1a), with corresponding maximum percentage reductions

in DRP concentrations of 32, 44, and 21%. For floodwater, the maximum magnitude of reduction in DRP concentration was 0.20 mg L^{-1} for Pembina soils at 56 DAF, and 0.37 and 0.99 mg L^{-1} for Denham and Dencross soils, respectively, at 21 DAF (Fig. 1b). The maximum percentage decreases in floodwater DRP concentrations with gypsum amendment were observed at 14, 21, and 7 DAF with 39, 57, and 35% reductions for Pembina, Denham, and Dencross soils, respectively.

The effectiveness of gypsum in decreasing the P concentration in runoff water from agricultural soils has been previously reported using natural, synthetic, recycled wallboard, and flue gas desulfurization (FGD) gypsum (Favaretto et al., 2006; Norton, 2008; Watts and Torbert, 2016). The application of gypsum (analytical grade) at 5 Mg ha^{-1} to the surface just before the rain decreased the mass loss of DRP and total P in runoff by 83 and 52%, respectively (Favaretto et al., 2006). In a more recent field study, two applications of FGD gypsum at 2.24 Mg ha^{-1} significantly reduced DRP loads in surface runoff by 41%

(King et al., 2016), whereas in another field study, amendment of phophogypsum at 4.1 Mg ha^{-1} reduced the DRP losses in runoff by one-third (Ekholm et al., 2012). In the present study, with wallboard gypsum applied to soils prior to flooding at similar rates as in previous studies (Favaretto et al., 2006; King et al., 2016), the reduction in apparent mobilization of P from flooded soils was substantial. This is evident from the maximum percentage decrease in floodwater DRP concentration (35–57%) as compared with the unamended control, depending on the soil.

To further elucidate the effect of gypsum in reducing P release from flooded soils, the relationships between DRP concentrations between floodwater and pore water was examined. In Pembina and Denham soils, floodwater DRP was poorly correlated with pore water DRP; however, in the Dencross soil, which had pore water DRP concentrations >3.0 mg L^{-1}, a significant ($p < 0.001$), positive relationship was observed, with ~1.2-fold increase in floodwater DRP concentration per unit increase in pore water DRP concentration (Fig. 2). Even though both pore water and floodwater DRP concentrations were lower in the gypsum-amended than unamended Dencross soil, it is interesting to note that the same regression line also appeared to fit the floodwater versus pore water DRP concentrations in both treatments. The results, therefore, suggest that gypsum amendment reduced the DRP concentration in pore water and floodwater in a similar manner. In Pembina and Denham soils, a significant relationship between floodwater and pore water DRP concentration was not observed, probably due to very low DRP concentrations. In coarse-textured Denham soil, pore water DRP concentration decreased with a simultaneous increase in the floodwater DRP concentration with DAF, which could be attributed to the sandy nature of the soil (Table 1) favoring faster diffusion of P from pore water to floodwater.

Factors Influencing Dissolved Reactive Phosphorus Concentrations in Pore Water and Floodwater in Unamended and Gypsum-Amended Soils

A multitude of complex chemical and biochemical processes govern the release of P from flooded soils to pore water and subsequent diffusion to floodwater. A complete understanding of these complex reactions could only be attained by an in depth study of the dynamics of chemical species associated with those reactions. However, to identify the key factors that govern the effectiveness of gypsum in reducing the DRP concentrations in pore water and floodwater, changes in soil Eh, pH, and cation concentrations in both pore water and floodwater with flooding time were determined.

Change in Redox Potential

On the day of flooding, Eh of soils at the 5-cm depth ranged from +359 to +544 mV and decreased with time of flooding to Eh values of +12 to +205 mV by the end of the incubation period (Fig. 3a). The main effect of soil was highly significant ($p < 0.001$), whereas the interaction of DAF × gypsum amendment was significant ($p < 0.05$). Soil Eh decreased with time after flooding in all three soils, with the greatest decrease in the Dencross series (Fig. 3a). By the end of the incubation period, soil Eh in unamended treatments decreased to around +100 mV in Pembina soil and close to zero mV in Dencross soil, suggesting a possibility of microbially mediated reductive dissolution of Fe and Mn phosphates releasing P. Microbial reduction of Fe^{3+} to Fe^{2+} takes place when soil Eh falls below +100 mV (Gotoh and Patrick, 1974), whereas reduction of Mn^{4+} to Mn^{2+} takes place at higher Eh than Fe^{3+} reduction (Patrick and Jugsujinda, 1992; Amarawansha et al., 2015).

