

**EVALUATING THE RESIDUAL BENEFITS OF SOIL AMENDMENTS IN
REDUCING PHOSPHORUS LOSSES TO SNOWMELT RUNOFF FROM
AGRICULTURAL FIELDS**

By

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Abstract

Phosphorus (P) in snowmelt runoff from agricultural fields across the Canadian prairies is a major source of nutrient pollution to freshwater bodies, such as Lake Winnipeg. The use of soil amendments, such as alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and magnesium-sulphate (MgSO_4) have previously shown to reduce P losses from soils with snowmelt in the field, and under simulated snowmelt flooding in the laboratory through converting P to less soluble forms; however, their long-term effectiveness has not been investigated. This thesis examined the effectiveness of alum, gypsum, and magnesium-sulphate after 12 - 18 months after amendment application in (a) reducing dissolved reactive P (DRP) loss with snowmelt runoff in field plots, (b) reducing DRP concentrations in floodwater of intact soil columns with simulated snowmelt flooding, and (c) reducing potential P mobility through changes to P fractions and speciation. Amendments were applied in the fall of 2020 at a rate of 2.5 Mg ha^{-1} in plots arranged in a randomized complete block design, consisting of 4 replicates of 4 amendments (alum, gypsum, magnesium sulphate, and unamended) for a total of 16 field plots. During the snowmelt period, concentrations of DRP and cations, as well as pH in snowmelt were determined. Using intact soil columns taken from the same field plots, a more controlled laboratory study was conducted, where soil columns were flooded and incubated at $4 \text{ }^\circ\text{C}$ to simulate snowmelt conditions. Porewater and floodwater samples were extracted weekly and analyzed for DRP, cation concentrations, pH, and soil redox potential. Phosphorus species in porewater were predicted using Visual MINTEQ 3.1. on days 0, 28 and 49 during the laboratory study. Phosphorus fractions were also determined using a modified sequential fractionation method. In the field, snowmelt DRP concentrations

increased over the sampling period regardless of amendment, with higher concentrations seen after the soil had thawed. In the latter days of sampling, the alum, gypsum, and magnesium sulphate-amendments decreased DRP concentrations in snowmelt by 9 – 31% relative to the control. However, differences between treatments and the control were not statistically significant. Snowmelt DRP loads (calculated using DRP concentrations and snowmelt volume) showed a significant positive relationship with snowmelt volume, whereas the relationship with DRP concentration was not significant. During the laboratory study, redox potential in all treatments decreased with time of flooding. Soil columns taken from alum-amended field plots had significantly lower DRP concentrations in porewater when compared to all other treatments, but this effect was not observed for floodwater. Predicted P species showed slight changes in alum-amended soils, suggesting the potential for alum to delay the reductive dissolution of ferric phosphate (strengite, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), thereby delaying the P release. However, P fractionation analysis did not show significant differences in soil P fractions between treatments. The results of this research suggest that the effectiveness of these amendments in reducing P loss to snowmelt is very small to negligible one year after application, or after one snowmelt flooding event. This implies that re-application of amendments on a more frequent basis or application at a higher rate may be necessary for amendments to be effective in reducing P loss to snowmelt. However, more field scale research is necessary to provide recommendations to farmers regarding the use of soil amendments for this purpose.

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Table of Contents

<i>Abstract</i>	<i>iii</i>
<i>Acknowledgements</i>	<i>v</i>
<i>List of Tables</i>	<i>ix</i>
Chapter 1. Literature Review	1
1.1. Phosphorus use in agriculture	1
1.2. Phosphorus accumulation, fractions, and speciation in soils.....	1
1.3. Eutrophication of water bodies.....	4
1.4. Phosphorus transport through runoff and best management practices (BMPs)	5
1.5. Prairie snowmelt flooding and P losses.....	6
1.6. Strategies for reducing P losses through snowmelt runoff.....	7
1.7. Thesis overview and overall objectives.....	9
1.8. References	11
Chapter 2. Field evaluation of residual benefits of alum, gypsum, and magnesium sulphate amendments in reducing phosphorus losses to snowmelt runoff	16
2.1. Introduction	17
2.2. Materials and Methods	20
2.2.1. Site Location and Description	20
2.2.2. Experimental Setup	20
2.2.3. Analysis of snowmelt samples	21
2.2.4. Statistical Analysis	22
2.3. Results	23
2.3.1. Air Temperature over the sampling period.....	23
2.3.2. Mehlich 3 extractable P concentrations	23
2.3.3. Dissolved reactive phosphorus concentrations and loads in snowmelt.....	24
2.3.4. Relationship between cations, pH and DRP concentrations in snowmelt.....	29
2.4. Discussion	33
2.4.1 Increase in snowmelt DRP concentration with time.....	33
2.4.2 Residual amendment effects on DRP release to snowmelt	35
2.4.3 Soil available P after snowmelt with different treatments	37
2.4.4 Major controllers of snowmelt DRP load.....	38
2.5. Conclusions	38
2.6. References	40
Chapter 3. Residual benefits of soil amendments in reducing phosphorus losses from soils during simulated snowmelt flooding	44
3.1. Introduction	45
3.2. Materials and Methods	47
3.2.1. Site Location and Description	47
3.2.2. Experimental Setup	48
3.2.3. Collection of porewater and floodwater samples	48

3.2.4. <i>Sample Analysis</i>	48
3.2.5. <i>Statistical Analysis</i>	49
3.3. Results	50
3.3.1. <i>Dissolved reactive phosphorus (DRP) concentrations in porewater and floodwater</i>	50
3.3.2. <i>Changes in pH, cation concentration in porewater and floodwater, and redox potential</i>	51
3.3.3. <i>Relationship between porewater and floodwater concentrations of DRP, Ca, Mg, Fe & Mn</i> ...	57
3.4. Discussion	60
3.5. Conclusions	64
3.6. References	65
<i>Chapter 4. Phosphorus speciation and fractionation during simulated snowmelt flooding with soil amendments</i>	68
4.1. Introduction	69
4.2. Materials and Methods	71
4.2.1. <i>Site Location and Description</i>	71
4.2.2. <i>Experimental Setup</i>	72
4.2.3. <i>Collection of porewater and soil samples</i>	72
4.2.4. <i>Sample Analysis</i>	73
4.2.5. <i>Predicting P Species</i>	73
4.2.6. <i>Sequential P Fractionation</i>	74
4.2.7. <i>Statistical Analysis</i>	75
4.3. Results	76
4.3.1. <i>Phosphorus species as predicted by the Visual MINTEQ model</i>	76
4.3.2. <i>Phosphorus fractions in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soils</i>	78
4.4. Discussion	78
4.5. Conclusions	80
4.6. References	82
<i>Chapter 5. General discussion, conclusions, and recommendations for future research</i>	85
5.1. <i>Summary of results</i>	85
5.2. <i>General discussion and conclusions</i>	86
5.3. <i>Limitation of the study and recommendations for future research</i>	88
5.4. References	90
Appendix	92
6.1. <i>Dissolved reactive P analysis (Murphy & Riley, 1962)</i>	92
6.2. <i>Mehlich 3 Extraction (Mehlich, 1984)</i>	92
6.3. <i>Thermodynamic modelling using Visual MINTEQ 3.1.</i>	93
6.4. References	98

List of Figures

Figure 2.1. Daily average, minimum, and maximum air temperature for the Kleefeld, MB weather station obtained from Environment Canada. Arrows indicate the sampling days.

Figure 2.2. Mean dissolved reactive P concentrations (a) daily snowmelt volume (b) and daily DRP loads (c) in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots with sampling date. Vertical error bars represent standard error of the mean.

Figure 2.3. Relationship between a) DRP load and snowmelt volume and b) DRP concentration and snowmelt volume of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots. Significance determined at $p < 0.05$.

Figure 2.4. Mean cumulative DRP loads in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots with snowmelt sampling day. Vertical error bars represent standard error of the mean.

Figure 2.5. Mean volume-weighted DRP concentrations in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots.

Figure 2.6. Mean pH in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots with snowmelt sampling day.

Figure 2.7. Mean concentrations of a) Ca, b) Mg, c) Fe and d) Mn in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots.

Figure 2.8. Relationship between DRP, a) Mn, b) Fe, c) Ca and d) Mg concentrations in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots. Significance determined at $p < 0.05$.

Figure 2.9. Relationship between DRP and pH in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots. Significance determined at $p < 0.05$.

Figure 3.1. Mean pore water and flood water dissolved reactive P concentrations in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths with time. Vertical error bars represent standard error of the mean.

Figure 3.2. Mean pore water and flood water pH in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths with time. Vertical error bars represent standard error of the mean.

Figure 3.3. Mean pore water and flood water concentrations of calcium in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths. Vertical error bars represent standard error of the mean.

Figure 3.4. Mean pore water and flood water concentrations of magnesium in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths. Vertical error bars represent standard error of the mean.

Figure 3.5. Mean pore water and flood water concentrations of iron in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths. Vertical error bars represent standard error of the mean.

Figure 3.6. Mean pore water and flood water concentrations of manganese in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths. Vertical error bars represent standard error of the mean.

Figure 3.7. Soil redox potential in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths over the 49-day incubation period.

Figure 3.8. Relationship between pore water DRP, a) Mn, b) Fe, c) Ca and d) Mg concentrations of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soil monoliths. Significance determined at $p < 0.05$.

Figure 3.9. Relationship between flood water DRP and pore water a) Mn, b) Fe, c) Ca and d) Mg concentrations of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soil monoliths. Significance determined at $p < 0.05$.

Figure 3.10. Relationship between flood water and pore water DRP concentrations in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soil monoliths. Significance determined at $p < 0.05$.

Figure 3.11. Relationship between a) flood water b) pore water DRP concentrations and pore water pH in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soil monoliths. Significance determined at $p < 0.05$.

Figure 4.1. Mean phosphorus fractions in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soil monoliths.

List of Tables

Table 4.1. Saturation index values (SI) of P species in pore water of unamended, alum-amended, gypsum-amended, and magnesium-sulphate amended monoliths on days 0, 28 and 49 after flooding as predicted by Visual MINTEQ modeling.

Chapter 1. Literature Review

1.1. Phosphorus use in agriculture

Phosphorus (P) is an essential nutrient required for plant growth (Daly et al., 2015). The availability of P in the soil can be a limiting factor in crop growth, as P has a high sorption capacity, especially in calcareous soils (Abdala et al., 2015). Generally, soils contain enough P to meet crop requirements, however most of this P is found in unavailable forms; therefore, application of P in the form of fertilizer or manure is required to supply sufficient amounts of P in plant available forms (Government of Manitoba, 2013). Plants typically use less than 20% of applied P, and the remaining portion is immobilized over time (Roberts & Johnston, 2015). Over the last few decades, soil P has been increasing as a result of heavily managed agricultural soils, although it is abundant in forms unavailable for plant uptake (Koopmans et al., 2002; Chen et al., 2022; Pradhan et al., 2021). The use of animal manures can be a cost-effective way to meet nutrient requirements of a crop, however it is difficult to apply manure to supply adequate amounts of both nitrogen (N) and P. Using synthetic fertilizers allows farmers to supply the appropriate amounts of nutrients, although it can be expensive (Government of Manitoba, 2013). Intensification of agriculture has led to significant increases in P losses although many of the processes responsible for P loss are naturally occurring (Grewal et al., 2020).

1.2. Phosphorus accumulation, fractions, and speciation in soils

There are many factors that can contribute to a soil's ability to immobilize P which include many physical and chemical processes (Sample, Soper & Racz, 1980). In

calcareous soils, when P is applied in excess, large amounts are retained through various processes such as adsorption to calcite, precipitation with calcium (Ca) and magnesium (Mg), and immobilization by soil microbes, while a small proportion of P may be retained through sorption to Al and Fe-oxides (Ajiboye et al., 2007; Kolahchi & Jalali, 2013). The use of P fertilizers in calcareous soils has resulted in an increased concern of P accumulation, due to high P fixation (Halajnia et al., 2008). However, under certain circumstances, this phosphorus that is accumulated in the surface layers of soils can be highly susceptible to losses (Kleinman et al., 2011; Amarawansa et al., 2015). In calcareous soils, which are predominated by the Ca-P system, a large portion of P exists as various Ca-P species, with a smaller abundance of other species like Al- and Fe-P (Shariatmadari et al., 2007). When manure is continuously applied to the soil, P speciation can be altered (Weyers et al., 2016; Halajnia et al., 2009).

To gather a better understanding of soil P availability and mobility, P can be fractionated into various pools (Jiang & Gu, 1989). Most fractionation methods have been adapted from the Hedley fractionation scheme (Hedley, 1982), with modifications to suit various soil and environmental conditions such as highly calcareous soils, water-logged soils, etc. Sequential extraction methods considered to be more effective for calcareous soils are able to divide the Ca-P pool into three fractions (Ca₂-P, Ca₈-P & Ca₁₀-P), as well as the fractions including Al-P, Fe-P, and P occluded to Fe oxides (Jiang & Gu, 1989). The Ca₂-P, Ca₈-P and Ca₁₀-P pools represent labile P, partially available P, and unavailable P, respectively (Shariatmadari et al., 2007). In many calcareous soils, P species decrease in abundance in the following order: Ca₁₀-P > Ca₈-P > Al-P > Fe-P > Occl-P > Ca₂-P.

Phosphorus species that are unavailable or only partially available are generally the most

abundant due to the rapid formation of less soluble P species (Cerozi & Fitzsimmons, 2016). In addition to these fractionation methods that separate P into operationally defined pools, P speciation is another important tool to gather information on exact P species (Gatiboni et al., 2021). The dominant P species in calcareous soils include: α -tricalcium phosphate, β -tricalcium phosphate, octacalcium phosphate, and hydroxyapatite (Lindsay, 1979). Using multiple analytical techniques for identifying P species, Weyers et al. (2016) determined that in a calcareous soil, approximately 54% to 74% of phosphorus species are calcium-phosphates. Whereas, only about 25% to 35% of phosphorus was found as adsorbed species, and 0% to 19% as organic phosphorus, predominantly phytic acid (Weyers et al., 2016). The Ca/Mg ratio of a soil can also have an impact on P speciation (Manimel Wadu et al., 2013). It was determined that in soils with 100% to 50% Ca saturation, dicalcium phosphate dihydrate ($\text{Ca}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$) was the dominant phosphorus species, whereas in soils where magnesium saturation is 70% to 100%, magnesium phosphate trihydrate ($\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$) was identified as an important phosphorus phase (Manimel Wadu et al., 2013). However, in highly calcareous soils, P immobilization is highly correlated to the formation of Ca-P species (Ann, Reddy & Delfino, 1999).

There are many analytical techniques for identifying P species in soils including x-ray absorption near edge structure (XANES), Raman, IR, and nuclear-magnetic resonance (NMR) spectroscopy (Kruse et al., 2015; Hashimoto & Watanabe, 2014; Weyers et al., 2016). These analytical techniques can identify specific minerals and are quite accurate (Ajiboye et al., 2007). In addition to these analytical techniques, modeling methods such as Visual MINTEQ (a computerized chemical model for speciation and mineral equilibria

of natural waters (Gustafsson, 2011)) can be useful in predicting P species based on various input parameters, including pH, ion concentrations, redox potential and solubility, although these models should be used in combination with other direct speciation techniques such as XANES and NMR (Lindsay, 1979).

1.3. Eutrophication of water bodies

Nutrients like P, which are transported from agricultural land to waterbodies, can contribute to the eutrophication and deterioration of aquatic environments (Liu et al., 2013). Dissolved reactive P (DRP) is readily bioavailable for use by plants and algae and is the dominant form of P transported to waterbodies from agriculture in cold climate regions (Hoffman et al., 2019). Particulate P losses through runoff in warmer regions can also contribute to the increase in algal blooms seen in many freshwater bodies (Grewal et al., 2020). Phosphorus is considered to be a major water pollutant and even at low concentrations can be responsible for stimulating significant algal growth (Schindler et al., 2012). Previous studies have found that in snowmelt runoff events DRP is the dominant form of P being exported to surface waters (Hoffman et al., 2019). Lake Winnipeg, the 10th largest lake in the world spanning an area of 24,500 km² is a perfect example of a freshwater lake that has been adversely impacted by excessive nutrient runoff from many sources, including agriculture (Liu et al., 2013). Lake Winnipeg water quality has been rapidly deteriorating over many decades which is largely caused by the abundance of nitrogen-fixing cyanobacteria; this rapid deterioration is linked to the transformation of much of the native grasslands to agriculture (Schindler et al., 2012).

1.4. Phosphorus transport through runoff and best management practices (BMPs)

Agricultural practices that increase or aim to maintain high levels of nutrients within the soil have been linked to increasing nutrient loads in runoff (Liu et al., 2013). The transport of P, through mechanisms such as runoff, is of major concern as these runoff events can contribute a significant portion of total annual P loads (Hoffman et al., 2019). Typically, P is transported from soils as particulate-bound through erosion, or as dissolved forms in water (Cober et al., 2019). Phosphorus losses through rain runoff events are dominated by particulate-bound P (Hoffman et al., 2019). There can be a very high degree of variability in surface runoff P concentrations, making it difficult to extrapolate small scale studies to $\text{kg of P ha}^{-1} \text{ year}^{-1}$ (Heathwaite & Dils, 2000). For this reason, quantifying total P losses from agricultural fields can be challenging with inconsistent results. Although, the mean total P (TP) concentrations in surface runoff from agriculture has been reported as being significantly higher than TP concentrations in runoff from grassland catchments (Heathwaite & Dils, 2000). Particulate P transported through runoff, in aerobic waters, can have a portion of P desorbed and become available for primary producer use (Uusitalo et al., 2003). Whereas, when particulate P is transported to anaerobic waters, its availability is dependent on redox induced dissolution reactions. Primary drivers of increased P losses from agricultural fields to runoff include tillage, removal of native vegetation, and poor cropping practices (Grewal et al., 2020). While some P losses may occur through below surface processes, overland transport of P is the main pathway to freshwater systems during storm runoff events (Hart et al., 2004).

While P losses from soils during surface runoff events are a major source of P loading to freshwater systems, there are many BMPs which have been identified to reduce P losses (Rao et al., 2009). Many of these BMPs are effective in reducing particulate P losses (Hoffman et al., 2019). Some BMPs that have proven to be effective in reducing P losses to runoff include cover cropping, buffer strips, and conservation tillage (Blanco-Canqui, 2018; Roberts et al., 2012; Tiessen et al., 2010).

1.5. Prairie snowmelt flooding and P losses

Prairie regions are often characterized by poor drainage due to their flat topography and low soil permeability. These conditions, coupled with large amounts of winter and spring precipitation, can contribute to flooding events which can enhance nutrient losses through runoff (Liu et al., 2013). Prolonged flooding can contribute to various changes in biogeochemical processes which can greatly impact P retention in the soil (Ponnamperuma et al., 1972; Jayarathne et al., 2016). Flooding can induce anaerobic soil conditions by decreasing soil redox potential (Ponnamperuma et al., 1972; Maranguit et al., 2017). This decrease in redox potential is caused by the respiration of soil microbes until there is no oxygen (O₂) left (Ponnamperuma, 1972). Once the system is depleted of O₂, those microbes which can anaerobically respire are favoured; these microbes can then use other electron acceptors for respiration subsequently reductively dissolving many P species (Maranguit et al., 2017). Phosphorus species which are redox sensitive include P associated with Fe and Mn. When soils become more reduced during flooding events, increases in concentrations of DRP, Fe and Mn in floodwater are likely to be observed (Amarawansa et al., 2015). In addition to the effect of flooding on soil redox potential, impacts to soil pH may also be observed (Ponnamperuma, 1972). As a soil becomes

flooded, various chemical reactions occur shifting soil pH towards neutrality (pH ~ 7.0); this means that a flooded acidic soil will see an increase in pH, whereas a flooded alkaline soil will see a decrease in pH (Shenker et al., 2005). While P species such as Fe and Mn-P are redox sensitive, P associated with Ca and Mg is not; these species, as well as Fe and Mn-P are affected by changes in pH (Sample, Soper & Racz, 1980). Calcium phosphates are quite stable in calcareous soils with an alkaline pH. However, as pH decreases, the solubility of these species is increased (Ponnamperuma, 1972). Although, there are many governing factors, the degree of P loss is dependent on the soil properties and length of flooding conditions (Kumaragamage et al., 2019).

Runoff events caused by snowmelt account for approximately 90% of annual runoff volume and can contribute a significant portion of total P as dissolved P (Hoffman et al., 2019). As the snowpack begins melting while the soil surface remains frozen, infiltration is inhibited, and this often contributes to an increase of DRP in runoff. According to Heathwaite & Dils (2000), about 62% of total P lost during surface runoff events is characterized as DRP, 70% of which is dissolved inorganic phosphorus (DIP). A multi-year study, conducted in Wisconsin, found that P exported through snowmelt runoff can represent anywhere from 12-62% of annual total phosphorus (TP) export (Hoffman et al., 2019).

1.6. Strategies for reducing P losses through snowmelt runoff

Most BMPs (conservation tillage, riparian buffers, etc.) are effective in targeting P retention during the warmer months or in warmer climates where erosion due to rain-runoff is the mode of P transport; however, these practices are often ineffective in cold climates with snowmelt-driven P loss (Hoffman et al., 2019). Majority of the BMPs used

in warmer climates focus on the transport of particulate-bound P through erosion and are ineffective in decreasing losses from the dissolved fraction (Hoffman et al., 2019).

