

Article



## Alum and Gypsum Amendments Decrease Phosphorus Losses from Soil Monoliths to Overlying Floodwater under Simulated Snowmelt Flooding

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**Abstract:** Phosphorus (P) loss from soils poses a threat of eutrophication to downstream waterbodies. Alum (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O) and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) are effective in reducing P loss from soils; however, knowledge on their effectiveness under cold temperatures is limited. This study examined the reduction of P loss from soils with alum and gypsum amendment under simulated snowmelt flooding. Intact soil monoliths (15 cm depth) collected from eight agricultural fields in flood-prone areas of Manitoba, Canada, were surface amended with alum or gypsum, pre-incubated for 2 weeks, then flooded and incubated at 4 °C for 8 weeks. Porewater and floodwater samples collected weekly were analyzed for dissolved reactive P (DRP), dominant cations and anions. An enhanced P release with flooding time was observed in all soils whether amended or unamended; however, alum/gypsum amendment reduced DRP concentrations in porewater and floodwater DRP concentrations (maximum DRP concentration during flooding) with alum and gypsum ranged from 34–90% and 1–66%, respectively. Based on Visual MINTEQ thermodynamic model predictions, precipitation of P and formation of P-sorbing mineral species with alum and gypsum amendment reduced DRP concentrations at latter stages of flooding.

Keywords: agricultural soils; floodwater; non-point source pollution; porewater; thermodynamic model

## 1. Introduction

Phosphorus (P) is a major, non-point source pollutant of surface water bodies [1,2]. Elevated soluble P concentrations in surface water bodies stimulate algae growth, thus degrading water quality [3,4]. Agricultural soils can significantly contribute towards P enrichment in water bodies through P losses via different pathways [4,5]. In cold climatic regions, spring snowmelt runoff over frozen soils is a dominant pathway of P losses from soils [6–9]. During the snowmelt period in the Canadian prairies, agricultural fields remain flooded for periods ranging from a few days to several weeks [10], depending on soil type, and drainage/landscape position. Prolonged flooding leads to a depletion of dissolved  $O_2$  in soil because of microbial respiration, thus creating anaerobic conditions [11]. Even under cold temperatures characteristic of spring snowmelt, continuous flooding led to anaerobiosis in soil with a corresponding decrease in redox potential [12,13]. Subsequent anerobic microbial respiration results in a sequence of redox reactions [11,14] causing microbially mediated reductive dissolution of P bound to redox sensitive elements such as Fe and Mn [15,16].



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Significant enhancement of P release from soils to soil solution and/or floodwater under flooded, anaerobic conditions has been reported across a wide range of agricultural soils under varying environmental conditions [15–19]. The magnitude of P release from soils to floodwater varied depending on soil properties [17,20,21] and flooding conditions, with greater losses under warm (~20 °C) than under cold (~4 °C) temperatures [12,13,22]. Enhanced P release from flooded soils has been attributed to a combination of physical and reductive dissolution reactions triggered by the changes in soil pH and redox status [16–18]. Organic P in soils can contribute to P release through mineralization as well; however, it has been shown that continuous flooding suppressed organic P mineralization due to inhibition of microbial and root activity with a corresponding decrease in root phosphatase activity [23].

Soil amendments containing Ca, Al and Fe have been demonstrated to be effective in reducing P runoff and leaching losses from soils through the conversion of soil P to less soluble forms [24–28]. Application of natural, synthetic, recycled wallboard, and flue gas desulfurization (FGD) gypsum (CaSO<sub>4</sub> $\cdot$ 2H<sub>2</sub>O) to soils effectively reduced P runoff losses by favoring the precipitation of insoluble Ca phosphates [26,29–31]. Lizarralde et al. [32] evaluated seven amendments including gypsum and alum  $(Al_2(SO_4)_3 \cdot 18H_2O)$  and reported greater cost-effectiveness with alum than gypsum in reducing water extractable P in soils, while the decrease in water extractable P was proportional to the rates of amendment application. Amending flooded soils with P-fixing materials such as gypsum, calcite (CaCO<sub>3</sub>), slaked lime  $(Ca(OH)_2)$ , dolomite  $(CaMg(CO_3)_2)$ , alum, magnesium sulfate  $(MgSO_4)$  and ferric chloride (FeCl<sub>3</sub>) have shown varying degrees of effectiveness in reducing P release to floodwater, depending on the type of amendment, rate, soil properties and flooding environment [33–36]. In packed soil columns using three manure-amended, calcareous agricultural soils, application of recycled, wallboard gypsum at a rate of 2.5 g kg<sup>-1</sup> prior to flooding resulted in a significant, and up to 57%, decrease in dissolved reactive P (DRP) concentration in floodwater, while the magnitude of decrease was dependent on the soil and time of flooding [35]. The authors attributed the decrease in P release from soils to floodwater with gypsum amendment to a combination of effects; a delay in Eh reduction beyond +200 mV, a decrease in porewater pH, and an increase in Ca, Mg, and Mn concentrations in porewater favoring precipitation of P with these cations. In addition, the change in the soil solution composition and increase of ionic strength with soil amendments will increase P sorption as previously reported [37–39]. In packed soil columns using an organic soil from a constructed wetland, the effectiveness in reducing floodwater P concentration was in the order:  $FeCl_3 > alum > Ca(OH)_2 > calcite > dolomite [33]$ . Prediction of P speciation using SOILCHEM [40] and Visual MINTEQ [41] software suggested that non-apatite Ca-P (tri calcium phosphate and octa calcium phosphate), amorphous Al hydroxide, and iron oxide phosphate compounds probably controlled soluble inorganic P in the porewater and overlying floodwater in chemically amended soils [33,42]. Although the effectiveness of various amendments in reducing P release is well documented under summer flooding or warm temperatures, very little information is available on their effectiveness under cold flooding, characteristic of snowmelt conditions.

