

**EFFECT OF MANURE APPLICATION METHODS ON NUTRIENT AND METAL  
MOBILIZATION WITH SNOWMELT FLOODING IN A MANURED AGRICULTURAL  
LAND**

By

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## ABSTRACT

Viranga Weerasinghe, M.Sc., The University of Manitoba, September 2023. Effect of manure application methods on nutrient and metal mobilization with snowmelt flooding in a manured agricultural land. Advisors: Dr. Inoka Amarakoon, Dr. Darshani Kumaragamage.

Accumulation of phosphorus (P), nitrogen (N), and metal(loid)s with manure applications to agricultural lands and their subsequent losses via runoff and leaching pose a potential risk of water quality deterioration. In the Canadian prairies, snowmelt flooding contributes to the majority of annual runoff. Injection of liquid swine manure (LSM) has been well documented as a manure application method to reduce nutrient loss with rainfall-runoff; however, its effectiveness in reducing snowmelt-driven nutrient and metal(loid) runoff has not been studied to our knowledge. This thesis examined the (a) release of P and metal(loid)s [zinc (Zn), manganese (Mn), iron (Fe), magnesium (Mg), calcium (Ca), and arsenic (As)] to floodwater under simulated snowmelt flooding, and (b) losses of P, N, Zn, Mn, Fe, Mg, and Ca to snowmelt runoff from field plots, with LSM injection and surface application. LSM was applied in the Fall of 2021 to four replicated field plots with three treatments: manure injected, surface-applied, and unmanured (control). For the simulated snowmelt study, intact soil columns were extracted from each plot after two weeks of manure application. The columns were flooded with ultrapure water at  $4\pm 1$  °C to simulate snowmelt flooding. Porewater and floodwater samples were extracted for 8 consecutive weeks and analyzed for dissolved reactive P (DRP), pH, and metal(loid)s concentrations. For the field study, snowmelt was collected from installed boxes in each plot in the 2022 spring for 10 days when the temperature was above 0 °C and snowmelt was present. The snowmelt samples were analyzed for DRP, nitrate-N, metals (Zn, Mn, Fe, Mg, and Ca), and pH. Significant differences in DRP concentrations in porewater or floodwater were not observed among the three treatments in the simulated snowmelt study; however, concentrations of DRP in floodwater increased (1.5-fold and

5-fold in porewater and floodwater, respectively) under prolonged flooding conditions irrespective of the treatment. Metal concentrations in porewater or floodwater did not show significant differences among the three treatments in the simulated snowmelt study, with the exception of porewater Mg concentration on day 0 and floodwater Zn concentration on day 7. In the field, the DRP concentrations in snowmelt were significantly higher in surface-applied manure treatment than in injected and control treatments from day 7 to 8. The concentrations of nitrate-N or any of the metals were not significantly different among the treatments. However, DRP, nitrate-N, and metal concentrations increased with time during the snowmelt period. There was a dramatic spike in nitrate-N concentration towards the end of the sampling period, where the increase in nitrate-N concentration was 44-fold compared to day 1. We also found significant correlations and positive linear relationships between snowmelt volume and DRP and metals loads, suggesting that snowmelt volume was the main driving factor of DRP and metal (Zn, Mn, Fe, and Ca) loss with snowmelt. The results of this research suggest that the management practices should be focused not only on reducing concentrations of nutrients and metals in snowmelt but also on reducing the snowmelt volume and snowmelt flooding duration.

**Keywords:** snowmelt, liquid-swine-manure, injection, dissolved reactive phosphorus, nitrate-N, metals.

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## **FOREWORD**

This thesis is prepared in accordance with the Department of Soil Science, University of Manitoba guidelines, focusing on two manuscripts that will be submitted for publication (Chapters 2 and 3). Chapter 2 is being prepared for submission to the Journal of Environmental Quality (JEQ), and Chapter 3 is being prepared for submission to Catena. Viranga Weerasinghe, who worked on conducting experiments, sample collections, data analysis, interpretation of results, and writing manuscripts, will be the first author of each of the manuscripts. Dr. Inoka Amarakoon and Dr. Darshani Kumaragamage, who led defining the research problem, formulating the study design, acquiring project funding, providing supervision, approach in statistics and data analysis, interpretation of data, and providing editorial guidance on writing, will be co-authors on both manuscripts. Dr. Nora Casson, Dr. Douglas Goltz, Dr. Srimathie Indraratne, and Dr. Xiaopeng Gao, who reviewed and provided editorial guidance on both manuscripts, will also be co-authors.