Previous research has even shown increases in DRP concentration in snowmelt runoff through BMPs such as conservation tillage and cover crops (Hoffman et al., 2019; Liu et al., 2014). Soil amendments, such as alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and magnesium-sulphate (MgSO_4) have been evaluated as a method to reduce P losses from soils during snowmelt runoff in field and under simulated snowmelt flooding events in the laboratory (Lasisi et al., 2023; Kumaragamage et al., 2022; Vitharana et al., 2021; Dharmakeerthi et al., 2019^a; Dharmakeerthi et al., 2019^b). Soil amendments stabilize soil P through various processes (Attanayake et al., 2022). With the addition of soil amendments such as magnesium sulphate and gypsum, precipitation reactions that occur between the added Ca/Mg and P are favored, whereas soils amended with alum may see an increase in P adsorption to Al (Lasisi et al., 2023). These amendments can alter P fractions and species, therefore, having a direct impact on the solubility of P species (Fan et al., 2019). In addition to the increased precipitation and adsorption reactions that may occur as a result of amendment application, it has been observed that with the addition of gypsum, there may be a delay in the decrease in redox potential, subsequently inhibiting the reductive dissolution reactions that may release P to soil solution (Dharmakeerthi et al., 2019^b). Soil amendments have also been used to either increase or decrease soil pH. As soil pH is affected by flooding, the application of soil amendments has shown to help buffer some of those changes in pH, which again may indirectly reduce P losses (Ann, Reddy & Delfino, 1999). Soil amendments have also been shown to impact soil

aggregation and structure, which may impact the infiltration of snowmelt therefore, reducing runoff volume and ultimately P loss (Lasisi et al., 2023).

1.7. Thesis overview and overall objectives

While the use of soils amendments as a means to reduce P losses from soils to snowmelt has been studied by many researchers in laboratory simulated studies, field research is required to fully understand the capacity of these amendments. A recent study conducted by Lasisi et al (2023) showed that alum, gypsum and magnesium-sulphate applied in the fall reduced the P loss to snowmelt by 42-68% in a manured field site, and by <20% in an unmanured field site, with the magnesium sulphate amendment showing a significant decrease in snowmelt DRP loss in the manured site; however, the long-term benefits of these amendments have not been evaluated. This study was conducted at the same manured site, with the same field plots used by Lasisi et al (2023) where the amendments had been applied 12-18 months prior to the initiation of the study. The research aims to identify the long-term and residual benefits of alum, gypsum, and magnesium-sulphate in reducing P losses from soil to snowmelt.

This thesis is organized into the following 5 chapters:

- Chapter 1: *Literature Review*
- Chapter 2: *Field evaluation of residual benefits of alum, gypsum, and magnesium sulphate amendments in reducing phosphorus losses to snowmelt runoff*
- Chapter 3: *Residual benefits of soil amendments in reducing phosphorus losses from soils during simulated snowmelt flooding*
- Chapter 4: *Phosphorus speciation and fractionation during simulated snowmelt flooding with soil amendments*
- Chapter 5: *General discussion, conclusions, and recommendations for future research*

The overall objective of this thesis was to determine the long-term and residual benefits of soil amendments in reducing P losses through snowmelt runoff and simulated snowmelt flooding. The inorganic soil amendments chosen for this research were: alum, gypsum, and magnesium-sulphate. To better understand soil P dynamics with these amendments, soil P fractionation and P speciation using Visual MINTEQ thermodynamic modelling software were conducted. It was hypothesized that a) alum, gypsum, and magnesium sulphate would reduce DRP concentrations and loads in snowmelt 18 months after application b) amended soils would have lower DRP concentrations in floodwater than unamended soils with simulated flooding under controlled conditions and c) amended soils would have observable differences in P species/fractions with a greater proportion of P found in the less soluble P fractions.

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Chapter 2. Field evaluation of residual benefits of alum, gypsum, and magnesium sulphate amendments in reducing phosphorus losses to snowmelt runoff

Abstract

Phosphorus (P) in snowmelt runoff from agricultural fields across the Canadian prairies is a major source of nutrient pollution to freshwater bodies, such as Lake Winnipeg. The use of soil amendments, such as alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and magnesium-sulphate (MgSO_4) have previously shown a decrease in P release from various soils, through field experiments and simulated snowmelt studies. This study examined the effectiveness of alum, gypsum, and magnesium-sulphate in reducing P losses from a field site 18 months after amendment application. The study was conducted on a silt clay loam soil in SE Manitoba. Amendments were applied in the fall of 2020 at a rate of 2.5 Mg ha^{-1} as a randomized complete block, consisting of 4 replicates of 4 amendments (alum, gypsum, magnesium sulphate, and unamended) for a total of 16 field plots. Daily snowmelt volume was collected from each field plot in spring of 2022 and analyzed for dissolved reactive P (DRP), pH, and cations. Dissolved reactive P concentrations increased over the sampling period regardless of amendment, with higher concentrations seen after the soil was suspected to have thawed. In the latter days of sampling, the alum, gypsum, and magnesium sulphate-amendments decreased DRP concentrations in snowmelt by 9 – 31% relative to the control. However, differences between treatments and the control were not statistically significant. Snowmelt DRP loads showed a significant positive relationship with snowmelt volume, whereas the relationship between DRP concentration and loads was not significant. The results of this study add to the body of evidence suggesting that DRP load is largely controlled by the

volume of water rather than the concentration of P in the snowmelt, and also suggests that the amendments were not effective in reducing DRP loads 18 months after application.

2.1. Introduction

Phosphorus (P) losses from agricultural soils are a major concern, as P is generally considered the most limiting nutrient for algal growth and eutrophication (Schindler et al., 2012). In the Canadian prairies, nutrients like nitrogen (N) and P are often applied to agricultural soils in the form of fertilizer or manure in order to improve crop yields and soil health (Government of Manitoba, 2013). It is estimated that only about 20% of P applied as fertilizer is used by plants in annual cropping systems, while the remainder becomes immobilized within the soil (Roberts & Johnston, 2015). This added P is retained in the soil through adsorption onto (hydr)oxides of aluminum (Al), iron (Fe) and manganese (Mn), calcium carbonates (CaCO_3), and clay minerals, as well as through precipitation with dissolved ions like calcium (Ca), magnesium (Mg), Mn, Al, and Fe (Sample, Soper & Racz, 1980).

In the Canadian prairies, a large portion of annual precipitation falls over the winter months in the form of snow, which accumulates on the soil surface while temperatures are below 0°C (Schneider et al., 2019). As the Canadian prairies have relatively flat landscapes, the lands are susceptible to spring flooding which can often last for a period of few days to weeks (Bedard-Haughn, 2009). As the ground remains frozen, snowmelt is unable to infiltrate into the soil (Li et al., 2021; Dumanski et al., 2015). Therefore, a rapid accumulation of meltwater occurs in these flat, low-lying areas (Liu et al., 2014). The rapid snowmelt, flat landscapes, and frozen soil surface are the perfect conditions to allow for prolonged flooding (Li & Simonovic, 2002). Runoff caused by snowmelt is one

of the main events in which nutrients are transported from agricultural lands to freshwater systems on the Canadian prairies (Rattan et al., 2017).

When anaerobic conditions occur as a result of flooding, microbial activity within the soil shifts to those microbes that have the ability of anaerobic respiration, using electron acceptors like nitrate (NO_3^-), Mn and Fe to maintain their metabolism (Maranguit et al., 2017). These anaerobic microbes typically use whatever is most readily available, therefore reducing $\text{Mn}^{3+}/\text{Mn}^{4+}$ to Mn^{2+} , and Fe^{3+} to Fe^{2+} . Any P that may have been associated with Mn and Fe can become mobilized due to their higher solubility (Amarawansa et al., 2015; Kumaragamage et al., 2019). In flooded, anaerobic soils, Rakotoson et al. (2016) observed an increase in available soil P from 1.4 to 60 mg kg^{-1} when compared to aerobic soils. Consequently, an increase in P concentration in floodwater is often seen in combination with an increase in Fe^{2+} and Mn^{2+} concentrations (Amarawansa et al., 2015; Maranguit et al., 2017). Soil pH also plays an important role in the solubility of P in anaerobic soils; as when an alkaline soil is flooded, pH decreases, subsequently increasing the solubility of hydroxyapatite ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_3$), a common Ca-P species (Ponnamperuma, 1972). Due to the changes in pH that accompany the reduction in soils, Ca and Mg-phosphates play an important role in the release of P in calcareous soils (Jayarathne et al., 2016). However, while Ca and Mg-P species are sensitive to changes in pH, they are not sensitive to changes in redox potential (Shenker et al., 2005). During the early stages of flooding, before soils become completely anaerobic, the role of Ca and Mg in the release of P is considered to be more important than that of Fe and Mn (Jayarathne et al., 2016). However, the opposite can be said in the latter stages of flooding, as soils become more anaerobic.

Additions of soil amendments, such as alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and magnesium-sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) have been shown to effectively decrease P release from soils to porewater and overlying floodwater in the laboratory under simulated snowmelt conditions (Dharmakeerthi et al., 2019^a; Dharmakeerthie et al., 2019^b; Vitharana et al., 2021). Soil amendments can favor the formation of less labile P species through precipitation and adsorption reactions, subsequently immobilizing P within the soil (Attanayake et al., 2022; Kumaragamage et al., 2022). More recently, Lasisi et al. (2023) evaluated the immediate benefits of fall-applied amendments such as gypsum, alum, and magnesium-sulphate in reducing P losses to snowmelt in the following spring season and found that the P loss to snowmelt in the spring (six months after application) was reduced by 42-68% in a manured field site, and by <20% in an unmanured field site, with magnesium sulphate amendment showing a significant decrease in snowmelt DRP loss in the manured site; however, identifying their long-term and residual benefits has yet to be established. This study aims to determine if alum, gypsum, and magnesium-sulphate are effective in reducing P concentration and loads in snowmelt, 18 months after amendment application. This information will be useful in deciding the frequency of amendment application to reduce P loss to snowmelt. The relationship between P and cations (Ca, Mg, Fe, and Mn), and pH will be investigated in order to help determine the mechanisms that govern the release of P from soil to snowmelt. We hypothesized that the plots amended with alum, gypsum, and magnesium sulphate would reduce DRP concentrations and loads in snowmelt, even 18 months after application, although likely to a lesser degree compared to a snowmelt event immediately after amendment application.

2.2. Materials and Methods

2.2.1. Site Location and Description

A site located on a manured, agricultural field in the Red River Basin, South-East of Winnipeg (49° 32' N, 96° 51' W) near Randolph, Manitoba was chosen for this study. This site was selected because it is in a region identified as a P hotspot (areas that contribute large amounts of P to Lake Winnipeg) based on the Lake Winnipeg Basin Community Based Monitoring Data (<https://doi.org/10.25976/hxqe-py39>).

The soil at this site is clay in texture, classified as a Rego Humic Gleysol, and part of the Osborne Series (Government of Manitoba, 2010), with a pH of 7.7, organic matter content of 75 g kg⁻¹ and Olsen P of 80 mg kg⁻¹. More details of soil characterization are provided in Lasisi et al. (2023).

2.2.2. Experimental Setup

This study is the second phase of a multi-year project. The immediate benefits of the soil amendments in reducing P loss to snowmelt were investigated in 2020/2021 (Lasisi et al., 2023). In the fall of 2020, field plots were laid out as a randomized complete block design consisting of 4 replicates of each treatment. The treatments were a) alum amendment, b) gypsum amendment, c) magnesium-sulphate amendment, and d) an unamended-control. Runoff boxes were installed in each plot. Soil amendments were applied at a rate of 2.5 Mg ha⁻¹ and incorporated into the top 0-5 cm of the soil. Details on experimental setup, collection, and analysis of snowmelt runoff in the spring of 2021 were previously reported (Lasisi et al., 2023).

In the fall of 2021 soil samples (0 – 15 cm) were collected from each plot. The runoff boxes were then re-installed in each plot to collect snow over the 2021/2022 winter to evaluate the residual benefits of soil amendments in reducing P loss with snowmelt. In the spring of 2022, once temperatures increased above 0° C, the total volume of snowmelt was pumped out of each plot daily using a Mastercraft 12V Rubber Impeller Transfer Pump, collected into a 22.73L pail and the daily snowmelt volume was measured from each runoff box. A snowmelt sub-sample of about 250mL from each plot was then transported immediately to the laboratory for analysis. In the laboratory, a sub-sample was filtered through a 0.45 µm pore size syringe filter, stored in a walk-in cooler at 4°C overnight before analysis. Snowmelt collection began on March 20th and continued for 5 consecutive days (sampling days 1 to 5) until average daily temperatures dropped below 0°C. Collection resumed on March 29th, April 1st, and April 4th (sampling days of 6, 7 and 8, respectively). Soil samples (0-15 cm) were collected from each plot soon after snowmelt collection had ended.

2.2.3. Analysis of snowmelt samples

Dissolved reactive P concentrations were determined in the snowmelt samples within 24 hours of collection using the molybdate blue color method (Murphy & Riley, 1962).

Snowmelt pH of each sample was measured using a Fisher Accumet AB15 pH meter.

Snowmelt samples were also analyzed for the concentrations of Ca, Mg, Fe and Mn using flame atomic absorption spectroscopy (AAAnalyst 400, PerkinElmer). Daily DRP and cumulative loads were calculated by the following formulas:

$$\text{Daily DRP Load (mg)} = \text{DRP concentration} \left(\frac{\text{mg}}{\text{L}} \right) \times \text{daily snowmelt volume (L)}$$

$$\text{Cumulative Load (mg)} = \sum_{i=1}^n \text{Daily DRP Load (mg)}$$

where i is the day of the i^{th} sample and n is the number of sampling days.

The volume-weighted concentrations were calculated by the following formula:

$$\text{volume-weighted concentrations} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{\text{cumulative DRP load (mg)}}{\text{cumulative snowmelt volume (L)}}$$

Soil samples (0 – 15 cm), which were collected in the fall of 2021 and spring of 2022, were analyzed for available P using the Mehlich method (Mehlich, 1984) and P concentration in the extracts was determined using the molybdate-blue colour method (Murphy & Riley, 1962).

2.2.4. Statistical Analysis

Statistical analysis was conducted using R Studio Programming, version 1.4.1106 (RStudio Team, 2021). The data were tested for normality using the Shapiro-Wilks test. All non-normal data were log-transformed to conform to normality. Repeated measures ANOVA was used to determine a significant effect of treatment, sampling day or their interaction (day \times treatment) (rstatix package in Rstudio).

A paired T-test was performed to compare the fall vs spring Mehlich 3 extractable P from soil, as well as an ANOVA to identify differences in volume-weighted DRP concentrations as well as Mehlich 3 P between treatments in both spring and fall samples. Regression analysis was used to determine the relationship between DRP and pH, Ca, Mg, Mn, and Fe concentrations. For all statistical analysis, significance was determined at $p = 0.05$.

2.3. Results

2.3.1. Air Temperature over the sampling period

Mean daily air temperature varied from -13.1 °C to 4.3 °C over the sampling period. On days where snowmelt was present in each plot, maximum daily air temperature varied from 2.7 °C to 9.4 °C.

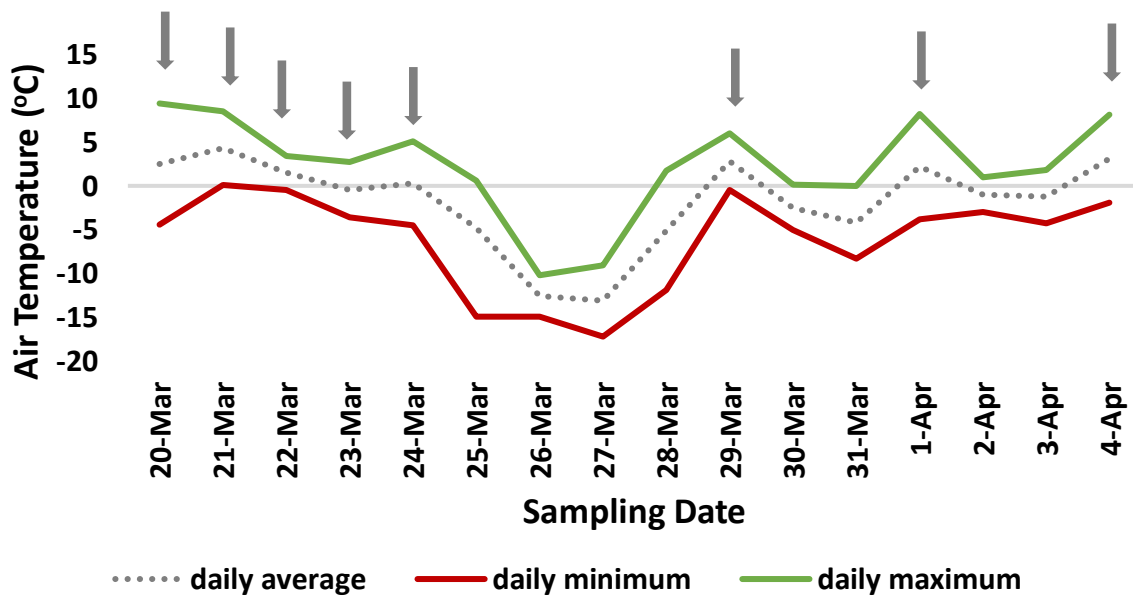


Figure 2.1. Daily average, minimum, and maximum air temperature for the Kleefeld, MB weather station obtained from Environment Canada. Arrows indicate the sampling days.

2.3.2. Mehlich 3 extractable P concentrations

Mean Mehlich 3 extractable P ranged from 145.05 to 206.3 mg kg⁻¹ in the fall and from 208 to 354.3 mg kg⁻¹ in the spring, depending on treatment. There were no significant differences between treatments in either the fall or spring samples. However, a paired T-

test revealed that Mehlich extractable P was significantly greater ($p < 0.05$) in samples collected in the spring for all amended and unamended plots, compared to samples collected in the fall.

2.3.3. Dissolved reactive phosphorus concentrations and loads in snowmelt

Mean DRP concentrations in snowmelt of different treatments ranged from 0.27 mg L^{-1} to 1.33 mg L^{-1} throughout the sampling period. Results of an ANOVA identified no significant treatment effect or interaction effect of treatment \times sampling day. However, the effect of sampling day alone was significant ($p < 0.001$) (Table 6.1; Appendix). Regardless of amendment, there was a significant increase in DRP concentrations over the sampling period with a greater increase seen on sampling days 6-8, although the differences between treatments were not significant (Figure 2.2a). On sampling days 6, 7 and 8 the alum-amended plots had 20 – 31.3% lower DRP concentrations compared to the unamended plots, whereas on days 7 and 8 all amended plots (alum, gypsum, and magnesium-sulphate) had 9.4 – 31.3% lower DRP concentrations than the unamended plots. However, these differences were not statistically significant.

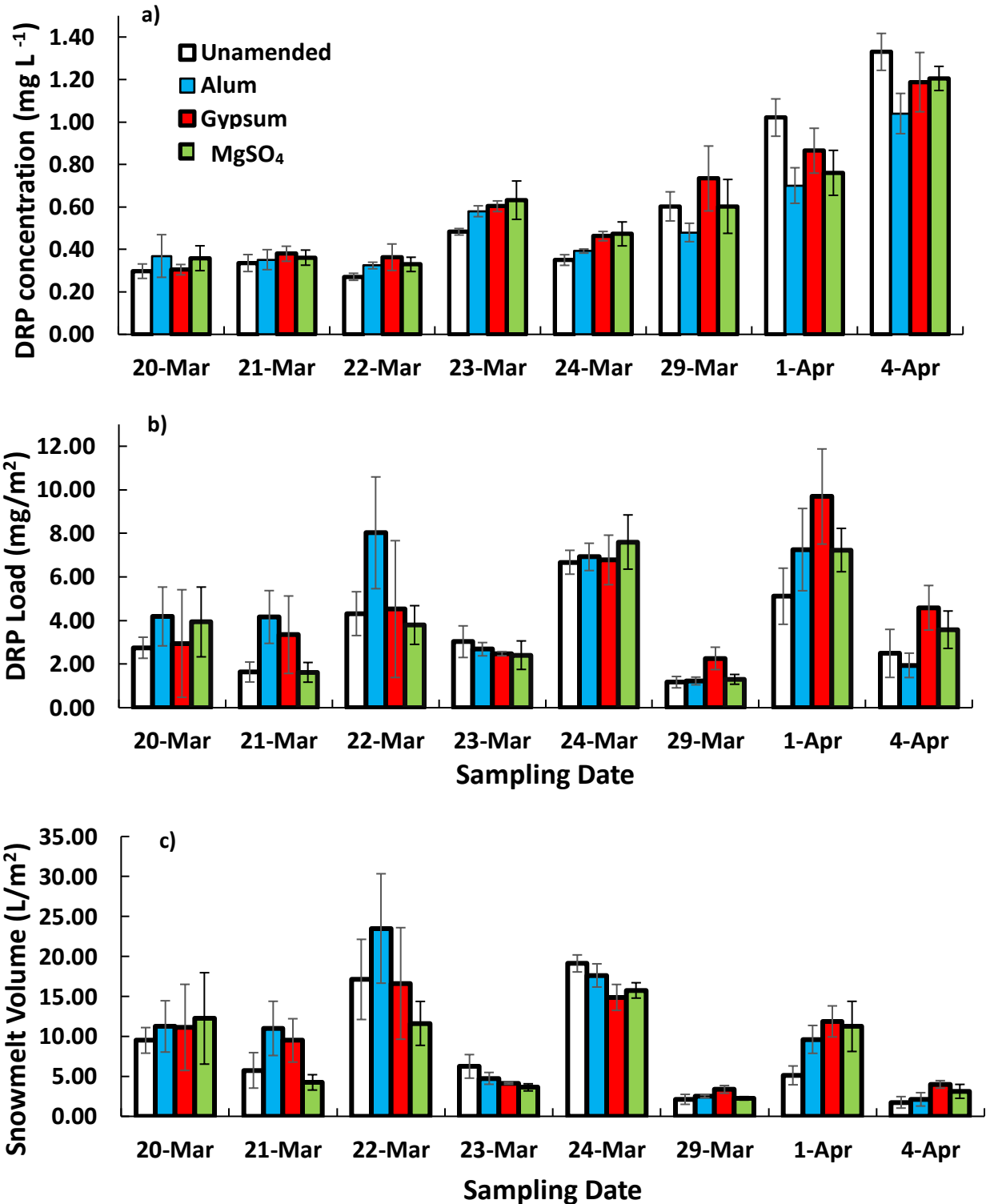


Figure 2.2. Mean dissolved reactive P concentrations (a) daily snowmelt volume (b) and daily DRP loads (c) in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots with sampling date. Vertical error bars represent standard error of the mean.