Gypsum amendment did not seem to influence the decrease in Eh at the initial stages of flooding; however, when Eh dropped to about +200 mV, further decrease in Eh with flooding time was somewhat delayed in gypsum-amended, than unamended, soils (Fig. 3a). The Eh did not drop below +200 mV in gypsum-amended Pembina soil and both unamended and gypsum-amended Denham soil. In unamended Dencross soil, Eh decreased below +200 mV after ~28 DAF and continued to decrease thereafter. In contrast, Eh of the gypsum-amended Dencross soil remained above +200 mV until ~42 DAF and then decreased. Thus, our results suggest that in addition to P removal from solution through precipitation reactions (Elrashidi et al., 2010; Murphy and Stevens, 2010), gypsum may have directly reduced the redox-induced P release from soils, since the decrease
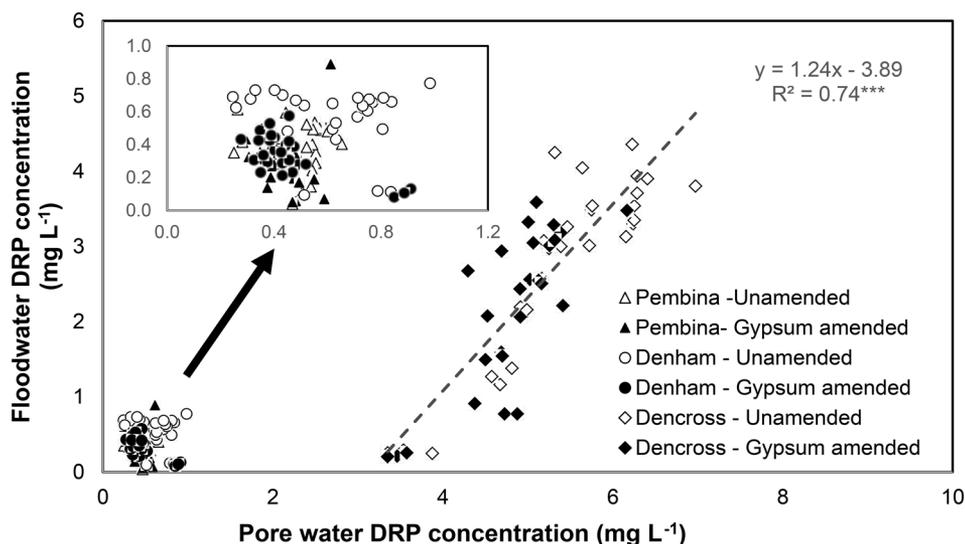