Most studies investigating amendment effects on P release from flooded soils used packed columns or mesocosms [33–35]. Compared to previous studies with packed soil columns, more recent studies have shown that flooding of intact soil monoliths resulted in a more rapid development of anaerobic conditions resulting in substantial P release from soils to floodwater [13,43]. The objective of this research was to evaluate and compare P release from flooded intact monoliths of unamended, gypsum-amended, and alumamended soils under simulated snowmelt conditions and to identify possible inorganic P transformations using Visual MINTEQ modeling software. We hypothesized that gypsum and alum amendment will reduce the magnitudes of P release from soils to floodwater with flooding even under cold temperatures.

## 2. Materials and Methods

#### 2.1. Collection of Soil Monoliths and Soil Characterization

Intact soil monoliths were collected from eight poorly drained agricultural fields located in the Red River Valley of Manitoba, Canada, in October 2019. The eight soils belonged to four soil series, Dencross (two soils named as Dencross 1 and Dencross 2), Lakeland (one soil), Osborne (three soils identified as Osborne 1, Osborne 2 and Osborne 3) and Scanterbury (two soil identified as Scanterbury 1 and Scanterbury 2) series. According to the Canadian system of soil classification, Dencross, Lakeland and Scanterbury series belong to Gleyed Rego Black Chernozem subgroup while Osborne series belongs to Rego Humic Gleysol [44]. The equivalent FAO classification for Dencross, Lakeland and Scanterbury series is Calcic Chernozems and for Osborne series is Mollic Gleysol [45]. All fields were cultivated to annual field crops but had not received fertilizer or manure within four months prior to the sampling date. All sites selected are prone to flooding during spring snowmelt period.

To collect intact soil monoliths, we used polyvinyl chloride (PVC) tubes (10 cm internal diameter, 30 cm long), each with a drilled hole (3 mm) at 20 cm from the top. Soil monoliths were collected by pushing PVC cylinders into the soil using a drop hammer to a 15 cm depth (so that the drilled hole is 5 cm below the soil surface). Soil monoliths were sealed on the bottom end by gluing a PVC cap.

From each site, a composite surface soil sample (0–15 cm depth) was taken for soil characterization. Soil samples were air-dried and passed through a 2 mm sieve prior to analysis for physical and chemical properties. Soil texture was analyzed using the pipette method [46]. Soil pH was determined in 1:2 soil-water suspension using a pH meter (Fisher Accumet AB15). Soil P status was determined by the Mehlich-3 [47] method. The P concentration of filtered Mehlich-3 extracts were determined using the molybdate blue method [48]. Organic matter and calcium carbonate equivalent (CCE) of soils were determined using a modified loss-on-ignition method [49]. Mehlich-3 extractable Ca, Mg, Fe and Mn concentrations were determined by extracting soil samples with Mehlich-3 extractant [47] and measuring the cation concentrations in the extract using flame atomic absorption spectroscopy (AAnalyst 400, PerkinElmer, Waltham, MA, USA).

### 2.2. Incubation Study with Intact Soil Monoliths

Triplicate monoliths from each soil were subjected to three treatments; unamended, alum (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O)-amended or gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O)-amended. The monoliths were amended with alum (VWR International, Radnor, PA, USA) or gypsum (Fisher Scientific, Hampton, NH, USA) at a rate of 5 Mg ha<sup>-1</sup> by uniformly applying the weighed chemical to the soil surface based on the surface area of the monolith. A Rhizon-MOM soil solution sampler (2.3 mm outer diameter, 0.15 µm pore size; Rhizosphere Research Products, Wageningen, Netherlands) was placed horizontally through the drilled hole at 5 cm below the soil surface to extract porewater. Unamended and amended soil monoliths were pre-incubated for 2 weeks in field moist conditions at  $4 \pm 1$  °C.

Soil monoliths were flooded after pre-incubation by adding ultrapure water (Milli-Q; 18 M $\Omega$  cm) from the top along the sides of the PVC tube, to maintain a 10 cm head of water. To measure the soil redox potential (Eh), a redox probe with a platinum sensor (Paleo Terra, Amsterdam, Netherlands) was inserted vertically soon after flooding, ensuring that the sensor was at 5 cm depth (same depth as porewater samplers) in each monolith. Unamended, alum-amended and gypsum-amended monoliths were incubated for 56 d in a cooler at 4 ± 1 °C to simulate snowmelt flooding.