Mean snowmelt volume ranged from 1.75 L to 23.5 L (Figure 2.2b). There was a significant ($p < 0.001$) decrease in snowmelt volume with sampling day (Table 6.1; Appendix). However, the differences among treatments were not significant. Mean DRP loads, calculated using DRP concentration and snowmelt volume, varied from 1.17 mg to 9.69 mg per runoff box (equivalent to 0.01 – 0.09 kg ha⁻¹), depending on treatment and snowmelt sampling day (Figure 2.2c). There was no significant interaction between sampling day \times treatment or treatment alone, however there was a significant ($p < 0.001$) effect of sampling day (Table 6.1; Appendix). A significant ($p < 0.001$) positive relationship was observed between snowmelt volume and DRP load, regardless of amendment (Figure 2.3a), as well as a significant negative relationship between snowmelt volume and DRP concentration ($p < 0.001$; Figure 2.3b). The relationship between DRP load and DRP concentration was not significant (Figure 2.3c).

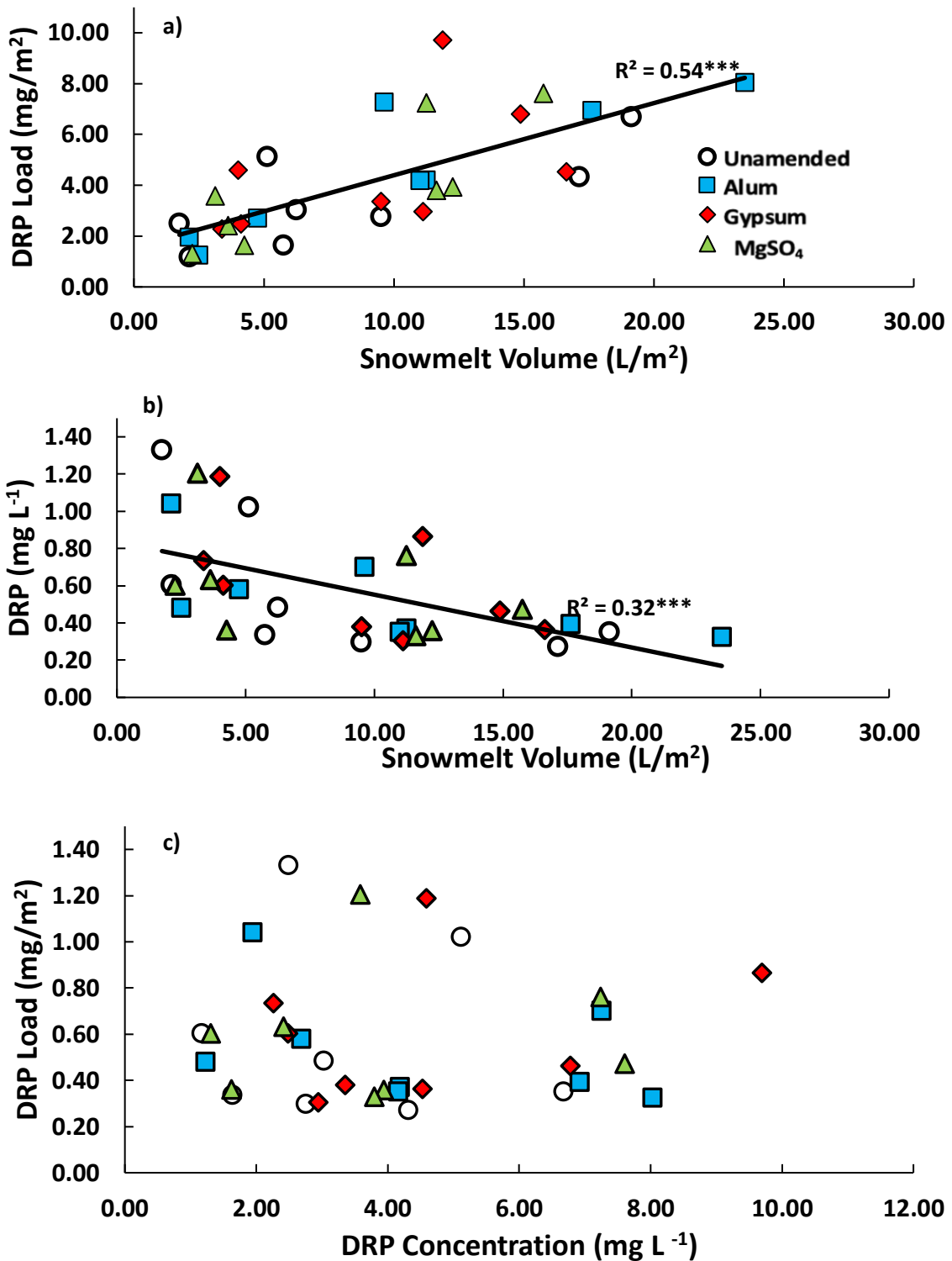


Figure 2.3. Relationship between a) DRP load and snowmelt volume, b) DRP concentration and snowmelt volume and c) DRP load and DRP concentration of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots. Significance determined at $p < 0.05$.

Mean cumulative DRP loads ranged from 27.19 – 36.62 kg ha⁻¹, depending on treatment (Figure 2.4). Even though the DRP concentrations in snowmelt were greater in unamended than in amended plots, the cumulative DRP loads in the unamended plots were often lower than in amended plots because of the lower snowmelt volume in the unamended plots. Volume-weighted concentrations varied from 0.4 mg L⁻¹ to 0.49 mg L⁻¹ depending on treatment (Figure 2.5). There was no significant difference observed among the treatments.

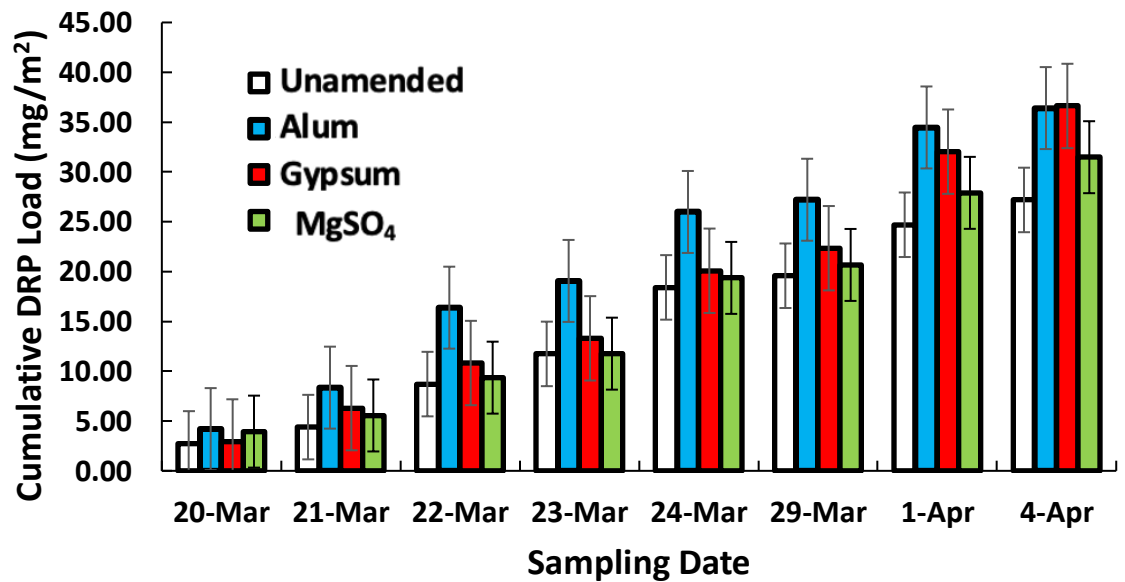


Figure 2.4. Mean cumulative DRP loads in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots with snowmelt sampling day. Vertical error bars represent standard error of the mean.

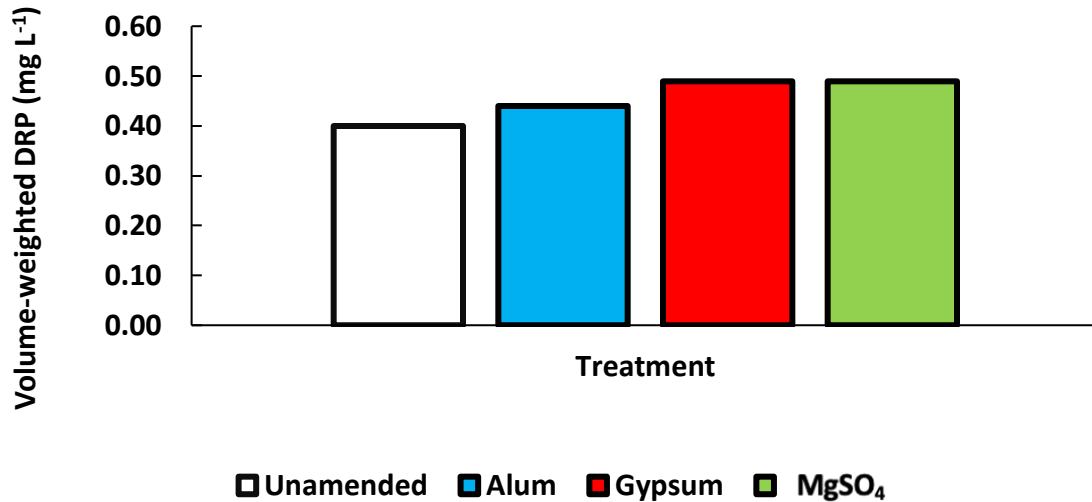


Figure 2.5. Mean volume-weighted DRP concentrations in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots.

2.3.4. Relationship between cations, pH and DRP concentrations in snowmelt

Mean snowmelt pH varied from 7.16 to 7.83 depending on treatment and snowmelt sampling day (Figure 2.6) and there was a significant ($p < 0.001$) day effect (Table 6.1; Appendix).

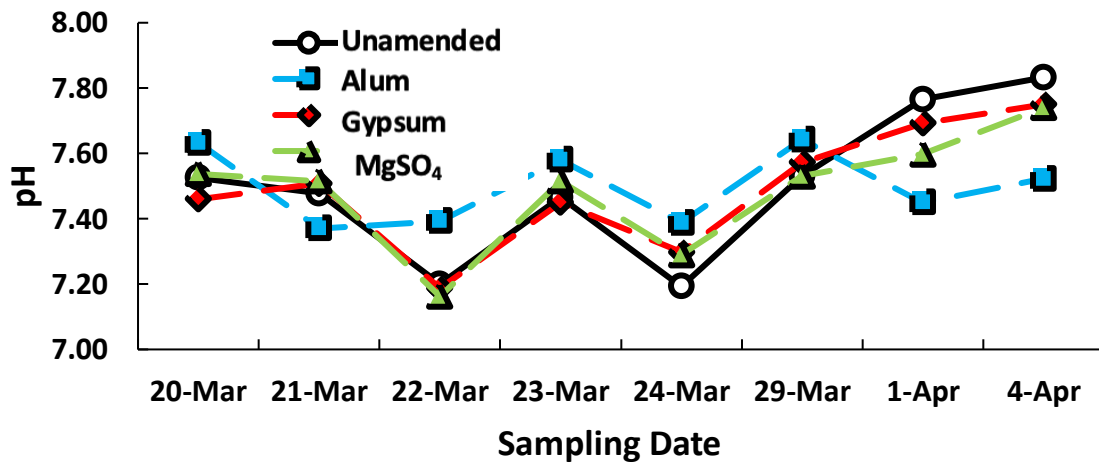


Figure 2.6. Mean pH in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots with snowmelt sampling day.

Mean Ca and Mg concentrations ranged from 0.4 mg L⁻¹ to 150.15 mg L⁻¹ and 2.16 mg L⁻¹ to 101.71 mg L⁻¹, respectively (Figure 2.7a & b). Both Ca and Mg concentrations significantly increased over the sampling period ($p < 0.001$; Table 6.1; Appendix). No significant effect of treatment or the interaction between treatment and sampling day was observed.

Mean Fe and Mn concentrations varied from 0.046 mg L⁻¹ to 0.21 mg L⁻¹ and 0.0031 mg L⁻¹ to 0.079 mg L⁻¹, respectively (Figure 2.7c & d). There was no significant interaction between sampling day and treatment on Fe concentrations. However, a significant interaction was observed with Mn concentrations ($p < 0.05$). Mn concentrations significantly increased in unamended plots ($p < 0.05$) and over the sampling period ($p < 0.001$). In contrast, there was a significant ($p < 0.001$) decrease in Fe concentrations, regardless of treatment, over the sampling period (days 1-8) (Table 6.1; Appendix).

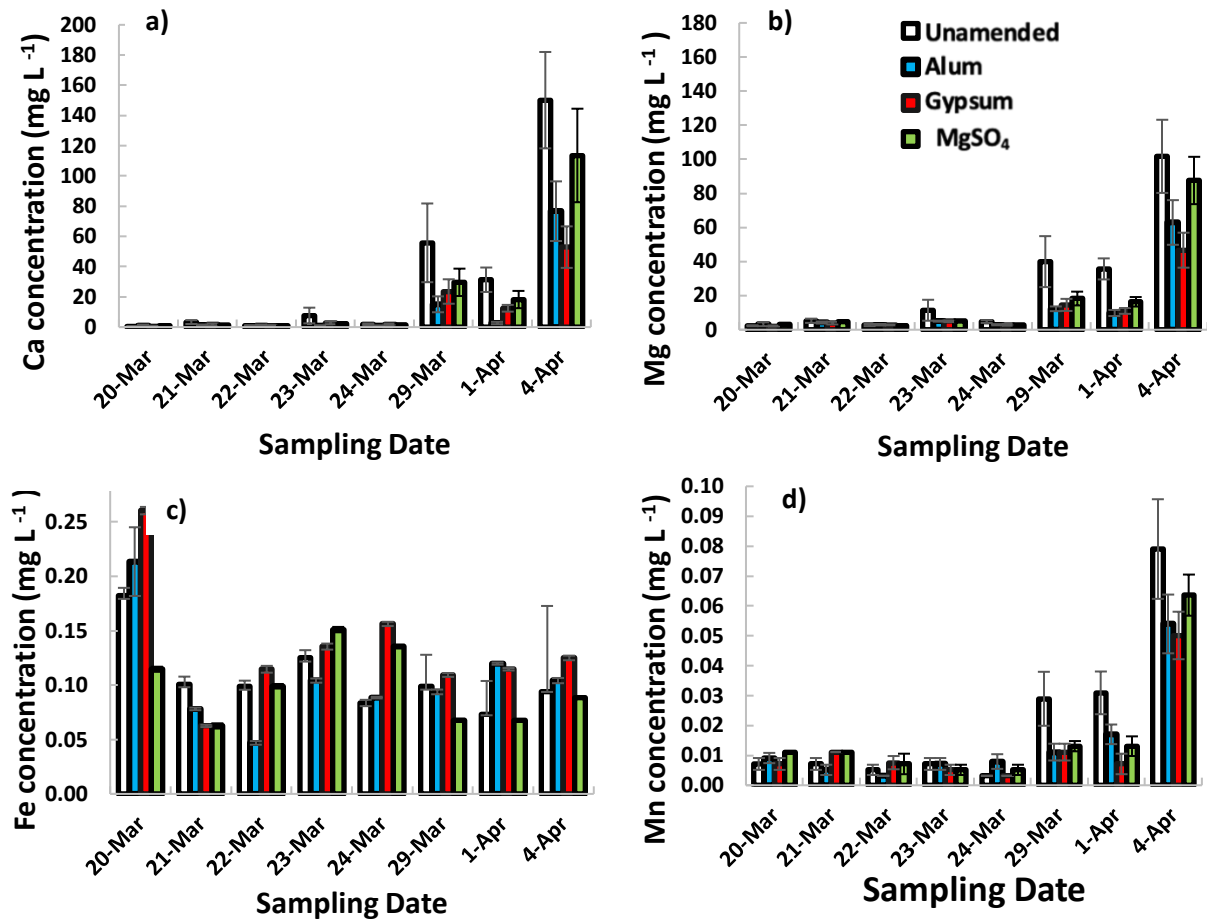


Figure 2.7. Mean concentrations of a) Ca, b) Mg, c) Fe and d) Mn in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots.

Regardless of treatment, regression analysis of all data showed that snowmelt Mn concentrations and DRP concentrations had a significant positive relationship ($p < 0.001$; Figure 2.8). However, Fe concentrations in snowmelt did not have a significant relationship with DRP concentrations. The relationships between Ca/Mg and DRP concentrations were also positive and significant ($p < 0.001$; Figure 2.8) in all treatments.

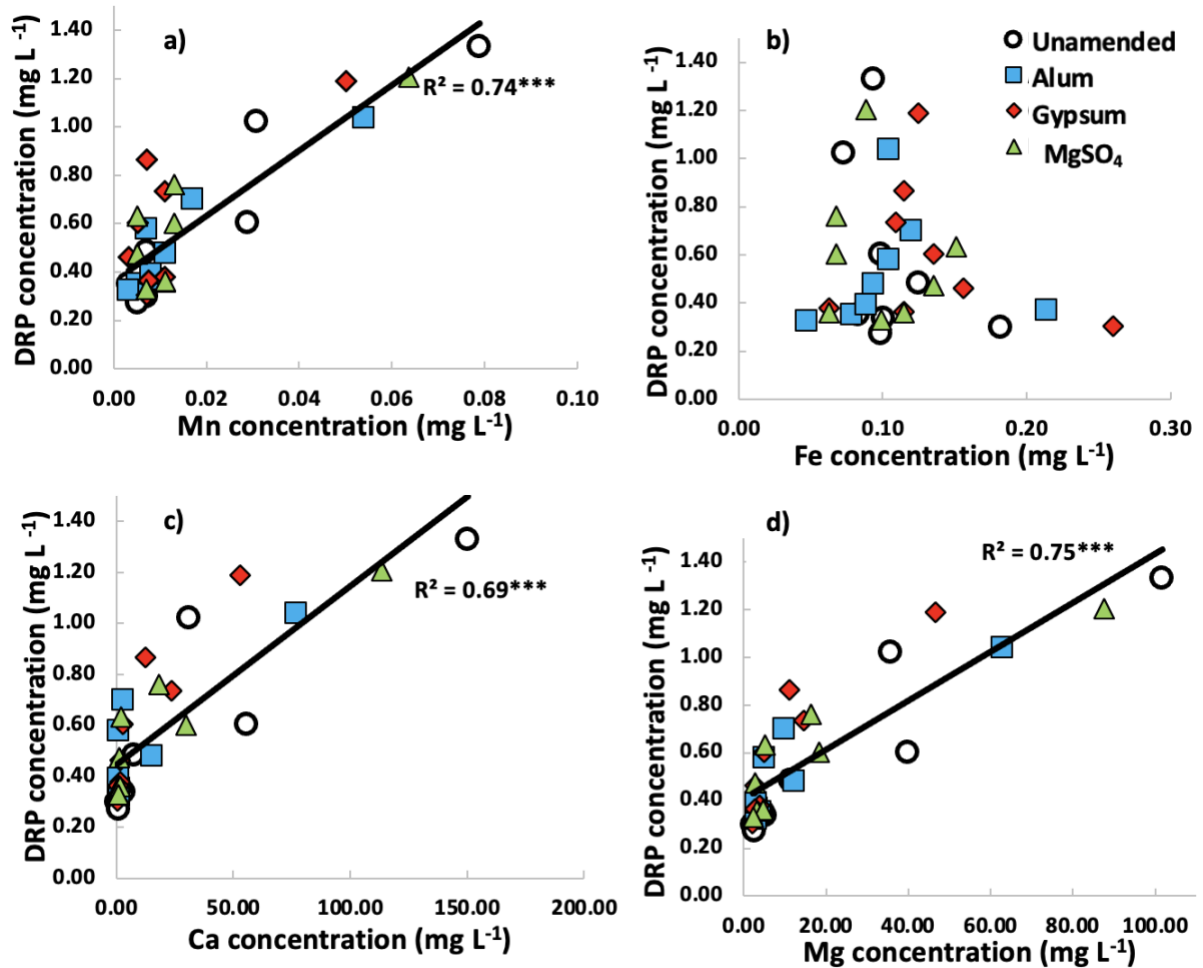


Figure 2.8. Relationship between DRP, a) Mn, b) Fe, c) Ca and d) Mg concentrations in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots. Significance determined at $p < 0.05$.