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## **1. GENERAL INTRODUCTION**

### **1.1 Agriculture in Manitoba**

Canadian agriculture and agri-food system is one of the country's five major industries, accounting for 7.4% (\$139.3 billion) of the country's GDP (Statistics Canada, 2020). With the expansion and intensification of agriculture in the southern Lake Winnipeg catchment during the 20th century, the Province of Manitoba has been a key contributor to Canadian agriculture and agri-food system. Manitoba agriculture was recognized as a very stable agriculture industry in Western Canada, and the province was cited for having the most income from field crops, while the second most income was from livestock in 1947 (Grosse, 1948). This trend has continued up to date, where crop and animal production are the top two agricultural industries that contribute to 5% of the provincial GDP (Manitoba Analytics, 2020). Wheat, canola, dry pea, sunflower, corn, oats, potato, and soybean are major crop production sectors in Manitoba, while the swine manure operation tops the livestock production. The revoking of the Western Grain Transportation Act in 1995 led to the expansion of the hog industry because farmers started feeding grain crops to livestock to increase profits (Schindler et al., 2012). This thriving livestock sector produced and sold over 8.4 million hogs in 2021, earning a revenue of \$ 1.4 billion (Government of Manitoba, 2022).

### **1.2 Crop nutrient requirements**

The requirement of providing essential plant nutrients to meet the crop requirement was raised as a concern with the expansion of crop production as it directly impacts crop yields. While nutrient uptake varies with the crop type, 17 essential elements are considered plant nutrients. Nitrogen (N), phosphorus (P), potassium (K), and sulfur (S) are closely monitored in crop production due to their major roles in plant development (Whalen et al., 2021). Out of 17 essential plant nutrient elements, seven [chlorine (Cl), boron (B), copper (Cu), iron (Fe), manganese (Mn), molybdenum

(Mo), nickel (Ni), and zinc (Zn)] are recognized as micro-nutrients (Whalen et al., 2021). These nutrients are provided to crops on recommendations based on proper soil tests, mainly through commercial fertilizers, since they are very soluble and readily available for plant uptake. However, nutrients such as P and N are challenging to maintain in plant-available forms in the soils due to the complexation and frequent losses. Since addressing nutrient requirements with only commercial fertilizer can be expensive, manure is used as a cost-effective substitute.

### **1.3 Manure composition and usage in agriculture**

A large extent of animal waste generated during livestock production is recycled as a soil amendment (Khaleel et al., 1980; Choudhary et al., 1996). In Manitoba, swine manure can be used sustainably as most swine livestock operations are associated with agricultural croplands, making it readily available. Presence of certain metals and metalloids such as Cu, Zn, chromium (Cr), lead (Pb), cadmium (Cd), Selenium (Se), nickel (Ni) in manures such as liquid swine manure (Olatuyi et al., 2014; Rayne & Aula, 2020; Nicholson et al., 1999) could contribute to non-point source pollution. Some of these elements are provided to pigs with the diet at low levels to enhance growth and reproduction as well as sanitary and pharmaceutical purposes (Moreno-Caselles et al., 2002; Government of Manitoba, 2007). Manures do not contain high concentrations of heavy metals as some other waste materials such as sewage sludge; however, the presence of heavy metal in swine and cow manure has been reported (Moreno-Caselles et al., 2002). Thus manure should be applied to crops after proper soil testing. Manure is not only an excellent source of essential plant nutrients but also has numerous benefits, such as improving soil health via the addition of organic matter, improving soil structure, aeration, water holding capacity, maintaining soil pH, and sequestering C (Risse et al., 2020; Rayne & Aula, 2020). Moreover, the slow release rates of manure nutrients improve plant uptake and reduce nutrient losses. However, it should be carefully managed to reap

the benefits of manure use in agriculture and minimize the potential environmental risks associated with manure use.