During the day of flooding and thereafter at 7 d intervals, porewater and floodwater samples were collected. Porewater samples were extracted by applying suction using a syringe attached to the end of the Rhizon-MOM samplers. Overlying floodwater samples were extracted using syringes from flooded monoliths. After each sampling, ultrapure water was added to each soil monolith to maintain a 10 cm head. Floodwater samples were filtered through 0.45  $\mu$ m membrane filters. Both porewater and floodwater samples

were analysed for DRP concentrations immediately after sampling by the molybdate blue method [48]. Porewater and floodwater samples were also analyzed for pH using a pH meter (Fisher Accumet AB15) and Ca, Mg, Fe and Mn concentrations using flame atomic absorption spectroscopy (AAnalyst 400, PerkinElmer). Soil Eh was measured on the day of flooding and at 7 d intervals (same day of water sampling) by temporarily inserting a Ag-AgCl reference electrode to the soil-floodwater interface and the permanently installed redox probe using a high impedance volt meter. Recorded Eh values were corrected to the standard hydrogen electrode potential by adding the potential of the reference electrode at +4 °C. The overall redox status was described using pe + pH as suggested by Lindsay [50], where pe is the electron activity. We calculated pe 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 Coulombs), R is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), and the T is the absolute temperature in K (277.15 K because the experiment was done at 4 °C).

## 2.3. Predicting Phosphorus Transformations with Flooding in Amended and Unamended Soil

Phosphorus transformations with flooding of unamended and amended soil monoliths were examined in two selected soils with contrasting properties, Dencross 2 and Lakeland series, using a thermodynamic modeling software Visual MINTEQ 3.1 with NICA-Donnan model [41]. Based on the input parameters, the thermodynamic model was used to calculate the equilibrium composition of porewater and to identify minerals that can potentially be precipitated.

To obtain the parameters to input into the modeling software, porewater samples collected on 0, 14, 28, 42 and 56 days after flooding (DAF) were analyzed for electrical conductivity (EC) using a Fisher Accumet AB30 conductivity meter. Dissolved organic carbon (DOC) was determined using the APHA Method 5310C [51] with a Fusion Total Organic Carbon Analyzer (Teledyne Tekmar Inc.). Porewater samples were also analyzed for  $Cl^-$ ,  $F^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$ , and  $SO_4^{2-}$  using ion chromatography (Metrohm Eco IC), and for total Al and dissolved P concentrations using inductively coupled plasma atomic emission spectroscopy (Thermo iCAP 6500 Duo). The EC values (S m<sup>-1</sup>) were converted to ionic strength (mol L<sup>-1</sup>), using the equation [52]:

*Ionic strength* = 
$$\frac{EC}{6.67} \times \frac{1}{0.991}$$

For gypsum-amended treatments, we assumed the presence of  $CaSO_4 \cdot 2H_2O$  throughout the flooding period at a concentration of 0.0145 mol L<sup>-1</sup> based on the solubility of gypsum and calculated using the Visual MINTEQ software. For the NICA-Donnan model we used a ratio of active DOM to DOC of 1.65 (assuming that 82.5% of DOM is active and consists of 50% carbon by weight) with 100% of the active DOM considered to be fulvic acid [53]. The mineral species that could be potentially formed were indicated by saturation indices in the output of the software, with positive saturation indices for minerals that are likely to be precipitated and negative saturation indices when the precipitation of the mineral is not thermodynamically favored [41]. The input parameters used for modeling are given in Supplemental Table S1.

#### 2.4. Statistical Analysis

The incubation experiment was conducted as a randomized complete block with three amendment treatments (unamended, alum-amended and gypsum-amended) and eight soils as fixed effects and DAF as the repeated measures factor. ANOVA was conducted using the generalized linear mixed model (GLIMMIX) procedure for repeated measures in SAS 9.4 [54]. The Tukey–Kramer multiple mean comparison was used to compare the treatment effects. Regression analysis was performed with data from all soils assuming normal

distribution of data to identify the relationships between porewater ion concentrations with flooding time or redox status (pe + pH). For all statistical analyses, significance was set at p < 0.05.

## 3. Results

## 3.1. Soil Characterization

The textural class of all the soils in this study were clay (USDA classification) and the clay content ranged between 481 and 768 g kg<sup>-1</sup> with a sand content <147 g kg<sup>-1</sup> (Supplemental Table S2). These soils were moderately to strongly calcareous with CCE values between 89 and 167 g kg<sup>-1</sup>. Except for the two Scanterbury series soils with near neutral pH values, other soils were alkaline in reaction with pH values ranging from 7.9 to 8.3. All soils had high organic matter contents ranging from 87 to 113 g kg<sup>-1</sup>. The available P in all soils were medium to high, but not excessively high, ranging from 14 to 85 mg kg<sup>-1</sup> of Mehlich-3 P. Mehlich-3 extractable cations were in the range of 1378 to 3872 mg kg<sup>-1</sup> for Ca, 956–2008 mg kg<sup>-1</sup> for Mg, 61 to 147 mg kg<sup>-1</sup> for Fe, 21 to 88 mg kg<sup>-1</sup> for Mn, and 22 to 648 mg kg<sup>-1</sup> for Al. Bulk density of intact soil monoliths used for the flooding study varied from 0.81 to 1.36 Mg m<sup>-3</sup>.

# 3.2. Dissolved Reactive P and Total P Concentrations in Porewater and Floodwater with Days of Flooding (DAF)

The porewater DRP concentrations varied from 0.03 to 3.06 mg  $L^{-1}$  depending on the soil, treatment, and the DAF (Supplemental Table S3). The total P concentrations in porewater were slightly greater than the respective DRP concentrations and ranged between 0.09 and 3.10 mg  $L^{-1}$  (data not shown). The non-molybdate reactive P (considered as the dissolved organic P) calculated using the difference between total P and DRP concentrations was less than 25% of total P with a median of 12% (data not shown). In all soils, porewater DRP concentrations were greater in unamended, than gypsum- or alumamended treatments for most DAFs, and often the differences were statistically significant (Figure 1; Supplemental Table S4). The changes in porewater DRP concentration with DAF was inconsistent among soils and treatments (Figure 1). In unamended monoliths of Dencross 1, Osborne 1, Osborne 2, Osborne 3 and Scanterbuty 2, porewater DRP concentrations remained relatively stable or slightly decreased towards the latter stages of flooding. However, the alum- and gypsum-amended monoliths of the same soils often showed an increasing trend with DAF. In Lakeland and Scanterbury 1 soils which had relatively lower Mehlich-3 P values, all treatments showed somewhat similar, increasing trend in porewater DRP concentration with DAF. In contrast, monoliths of all treatments in the highly calcareous Dencross 2 soil showed a decreasing or somewhat stable DRP concentration with DAF.