The relationship between DRP concentrations and pH in snowmelt was positive and significant ($p < 0.001$), but only for gypsum-amended, magnesium sulphate-amended and unamended plots. There was no significant relationship between DRP concentration and pH in the alum-amended plots (Figure 2.9).

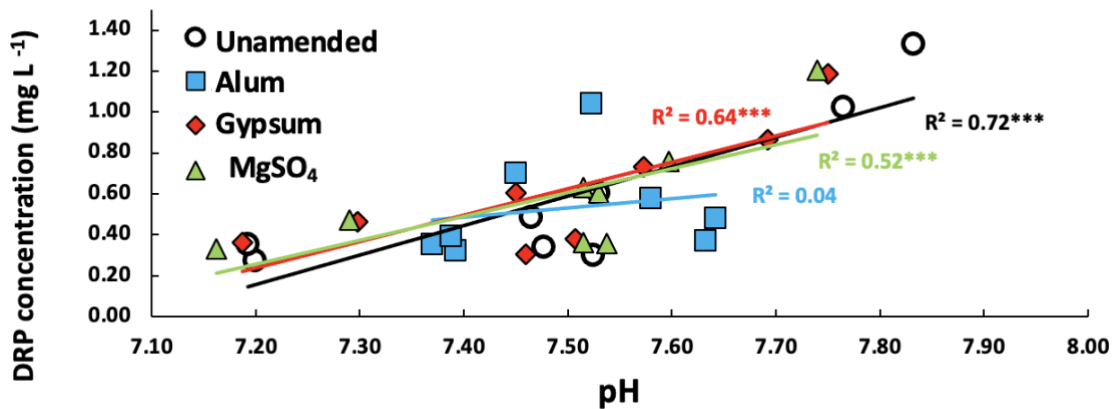


Figure 2.9. Relationship between DRP and pH in snowmelt of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended plots. Significance determined at $p < 0.05$.

2.4. Discussion

2.4.1. Increase in snowmelt DRP concentration with time

Snowmelt DRP concentrations were higher in the current study than in the first year of the study, with the highest concentrations observed in the first year reaching 1.06 mg L^{-1} (Lasisi et al., 2023). Whereas, in the current study, DRP concentrations reached 1.33 mg L^{-1} by the end of the sampling period. Dissolved reactive P concentrations in snowmelt, during the first five days of collection, were lower than DRP concentrations in the last 3 days. As reported in another study, the interaction between the soil and overlying snowmelt can be inhibited by the frozen soil surface as less P is released to snowmelt compared to when the soil has thawed (Kumaragamage et al., 2020). In addition, the cold temperatures hinder microbial activity, delaying the release of P in colder climates (Jefferies et al., 2010). The greater increases in DRP concentrations observed in the last three days of collection suggest that P release from frozen soil to overlying snowmelt was enhanced after the top layer of soil had thawed, and there is sufficient interaction between

the soil and overlying snowmelt (Tang et al., 2016; Weerasekara et al., 2021). While P release from soils may be governed by multiple biogeochemical processes and their interactions, microbial-mediated reductive dissolution reactions play an important role in flooded soils (Arenberg & Arai, 2019). The effects of flooding events on soil redox conditions can cause an increased release of P from the soil to pore water, and overlying floodwater (Ponnamperuma, 1972; Amarawansa et al., 2015; Jayarathne et al., 2016). While P release to snowmelt in cold climates is less severe than release to floodwater in warmer climates, P losses with snowmelt flooding is substantial in the Red River Basin (McCullough et al., 2012). In this study, since the total volume of melted snow was removed from each runoff box on each collection day, a prolonged flooding condition was not created; however, it is possible that beneath the frozen soil layer, conditions were anaerobic as indicated by low redox potential readings in the previous year at the same site during the snowmelt period (Lasisi et al., 2023). Increases in DRP concentrations with time in actual snowmelt in the field, and in floodwater with simulated flooding in the laboratory, has been previously reported by researchers in this region (Lasisi et al., 2023; Vitharana et al 2021; Van et al., 2022; Kumaragamage et al., 2022; Amarawansa et al., 2015; Dharmakeerthi et al., 2019^a; Dharmakeerthi et al., 2019^b).

Initial increases in DRP concentrations, during early stages of flooding, are usually attributed to the dissolution of Ca and Mg phosphates, (Jayarathne et al., 2016), whereas during the latter stages, increasing DRP concentrations in snowmelt are likely due to the decrease in redox potential, increase in microbial mediated reductive dissolution reactions where $\text{Fe}^{3+}/\text{Mn}^{3+}$ is reduced to $\text{Fe}^{2+}/\text{Mn}^{2+}$, which subsequently releases chemically bound P, increasing the release of P to floodwater (Amarawansa et al., 2015;

Vitharana et al., 2021; Scalenghe et al., 2010; Ponnampereuma, 1972; Kumaragamage et al., 2020). During snowmelt collection, concentrations of both Ca and Mg increased slowly in the first 5 days of collection. The frozen soil layer and colder temperatures likely inhibited the dissolution reactions that would normally take place in the early stage of spring melt (Kumaragamage et al., 2020). In the last 3 days of collection, concentrations of Ca, Mg, Mn and DRP increased significantly, suggesting that both the dissolution of Ca and Mg-phosphates as well as the reductive dissolution of Mn may have contributed to the increased DRP concentrations in snowmelt at this stage. It is also possible that the increase in DRP concentrations observed is more related to the increase in temperature, enhancing dissolution reactions. The release of P to floodwater in controlled laboratory studies has been associated with increased concentrations of Mn and Fe, especially as anaerobic conditions progress (Vitharana et al., 2021). Although the relationship between DRP and Mn was observed and suggests increased reductive dissolution of Mn-P, the role of redox conditions can only be speculated based on the results published by Lasisi et al. (2023), as redox potential was not measured in this year of the study. Lasisi et al (2023), reported reducing conditions (100-242 mV) in all soils which suggested the reductive dissolution of Mn was a possible mechanism for P release.

2.4.2. Residual amendment effects on DRP release to snowmelt

The decreases in snowmelt DRP concentration with alum, gypsum and magnesium sulphate were not significantly different to that of the unamended control, contrary to the past research that has shown significant decreases in floodwater DRP concentrations with the use of alum (Kumaragamage et al., 2022), gypsum (Kumaragamage et al., 2022) and magnesium sulphate (Vitharana et al., 2021) amendments. However, these previous

studies were conducted shortly after amendment application to intact soil monoliths in the laboratory under simulated spring flooding. Lasisi et al. (2023) noted that the cumulative DRP load in snowmelt was reduced by 51, 48 and 62% in alum, gypsum and magnesium sulphate-amended plots compared to unamended treatment, when amendments were applied in the preceding fall (~6 months prior to snowmelt), however, the difference was significant only for the magnesium sulphate treatment. In the current field study using the same field plots used by Lasisi et al. (2023) 18 months after amendment application, alum, gypsum, and magnesium sulphate amendments decreased DRP concentrations in snowmelt by 31.3%, 15.3% and 25.5%, respectively, although, they had no effect on DRP loads or cumulative DRP loads because of the high variability in snowmelt volume among treatments. Therefore, results suggest that the amendments, even if effective in the first snowmelt season after application, may not be effective in reducing P loss to snowmelt for more than one snowmelt flooding season. Reductions in P release from soils amended with alum, gypsum and magnesium sulphate have been attributed to the amendments effect on the oxidation-reduction of soils as well as their ability to enhance precipitation reactions (Attanayake et al., 2022; Vitharana et al., 2021). Past research has also indicated that amendments like alum and gypsum can be more effective at immobilizing P when DRP concentrations in floodwater are greater than 0.15 mg L^{-1} (Kumaragamage et al., 2022). This is somewhat consistent with this study where the decreases in DRP with amendments were more observable in the last 3 days of collection, when DRP concentrations were greater than 0.5 mg L^{-1} , however, these decreases were still not statistically significant.

The significant positive relationship observed between pH and DRP concentrations in this study suggest that P availability was significantly tied to pH. Changes in pH observed with flooding can impact the solubility of certain P species (Ponnamperuma, 1972), leading to an increase in P loss from the soil. In the current study, the alum amended plots had significantly lower pH, compared to the unamended control, in the last two days of collection and subsequently, no relationship between pH and DRP concentration with the alum amendment was observed. The pH decrease was very slight in alum amended treatment and was observed only during the last 2 days of collection, compared to all other treatments, and it remained above the threshold for significant Ca-P dissolution (Ponnamperuma, 1972).

2.4.3. Soil available P after snowmelt with different treatments

The available soil P measured as Mehlich 3 extractable P was greater in spring soil samples when compared to fall samples, although no significant differences among treatments was observed. Significant increases in spring versus fall available soil P concentrations have been observed in previous studies (Lasisi et al., 2023). Anderson et al. (2021) also reported an increase in available P in soils after simulated flooding compared to pre flooding. This increase in available soil P, may be linked to the anaerobic soil conditions induced by the prolonged flooding and the subsequent increase in the solubility of P species (Anderson et al., 2021; Vitharana et al., 2021). Xu et al. (2020) reported increases in labile P fractions from 31% to 50% after flooding, attributed to the reductive dissolution of Fe-P. Mineralization also plays an important role in the increase in labile P after freeze-thaw events (Vaz et al., 1994). In addition, the presence of crop residue in soils have shown to contribute to enhance P availability in soils

subjected to multiple freeze thaw cycles (Messiga et al., 2010). Sui et al. (2022) also found that soils undergoing freeze thaw events showed significant increases in labile P when compared to soils under thermostatic incubation.

2.4.4. Major controllers of snowmelt DRP load

A positive relationship between snowmelt volume and DRP load was observed in this study, and is consistent with past research (Wilson et al., 2019; Lasisi et al., 2023; Liu et al., 2013). While concentration of DRP in snowmelt is a contributing factor, it does not have as strong of a relationship with DRP loads as snowmelt volume. However, a strong negative relationship between snowmelt volume and DRP concentration was observed and suggests a dilution effect does occur. The dilution effect is further suggested by the lack of significant difference between the volume-weighted concentrations for each treatment. The unamended plots had lower snowmelt volume collected from each plot, however had similar volume weighted DRP concentrations compared to the amended plots. This dilution effect is predicted to be more prominent in snowmelt flooding where the frozen soil surface delays the release P compared to rainfall flooding events (Wilson et al., 2019). Even with this dilution effect, McCullough et al. (2012) reported that P loads in the Red River basin were 2.5 times greater in significant spring flooding years compared to non-flooding years. The relationships identified between snowmelt volume and DRP loads/concentration explain the slight decreases with amendment application when assessing DRP concentration but not with DRP loads, as the volume of water collected from the unamended plots was often less than that of the amended plots.

2.5. Conclusions

The use of soil amendments to decrease the P loss from soil to snowmelt is an important strategy for reducing overall P loads to waterways, however, our results imply that the snowmelt volume, rather than the P concentration in snowmelt, is the driving force affecting loading. A strong negative relationship between snowmelt volume and DRP concentration in snowmelt suggest a dilution effect, which is a prominent process in snowmelt flooding conditions. Results of this study evaluating the effectiveness of amendments 18 months after amendment application, suggest that alum, gypsum, and magnesium sulphate applied at a rate of 2.5 Mg ha⁻¹ were not effective in reducing P loss to snowmelt even though magnesium sulphate showed a significant effectiveness 6 months after application. The results suggest that to effectively reduce P loss from soils to snowmelt, amendments that are effective may need to be reapplied each fall, as amendment effectiveness decreased with the second spring snowmelt, or amendments would need to be applied at a higher rate in alternate years. However, due to the high variability in field conditions, multi-year, multi-site research evaluating soil amendments are needed to validate the results.

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Chapter 3. Residual benefits of soil amendments in reducing phosphorus losses from soils during simulated snowmelt flooding

Abstract

In the Canadian prairies, snowmelt runoff is the dominant pathway of nutrient transport from agricultural lands to freshwater systems. Spring snowmelt occurs rapidly and causes flooding in low lying areas, inducing anaerobic soil conditions, which may lead to an enhanced phosphorus (P) release from the soil into porewater and floodwater. Previous studies have shown that additions of soil amendments, such as gypsum, alum, and magnesium-sulphate were effective in decreasing P release from soils to porewater and floodwater. However, little is known on their long-term benefits. This study investigated the effects of gypsum, alum, and magnesium-sulphate in reducing P losses, one year after amendment application, in a simulated snowmelt flooding experiment. Dissolved reactive P (DRP) concentrations in both porewater and floodwater were determined and compared to identify any long-term benefits of these soil amendments. Sixteen intact soil columns were collected in the fall of 2021 from field plots which were amended with gypsum, alum, and magnesium-sulphate in the fall of 2020, as well as an unamended control. Soil columns were flooded at +4 °C for 49 days to simulate spring snowmelt flooding. Weekly, redox potential measurements were taken, and samples of porewater and floodwater were extracted and analyzed for DRP, and pH. For all treatments, pH ranged from neutral to slightly alkaline throughout the flooding period. In addition, all treatments saw a decrease in redox potential with a lesser decrease observed in the alum-amendment. Soil columns taken from alum-amended field plots had significantly lower DRP concentrations in porewater when compared to all other treatments, including the

unamended control. However, this effect of alum in reducing DRP concentrations was not observed for floodwater.

3.1. Introduction

Phosphorus (P) losses from soil are a major contributor to P loading into freshwater bodies (Schindler, Hecky & McCullough, 2012). In the prairie regions, high volumes of precipitation in the form of snow are received over the winter, which can rapidly melt in the spring, causing major snowmelt flooding events (Schindler et al., 2012). Spring snowmelt flooding is a main driver of P losses from the soil (Liu et al., 2019). Farmers often apply P to the soil as synthetic fertilizer or manure (Government of Manitoba, 2013). The application of manures and fertilizer P, in excess of plant requirements, may cause an accumulation of P in the soil, in forms unavailable for plant uptake (Yan et al., 2018). The rapid spring snowmelt, coupled with the accumulation of P in soil can increase P release during flooding events (Schärer et al., 2009). Prolonged flooding can cause anaerobic soil conditions, which exacerbates P release from the soil into the porewater and overlying floodwater (Amarawansa et al., 2015; Dharmakeerthi et al., 2019^a; Dharmakeerthi et al., 2019^b; Kumaragamage et al., 2020). Within as little as a few hours after flooding, microorganisms in flooded soils will use substantial amounts of oxygen (Ponnamperuma, 1972), making the soils anaerobic. Microbial communities capable of using electron acceptors other than oxygen will become more prevalent as the soil redox potential decreases (Smith et al., 2021). Thus, a shift in microbial communities occurs and the microbially mediated reductive dissolution of Mn^{3+}/Mn^{4+} to Mn^{2+} , and Fe^{3+} to Fe^{2+} begins (Barcala et al., 2023). These reductive dissolution processes are responsible for the release of significant amounts of P from the soil to porewater and

overlying floodwater (Scalenghe et al., 2010; Amarawansa et al., 2015). While forms of P associated with Mn and Fe are redox-sensitive, P associated with cations such as calcium (Ca^{+2}) and magnesium (Mg^{+2}) are not (Jayarathne et al., 2016). However, both Ca-P and Mg-P species are affected by changes in pH. This is an important consideration as prolonged flooding of soils can also impact soil pH (Ponnamperuma, 1972). As soils are flooded, pH may shift; acidic soils may see an increase in pH, while alkaline soils may see a decrease in pH (Amarawansa et al., 2015). In alkaline soils, as pH decreases, both Ca-P and Mg-P species increase in solubility and can subsequently release P into pore water and floodwater, whereas when pH increases, Ca-P and Mg-P become more stable (Cerozi & Fitzsimmons, 2016). Changes in pH and the associated dissolution of Ca-P and Mg-P, as well as, decreases in redox potential and associated reductive dissolution of Fe-P and Mn-P are two major processes that can influence P release in flooded soils (Scalenghe et al., 2010; Vitharana et al., 2021).

Soil amendments can reduce P losses from flooded soils and can impact various soil processes (Dharmakeerthi et al., 2019^a; Dharmakeerthi et al., 2019^b; Vitharana et al., 2021; Attanayake et al., 2022; Kumaragamage et al., 2022; Van et al., 2022).

Dharmakeerthi et al. (2019^a) found that with the addition of gypsum, the decrease in redox potential below +200mV was delayed compared to unamended soil. This delay in the decrease of a soil's redox potential can inhibit the microbially-mediated reductive dissolution of Mn and Fe-P species, thereby reducing P release from the soil.

Additionally, amendments may also have an effect on soil pH (Ann, Reddy & Delfino, 1999). For pH-sensitive P species, such as hydroxyapatite ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_3$), an increase or stabilization in pH could inhibit dissolution reactions (Ponnamperuma, 1972).

Soil amendments can also directly reduce P losses from the soil through precipitation reactions with the added ions (Kumaragamage et al., 2022), as well as through increased ionic strength, which can increase sorption at an alkaline pH (Huang et al., 2013).

Previous researchers have found that the use of soil amendments in controlled incubation experiments significantly reduced P release from soil to porewater and overlying floodwater to varying degrees (Dharmakeerthi et al., 2019^a; Dharmakeerthi et al., 2019^b; Vitharana et al., 2021; Kumaragamage et al., 2022; Van et al., 2022). However, these studies were conducted immediately after the amendments were applied. This study aims to determine whether alum, gypsum, and magnesium-sulphate are effective in reducing DRP concentrations in porewater and floodwater, one year after amendment application. In addition, other parameters such as soil redox status, pH, and cation concentrations were analyzed and used to better understand the mechanisms responsible for P release in flooded soils. We hypothesized that the amendments will show some residual effectiveness, one year after application, although the extent to which they are effective is expected to be less than immediately after application.

3.2. Materials and Methods

3.2.1. Site Location and Description

Soil columns were extracted from a field site in the Red River Basin, South-East of Winnipeg (49° 32' N, 96° 51' W) near Randolph, Manitoba. This agricultural field has a history of manure application and liquid swine manure was last applied to the field in the fall of 2020 (Lasisi et al., 2023). The soil is a Rego Humic Gleysol, and part of the Osborne Series (Government of Manitoba, 2010), clay in texture, with a pH of 7.7,

organic matter content of 75 g kg^{-1} , Olsen P of 80 mg kg^{-1} , and a CEC of $69.7 \text{ cmol}_c \text{ kg}^{-1}$. More details of soil characterization are provided in Lasisi et al. (2023).

3.2.2. Experimental Setup

The experimental plots with four treatments were set up as a randomized complete block design with 4 replicates of each treatment. Treatments were a) alum, b) gypsum, c) magnesium-sulphate, and d) an unamended-control applied in the fall of 2020 at a rate of 2.5 Mg ha^{-1} . More details on the rate and method of amendment application are provided elsewhere (Lasisi et al., 2023). Sixteen soil columns (15-cm depth) were collected in 30 cm PVC piping, in the fall of 2021, one year after the amendment application. An incubation study was conducted with flooded soil columns (10-cm head) under simulated snowmelt conditions, and porewater and floodwater samples were periodically collected and analyzed. More details pertaining to the collection and setup of the soil columns can be found in Kumaragamage et al. (2022).

3.2.3. Collection of porewater and floodwater samples

Sample collection began on the first day of flooding (day 0) and continued on a weekly basis for a total of 7 weeks (day 0 – 49). On each sampling day, 20 ml of floodwater was collected through a syringe and then filtered through a $0.45 \mu\text{m}$ pore size syringe filter. Porewater (20 mL) was collected through a pre-installed Rhizon-MOM sampler ($0.15 \mu\text{m}$ pore size; Rhizosphere Products, Netherland) using a syringe. After each sampling day, deionized water was added to maintain the 10-cm head above the soil surface.

3.2.4. Sample Analysis

Dissolved reactive P (DRP) concentrations were determined in both floodwater and porewater samples using the molybdate blue color method (Murphy & Riley, 1962) and

measuring the absorbance at 882 nm wavelength using a UV visible spectrophotometer (Ultraspec 500 pro UV–visible spectrophotometer). The pH of each sample was measured using a Fisher Accumet AB15 pH meter. Both porewater and floodwater samples were also analyzed for the concentration of Ca, Mg, Fe and Mn using flame atomic absorption spectroscopy (AAAnalyst 400, PerkinElmer). On each sampling day, the redox potential of each column was measured by inserting an Ag-AgCl reference electrode with KCl electrolyte into the soil-floodwater interface and a pre-installed platinum redox probe installed at 5-cm depth on the day of flooding, allowing the voltmeter to stabilize before taking the reading (Patrick, Gambrell & Faulkner, 1996). The recorded Eh values were corrected to the standard hydrogen electrode potential by adding +200 mV, the potential of the reference electrode. Redox potential measurements from one replicate of each treatment will be reported to show the trend in redox potential over the flooding period.