#### **1.4 Nutrients and metal accumulation in agricultural soils.**

Inappropriate agricultural management practices and over-application of manure can result in the build up of contaminants and pollutants in agricultural soils. The most concerned pollutants are excess P & N, pathogens, hormones (Risse et al., 2020), and metal(loid)s. Agriculture is known to be the leading nonpoint source of water pollution, while P and N are the major nutrients that contribute to water pollution(US EPA, 2002). Repeated manure application causes P accumulation in agricultural lands (Kokulan et al., 2022; Qin et al., 2020). The available N to P ratio in manure is an indicator of the amount of P applied per unit of available N. In general, most crops should be provided around 3 to 4 units of available N per unit of removed P, whereas N:P ratio in manure is 3:1 or less (Government of Manitoba, 2015; Flaten et al., 2003). Therefore, to address this disproportionate between N and P crop requirements, two manure application strategies were introduced as N- and P-based applications (Olson et al., 2009). Traditionally, manure applications have been practiced in Europe and North American regions, including Manitoba, based on crop N requirements (Miller et al., 2011; Karimi et al., 2017). However, the higher N:P ratio of the crop uptake than the ratio in the manure resulted in P accumulation in agricultural soils in the N-based manure management (Eghball, 2002). The organic N forms in the manure can be gradually turned into inorganic forms via decomposition (Rasouli et al., 2014), which is accumulated in the soil. Once the N inputs are recovered through crop biomass, the remaining mineral N in the soil is called residual soil N. Jayasundara et al. (2007) reported that 45 to 69% of N applied remained in the soil after harvest and the N mineralization process continued until the soil froze, thus increasing the risk of mobilization.

Metal elements are present in manure since not all the additives in animal feed are digested and absorbed in animal bodies (Feng et al., 2018). The continuous application of manure (Rashid et al., 2023) and bioaccumulation of naturally occurring metal elements causes the eventual building up of metal(loid)s in the agricultural soils. Accumulation and loss of nutrients and metals are influenced not only by fertilizer and manure inputs but also by factors such as soil texture, crop rotation, tillage practices, precipitation, hydrological pathways, and drainage (Government of Manitoba, 2007; Zanon et al., 2020; Li et al., 2023; Lv et al., 2023).

## **1.5 Forms of nutrients and metals in soils.**

### **1.5.1 Phosphorus in soil**

The soil P can be mainly grouped into soil solution P, labile P, and non-labile P (Brady & Weil, 2016). The soil solution P (mostly composed of inorganic P with a small amount of organic P) is the fraction of soil P that is plant-available. Labile P forms generally consist of P adsorbed onto silicate clay mineral surface, oxides and hydroxides of the Fe and Al (aluminum) of soil sheets and/or humus particles, and mineralizable organic P (Antelo et al., 2005; Asomaning, 2020; Xiong et al., 2022). Labile P forms have the ability to release inorganic P into the soil P solution. Non-labile P fraction consists of insoluble P that is strongly fixed with Fe and Al minerals (occluded P), insoluble inorganic P compounds with larger molecular masses, and insoluble organic compounds that are very stable and not subjected to microbial mineralization and are not available for plant uptake (Costa et al., 2016; The Soil P Cycle, 2023). Chemically, inorganic P in soils is found as orthophosphates ( $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ ) in soil solution, non-occluded Al and Fe bound P, occluded P bound with Al and Fe oxides and hydroxide, and Mg and Ca bound P (Vadas & Sims, 1998). The availability of orthophosphate species is pH-dependent. Al and Fe-bound P are dominant in acidic soils, while Ca-bound P is dominant in alkaline soils (Zhao et al., 2023), which is abundant in southern Manitoba. There is a large variety of soil organic P compounds; however, they are

generally classified into four main groups, namely, monoester phosphates, diesters phosphates, phosphonates, and organic polyphosphate (Turner et al., 2005; Huang et al., 2017; Ducousso-Détrez et al., 2022). Organic P could be mineralized by microorganisms, which releases soluble P forms such as orthophosphates into soil solution.