The DRP concentrations in floodwater were lower than in porewater and were often less than detectable ranges at 0 DAF, with the maximum concentration of 0.98 mg L<sup>-1</sup> in unamended Osborne 3 soil at 56 DAF (Supplemental Table S5). Floodwater DRP concentrations showed highly significant correlations with porewater DRP concentrations across soils, treatments, and DAFs (r = 0.57, n = 216). As with porewater, the total dissolved P in floodwater was slightly greater than DRP concentrations and the proportion of non-molybdate reactive P (considered as the dissolved organic P) was less than 35% in all samples with a median of 21% (data not shown). Thus, our discussion will only focus on DRP or "inorganic" P, measured as molybdate reactive P.



**Figure 1.** Mean porewater dissolved reactive P concentrations in unamended, alum-amended and gypsum-amended soil monoliths with time of flooding. The vertical bars indicate the standard deviation of the means (n = 3).

In general, floodwater DRP concentrations increased with DAF in all soils and treatments, reached a peak, and then declined or remained relatively stable, likely due to reprecipitation of released P. In a few soils (Dencross 1, Dencross 2 and Osborne 3), floodwater DRP concentrations increased continuously up to 56 DAF suggesting enhanced P release with the development of anaerobic conditions. In general, the unamended monoliths had greater floodwater DRP concentrations than gypsum- or alum- amended treatments, particularly at the latter stages of flooding, with significant differences at certain DAFs (Figure 2; Supplemental Table S4). The differences between floodwater DRP concentration in unamended and amended monoliths increased with DAF and became significant at latter stages of flooding in all soils except Lakeland, which had relatively low floodwater DRP concentrations throughout the flooding period. Thus, the amendments seem to be more effective in immobilizing P at higher DRP concentrations. In Lakeland soil which had the lowest Mehlich-3 P ( $<15 \text{ mg kg}^{-1}$ ; Supplemental Table S2), the floodwater DRP concentrations were less than 0.15 mg  $L^{-1}$  throughout the flooding period even in unamended monoliths (Figure 2). In Dencross 1, Dencross 2, Osborne 2, and Osborne 3 soils, the alum-amended monoliths had significantly lower floodwater DRP concentrations than gypsum-amended monoliths for certain DAFs suggesting greater effectiveness of alum in immobilizing P than gypsum. In contrast, Scanterbury 1 soil had greater floodwater DRP concentration in gypsum-amended monoliths from 0 to 28 DAF (significant on 21 DAF) compared to both alum-amended and unamended monoliths; however, after 28 DAF, unamended monoliths had greater DRP concentrations in floodwater than gypsum- or alum-amended monoliths.

## 3.3. Changes in Overall Redox Status and Release of Cations with Time of Flooding

All soil monoliths were moderately to well oxidized on the day of flooding with Eh values (at 5 cm depth) ranging from 323 to 507 mV. With time of flooding, monoliths from different soil series and treatments became progressively anaerobic, and their Eh values steadily decreased. By the 56 DAF all soil monoliths were moderately to severely reduced with Eh ranging from +23 to 236 mV (Supplemental Table S6). In general, different amended treatments of the same soils did not show significant differences in Eh for most DAFs.

Porewater pH of all unamended soil monoliths were slightly alkaline on 0 DAF (ranging from 7.8 to 8.2) except for Scanterbury 1 and Scanterbury 2, which were slightly acidic to neutral (6.8 and 7.1). On the 0 DAF, porewater pH was significantly (p < 0.05) lower in alum-amended monoliths compared to unamended or gypsum-amended monoliths, however, with time of flooding, porewater pH increased in alum-amended monoliths and the differences were not significant at latter stages of flooding (Supplemental Table S7). Porewater pH in monoliths of unamended and gypsum-amended treatments remained relatively stable or slightly decreased over flooding period in all soils. Similar observations were made for floodwater pH (data not shown). Irrespective of the amended treatments, floodwater pH steadily and significantly increased with DAF in all soils.

The pe + pH values in all monoliths on 0 DAF were near or above 14 except for alumamended monoliths of a few soils where pe + pH values were around 12. In all unamended and amended soil monoliths pe + pH steadily decreased with time of flooding (Figure 3). Porewater Ca and Mg concentrations showed an increasing trend with flooding time, but only in unamended monoliths with significant (p < 0.01), positive, linear relationships (Figure 4). This is likely due to the increased solubility of Ca and Mg minerals with flooding time. In contrast, porewater Ca concentrations decreased with flooding time in alum amended monoliths with a highly significant (p < 0.001) negative relationship. At a given DAF, porewater Ca concentrations were greater in gypsum and alum-amended monoliths than in unamended counterparts, however this trend was not observed with Mg.