3.2.5. Statistical Analysis

Data analysis was conducted using Rstudio programming version 1.4.1106 (RStudio Team, 2021). All data were tested for normality using the Shapiro-Wilks test. All non-normal data were log-transformed to conform to normality. Repeated measures ANOVA was used to determine a significant effect of treatment, sampling day or their interaction (day \times treatment). Regression analysis was used to determine the relationships between pH, DRP, Ca, Mg, Mn, and Fe concentrations in porewater and floodwater. For all statistical analyses, significance was determined at $p = 0.05$.

3.3. Results

3.3.1. Dissolved reactive phosphorus (DRP) concentrations in porewater and floodwater

Dissolved reactive P concentrations ranged from 0.82 mg L⁻¹ to 1.67 mg L⁻¹ in porewater and from 0.11 mg L⁻¹ to 0.64 mg L⁻¹ in floodwater. A paired T-Test revealed that DRP concentrations in porewater were significantly ($p < 0.0001$) greater than in floodwater.

There was a significant ($p < 0.001$) effect of day on DRP concentrations for both porewater and floodwater, however the interaction between the two was not significant (Table 6.2b; Appendix). The alum amendment significantly ($p < 0.05$) decreased porewater DRP concentrations by 24.5% - 40.7% compared to all other treatments including the unamended control (Fig 3.1) (Table 6.2a; Appendix). Although, this effect of alum was not seen for floodwater DRP concentrations.

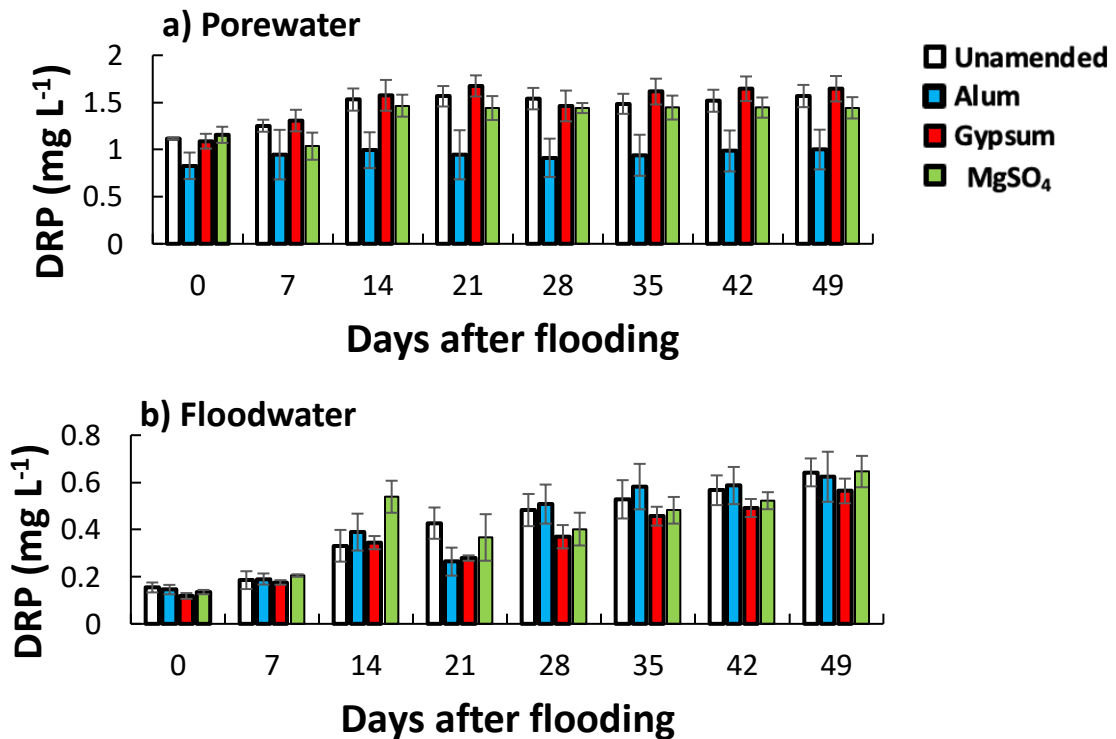


Figure 3.1. Mean a) porewater and b) floodwater dissolved reactive P concentrations in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths with time. Vertical error bars represent standard error of the mean.

3.3.2. Changes in pH, cation concentration in porewater and floodwater, and redox potential

Mean pH ranged from 7.4 to 7.8 in porewater and from 6.4 to 7.5, in floodwater (Fig 3.2). Both porewater and floodwater pH increased significantly ($p < 0.001$) with flooding time (Table 6.2a & b; Appendix). There was no significant effect of treatment or the interaction between day after flooding and treatment. Mean concentrations of Ca ranged from 433.02 mg L⁻¹ to 1209.7 mg L⁻¹ in porewater and from 2.13 mg L⁻¹ to 158.5 mg L⁻¹ in floodwater (Fig 3.3a & b). Concentrations of Mg ranged from 144 mg L⁻¹ to 663.9 mg L⁻¹, in pore water and from 5.39 mg L⁻¹ to 83.17 mg L⁻¹ in floodwater (Fig 3.4a & b). Porewater Ca and Mg concentrations decreased significantly ($p < 0.001$) with time whereas floodwater Ca and Mg concentrations significantly increased with time ($p < 0.001$) (Table 6.2a & b; Appendix).

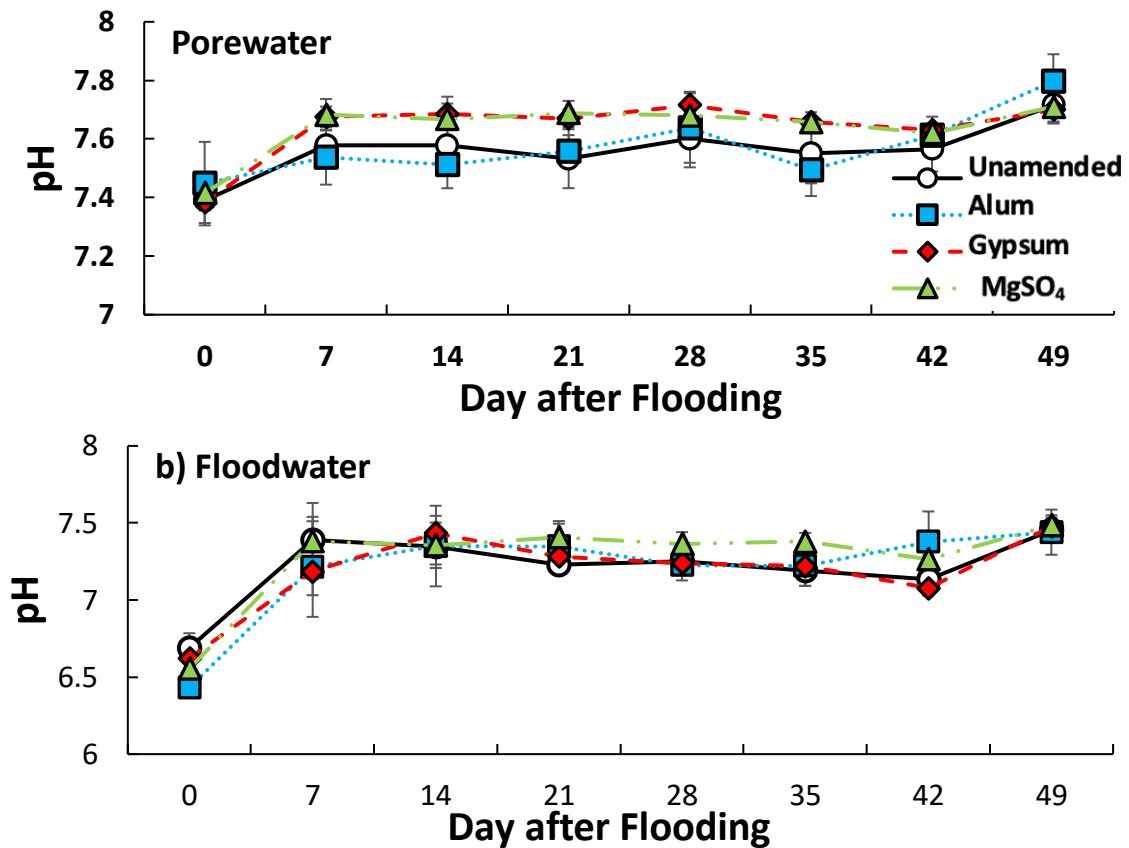


Figure 3.2. Mean a) porewater and b) floodwater pH in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths with time. Vertical error bars represent standard error of the mean.

Mean concentrations of Fe varied from 0.047 mg L⁻¹ to 0.315 mg L⁻¹ in porewater and from 0.074 mg L⁻¹ to 0.34 mg L⁻¹ in floodwater (Fig 3.5a & b). In both porewater and floodwater, Fe concentrations decreased initially, before increasing with time towards the end of the flooding period (Table 6.2a & b; Appendix). Mean concentrations of Mn ranged from 0.018 mg L⁻¹ to 0.06 mg L⁻¹ in porewater and from 0.00 mg L⁻¹ to 0.06 mg L⁻¹ in floodwater (Fig 3.6a & b). The change in both Fe and Mn concentrations was significant (p<0.001) over the flooding period. Mn concentration in porewater followed a similar trend to Fe concentrations in both pore and floodwater (Table 6.2a & b; Appendix). However, Mn concentrations in floodwater decreased with time and in some cases were even below a detectable level (0.01 mg L⁻¹), especially in the last few weeks

of flooding. Redox potential measured in one replicate of each treatment decreased from 502.5 mV on day 0, to 258.1 mV on day 49 (Fig 3.7). A decrease in redox potential was observed for all treatments over the flooding period.

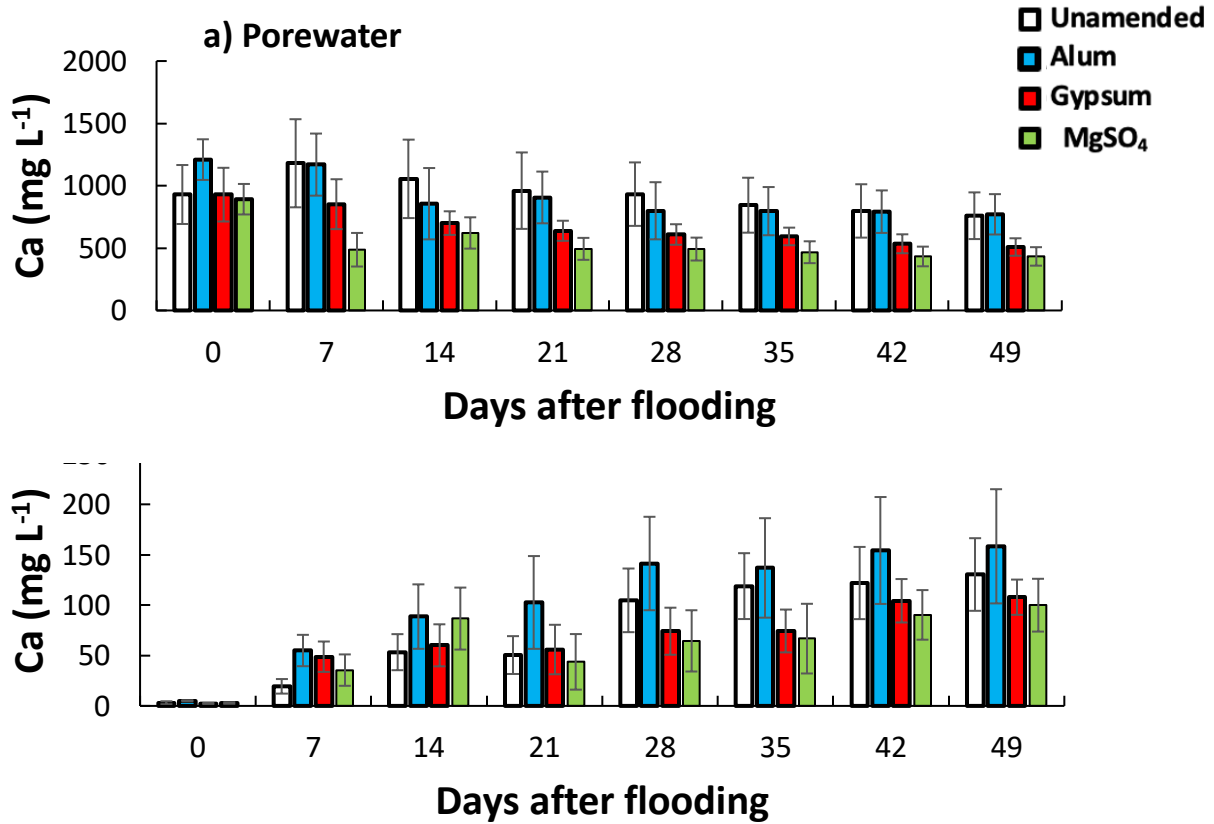


Figure 3.3. Mean pore water and floodwater concentrations of calcium in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths. Vertical error bars represent standard error of the mean.

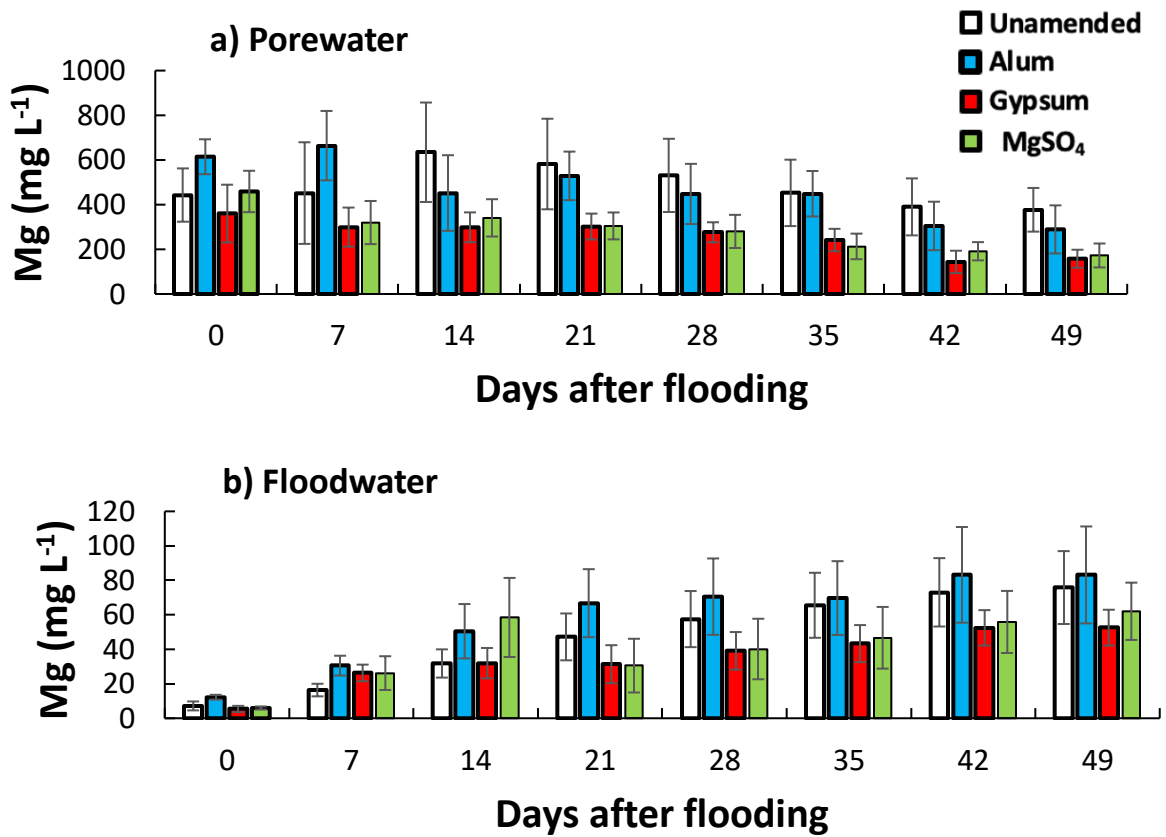


Figure 3.4. Mean porewater and floodwater concentrations of magnesium in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths. Vertical error bars represent standard error of the mean.

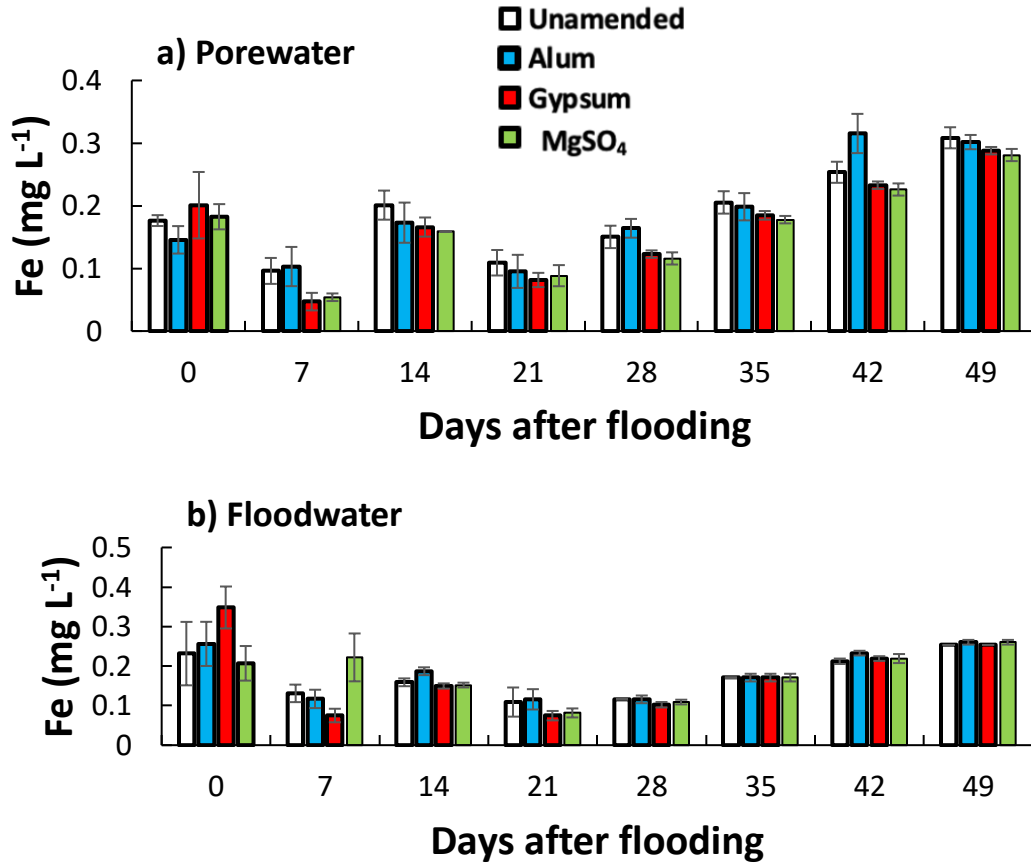


Figure 3.5. Mean porewater and floodwater concentrations of iron in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths. Vertical error bars represent standard error of the mean.

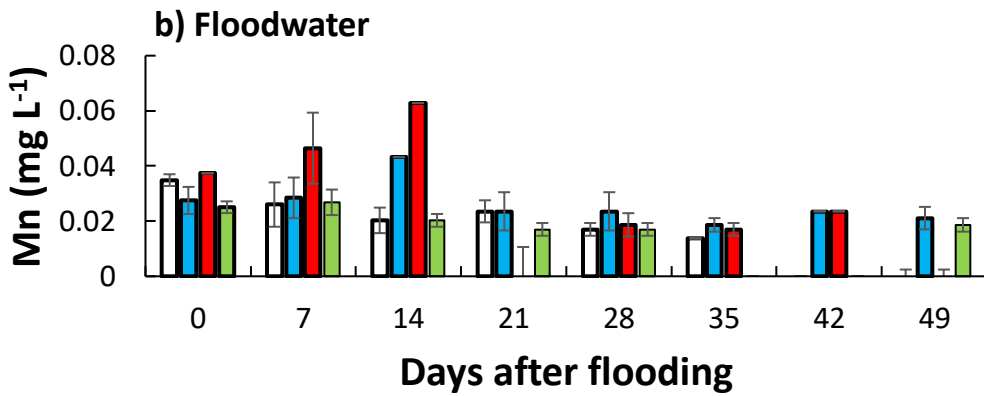
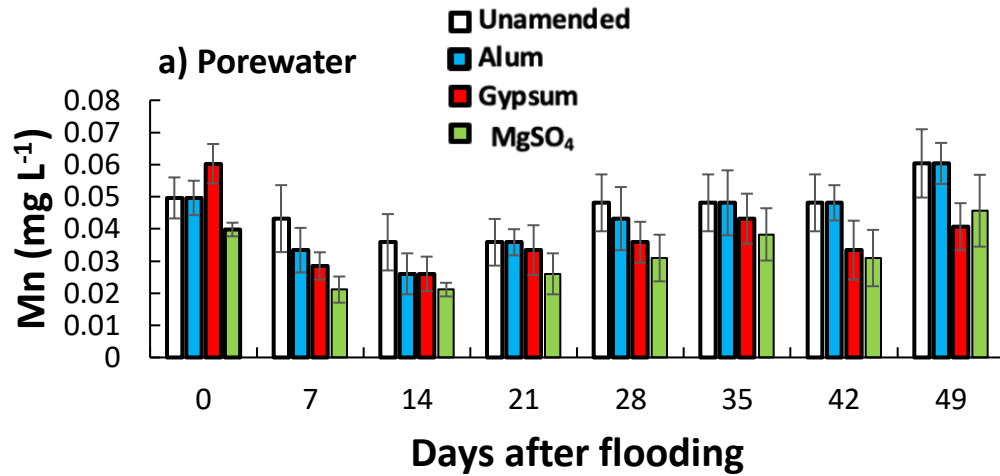


Figure 3.6. Mean porewater and floodwater concentrations of manganese in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths. Vertical error bars represent standard error of the mean.