The P in natural water is grouped into three categories: soluble reactive P (SRP), soluble unreactive P (SUP), and particulate P (Carlson & Simpson, 1996). The total of SRP and SUP is known as soluble P (SP), and the total of all P components is called total P (TP). Particulate P is separated by filtering through a 0.45-micron membrane filter. SRP, which is also termed dissolved reactive P (DRP), contains the soluble portion of P (filtered through a 0.45-micron membrane filter) and all forms of reactive P, including some organic P with testing reagents (Carlson & Simpson, 1996). DRP accounts for a large portion of orthophosphate that is consumed directly by algae. Therefore, DRP is an index to measure the amount of P available for algae in water (Carlson & Simpson, 1996). SUP is the soluble P portion present in water that is not reactive with testing reagents and are complex organic P forms and bulky chains of inorganic P molecules. These molecules can not be directly available for algal consumption and have to be converted to orthophosphate.

### **1.5.2 Nitrogen in soil**

Over 90% of the total N in most soils is found in organic forms (Cruz et al., 2021), which can be divided into two broad categories as N from organic residue from undecayed animal and plant matter and N from soil organic matter or humus (Kelley & Stevenson, 1995; Francisco da Silva et al., 2020). Some forms of organic N are soluble and are called dissolved organic N (DON). Microbial degradation of proteins and amino acids can also contribute to the formation of DON forms in soils (Rasouli et al., 2014). Organic N is mineralized mainly in the growing seasons in agricultural soils (Rasouli et al., 2014). The major inorganic N forms found in the soil are nitrite



(NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), exchangeable NH<sub>4</sub><sup>+</sup>, non-exchangeable (mineral-fixed) NH<sub>4</sub><sup>+</sup>, nitrous oxide (N<sub>2</sub>O) and dinitrogen gas (N<sub>2</sub>) (Cruz et al., 2021). Nitrite, nitrate, and ammonium are found as soluble inorganic N forms (Yang et al., 2019). Nitrite is transitory, and both nitrite and ammonium are found in low concentrations relative to nitrate in soil solutions in aerated soils (Maynard et al., 2007; Fu et al., 2010). Nitrate is readily plant available and found to be higher in concentrations in soil solution due to the interaction of the overall negative charge between soil and the nitrate anion (Cruz et al., 2021). Ammonium ions are found as exchangeable cations in the soil solution due to their attraction to the negatively charged soil particles. Non-exchangeable ammonium ions are immobilized by the fixation with clay minerals (Scherer, 1993). In agricultural soils, a residual soil N pool is present after crop harvest, which contains soluble N compounds mainly composed of nitrate (Rasouli et al., 2014). The residual soil N pool is converted into gaseous N (NH<sub>3</sub>, N<sub>2</sub>O, N<sub>2</sub>) by the microbial activity and chemical and biological transformations in the soil, which is a way soil loses N. The N in the drainage and runoff water can be categorized into two groups: dissolved N compounds (DON, NH<sub>4</sub>-N, and NO<sub>3</sub>-N) and particulate N compounds (organo-mineral complexes and fixed NH<sub>4</sub>-N) (Rasouli et al., 2014).

### **1.5.3 Metals in soil**

Frequently found metals in agricultural soils can be categorized as light or heavy metals and metalloids. Furthermore, they can be classified based on their chemical, physical, and physiological characteristics as transition metals: Mn, Fe, Cr, Ni, Cu; post-transition metals: Zn, Al, Cd, and Pb; alkaline earth metals: Ca and Mg; and metalloids: As (Rashid et al., 2023). Metals in agricultural soils could be in different chemical forms, such as water-soluble or insoluble, adsorbed to soil colloidal surfaces, in organic material complexes, bonded with inorganic minerals, etc. (Lindsay, 1979). Metal concentrations in the soil are controlled by the pH and organic matter

of the soil (Rashid et al., 2023). Alkaline soils with high organic matter have low  $H^+$  concentrations that allow metal cations to bind tightly with negatively charged soil particles and organic matter. Due to this strong bonding, most metals are less available for plant uptake. Most inorganic forms of metals within the soil are available for plant uptake, while organic forms are required to be degraded or converted by microbial decomposition (Rashid et al., 2023). Excessive P in soils can result in Zn, Mn, and Fe deficiencies (McBride, 2022), where P forms precipitates and complexes with these metal ions (Mortvedt, 1991; Jones, 2020). In alkaline soils, precipitation reactions and formation of metal oxides, phosphates, silicates, carbonates, sulfides, etc., make metals biologically unavailable and less mobile, while the availability of metals are higher in acidic soil due to increased solubility (Gadd & Griffiths, 1977). The plant rhizosphere also plays an important task where the metals are chelated with plant secretion and organic molecules.