**Figure 2.** Mean floodwater dissolved reactive P concentrations in unamended, alum-amended and gypsum-amended soil monoliths with time of flooding. The vertical bars indicate the standard deviation of the means (n = 3).



**Figure 3.** Change in pe + pH in unamended, alum-amended and gypsum-amended soil monoliths with time of flooding. The vertical bars indicate the standard deviation of the means (n = 3).



Days after flooding

**Figure 4.** Relationships between days after flooding and porewater concentrations of Ca and Mg in unamended, alum-amended and gypsum-amended monoliths. Note: Linear relationships are shown only when significant at p < 0.05. Superscripts \*\*\* and \*\* followed by R<sup>2</sup> indicates significant at p < 0.001 and p < 0.01, respectively (n = 72).

In unamended, gypsum-amended, and alum-amended monoliths, the decrease in pe + pH resulted in an increase in porewater Fe and Mn concentrations, and the relationship was exponential (Figure 5) and highly significant (p < 0.01). The concentrations of Fe and Mn were undetectable at the beginning of flooding when pe + pH values were above 12, however once pe + pH values decreased below 12, porewater Fe and Mn concentrations exponentially increased, with a greater increase in unamended and gypsum-amended monoliths than in alum-amended monoliths.



**Figure 5.** Exponential relationships between pe + pH and porewater concentrations of Fe and Mn in unamended, alum-amended and gypsum-amended monoliths. Note: Values in x-axis are in reverse order. Superscripts \*\*\* and \*\* followed by  $R^2$  indicates significant at p < 0.001 and p < 0.01, respectively (n = 72).

## 3.4. Predicted P Transformations with Amended Treatments and Flooding

The output tables from Visual MINTEQ software lists the saturation index (SI) values calculated simply as log IAP–log K<sub>sp</sub>, where K<sub>sp</sub> is the solubility product from the thermodynamic database, after correction for temperature effect and IAP is the ion activity product of all solids that can potentially precipitate out of solution. A negative SI (IAP < K<sub>sp</sub>) indicates that the solution is undersaturated with respect to the species and the species is not likely to be formed, while a positive SI (IAP > K<sub>sp</sub>) indicates that the solution is supersaturated with respect to the species, and the species is likely to precipitate.

Saturation index values for various amended treatments are shown in Table 1. Only the values for possible P species that can be formed are presented at 0, 28 and 56 DAF. At 0 DAF, SI values in unamended Dencross 2 and Lakeland soils were positive with respect

to hydroxyapatite  $[Ca_{10}(PO_4)_6(OH)_2]$  and  $\beta$ -tricalcium phosphate  $[\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>], whereas only in Dencross 2 soil, SI value was positive with respect to MnHPO<sub>4</sub>. Gypsum-amended treatments showed a similar trend, but SI values with respect to variscite  $[AIPO_4 \cdot 2(H_2O)]$ were positive as well in both soils. In alum-amended Dencross 2 soil, SI values were negative with respect to hydroxyapatite,  $\beta$ -tricalcium phosphate and MnHPO<sub>4</sub>, however, it was positive with respect to variscite, while in the alum-amended Lakeland soil, positive SI values were observed for hydroxyapatite,  $\beta$ -tricalcium phosphate and variscite.

**Table 1.** Saturation index values  $\dagger$  (SI = log IAP–log K<sub>sp</sub>) of P minerals in equilibrium solution in unamended (control), alum-amended and gypsum amended soils at 0, 28 and 56 days after flooding (DAF) as predicted by Visual MINTEQ modeling.

Mineral	SI at 0 DAF			SI at 28 DAF			SI at 56 DAF		
	Unamended	Alum- Amended	Gypsum- Amended	Unamended	Alum- Amended	Gypsum- Amended	Unamended	Alum- Amended	Gypsum- Amended
Dencross 2 soil									
AlPO <sub>4</sub> ·1·5H <sub>2</sub> O	-4.1	-0.9	-1.1	0.7	1.1	0.6	-1.1	-0.4	0.6
$\begin{array}{c} Ca_3(PO_4)_2\\ (beta) \end{array}$	1.6	-6.8	2.6	1.4	-1.1	1.8	0.3	-0.8	2.0
Hydroxyapatite	8.6	-6.0	10.0	8.0	4.1	8.7	6.1	4.5	8.9
MnHPO <sub>4</sub> (s)	1.3	-0.6	0.5	2.2	1.2	1.8	2.6	1.8	2.5
Variscite	-2.5	0.7	0.5	2.3	2.7	2.2	0.5	1.2	2.2
Lakeland soil									
$\begin{array}{c} Ca_3(PO_4)_2\\ (beta) \end{array}$	0.8	0.1	0.7	1.1	1.5	1.3	0.9	0.6	1.1
Hydroxyapatite	7.8	6.6	7.2	8.1	8.9	8.5	7.8	7.3	8.2
MnHPO <sub>4</sub> (s)	-0.1	-0.7	-0.5	1.9	1.6	1.7	2.5	2.1	1.7
Variscite	-3.3	0.6	0.3	-1.2	0.6	0.5	-0.1	0.7	-2.0

+ Positive SI values (in red text) indicate oversaturation. IAP ion activity product, K<sub>sp</sub> solubility product constant.