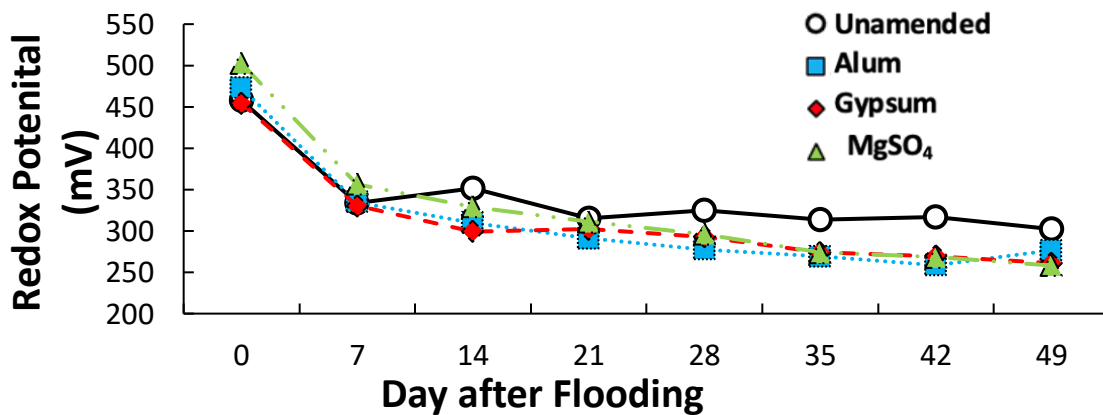


Figure 3.7. Soil redox potential in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended monoliths over the 49-day incubation period.

3.3.3. Relationship between porewater and floodwater concentrations of DRP, Ca, Mg, Fe & Mn

Porewater DRP concentrations showed significant negative relationships with porewater Ca ($p < 0.05$) and Mg ($p < 0.01$) concentrations (Fig 3.8a & b). However, no relationship between porewater DRP and Fe or Mn concentrations were observed (Fig 3.8c & d). A significant negative relationship between floodwater DRP concentrations and porewater concentrations of Ca ($p < 0.01$) and Mg ($p < 0.01$) were also identified (Figure 3.9a & b). In addition, floodwater DRP showed a significant ($p < 0.0001$) positive relationship with porewater Fe concentrations (Figure 3.9c), but no relationship between floodwater DRP and porewater Mn concentrations was identified (Figure 3.9d). Significant positive relationships were also identified between floodwater and porewater DRP concentrations ($p < 0.01$) (Figure 3.10), as well as porewater pH with both floodwater ($p < 0.001$) and porewater ($p < 0.05$) DRP concentrations (Figure 3.11 a & b)

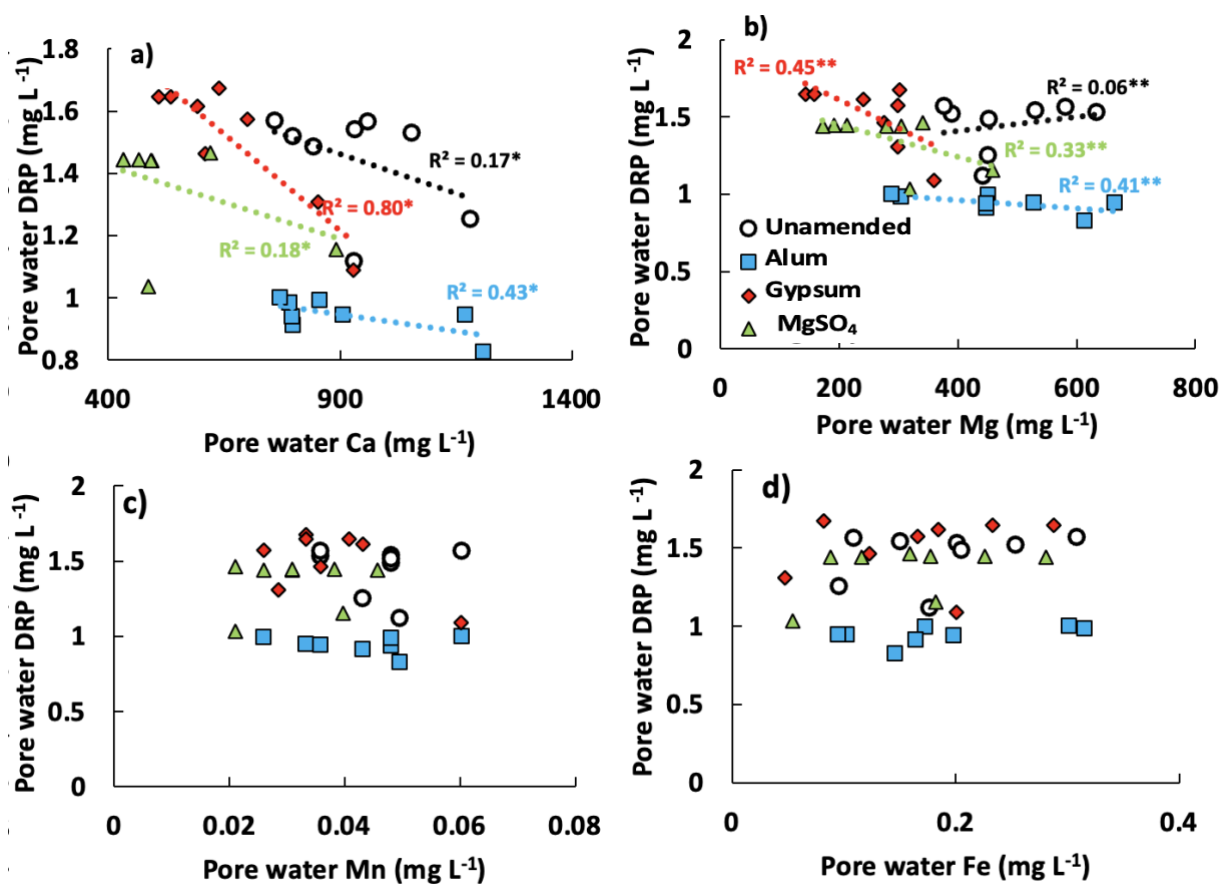


Figure 3.8. Relationship between mean porewater DRP, a) Ca, b) Mg, c) Mn and d) Fe concentrations of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soil monoliths. Significance determined at $p < 0.05$.

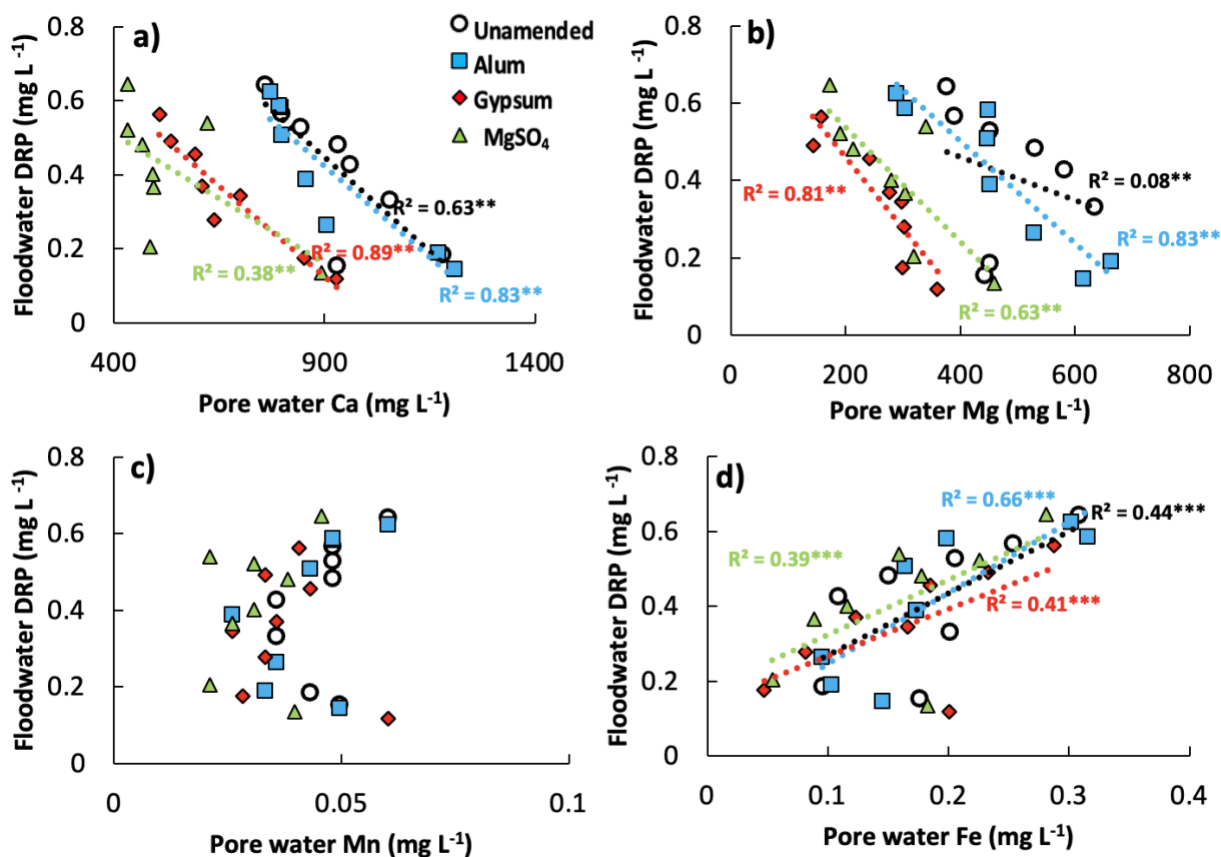


Figure 3.9. Relationship between mean floodwater DRP and porewater a) Mn, b) Fe, c) Ca and d) Mg concentrations of unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soil monoliths. Significance determined at $p < 0.05$.

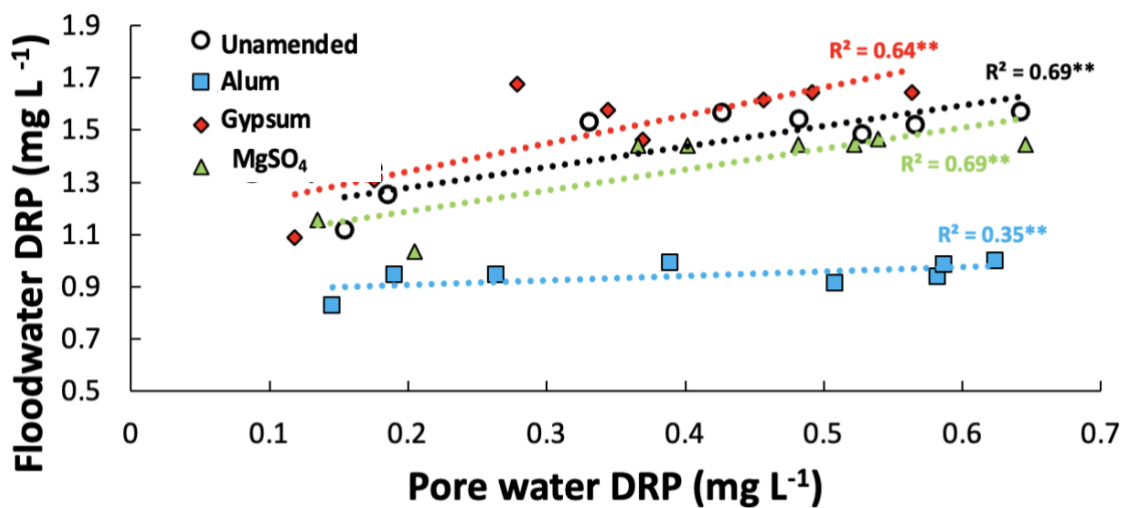


Figure 3.10. Relationship between mean floodwater and porewater DRP concentrations in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soil monoliths.

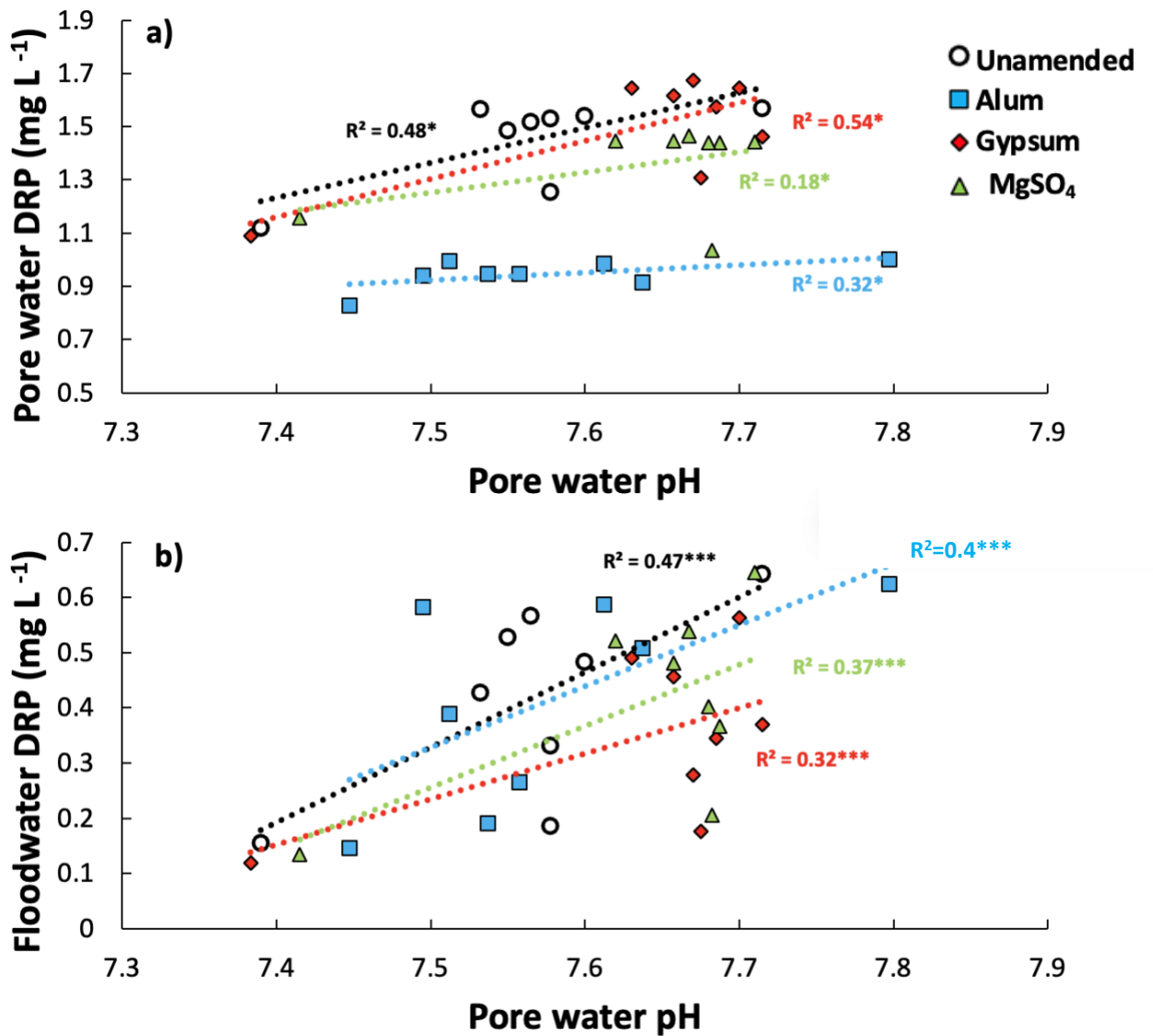


Figure 3.11. Relationship between a) mean floodwater b) mean porewater DRP concentrations and pore water pH in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soil monoliths. Significance determined at $p < 0.05$.

3.4. Discussion

The alum amendment decreased porewater DRP concentration by 24.5 – 41%, although the factors governing these decreases are unclear due to the high variability between replicates. The effects of gypsum and magnesium sulphate on the release of P from soil to porewater were not significant in this study. Past research has shown significant

decreases with the use of these amendments; however, these experiments were conducted shortly after amendment application (Dharmakeerthi et al., 2019^a; Dharmakeerthi et al., 2019^b; Vitharana et al., 2021; Kumaragamage et al., 2022). Previous studies have also shown the effect of amendments on pH and redox conditions (Dharmakeerthi et al., 2019^a; Dharmakeerthi et al., 2019^b; Amarawansa et al., 2015; Vitharana et al., 2021; Kumaragamage et al., 2022; Van et al., 2022), however, no significant effect of the amendments on redox and pH was observed in the current study, probably because the amendments were applied one year prior to the flooding study. Soils amended with gypsum usually see an increase in soil pH (Kordlaghari & Rowell, 2006), whereas soils amended with alum may see a decrease in soil pH (Ann, Reddy & Delfino, 1999). However, both alum and gypsum have shown to be effective in reducing P losses in various soils with varying characteristics (Kumaragamage et al., 2022). The relationships between porewater cation (Ca^{2+} & Mg^{2+}) concentrations and DRP in both pore and floodwater exhibited similar trends in the unamended and alum-amended monoliths. However, soils amended with alum had much higher concentrations of Ca and Mg in floodwater compared to other amendments. This could be caused by the cation exchange between Al and Ca/Mg in the soil, as well as the slightly lower pH observed at early stages of flooding which may have contributed to solubility of Ca-carbonates. However, Ann, Reddy & Delfino (1999), identified in their study that the application of alum had little effect on Ca and Mg-bound P.

In this study, the flooded soil became increasingly anaerobic, as shown by the decrease in redox potential, over the flooding period. A decrease in soil redox potential has been observed with prolonged flooding in many studies with many different soil types in

similar flooding studies using soil columns (Kumaragamage et al., 2022; Kumaragamage et al., 2020; Vitharana et al., 2021; Van et al., 2022). As the redox potential decreased, increases in DRP concentrations were observed early on, although concentrations eventually plateaued near the end of the flooding period in porewater, while they continued to increase in floodwater. Increases in porewater and floodwater DRP concentrations during prolonged flooding events, where soils become increasingly reduced, are common (Dharmakeerthi et al., 2019^a; Dharmakeerthi et al., 2019^b; Kumaragamage et al., 2022). Different trends in porewater and floodwater DRP concentrations, with flooding time, has been observed depending on soil and environmental conditions (Amarawansa et al., 2015; Kumaragamage et al., 2022). However, in the current study, porewater DRP concentrations plateaued, and floodwater concentrations continued to increase. A similar trend in porewater and floodwater DRP concentrations was observed by Van et al. (2022) where porewater DRP concentrations eventually decreased and floodwater DRP concentrations increased. Increased DRP diffusion is likely to occur from porewater to floodwater when there is a concentration gradient (Tian et al., 2017), potentially contributing to these results.

The significant positive correlation between floodwater DRP and porewater Fe suggests that the reductive dissolution of Fe-P species is a likely process governing the release of P from the soil to porewater, while diffusion of P controlled the P transfer from porewater to floodwater. Phosphorus release from flooded soils has often been linked to the changes in redox conditions and the subsequent reductive dissolution of Fe and Mn-P species (Dharmakeerthi et al., 2019^b). Some researchers have found that Mn, being reduced at a higher redox potential (~200mV), is more responsive than Fe, and likely governing P

release to porewater and overlying floodwater (Amarawansa, et al., 2015). However, in this study, there was no correlation between pore water Mn and floodwater/porewater DRP, whereas there was a significant correlation between floodwater DRP and porewater Fe. In the results reported by Amarawansa et al. (2015), a strong positive correlation between pore water DRP and porewater Fe was observed, although in the current study, porewater Fe was only correlated with floodwater DRP, but not with porewater DRP, likely because of effective transfer of P from porewater to floodwater. Concentrations of Ca and Mg in porewater were negatively correlated with both porewater and floodwater DRP concentrations. The initially high concentrations of both Ca and Mg in porewater observed are likely due to the dissolution of Ca and Mg during the early stages of flooding (Jayarathne et al., 2016). Generally, concentrations of Ca/Mg increase with simultaneous increases in DRP (Shenker et al., 2005). However, processes other than the dissolution of Ca/Mg-P may control the release of P from the soil to porewater (Shenker et al., 2005). While Ca and Mg may have initially contributed to P release in this study, the negative correlations between DRP in both porewater and floodwater and porewater Ca and Mg suggest that re-precipitation of Ca and Mg with other anions may also be occurring (Van et al., 2022).