Fig. 2. Relationship between pore water dissolved reactive P (DRP) and surface floodwater DRP concentrations for Pembina, Denham, and Dencross soils.
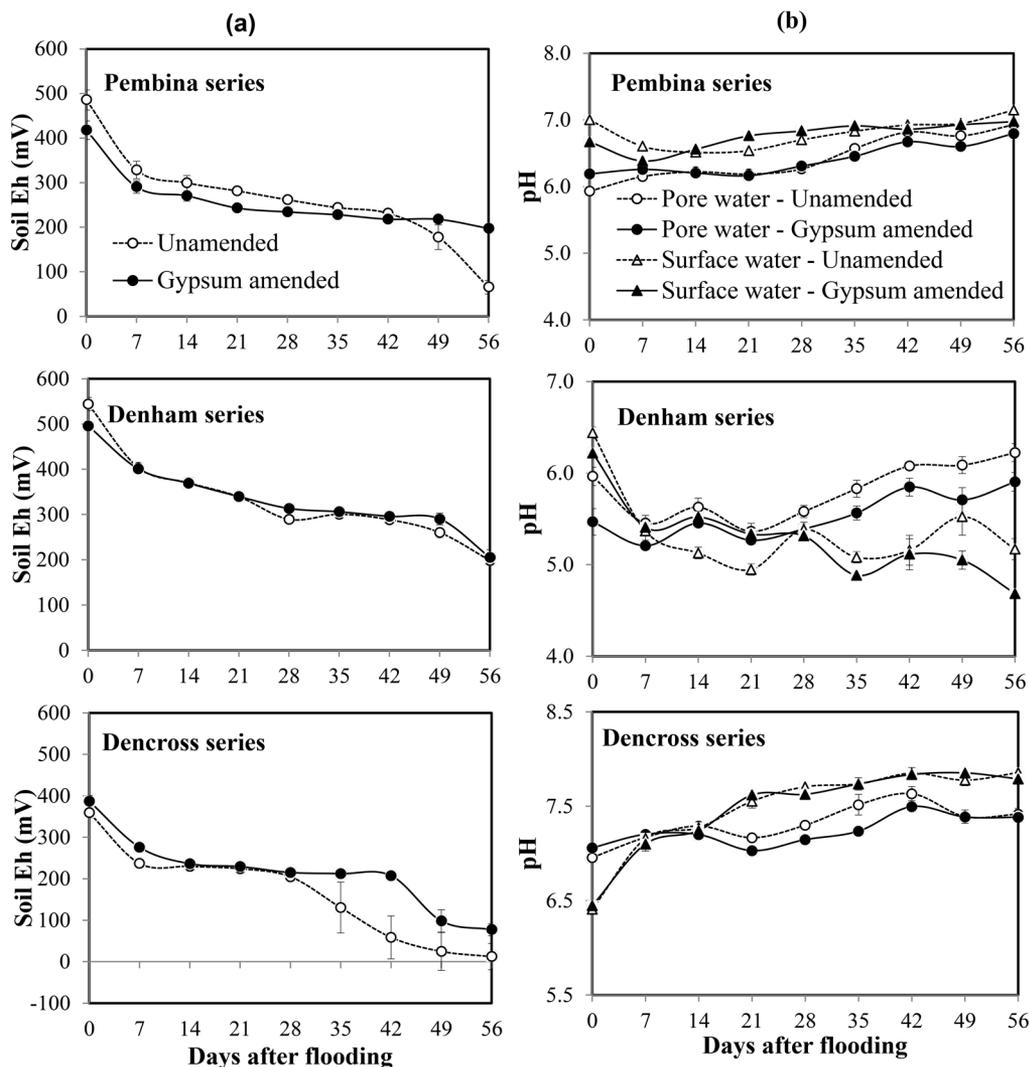
Fig. 3. Changes in (a) soil redox potential (Eh) and (b) pore water and floodwater pH with time of flooding in unamended and gypsum-amended Pembina, Denham, and Dencross soils. Vertical error bars represent the SEM value ($n = 3$).

in Eh with flooding was delayed in gypsum-amended treatments when soil reached a redox potential of about +200 mV, whereas Eh of unamended soils continued to decline.

Changes in Pore Water and Floodwater pH

The floodwater and pore water pH during the flooding period was influenced by the DAF × amendment × soil interaction effect ($p < 0.01$ and 0.05, respectively). In Pembina and Dencross soils, pH in pore water increased with flooding time by ∼0.4 to 0.8 units, whereas the difference among gypsum-amended and unamended soil varied depending on DAF (Fig. 3b). In Denham soil, pore water pH in the gypsum-amended treatment was significantly less than in the unamended treatment for most time periods, whereas in both the unamended and gypsum-amended treatments, pore water decreased initially up to about 7 DAF and then increased. Floodwater pH was greater than pore water pH for most DAFs in all soils (Fig. 3b), thus favoring precipitation of P with Ca and/or Mg (Ramasahayam et al., 2014; Song et al., 2002).

The decrease in pH with gypsum amendment was significant for pore and floodwater in the Denham soil and for pore water in Dencross soils for most DAFs (Fig. 3b). The lowering of pH with application of gypsum was previously reported for both alkaline

and acidic soils (Sun et al., 2000; Vizcayno et al., 2001; Murphy and Stevens, 2010; Temiz and Cayci, 2018) and was attributed to the exchange of Ca^{2+} for H^+ and Al^{3+}. The decrease in soil pH will enhance the solubility of Ca and Mg phosphates but favor precipitation of Mn and Fe phosphates (Hsu, 1973; Boyle and Lindsay, 1986; Gomez et al., 1999).

Changes in Calcium and Magnesium Concentrations in Pore Water and Floodwater

The main effect of treatment was highly significant ($p < 0.0001$) for pore water Ca and Mg concentrations, whereas the main effect of soil was significant only for pore water Mg ($p < 0.01$), but not for Ca. For both pore water Ca and Mg concentrations, soil × treatment and all interactions with DAF were not significant. In gypsum-amended soils, pore water Ca and Mg concentrations were significantly greater in all three soils with the exception of 0 DAF (Supplemental Fig. S1a,c). This is to be expected, since recycled wallboard gypsum used in this study contained appreciable amounts of Mg ($10.1\ g\,kg^{-1}$) in addition to Ca ($213\ g\,kg^{-1}$). Presence of relatively high concentrations of Mg in wallboard gypsum has been previously reported (Patterson et al., 2009). In addition, Ca released from gypsum can effectively

compete for cation exchange sites and release exchangeable Mg (Uusitalo et al., 2012), thus increasing pore water Mg concentrations. In a study where gypsum was applied to a saline-sodic topsoil, it was found that 64 to 74% of the applied Ca was transferred to ion exchange sites, whereas one-third of this adsorbed Ca displaced exchangeable Mg (Armstrong and Tanton, 1992). In the current study, pore water Ca and Mg concentrations in both unamended and gypsum-amended treatments decreased with time of flooding in all soils, which may be due to both ionic diffusion to floodwater and precipitation reactions.