At 28 and 56 DAF, most treatments in both Dencross 2 and Lakeland soils had positive SI values with respect to hydroxyapatite,  $\beta$ -tricalcium phosphate, MnHPO<sub>4</sub>, and variscite. The exception to this was the alum-amended Dencross 2 soil with respect to  $\beta$ -tricalcium phosphate at both 28 and 56 DAF, and unamended treatment at 28 DAF and both unamended and gypsum-amended treatments at 56 DAF of Lakeland soil with respect to variscite. In Dencross 2 soil, SI values were positive with respect to AlPO<sub>4</sub>·1·5H<sub>2</sub>O for all treatments at 28 DAF and in gypsum-amended treatment at 56 DAF (Table 1).

In alum- or gypsum-amended Dencross 2 and Lakeland soils, the ionic strength of soil solution was greater (0.14–0.30 mol L<sup>-1</sup>) than their unamended counterparts (0.02–0.12 mol L<sup>-1</sup>; Supplemental Table S2). Visual MINTEQ output showed that in unamended Dencross 2 and Lakeland soils, SI values were positive only with respect to a few Al(hydr)oxide species, namely diaspore [ $\alpha$ -AlO(OH)] in Dencross 2 and both diaspore and gibbsite [Al(OH)<sub>3</sub>] in Lakeland soil. In contrast, alum-amended and gypsum-amended treatments showed supersaturation with respect to many P-sorbing Al and Fe (hydr)oxide species (Supplemental Table S8). With time of flooding, SI values changed from negative to positive for many P-sorbing Al and Fe (hydr)oxide species in all treatments; however, at 56 DAF, more P-sorbing mineral species were supersaturated in alum- and gypsum-amended treatments than in their unamended counterpart (Supplemental Table S8).

#### 4. Discussion

## 4.1. Redox, Ionic Strength, and pH Changes with Flooding and Amendments

The majority of soil monoliths were in the oxic range on the day of flooding with a few in the sub-oxic range, based on the Eh (>300 mV) and pe+pH values (10–16). With time of flooding, soil monoliths became progressively anaerobic and by the 56 DAF all monoliths

were either anoxic or sub-oxic (Eh < 250 mV, pe + pH of 7–12). Since the soil monoliths were amended with alum and gypsum 2 weeks prior to flooding, their effects on soil pore water pH were observed from the first day of flooding. Significantly lower pH down to 4 cm has been previously observed with alum amendment in a wetland organic soil [55]. Decrease in soil pH with alum-amendment is expected since dissolution of alum, followed by a series of hydrolysis reactions of dissolved  $Al^{3+}$  result in the generation of protons and thus, a decrease in pH [56,57]. We also noted that the initial lowering of pH with alum amendment was transitory, and the pH increased with the progression of flooding to values similar to those of the unamended counterparts. In contrast, application of gypsum decreased the initial pH values only slightly compared to those of the unamended counterparts, which could be attributed to the acidification that occurs when Ca<sup>2+</sup> is exchanged for Al<sup>3+</sup>, and by the neutralization that occurs when  $SO_4^{2-}$  replaces  $OH^{-}$  [27]. Applications of both alum and gypsum increased the ionic strength (measured only in Dencross 2 and Lakeland soils) by more than two-fold, since both amendments are highly soluble. Similar increases in ionic strength (or electrical conductivity) with the application of gypsum have been previously reported [31] at similar rates of gypsum amendment.

## 4.2. P Transformations and Release at Early Stages of Flooding in Amended and Unamended Soils

The porewater DRP concentrations on 0 DAF in alum- and gypsum-amended monoliths were in general, lower than in the unamended monoliths. Visual MINTEQ analysis with two soils (Dencross 2 and Lakeland) indicated that the P solubility in unamended and gypsum amended treatments was regulated mostly by the solid phases of Ca-P compounds, while in alum-amended treatments the P solubility was controlled by solid phases other than Ca-P, such as Al-P. For example, in Dencross 2 soil (pH of 7.5 to 8.0 on 0 DAF), P solubility in unamended and gypsum-amended monoliths was regulated mostly by the solid phases of  $\beta$ -tricalcium phosphate and hydroxyapatite, as previously reported in gypsumamended soils [42]. In alum-amended treatment (pH of 5.5 on 0 DAF), the soil solution was undersaturated with respect to solid phases of Ca-P compounds. Similar observations have been previously reported using P speciation modeling for alum-amended and unamended low pH soils [33]. Thus, the results suggest that P solubility in slightly acidic systems was controlled by solid phases of Al-P such as variscite (AlPO<sub>4</sub> $\cdot$ 2H<sub>2</sub>O). The low solubility of variscite under acidic conditions and in the presence of high Al<sup>3+</sup> concentrations is well known [58,59], which could be one reason for the significantly lower porewater DRP concentration in alum-amended, compared to unamended and gypsum-amended treatments. Significant decreases in Olsen-P and CaCl<sub>2</sub>-extractable P with alum amendment has been previously documented, which was mainly attributed to the transformation of P from Ca<sub>2</sub>-P and  $Ca_8$ -P to Al-P [60]. In the highly alkaline Lakeland soil however, alum amendment resulted only in about 0.3 unit decrease in pH compared to the unamended counterpart, and the decrease in porewater DRP on 0 DAF was slight. Visual MINTEQ predicted that in both unamended and amended Lakeland soils, P solubility at 0 DAF was regulated by the solid phases of Ca-P ( $\beta$ -tricalcium phosphate and hydroxyapatite), and only in amended soils, by Al-P (variscite) as well.