In the early stages of flooding, floodwater pH for all treatments was initially below 7, although pH increased above 7 after one week of flooding. This was likely caused by the addition of ultrapure water to the soil columns. Calcium and Mg-P have a greater solubility at low pH (Ponnamperuma, 1972), and therefore the initially lower pH may be the reason for the initial higher concentrations observed for both Ca and Mg in porewater. As pore water pH increased, after one week of flooding, both Ca and Mg concentrations

in porewater decreased. When soil pH increases, Ca and Mg are more likely to precipitate with anions (Tian et al., 2017), although, these precipitation reactions at a more alkaline pH, tend to involve Ca-P and Mg-P species (Kordlaghari & Rowell, 2006). However, in the current study, decreasing Ca and Mg concentrations in porewater were associated with increasing DRP concentrations, suggesting precipitation of Ca and Mg with anions other than P (Amarawansa et al., 2015). In addition, reductive dissolution of Fe-P may continue to release P to porewater.

3.5. Conclusions

Flooding under simulated snowmelt conditions enhanced P release from soils, irrespective of the amendment treatment. In this soil, reductive dissolution of Fe-P seems to be the controlling factor governing the flooding-induced P release. Gypsum, and magnesium-sulphate were not effective in reducing DRP concentrations in porewater and floodwater under simulated snowmelt flooding, 12 months after the amendment application. While the alum amendment showed a reduction in DRP concentrations, the effectiveness was inconsistent. These results suggest that one year after amendment application, amendments lose their ability to stabilize P in soils and reduce P losses. Therefore, more frequent application of amendments may be required to mitigate P losses from agricultural soils with snowmelt. In order to fully understand the capabilities of alum, gypsum, and magnesium sulphate in reducing P losses from soils under snowmelt conditions, more research using various soil types under field snowmelt flooding conditions is needed. More robust research can help determine if more frequent applications, or a higher amendment application rate will maintain the effects of amendments in reducing P losses through snowmelt.

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Chapter 4. Phosphorus speciation and fractionation during simulated snowmelt flooding with soil amendments

Abstract

In the Canadian prairies, during the spring snowmelt period, soils can experience prolonged flooding, resulting in changes to soil chemical and physical processes. These changes can contribute to transformations in phosphorus (P) speciation and fractions, therefore increasing P release from the soil to porewater and overlying floodwater. Soil amendments, such as alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and magnesium-sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) can alter soil P speciation and fractions therefore, reducing P release during snowmelt flooding. This study investigated the residual effects (12 months after application) of alum, gypsum, and magnesium-sulphate on P species, as predicted by Visual MINTEQ 3.1., as well as their residual effects on P fractions. Soil columns were collected from a field site in SE Manitoba and were flooded in the laboratory for 7 weeks at 4°C. Porewater samples were collected on a weekly basis and analyzed for pH, redox potential, temperature, electrical conductivity, concentration of cations (Ca, Mg, Mn (as Mn^{2+}), Al^{3+} & Fe (as Fe^{2+}) in mg L^{-1} , and concentration of anions (Cl^- , F^- , NO_3^- , DRP (as $\text{P}(\text{PO}_4^-)$, and SO_4^{2-}) in mg L^{-1} . Data from days 0, 28, and 49 were used in the Visual MINTEQ model which predicted the P species which are thermodynamically favored to form, based on the input parameters. Soil samples collected from the same field site were used to conduct a P fractionation to determine the distribution of P between its various pools. As predicted by the Visual MINTEQ model, the soils amended with alum showed some slight changes in P speciation compared to other treatments; on day 0, the alum amended soil was undersaturated with respect to strengite whereas, with all other amendments, strengite was predicted to be

supersaturated. However, based on the P fractionation, there were no significant differences in the distribution of P between its fractions. The results of this study suggest that the residual effects of these amendments in changing P speciation and fractions are negligible 12 months after application, or after an initial flooding event.

4.1. Introduction

In the Canadian prairies, P losses from the soil to snowmelt are mainly in the form of dissolved reactive P (DRP) (Liu et al., 2019). The overland flooding that occurs during the spring snowmelt period can cause soils to become anaerobic therefore, contributing to a change in chemical processes within the soil (Ponnamperuma, 1972). Repeated application of fertilizer or manure for farming can cause P accumulation in the soil (Sharpley et al., 1994) as amorphous and crystalline species with varying solubility and mobility (Lindsay, 1979). Since the ability of soil to physically or chemically retain P is finite, excessive buildup of P make it more susceptible to mobilization (Hao et al., 2008). In cold climatic regions such as the Canadian prairies, the application of P in excess of crop demands, combined with spring snowmelt flooding may enhance the release of P from soil and increase P loading to freshwater systems (Schneider et al., 2019).

Phosphorus speciation and fractions in soils are highly dependent on soil properties and chemical processes (Ponnamperuma, 1972). In many alkaline soils, such as agricultural soils typically found across the Canadian prairies, P is predominantly controlled by the calcium (Ca) P system (Lindsay, 1979). Phosphorus fractions can be determined by separating P forms based on their mobility (Zhang & Kovar, 2009). While fractionation methods provide a good estimation of the distribution of P species based on their solubility, these methods can lack in certainty (Hashimoto & Watanabe, 2014).

Phosphorus speciation techniques can be used as a compliment to fractionation in order to better understand the predominant forms of P within each fraction (Gatiboni et al., 2021). Other techniques suitable for P species determination include x-ray absorption near edge structure (XANES), IR, raman, nuclear-magnetic resonance (NMR) spectroscopy, and modeling methods such as Visual MINTEQ 3.1. (Kruse et al., 2015; Hashimoto & Watanabe, 2014; Lindsay, 1979). Visual MINTEQ 3.1 is a thermodynamic modeling software that uses the equilibrium composition of soil solution and thereby predicts the thermodynamically favoured phosphorus species based on various input parameters (Lindsay, 1979). This modelling software can be a useful tool, when paired with other techniques, in understanding P species behaviour (Attanayake et al., 2022). For highly calcareous soils, Jiang and Gu (1989) developed a P fractionation method which determined the fraction of P in three Ca-P pools (Ca₂-P, Ca₈-P, Ca₁₀-P), P bound to Al, P bound to Fe, and P occluded to iron oxides (Occl-P). As many agricultural fields in the Canadian prairie region are calcareous, this fractionation method has become more popular due to its ability to further separate the Ca-P pool into various other fractions (Weeks et al., 2020; Zhang et al., 2022; Attanayake et al., 2022). According to Shariatmadari et al. (2007), the Ca₂-P pool, which consists of monocalcium-phosphate and dicalcium phosphate, represents the readily available P pool. The Ca₈-P represents a partially available P pool while the Ca₁₀-P is considered as the P fraction unavailable for plants. In calcareous soils, the inorganic P fractions generally range in abundance in the following order: Ca₁₀-P (unavailable for plant use) > Ca₈-P (partially available) > Al-P > Fe-P > Occl-P > Ca₂-P (readily available).

Using soil amendments like alum, gypsum, and magnesium sulphate to reduce P losses can impact soil chemical and physical properties (Dharmakeerthi et al., 2019^a; Dharmakeerthi et al., 2019^b; Kumaragamage et al., 2022; Vitharana et al., 2021). Past research has shown that with the use of soil amendments, P speciation can be altered (Attanayake et al., 2022). With changes in P speciation, P fractions will also be altered (Fan et al., 2019). Soil amendments, such as gypsum, which continuously provide soluble Ca to the soil system have been found to increase the Ca-P pool (He, Li & Dong, 2018). Fan et al. (2019) found that with the use of alum, Ca-P pools were decreased, whereas Al- and Fe-P pools increased. While the effects of soil amendments on P fractions and speciation have been observed immediately after amendment application, the residual effects of these amendments, over time, on soil P fractions and P species is less understood. Therefore, this study aimed to examine the residual effects of these amendments on both P speciation and fractions. Based on the results of chapter 3, where soils amended with alum showed significant decreases in DRP concentrations when compared to the unamended soil, it is hypothesized that soils amended with alum would have observable differences in P speciation with a greater proportion of P found in the less soluble P fractions.

4.2. Materials and Methods

4.2.1. Site Location and Description

Soil columns were collected from a field site in the Red River Basin, South-East of Winnipeg (49° 32' N, 96° 51' W) near Randolph, Manitoba. This agricultural field has a history of manure application and liquid swine manure was last applied to the field by the farmer in the fall of 2020 (Lasisi et al., 2023). The soil is a Rego Humic Gleysol, and part

of the Osborne Series (Government of Manitoba, 2010), clay in texture, with a pH of 7.7, organic matter content of 75 g kg⁻¹, Olsen P of 80 mg kg⁻¹, and a CEC of 69.7 cmol_c kg⁻¹). More details of soil characterization are provided in Lasisi et al. (2023).

4.2.2. Experimental Setup

The treatments in the field were setup as a randomized complete block design with 4 replicates of each treatment. Treatments were a) alum, b) gypsum, c) magnesium-sulphate, and d) an unamended-control. Amendments were applied in the fall of 2020 at a rate of 2.5 Mg ha⁻¹. Soil columns (15-cm depth) were collected in 30 cm PVC piping, in the fall of 2021, one year after amendment application from each plot (total of 16 columns). Soil columns were flooded with deionized water (10 cm head) and kept at 4 °C to simulate snowmelt flooding. More details pertaining to the collection and setup of the soil columns can be found in Chapter 3.

4.2.3. Collection of porewater and soil samples

Porewater sample collection began on the first day of flooding (day 0) and continued on a weekly basis for a total of 7 weeks (day 0 – 49). On each sampling day, 20 ml of porewater was collected through the Rhizon-MOM sampler (0.15 µm pore size) by applying suction using a syringe. After each sampling day, deionized water was added to maintain the 10 cm head above the soil surface.

Soil samples (0-15 cm) were collected in the fall of 2021 from each plot in the field site and brought back to the laboratory, air-dried, and sieved (2 mm) prior to sequential P fractionation analysis.

4.2.4. Sample Analysis

The methods used for determining soil redox potential, and pH, dissolved reactive P (DRP) and cation concentrations in porewater are described in Chapter 3. Electrical conductivity (EC) of porewater samples was measured using a Fisher Accumet AB30 conductivity meter. Anion concentration was analyzed by Ion Chromatography (IC) (Methrom Eco IC).

4.2.5 Predicting P Species

Thermodynamic modelling was conducted using a geochemical equilibrium speciation modeling software called Visual MINTEQ 3.1. These models use chemical properties such as K_{sp} and ionic strength, as well as the calculated equilibrium composition of porewater to predict the formation of and identify minerals that are likely to be insoluble (Lindsay, 1979). The input parameters used in this study included pH, redox potential, concentration of cations (Ca, Mg, Mn (as Mn^{2+}), Al^{3+} & Fe (as Fe^{2+}) in $mg\ L^{-1}$, and concentration of anions (Cl^- , F^- , NO_3^- , DRP (as $P(PO_4^-)$, and SO_4^{2-}) in $mg\ L^{-1}$. Possible redox pairs were included in this model such as, Fe^{3+}/Fe^{2+} and Mn^{3+}/Mn^{2+} , and temperature was set in the model at 4 °C. Electrical conductivity (EC), which was measured in S/m, was converted to ionic strength (μ) before being entered into the model. In order to convert EC to the required units (mol/L), the following formula was used:

$$Ionic\ Strength\ \left(\frac{mol}{L}\right) = \left(\frac{EC}{6.67}\right)^{1/0.991} \quad (Sposito, 2008).$$

The saturation index is the difference between logarithmic Ion Activity Product (IAP) and the solubility product (K_{sp}) for the dissolution reaction of a mineral at a given temperature.

$$\text{Saturation Index} = \log(IAP) - \log(Ksp)$$

Supersaturation refers to the minerals that could be potentially precipitated and are indicated by the positive saturation index, undersaturation refers to the minerals that are not thermodynamically favoured for precipitation and are indicated by a negative saturation index, and minerals in equilibrium are represented by a value of 0.00 (Lindsay et al, 1979).

The model was run for days 0, 28 and 49 of the incubation experiment to predict the changes in P transformation throughout the flooding period, as the soil became increasingly anaerobic. The full results of the analysis of DRP concentration, cation concentration, pH and redox potential can be found in Chapter 3. The input parameters for each treatment that were used in the model can be found in the appendix (Table 6.3).

4.2.6. Sequential P Fractionation

The P fractionation method used is described in Shariatmadari et al. (2007). This method consisted of 6 sequential extraction steps each targeting a different P fraction; the extractants are as follows: 1) NaHCO₃, 2) NH₄Acetate, 3) NH₄F, 4) NaOH – Na₂CO₃ 5) Sodium Citrate + Sodium Dithionite, 6) H₂SO₄. The extractions were completed for all 4 replicates of each treatment using the field soil samples. Soil extracts were sent to a third-party laboratory (Farmers Edge) for analysis of total P.

This method is outlined below:

For determination of Ca₂P, 25 mL of 0.25 M NaHCO₃ (pH=7.5) was added to 0.5 g of soil and shaken for 1 hour. The slurry was centrifuged and the supernatant was removed. The soil was then washed with 95% alcohol (methanol). Ca₈P was determined by adding 25 mL of 0.5 M NH₄Acetate (pH=4.2) to the residue, left unshaken for 4 hours, and then

shaking the mixture for 1 hour before centrifuging and removing the supernatant. Soil was then washed twice with saturated NaCl. Al-P was determined by adding 25 ml of 0.5 M NH₄F to the residue and shaking for 1 hour. The mixture was then centrifuged, and supernatant removed. Soil was again washed with saturated NaCl. Fe-P determination required the addition of 25 mL 0.1 M NaOH – 0.1 M Na₂CO₃. The mixture was shaken for 2 hours and then left unshaken for 16 hours before being centrifuged and supernatant removed. Occluded P was determined by adding 20 mL of 0.3 M sodium citrate + 1 g sodium dithionite and heated to 80°C for 15 minutes. The mixture was then centrifuged, and supernatant removed. Lastly, Ca₁₀P was determined by adding 25 mL of 0.5 M H₂SO₄ before being shaken for 1 hour. The mixture was then centrifuged, and supernatant removed. All extracts were then sent to Farmers Edge Laboratories for determination of total dissolved P using inductively coupled plasma – optical emission spectrometry (ICP-OES).

The concentrations of total dissolved P measured during the fractionation were converted to mg kg⁻¹ using the following formula:

$$P \left(\frac{mg}{kg} \right) = \frac{\text{concentration (mg/L)} \times \text{Volume (L)}}{\text{Sample mass (kg)}}$$

4.2.7. Statistical Analysis

Statistical analysis was conducted using Rstudio version 1.4.1106 (RStudio Team, 2021).

An ANOVA was conducted to determine any differences between treatments for each P fraction extracted. Significance was set to p<0.05.

4.3. Results

4.3.1. Phosphorus species as predicted by the Visual MINTEQ model

The saturation index (SI) values for predicted P species on days 0, 28, and 49 are given in Table 4.2. On day 0, 28, and 49 SI values were positive with respect to am²-tricalcium phosphate, beta-tricalcium-phosphate, hydroxyapatite, and manganese-hydrogen-phosphate, regardless of treatment. On day 0, SI values were negative with respect to vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) and $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}(\text{s})$, regardless of treatment, and positive with respect to strengite ($\text{FePO}_4 \cdot 3\text{H}_2\text{O}$) except for the alum amendment, which indicated negative SI values with respect to strengite. On day 28, SI values with respect to strengite shifted to negative for the unamended, gypsum-amended, and magnesium sulphate amended monoliths, and remained negative until day 49. In contrast, the alum-amendment shifted to positive SI values with respect to strengite on day 28. Only the gypsum amendment indicated positive SI values with respect to vivianite, on day 28. For all other treatments, positive SI values with respect to vivianite did not appear until day 49. On day 28, SI values for $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}(\text{s})$ were positive for the unamended and gypsum-amended monoliths but remained negative for the alum and magnesium sulphate amendments. SI values were positive with respect to $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}(\text{s})$, am²-tricalcium phosphate, beta-tricalcium phosphate, manganese hydrogen phosphate, hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3$, and vivianite for all treatments, by day 49.

Table 4.1. Saturation index values (SI) of P species in pore water of unamended, alum-amended, gypsum-amended, and magnesium-sulphate amended monoliths on days 0, 28 and 49 after flooding as predicted by Visual MINTEQ modeling. Red values indicate supersaturation and blue values indicate undersaturation.

Mineral	Day											
	0				28				49			
	Alum	Unamended	Gypsum	MgSO4	Alum	Unamended	Gypsum	MgSO4	Alum	Unamended	Gypsum	MgSO4
Ca ₃ (PO ₄) ₂ (am2)	0.23	0.09	0.05	0.15	0.06	0.89	0.84	0.36	0.70	1.04	0.89	0.52
Ca ₃ (PO ₄) ₂ (beta)	2.77	2.63	2.59	2.70	2.60	3.43	3.38	2.91	3.25	3.58	3.43	3.06
Ca ₄ H(PO ₄) ₃ :3H ₂ O(s)	-0.39	-0.42	-0.44	-0.35	-0.66	0.53	0.46	-0.13	0.19	0.69	0.60	0.08
Hydroxyapatite	10.7	10.3	10.2	10.4	10.4	11.7	11.6	10.8	11.5	12.0	11.7	11.1
MnHPO ₄ (s)	0.78	1.00	1.28	1.02	0.83	1.23	1.12	1.16	1.12	1.42	1.41	1.42
<u>Strengite</u>	-0.19	0.43	0.80	0.97	0.34	-1.58	-0.81	-1.80	-0.21	-1.48	-0.46	-1.77
Vivianite	-1.15	-0.73	-1.25	-0.80	-1.02	-0.12	0.11	-0.23	0.62	1.30	1.42	1.47

4.3.2. Phosphorus fractions in unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soils

The distribution of P pools for each treatment are shown in Figure 4.1. The Ca₁₀-P (sparingly soluble P) pool was greatest in all treatments, except for the magnesium sulphate amended soil where the Ca₈-P pool was slightly greater. Apart from this slight difference with the magnesium sulphate amended soil, all treatments followed the trend of Ca₁₀-P > Ca₈-P > Occl-P > Al-P > Fe-P > Ca₂-P > Fe-P. An ANOVA revealed no significant differences in the distribution of P between each fraction was observed between treatments.

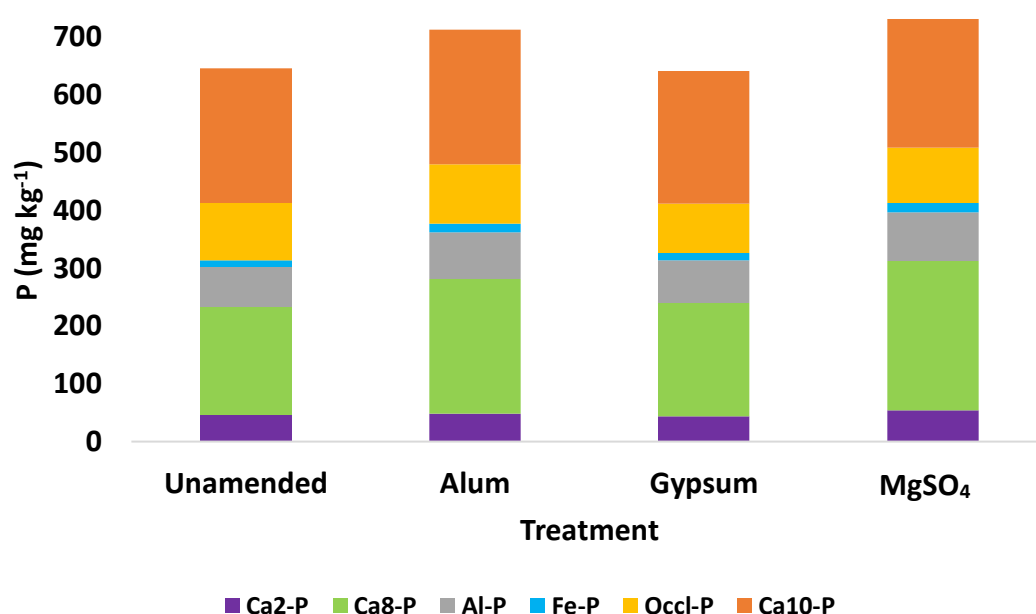


Figure 4.1. Mean phosphorus fractions in mg kg⁻¹ for unamended, alum-amended, gypsum-amended, and magnesium sulphate-amended soil monoliths.