For Ca and Mg concentrations in floodwater, the main effects of soil and treatment were highly significant ($p < 0.0001$) but soil × treatment interaction was not significant. The DAF × treatment interaction was also significant, and the magnitude of increase in floodwater Ca and Mg concentration with DAF varied among soils. Greater concentrations of Ca and Mg in floodwater were observed of gypsum-amended than unamended soils. Floodwater Ca and Mg concentrations increased initially up to about 28 DAF and then decreased or remained relatively stable, suggesting precipitation of Ca and Mg with anions such as phosphates (Supplemental Fig. S1b,d). Similarly, in previous studies, the decrease in runoff P concentration from gypsum-amended soils was attributed to the release of Ca to soil solution with the dissolution of gypsum, which reacts with phosphate to form sparingly soluble Ca orthophosphates (Zhu and Alva, 1994; Favaretto et al., 2006; Murphy and Stevens, 2010).

Changes in Iron and Manganese Concentrations in Pore Water and Floodwater

In most soil–treatment combinations, pore water Mn concentrations were below the detectable levels on the day of flooding but significantly increased with DAF (Supplemental Fig S2a). The main effects of soil, treatment, and their interaction, as well as all interactions with DAF, were highly significant for pore water Mn. Gypsum-amended treatment had significantly greater pore water Mn concentrations than unamended treatment in all soils, but the differences varied depending on soil and DAF. Gypsum amendment has been previously shown to increase Mn availability (Courtney and Timpson, 2005), as well as cause substantial leaching losses of Mn (Vidal et al., 2003). This was attributed to the increased acidity (or decreased pH) with gypsum application, which was also observed in the present study. With the development of anaerobiosis, pore water Mn concentrations in Pembina and Dencross soils steadily increased with DAF up to 42 to 56 DAF. In contrast, pore water Mn concentrations in Denham soil initially increased, reached a maximum around 14 DAF, and then declined with flooding time. Floodwater Mn concentrations were less than detectable levels in Pembina and Dencross soils for both treatments at all DAF, whereas detectable concentrations were observed only in Denham soil for the gypsum-amended treatment. In all soils, pore water and floodwater Fe concentrations were very low and often below the detectable range initially (at 0 DAF). Pore water concentrations of Fe increased to detectable levels by 56 DAF in all soils (Supplemental Fig. S2b), suggesting release of Fe through reductive dissolution of Fe compounds under anaerobic conditions, as previously observed in flooded soils (Amarawansha et al., 2015; Jayarathne et al., 2016).

In gypsum-amended soils, the observed delay in Eh decline beyond about +200 mV may reduce reductive dissolution of Fe and Mn compounds. This effect, however, was not reflected in the differences of Fe and Mn concentrations in pore water and floodwater between the unamended and gypsum-amended treatments, very likely due to the counteracting influence of increased acidity in gypsum-amended treatments. In addition, pore water Fe^{2+} and Mn^{2+}, while diffusing to floodwater, may get reoxidized at the soil–water interface and form precipitates (Young and Ross, 2001; Amarawansha et al., 2015; Jayarathne et al., 2016), which may mask the effect of gypsum in reducing Fe and Mn concentrations.

Influence of Initial Soil Phosphorus and Degree of Phosphorus Saturation

The magnitude of reduction in DRP concentrations with gypsum amendment was greater in the Dencross soil than in the other two soils for most DAFs. Dencross soil had a higher Olsen P concentration and DPS with consistently high DRP concentration in both pore water and floodwater compared with the other two soils, which may have favored precipitation of P as Ca and Mg phosphates. Our results corroborate the findings of a previous study comparing five contrasting grassland soils, where effectiveness of gypsum application in reducing DRP in soil solution was greater in high-P soil (Murphy and Stevens, 2010). Therefore, the benefits of gypsum application in controlling P release from flooded soils seem to be greater in soils with high available P and DPS, which contribute more to outflow of P when subjected to flooding.