Another reason for the lower DRP concentrations with alum amendment during the early stages of flooding could be the enhanced formation of P-sorbing amorphous and crystalline Al and Fe (hydr)oxides as predicted by the model, which may have enhanced P sorption to those mineral species, thus reducing P concentration in solution. In a previous study using alum-amended poultry litter, X-ray absorption near edge structure spectroscopy results indicated the precipitation of amorphous Al(OH)<sub>3</sub>, which then reacted with phosphate via adsorption mechanisms [61]. In addition, the application of gypsum or alum, which are reasonably soluble in aqueous environments, substantially increased the ionic strength of the soil solution in the current study (Supplemental Table S1) and increased the concentrations of other ions such as Mg and sulfate. While anions such as sulfate do not compete strongly with phosphate for anion adsorption sites on particle surfaces, if sulfate is high enough in concentration, it could cause some competition for adsorption sites with

phosphate [62]. Ionic strength is well known to play a role in P adsorption/desorption properties. In this study, the greater ionic strength in alum and gypsum-amended treatments may have also enhanced P adsorption as previously reported [37,39,63], resulting in lower DRP concentrations.

## 4.3. P Transformations and Release with Prolonged Flooding in Amended and Unamended Soils

Prolonged flooding of soil monoliths resulted in soils becoming progressively anaerobic to Eh values as low as 23 mV to 236 mV depending on the soil, with an accompanying release of P from soils to porewater and floodwater. Similar observations have been previously documented in packed soil columns and intact monoliths from a wide range of soils when flooded under room temperatures simulated summer flooding [15,33,64,65], as well as under simulated snowmelt flooding [12,13]. The increase in porewater and floodwater DRP concentrations with a simultaneous increase in Fe and Mn concentrations and decrease in Eh, suggest that reductive dissolution of Fe and Mn phosphates, and/or Fe and Mn (hydr)oxides with sorbed P, may have played a role in releasing P to solution, corroborating the findings of previous studies [16,66].

The DRP concentrations in floodwater were substantially lower than in porewater in all soils due to the slow rate of P diffusion from porewater to floodwater, and/or reprecipitation of diffused P with Fe or Mn at the oxidized interface as previously reported [15,66]. Despite having lower DRP concentrations in floodwater than porewater, the enhanced P release with flooding time in the current study was better reflected in DRP concentrations of floodwater than in porewater. The redox-induced P release with flooding of unamended and amended soils can be attributed to the changes in redox potential as well as pH changes associated with redox conditions caused by flooding and amendments. Such changes may result in enhanced dissolution of calcium phosphates and reductive dissolution of Fe/Mn phosphate and P-sorbing Fe/Mn minerals leading to P release from soil to solution as previously reported [15,16,18].

At a given DAF, both gypsum- and alum-amended monoliths maintained a higher porewater Ca concentration than unamended monoliths. Similar observations have been reported with enhanced Ca concentrations in runoff from manured soils where manure had been amended with alum [67,68]. A greater concentration of Ca with gypsum amendment is expected since dissolution of gypsum would release Ca to porewater. The increased Ca concentration with alum amendment is likely due to the initial low pH with alum amendment resulting in dissolution of Ca minerals, as well as the reaction of alum with calcium carbonate in these calcareous soils, forming more soluble Ca minerals such as gypsum [69]. Visual MINTEQ outputs of Dencross 2 and Lakeland soils predicted that the increase in pH with flooding time in alum-amended soils favored formation of  $\beta$ -tricalcium phosphate and hydroxyapatite. Supersaturation with respect to variscite was also indicated at 28 and 56 DAF in all treatments of Dencross 2 soil and in alum-amended Lakeland soil, whereas supersaturation with respect to  $MnHPO_4(s)$  was thermodynamically favored in all treatments in both soils. Such precipitation reactions might have regulated the P concentration in porewater, as seen with a slight decrease or stable DRP concentrations at latter stages of flooding.

Concentrations of Fe and Mn in porewater exponentially increased with the decrease in pe + pH, suggesting reductive dissolution of Fe(III) and Mn(IV,III) minerals. Concentrations of Mn started to increase earlier than Fe, which is to be expected since microbial reduction of Fe(III) minerals takes place at much lower Eh compared to reduction of Mn(IV, III) minerals [14,15]. Reductive dissolution reactions of oxides/oxyhydroxides of Fe and Mn may increase dissolved P in solution since P sorbed to such minerals gets released [21,34]. Therefore, despite being alkaline, the dominant mechanisms of P release in these soils were associated with reductive dissolution reactions involving Fe and Mn at latter stages of flooding when the soils were severely reduced.

Soils in this study were generally in the alkaline range, thus the presence of Fe(III) and Mn (IV,III) mineral species were indicated initially but mostly limited to amended

treatments based on the visual MINTEQ results with two soils. However, with time of flooding, precipitation of P-sorbing mineral species was favored, mostly in alum- and gypsum-amended treatments than in unamended treatment. The formation of these P-sorbing mineral species may facilitate re-adsorption of released P, as evidenced by the slight decrease, or relatively stable DRP concentrations towards the latter stages of flooding.