4.4. Discussion

The trends observed in the Visual MINTEQ model were not entirely consistent with past research where hydroxyapatite, beta-tricalcium-phosphate, and manganese-hydrogen

phosphate were predicted to be undersaturated during the early stages of the flooding period (Kumaragamage et al., 2022). Calcareous soils are characterized by an abundance of Ca/Mg-P species as these soils tend to be alkaline, favoring the formation of these species (Andersson et al., 2019). Some slight differences were observed with the alum amendment in the current study; on day 0, the alum amended soil was undersaturated with respect to strengite whereas, with all other amendments, strengite was predicted to be supersaturated. The reductive dissolution of strengite occurs as the soil redox potential decreases (Attanayake et al., 2022). The dissolution of strengite, caused by Fe^{3+} being reduced to Fe^{2+} can then favor the formation of vivianite. This relationship between the reductive dissolution of strengite and the formation of vivianite was observed in the current study. Over the flooding period, concentrations of Fe in porewater generally increased for all treatments. This trend in increasing Fe concentrations is consistent with the predicted P transformations which suggest that the reductive dissolution of Fe-P species is a key player in P solubility. In the study conducted by Kumaragamage et al. (2022), the alum amended soil was undersaturated with respect to hydroxyapatite, beta-tricalcium-phosphate, and manganese-hydrogen phosphate in the early stages of flooding, suggesting the Ca-P system controlling P solubility. Whereas, in this study, those trends were not observed. While the Ca-P system clearly plays an important role in P solubility in calcareous soils, this study confirms the importance of Fe and Mn in controlling P release during flooding events (Jayarathne et al., 2016).

Phosphorus pools generally decreased in abundance from $\text{Ca}_{10}\text{-P} > \text{Ca}_8\text{-P} > \text{Oocl-P} > \text{Al-P} > \text{Ca}_2\text{-P} > \text{Fe-P}$, with the exception of the magnesium sulphate amendment which had higher $\text{Ca}_8\text{-P}$. In a study conducted by Shariatmadari et al. (2007), the abundance of P

pools decreased from $\text{Ca}_{10}\text{-P} > \text{Ca}_8\text{-P} > \text{Al-P} > \text{Fe-P} > \text{Occl-P} > \text{Ca}_2\text{-P}$. While there are differences in the trends between the current study and the research by Shariatmadari et al. (2007), generally the most sparingly soluble forms of P were in highest abundance. This is to be expected as any P additions to the soil are often quickly immobilized as P easily forms insoluble compounds (Cerozi & Fitzsimmons, 2016). While it is true that flooding can increase the solubility of P within the soil, calcareous soils contain high concentrations of stable P species associated with Ca and Mg (Amarawansa et al., 2015). In addition, although dissolved organic carbon (DOC) was not measured in this study, it plays an important role in speciation and could have an impact on model predictions.

Additions of soil amendments in past studies have impacted the distribution of P fractions (Fan et al., 2019; He, Li & Dong, 2018). Although, these studies were conducted shortly after amendment application and under different conditions than the current study. No effect of the treatments on the distribution of P between its fractions was observed in this study, suggesting that amendments effectiveness in stabilizing P decreases after more than one flooding event and with time. The predicted P transformations using the Visual MINTEQ model were consistent with the results of the P fractionation. The increased abundance of Ca-P's compared to other P fractions, and the predicted supersaturation of various Ca-P species are expected in these soils, and have been shown in previous research (Kumaragamage et al., 2022; Attanayake et al., 2022).

4.5. Conclusions

Soil amendments such as alum, gypsum, and magnesium sulphate can influence the proportions of P in different soil P fractions. However, residual effects after one year of amendment application did not result in significant changes in soil P fractions and species

in this study, suggesting the amendments effect on stabilizing soil P decreases with time or after an initial flooding event. Monoliths amended with alum showed some slight differences in P speciation as predicted by Visual MINTEQ and these slight differences are consistent with the decrease in DRP concentrations observed with the alum amendment identified in Chapter 3; however, these differences were not significant. The results of this study suggest that in order for the amendments to continue to stabilize soil P and ultimately reduce P release, they would need to be re-applied prior to each flooding event. In order to gain a better understanding of the capacity of these amendments to stabilize P, more research with various soil types under various chemical and physical conditions is needed.

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Chapter 5. General discussion, conclusions, and recommendations for future research

5.1. Summary of results

Dissolved reactive P concentrations in snowmelt or overlying floodwater during simulated flooding increased over time, regardless of amendment application, in both the actual snowmelt and simulated snowmelt studies. While the amendments reduced P concentration in snowmelt compared to the unamended plots, the effects were not statistically significant. In addition to this, the amendments were not successful in reducing overall P loads suggesting that snowmelt volume, rather than the P concentration in floodwater from snowmelt, is the dominant driving factor. In the simulated snowmelt flooding study, only the alum amendment showed a significant decrease in DRP concentrations in porewater. Although, other amendments also decreased the DRP concentrations, these differences were not significant because of the high variability in DRP concentrations between replicates, suggesting the need to do more research to draw conclusions. The effect of amendments on soil redox potential or pH were not significant, in either study, further implying the decreased impact of the amendments on soil properties >12 months after application. In the simulated snowmelt study, the alum amendment showed some obvious differences in Ca, Mg and Mn concentrations compared to the unamended control. The alum amendment did have increased concentrations of Ca in pore water, which may result in formation of Ca-P. In addition, some slight differences were noted in predicted P species, with porewater of alum amended soils being supersaturated with strengite at 28 days after flooding unlike other treatments, suggesting a delay in reductive dissolution of strengite in alum-amended

soils. However, the decrease in P concentration observed with the alum amendment could be related to mechanisms other than those that were investigated in this research.

Evaluating the effectiveness of amendments 18 months after amendment application, in the field study, suggest that alum, gypsum, and magnesium sulfate applied at a rate of 2.5 Mg ha⁻¹ were not effective in reducing concentrations in snowmelt even though magnesium sulfate showed a significant effectiveness 6 months after application. In previous studies, it has been shown that soil amendments such as alum, gypsum, and magnesium sulphate can shift the proportions of P in different soil P fractions. However, one year after amendment application, we did not observe significant shifts in P fractions, suggesting the amendments effect on soil P fractions decreases with time and possibly after an initial flooding event. Monoliths amended with alum showed slight differences in P speciation as predicted by Visual MINTEQ and these slight differences are consistent with the decrease in DRP concentrations observed with the alum amendment identified in Chapter 3.

5.2. General discussion and conclusions

Soil amendments have shown to be effective in reducing P losses both in field and laboratory experiments, immediately after amendments are applied (Vitharana et al., 2021; Dharmakeerthi et al., 2019^a; Dharmakeerthi et al., 2019^b; Lasisi et al., 2023; Kumaragamage et al., 2022). The effect of these amendments has also been observed through changes to P speciation and fractions (Kumaragamage et al., 2022; Fan et al., 2019; He, Li & Dong, 2018; Kumaragamage et al., submitted 2023). As observed throughout this thesis, the alum amendment, did show some decreases in P release and changes in P speciation, 12 months after amendment application in a simulated snowmelt

study, as well as decreased P release 18 months after amendment application in a field study, even though the differences were not always significant. Regardless of amendment application, DRP concentrations in snowmelt and floodwater increased with time.

Hoffman et al. (2019) found that factors like air temperature, snowpack depth, and frozen soil surface all contribute to P release. It is likely that these factors contributed to the increase in P release with time.

The link between P speciation and P release has been identified in previous studies with the use of alum as a soil amendment (Kumaragamage et al., 2022; Fan et al., 2019). The addition of alum to the soil can contribute to the transformation of available P to less soluble forms, such as Al-P, thus reducing P loss (Fan et al., 2019). In a study conducted by Kumaragamage et al. (2023), using the soils collected by Lasisi et al. (2023), significant differences in the distribution of P between its fractions with the use of alum and magnesium sulphate were observed. These amendments had lower concentrations of Ca₈-P compared to the unamended and gypsum-amended soils and had greater concentrations of residual-P. Reduced concentrations of Ca₈-P with the use of these amendments were not observed in this research, where amendments were applied >12 months prior to soil sampling. While the distribution of soil P between its fractions is dependent on P speciation, the slight changes to P speciation observed with the alum amendment did not result in significant changes to soil P fractions compared to other treatments. The hypotheses of each chapter were reasonable, and the soils amended with alum, gypsum and magnesium-sulphate did show some minor differences when compared to the unamended soil, however the effects were not statistically significant therefore rejecting our initial hypotheses. The results of this study suggest that in order

for the amendments to continue to have an effect on soil P fractions, P speciation and ultimately P release, they would need to be re-applied more frequently, or applied at a higher rate than the rate used in this research.

5.3. Limitation of the study and recommendations for future research

This research focused on snowmelt P losses from agricultural soils under Manitoba conditions. In order to keep the study within this context, our research was conducted on a calcareous soil because agricultural soils in southern Manitoba are dominantly calcareous (Soper and ElBagouri, 1964). While this does limit the extent to which these results can be extrapolated, our findings could be transferable to calcareous soils of other regions. Since P mobility is impacted by various soil properties, in order to gain a better understanding of the capacity of these amendments in impacting soil P species, fractions, and P release, more research using various soil types under different environmental conditions is needed. Measuring and inputting DOC as a parameter in the Visual MINTEQ model can impact model outcomes. A study conducted by Cerozi & Fitzsimmons (2016), found that in removing DOC and alkalinity from the input parameters, the model predicts a decrease in orthophosphate due to the formation of calcium phosphates. It was also found that the model outcome was more similar to experimental results as DOC and alkalinity measurements were included. Other analytical techniques, such as XANES, IR, raman and NMR could also be used as a tool to better understand the differences in speciation (Kruse et al., 2015; Kumaragamage et al., submitted 2023), as Visual MINTEQ can only make predictions based on the input parameters (Lindsay, 1979).

A wide variety of inorganic soil amendments are found to be capable of reducing P losses from soil to snowmelt (Attanayake et al., 2022; Dharmakeerthi et al., 2019a; Fan et al., 2019), however, application costs and concerns around toxicities and bioaccumulation in the food chain can limit amendment choices (Kong et al., 2023). Alum, gypsum, and magnesium sulphate have been used as soil amendments for purposes other than P loss, therefore making them a safe choice for use in reducing P release (Crusciol et al., 2019).

While we investigated the impacts of these amendments in reducing P release from soil to snowmelt in Chapter 2, the natural snowmelt conditions were not allowed to develop as meltwater was fully collected from each runoff box daily. Future research should develop methods to allow for the prolonged flooding of the soil surface to develop as would naturally occur during prairie snowmelt flooding. Flooding may have an impact on the function of the soil amendments and should therefore be investigated further. Lastly, further research is necessary as field studies are highly variable, with field conditions difficult to reproduce. Keeping this in mind, multi-year and multi-site research is important to identify the capabilities of these amendments under a variety of climatic and environmental conditions.

5.4. References

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Appendix

6.1. Dissolved reactive P analysis (Murphy & Riley, 1962)

Soil extracts and water samples were analyzed for dissolved reactive P by adding 4 mL of filtered sample, and 4 mL of ascorbic acid reagent to a volumetric flask. The volumetric flask was then filled with ultrapure water to 25 mL and samples were shaken, capped, and left to develop for 20 minutes. A sub sample was then measured for absorbance at 882 nm wavelength using a UV visible spectrophotometer (Ultraspec 500 pro UV–visible spectrophotometer).

6.2. Mehlich 3 Extraction (Mehlich, 1984)

A solution of 1.5M NH_4F + 0.1M EDTA was prepared by dissolving 55.56 g of ammonium fluoride (NH_4F) in 600 ml of deionized water with 29.23 g of EDTA. The mixture was then filled to 1L, mixed thoroughly, and stored in a plastic bottle. 100ml of this stock solution was then added to 8L of deionized water with 200.1 g of ammonium nitrate (NH_4NO_3), 115 ml of acetic acid (CH_3COOH), 82 ml of 10% v/v nitric acid (10 ml concentrate 70% HNO_3 in 100ml of water). This mixture was then dissolved and filled to 10 L with deionized water and mixed thoroughly. In 50 ml centrifuge tubes, 2.5 g of air-dried soil samples (ground to less than 2 mm) and 25 ml of the Mehlich 3 stock solution (1:10 ratio) were added. Centrifuge tubes were shaken using a reciprocal shaker for 5 minutes at 120 strokes per minute. The extract was then filtered into plastic vials using medium retention filter papers (Whatman No.40). Available P was determined using the molybdate blue method (Murphy & Riley, 1962).

6.3. Thermodynamic modelling using Visual MINTEQ 3.1.

The input parameters required for this modelling method were pH, redox potential, concentration of cations (Ca, Mg, Mn (as Mn^{2+}), Al & Fe (as Fe^{2+}) in $Mg\ L^{-1}$, and concentration of anions (Cl^- , Fl^- , NO_3^- , DRP (as $P(PO_4^-)$), and SO_4^-) in $Mg\ L^{-1}$. Possible redox pairs were identified, such as, Fe^{3+}/Fe^{2+} and Mn^{3+}/Mn^{2+} and temperature was input in the model at 4°C. This model assumed the dominance of dissolution/precipitation reactions within these soils. This assumption was supported by past research which shows significant relationships between P in pore water and concentration of cations (Ca, Mg, Mn & Fe) (Dharmakeerthi et al., 2019). In calcareous soils, dissolution/precipitation reactions tend to be more dominant than adsorption/desorption reactions in the control of P release to soil solution (Daly et al., 2015). Visual MINTEQ 3.1. outputs data in the form of a saturation indices table. This output identifies minerals which are thermodynamically favoured and whether they are supersaturated, undersaturated or in equilibrium (Lindsay et al., 1979). The saturation index is the difference between logarithmic Ion Activity Product (IAP) and the solubility constant of the dissolution chemical reaction of a mineral (K_{sp}) at a given temperature (Saturation index= $\log IAP - \log K_{sp}$). Supersaturation refers to the minerals that could be precipitated and are indicated by a positive saturation index value, undersaturation refers to the minerals that are not thermodynamically favoured for precipitation and are indicated by a negative saturation index value, and equilibrium activity is represented by a value of 0.00 and indicates which minerals are in equilibrium.

Appendix Table 6.1. Mean day and treatment snowmelt concentrations for DRP, Fe, Mn, Ca and Mg, and DRP load, Snowmelt volume and pH. Note: Concentrations followed by the same lowercase letter are not significantly different at $p=0.05$.

Sampling Day	Concentration (mg L ⁻¹)							
	DRP	DRP Load (mg)	Snowmelt Volume (L)	pH	Fe	Mn	Ca	Mg
1	0.332d	3.454b	11.03b	7.48c	0.186a	0.009bc	0.738d	2.727d
2	0.357d	2.692bc	7.63ab	7.46c	0.075b	0.009bc	1.978cd	4.528cd
3	0.322d	5.165ab	17.22a	7.24d	0.089b	0.006cd	0.967cd	2.719d
4	0.574c	2.651bc	4.686ab	7.50c	0.128ab	0.006cd	3.386c	6.635c
5	0.419d	6.995a	16.84a	7.29d	0.116ab	0.005d	1.425c	3.34cd
6	0.605c	1.489c	2.557c	7.57bc	0.092b	0.016b	31.01b	21.27b
7	0.837b	7.324a	9.466b	7.63ab	0.094ab	0.017b	16.19b	18.22b
8	1.191a	3.147b	2.749c	7.71a	0.102ab	0.062a	98.33a	74.71a
Treatment								
<i>Unamended</i>	0.984	2.926	3.000	7.709	0.089	0.046a	79.082	59.111
<i>Alum</i>	0.740	3.475	4.750	7.538	0.106	0.027b	31.498	28.331
<i>Gypsum</i>	0.929	5.513	6.417	7.672	0.116	0.023b	29.649	24.079
<i>MgSO₄</i>	0.856	4.038	5.542	7.623	0.075	0.029ab	53.809	40.744
P Value								
<i>Sampling Day</i>	<0.0001	<0.0001	<0.0001	<0.0001	0.00039	<0.0001	<0.0001	<0.0001
<i>Treatment</i>	0.67	0.77	0.77	0.99	0.25	0.02	0.13	0.097
<i>Sampling day x Treatment</i>	0.55	0.71	0.85	0.1	0.45	0.02	0.75	0.31

Appendix Table 6.2a. Mean day and treatment pore water concentrations for DRP, Ca, Mg, Mn, Fe and pH. Note: Concentrations followed by the same lowercase letter are not significantly different at $p=0.05$.

Pore water Concentration (mg L ⁻¹)						
Sampling Day	DRP	pH	Ca	Mg	Mn	Fe
0	1.04b	7.40b	994.2a	476.3a	0.049a	0.17bc
7	1.14b	7.62b	922.3a	433.7a	0.032b	0.08d
14	1.39a	7.61b	808.3a	431.4a	0.027b	0.17bc
21	1.41a	7.61b	750.0a	429.3a	0.033b	0.09d
28	1.33a	7.66a	708.4a	383.8a	0.039a	0.14c
35	1.37a	7.59b	675.3a	339.0a	0.044a	0.19bc
42	1.40a	7.61b	639.6b	257.4b	0.040a	0.26ab
49	1.41a	7.73a	618.2b	249.1b	0.052a	0.29a
Treatment						
<i>Unamended</i>	1.45a	7.56	932.6	482.6	0.046	0.19
<i>Alum</i>	0.94b	7.57	912.6	468.7	0.043	0.19
<i>Gypsum</i>	1.52a	7.65	662.5	256.6	0.037	0.16
<i>MgSO₄</i>	1.36a	7.64	540.1	285.1	0.032	0.16
P-Value						
<i>Sampling Day</i>	<0.0001	<0.0001	<0.0001	<0.0001	0.042	<0.0001
<i>Treatment</i>	0.04	0.62	0.45	0.43	0.42	0.26
<i>Sampling Day x Treatment</i>	0.53	0.87	0.43	0.08	0.17	0.97

Appendix Table 6.2b. Mean day and treatment floodwater concentrations for DRP, Ca, Mg, Mn, Fe and pH. Note: Concentrations followed by the same lowercase letter are not significantly different at p=0.05.

Floodwater Concentration (mg L⁻¹)						
Sampling Day	DRP	pH	Ca	Mg	Mn	Fe
0	0.14d	6.57b	3.4d	7.8d	0.031a	0.25ab
7	0.19d	7.29a	39.7bc	24.4bc	0.032a	0.14b
14	0.40c	7.37a	73.1ab	43.9ab	0.028ab	0.16b
21	0.33c	7.32a	63.2ab	43.9ab	0.023ab	0.10b
28	0.44b	7.27a	96.3ab	51.8ab	0.019ab	0.11b
35	0.51a	7.25a	99.3ab	56.3a	0.016b	0.17b
42	0.54a	7.2ab	117.8a	66.1a	0.024ab	0.22ab
49	0.62a	7.46a	124.3a	68.4a	0.019ab	0.26a
Treatment						
<i>Unamended</i>	0.41	7.21	75.3	46.8	0.022	0.17
<i>Alum</i>	0.41	7.20	105.4	58.3	0.025	0.18
<i>Gypsum</i>	0.36	7.20	68.3	36.4	0.028	0.17
<i>MgSO₄</i>	0.41	7.27	61.3	40.7	0.021	0.18
P-Value						
<i>Sampling Day</i>	<0.0001	<0.0001	<0.0001	<0.0001	0.0001	<0.0001
<i>Treatment</i>	0.19	0.98	0.67	0.58	0.63	0.82
<i>Sampling Day x Treatment</i>	0.99	0.76	0.25	0.35	0.64	0.74

Appendix Table 6.3. Input parameters used in the Visual MINTEQ 3.1. model. Mean concentrations of, DRP cations, pH, ionic strength, and redox potential.

Day	Treatment	Concentration (mg L ⁻¹)										ionic strength	
		F ⁻	Cl ⁻	NO ₃ ⁻	DRP	SO ₄ ⁻	Ca	Mg	Fe	Mn	pH		Eh
0	<i>Alum</i>	0.30	79.12	38.66	0.87	16.37	1029.5	541.36	0.14	0.04	7.56	472.9	0.023
0	<i>Unamended</i>	0.22	63.63	38.40	1.11	12.84	786.97	372.73	0.17	0.04	7.43	457.7	0.017
0	<i>Gypsum</i>	0.10	44.67	29.96	0.99	10.83	538.16	127.17	0.10	0.05	7.46	454.5	0.011
0	<i>MgSO₄</i>	0.20	62.42	35.58	1.12	69.27	761.30	359.03	0.19	0.04	7.47	502.5	0.017
28	<i>Alum</i>	0.13	90.87	32.40	0.71	14.98	908.92	517.56	0.18	0.05	7.60	277.5	0.019
28	<i>Unamended</i>	0.20	89.73	34.24	1.61	13.78	817.27	439.24	0.14	0.05	7.67	325.1	0.017
28	<i>Gypsum</i>	0.19	69.58	26.91	1.49	13.75	607.54	273.25	0.13	0.03	7.71	292.9	0.012
28	<i>MgSO₄</i>	0.16	63.27	24.86	1.34	11.76	423.16	238.83	0.10	0.03	7.67	296	0.011
49	<i>Alum</i>	0.28	50.61	34.03	0.97	13.68	871.81	336.72	0.31	0.06	7.73	276.3	0.019
49	<i>Unamended</i>	0.23	43.51	24.05	1.65	10.94	657.74	321.49	0.30	0.06	7.77	302.2	0.015
49	<i>Gypsum</i>	0.18	30.03	17.74	1.74	10.94	514.69	173.01	0.29	0.04	7.68	261.1	0.012
49	<i>MgSO₄</i>	0.15	26.41	20.39	1.35	8.73	348.63	120.72	0.27	0.04	7.73	258.1	0.010

6.4. References

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