Changes in Soil Phosphorus Fractions

For the H_2O-extractable P fraction, soil × treatment interaction was significant ($p < 0.05$, Fig. 4a), but for other fractions, only the main effect of soil was significant (Fig. 4b) while the treatment effect and soil × treatment interaction were not significant. In all soils, H_2O-extractable P in unamended soils at the end of flooding period was greater than in preflooded soil, but the difference was significant only in Dencross soil with an increase of 18 to 20%. Our results suggest that flooding for a prolonged period of time converts P from other labile and recalcitrant fractions to water-soluble fractions, with the magnitudes varying depending on the soil. In gypsum-amended soils, the H_2O-extractable P at the end of flooding period was less than in unamended soils, but the difference was significant only in Denham soil. In Denham soil, gypsum amendment decreased the H_2O-extractable P after flooding by >42% compared with both preflooded soil and the unamended treatment at the end of flooding period (Fig. 4a). The decrease in H_2O-extractable P with gypsum amendment observed in all soils, with a significant decrease in Denham soil, suggests that water soluble P was converted to less labile forms with gypsum amendment. Reduction of the water-soluble P fraction in soils has been previously reported with the application of gypsum (Stout et al., 1999; Favaretto et al., 2006), but in these studies, soils were not kept under flooded, anaerobic conditions. Given the results of this study, we can speculate that the potential P release to floodwater, if flooding was continued beyond 56 DAF, would likely be less in gypsum-amended than unamended soils.
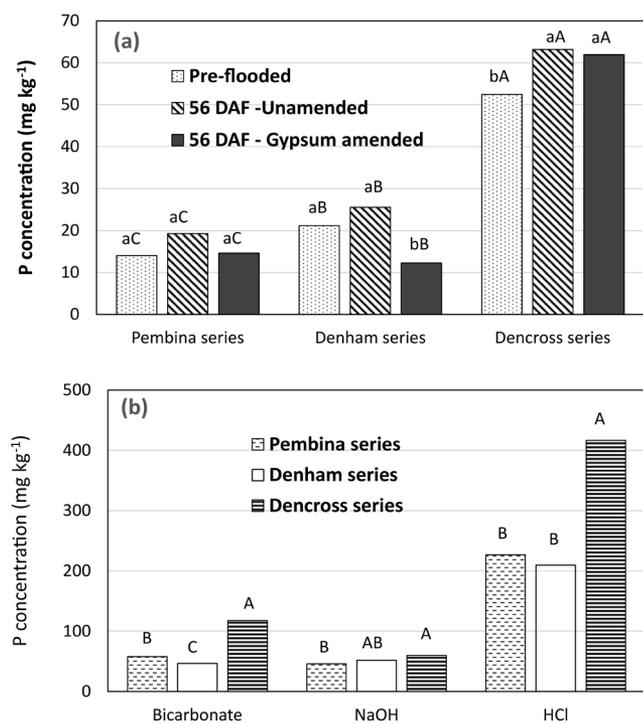
Fig. 4. Variation in P concentrations in different fractions: (a) H₂O-extractable P fraction as affected by soil type × incubation conditions and (b) HCO₃⁻-, NaOH-, and HCl-extractable P fractions as affected by soil type. Lowercase letters on bars indicate the significant differences ($p < 0.05$) among gypsum amendment and flooding within a soil series, whereas uppercase letters provide the significant differences among soil series within gypsum amendment and flooding in Panel a or different extractants in Panel b. The abbreviations DAF refers to days after flooding.

Conclusions

The increase in floodwater DRP concentration with time of flooding clearly demonstrates an enhanced P release from soils with the development of anaerobic conditions. Gypsum amendment at 5 Mg ha⁻¹ was effective in reducing redox-induced P release from flooded, anaerobic soils. A multitude of interactive factors seems to be responsible for reducing P release from flooded soils to floodwater with gypsum amendment. The contributive factors responsible for the reduction in P release from flooded soils with gypsum amendment may include (i) a delay in Eh reduction beyond +200 mV, (ii) a decrease in pore water pH, and (iii) an increase in Ca, Mg, and Mn concentrations in pore water favoring precipitation of P with these cations.

Supplemental Material

The supplemental material includes figures showing the changes in Ca and Mg concentrations in pore water and floodwater (Supplemental Fig. S1), and the changes in Fe and Mn concentration in pore water (Supplemental Fig. S2), in wallboard gypsum-amended and unamended treatments of Dencross, Denham, and Pembina series soils during the 56-d flooding period.

Acknowledgments

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