### **1.6 Snowmelt runoff in Prairie agricultural lands.**

Nutrients (P and N) and metals can be mobilized from agricultural lands through surface runoff, soil erosion, and leaching (He et al., 2004; Kieta et al., 2018; Yang et al., 2011; Liu et al., 2021). Runoff and leaching from livestock operations and fertilized/manured soils are responsible for 49% of the N loads found in Canadian surface water (Janzen et al., 2003). The water quality of the Canadian Prairies has been a growing concern due to the transport of nutrients. In Manitoba, particulate P is exported through erosion by water and to a lesser degree by wind (Manitoba Phosphorus Experts Committee, 2006). The major pathway of soluble P transport in Manitoba is through surface runoff (Salvano et al., 2009) because of the flat landscape. While the snowmelt contributes over 75% of the annual runoff in Manitoba (Liu et al., 2019), it accounts for the highest percentage of runoff volume (80%) received by Lake Winnipeg (Dibike et al., 2012). Thus, the snowmelt runoff is considered the dominant P transport pathway. Furthermore, a 3-year study in

Manitoba revealed that the snowmelt-associated surface runoff contributed to 22 to 91% of annual runoff, 24 to 98% of dissolved reactive P, and 29 to 97% of total P loss (Kokulan et al., 2019). It is reported that the total P concentrations in runoff events during rainfall and snow in frozen soils are dominated by DRP forms, while particulate P forms dominate in nonfrozen soil conditions (Zopp et al., 2019).

Due to the landscape features, poor infiltration and drainage, Canadian Prairie's agricultural lands are prone to temporary flooding during the spring snowmelt period, inducing reduced soil redox potentials (Amarawansa et al., 2015). These conditions occur due to microbial-mediated reactions reducing oxygen levels in the soil. The presence of organic matter enhances the development of reducing conditions and simultaneous changes in soil pH. Both laboratory and field studies conducted under snowmelt conditions have shown increased P release to soil porewater or overlaying floodwater during flooding (Concepcion et al., 2021; Weerasekara et al., 2021; Lasisi et al., 2023). During the initial phase of the snowmelt period, the soil is frozen, cold temperatures exist, and thus, microbial activities are inhibited in soils. Therefore, the nitrification rates are low in the topsoil. However, when the temperature rises in the spring, the nitrification rates increase and nitrate-N may add to the snowmelt water. Also, during the winter, microbial biomass immobilizes N within their cells (Brooks et al., 1998), and when the spring permits, the immobilized N is subsequently released with the lysis and collapse of the microbial cells (Isobe et al., 2018). Kokulan et al. (2019) reported that surface runoff contributes to 3-5% of annual nitrate losses associated with snowmelt in Manitoba. Therefore, surface runoff can play a significant role in N loss in agricultural lands.

### **1.7 Eutrophication and water quality risks.**

The mobilization of excess nutrients and metals in soils to surface water bodies causes deterioration of the water quality and eutrophication. P is considered the critical limiting factor for freshwater eutrophication; however, N is also important since a combination of P and N is needed for optimal algal growth (Rasouli et al., 2014). Release of high loadings of P and N into surface water results in eutrophication. Lake Winnipeg, the largest freshwater lake in Manitoba and the 10<sup>th</sup> largest freshwater lake in the world, has been dominated by nitrogen-fixing Cyanobacteria (Kling et al., 2011), and the intensity and frequency of occurrence of algal blooms have increased due to the dramatic increase in P concentration of the lake which started between 1990 and 2000s (McCullough et al., 2012). This has been attributed to increased livestock production, use of synthetic fertilizer, and increased frequency and intensity of spring floods in the Red River Valley watershed (Schindler et al., 2012). Therefore, concerns were raised suggesting the need to reduce nutrient mobilization to surface waters. The accumulated metals in agricultural soils can also be mobilized to natural waters through runoff events and contribute to nonpoint contamination, which may result in poor water quality.