#### 4.4. Effectiveness of Alum and Gypsum in Reducing P Release from Flooded Soils

The enhanced P release with time of flooding was observed in all soils whether amended or unamended; however, alum or gypsum amendment prior to flooding substantially reduced the DRP concentration in both porewater and floodwater in most soils. The decrease in porewater DRP concentrations (calculated based on the difference in maximum DRP concentrations during the flooding period) with alum and gypsum amendment ranged from 25% to 91%, and from 17% to 64%, respectively. For floodwater DRP concentrations, the decrease ranged from 34% to 90% and from 1% to 66% with alum and gypsum amendment, respectively. The decrease in P release from flooded soils with gypsum amendment has been previously reported using recycled wallboard gypsum applied at the rate of 0.25% on a weight basis [34,35], the same rate used in the current study but with chemical grade gypsum. The effectiveness of the alum amendment in reducing DRP concentration in the current study was more consistent across soils and often resulted in a greater magnitude of decrease in DRP concentrations, than gypsum amendment. Inconsistency of gypsum amendment in reducing flooding-induced DRP losses has been previously reported, with greater effectiveness in an acidic soil than in an alkaline soil, which was attributed to the enhanced stability of Ca-P ( $\beta$ -tricalcium phosphate and octa calcium phosphate), with the increase in pH with flooding in the acidic soil [42]. Comparing different rates of liming material, alum and FeCl<sub>3</sub>. Ann et al. [33] reported a substantial decrease in flooding-induced P release from an organic soil with all amendments tested, with alum amendment showing a greater effectiveness than Ca(OH)<sub>2</sub>, calcite and dolomite, but a lower effectiveness than FeCl<sub>3</sub>. In their study, the most effective rate of alum amendment to minimize P release from soil to overlying floodwater was 12 g kg<sup>-1</sup> [33], a rate that is about 4.8-fold greater than the rate used in the current study. Using intact soil monoliths from the same locations as in the current study, Vitharana et al. [36], observed 21% to 75% reduction in average pore water DRP concentration with flooding time with surface application of  $MgSO_4$  at a rate of 2.5 Mg ha<sup>-1</sup> (50% less than the rates used in the current study) which was mainly attributed to a reduction in redox-induced P release and re-precipitation of released P with Ca and Mg. None of these studies, however, looked into the long-term effectiveness of the amendments in reducing P release from soils with flooding events. Investigating the long-term effectiveness of amendments in reducing rainfall-driven P loss, Habibiandehkordi et al. [70] reported that effectiveness of aluminium-based water treatment residuals in reducing runoff P loss decreased during repeated runoff events, yet the DRP concentrations with the amendment was lower compared to the control treatment.

## 5. Conclusions

The overall redox status (pe + pH) decreased with flooding time in unamended, alumamended, and gypsum-amended soil monoliths, while DRP concentrations in porewater and floodwater increased in general, suggesting redox-induced P release. Amending the soil with alum (2 weeks prior to flooding) significantly reduced the porewater pH of flooded soil monoliths initially; however, this effect was transitory, and the pH increased with the progression of flooding to values similar to those in unamended monoliths. Porewater and floodwater DRP concentrations in general, were lower with alum and gypsum amendment as compared to unamended monoliths under simulated snowmelt flooding, while the magnitude of reduction varied depending on the soil. The decrease in floodwater DRP concentrations (calculated based on the difference in maximum DRP) ranged from 34% to 90% and from 1% to 66% with alum and gypsum amendment, respectively. Alum amendment was consistently more effective in reducing DRP concentration across soils often with a greater magnitude of decrease in DRP concentrations than gypsum amendment. Results of thermodynamic modeling using data from two soils suggest that the formation of P-sorbing mineral species (Al and Fe hydr(oxides)) was thermodynamically favored in gypsum- and alum-amended soils rather than in unamended soils, thus effectively reducing DRP concentrations through re-sorption of released P. Our results demonstrate the effectiveness of alum and gypsum in reducing P losses from soils to floodwater even when flooded under cold temperatures; thus, fall application of alum or gypsum could be practiced to reduce P losses from P-enriched agricultural fields during spring snowmelt runoff; however, more landscape-scale research is needed. In addition, the effect of a one-time fall application of gypsum or alum in reducing runoff P losses in subsequent snowmelt periods other than the spring snowmelt immediately after application should be investigated to evaluate the long-term benefits.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/w14040559/s1, Table S1. Input parameters used for the Visual MINTEQ model for unamended, alum-amended and gypsum-amended Dencross 2 and Lakeland soils for 0, 14, 28, 42 and 56 days after flooding (DAF); Table S2. Initial soil properties of the soils used in the experiment; Table S3. Mean porewater dissolved reactive P concentration (mg  $L^{-1}$ ) with days after flooding in unamended, alum-amended and gypsum-amended soils (n = 3). Standard error of mean is given in parentheses; Table S4. Main effects (P < F) of amended treatment, days after flooding (DAF), and their interactions on Eh, pore water dissolved reactive P (DRP) concentration and pore water pH (at 5-cm depth), and floodwater DRP concentration and floodwater pH; Table S5. Mean floodwater dissolved reactive P concentration (mg  $L^{-1}$ ) with days after flooding in unamended, alumamended and gypsum-amended soils (n = 3). Standard error of mean is given in parentheses; Table S6. Mean redox potential (Eh, mV) values with days after flooding in unamended, alum-amended and gypsum-amended soils (n = 3). Standard error of mean is given in parentheses; Table S7. Mean pore water pH values with days after flooding in unamended, alum-amended and gypsum-amended soils (n = 3). Standard error of mean is given in parentheses; Table S8. Saturation indext (SI = log  $IAP - logK_{sp}$ ) of P-sorbing mineral species in equilibrium solution in unamended (control), alumamended and gypsum amended soils at 0, 28 and 56 days after flooding (DAF) as predicted by Visual MINTEQ modeling.

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