### **1.8 Strategies to reduce nutrients and metal through runoff.**

Some of the best management practices (BMPs), such as conservation tillage and buffer strips, have been developed to reduce P and N loss from agricultural soils focusing on minimizing the nutrient runoff with soil particle runoff such as erosion (Tiessen et al., 2010; Peterjohn & Correll, 1984). However, these practices are ineffective in cold climate regions with flat landscapes such as Manitoba, where snowmelt runoff is the dominant pathway of nutrient and metal loss (Hoffman et al., 2019). Manure injection or subsurface application has significantly reduced concentrations of excess nutrients lost into the environment compared to a surface application under rainfall-runoff (Jokela et al., 2016; Eghball and Power, 1999; Tabbara, 2003). Therefore, this study was

designed to fill the research gap to investigate the effect of the manure application method on the P, nitrate-N, and metal concentrations under snowmelt runoff.

### **1.9 Objective**

The overall objective of this thesis was to determine the effect of liquid swine manure application method (injection and surface application of manure) and the duration of snowmelt flooding on the P, nitrate-N, and metal concentrations in snowmelt runoff.

### **1.10 Hypothesis**

- a) P, N, and metal loss are less with injected manure than surface-applied manure.
- b) P, nitrate-N, and metal concentrations in snowmelt will increase with the prolonged snowmelt flooding.

### **1.11 Thesis outline**

This thesis consists of four chapters. Chapter 1 is a general introduction to agriculture in Manitoba, manure usage, nutrient and metal accumulation, snowmelt runoff in the Canadian Prairies, and water quality issues caused by runoff of nutrients and metals. Chapter 2 is focused on release of phosphorus and metals from manured soils to floodwater during a laboratory simulation of snowmelt flooding. Chapter 3 compares the manure application methods on nutrient and metal loss with snowmelt flooding. Finally, Chapter 4 provides the overall synthesis of this research project.

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## **2. RELEASE OF PHOSPHORUS AND METAL(LOID)S FROM MANURED SOILS TO FLOODWATER DURING A LABORATORY SIMULATION OF SNOWMELT FLOODING.**

### **2.1 Abstract**

Phosphorus (P) and metal accumulation in manured agricultural soils and subsequent losses to waterways have been extensively studied; however, the magnitudes and the factors governing their losses during spring snowmelt flooding are less known. We examined the P and metal release from long-term manured soil to floodwater under simulated snowmelt flooding with recent manure additions. Intact soil columns collected from field plots two weeks after liquid swine manure treatments (surface-applied, injected, or control with no recent manure addition) were flooded and incubated for eight weeks at  $4\pm 1$  °C to simulate snowmelt conditions. Floodwater (syringe-filtered through  $0.45\ \mu\text{m}$ ) and soil porewater (extracted using Rhizon-Mom samplers) samples were periodically extracted and analyzed for dissolved reactive P (DRP), pH, zinc (Zn), manganese (Mn), iron (Fe), magnesium (Mg), calcium (Ca), and arsenic (As). Mean floodwater DRP concentrations ( $\text{mg L}^{-1}$ ) for manure injected ( $2.0\pm 0.26$ ), surface-applied ( $2.6\pm 0.26$ ), and control ( $2.2\pm 0.26$ ) treatments did not differ significantly. Despite manure application, DRP loss to floodwater did not significantly increase compared to the control, possibly due to the elevated residual soil P at this site from the long-term manure use. At the end of simulated flooding, the DRP concentrations increased by 1.5-fold and 5-fold in porewater and floodwater, respectively. The floodwater concentrations ( $\text{mg L}^{-1}$ ) of Mn ( $0.015\pm 0.0257$ ), Fe ( $0.071\pm 0.088$ ), Mg ( $12.3\pm 14.02$ ), and Ca ( $28.6\pm 27.52$ ) were not affected by manure treatments. While prolonged flooding increased the P release from soils irrespective of manure treatment, a similar effect was not observed for Mn, Fe, Mg and Ca.

**Keywords:** snowmelt, liquid-swine-manure, redox, dissolved-reactive-phosphorus, metal(loid)s

## 2.2 Introduction

Phosphorus (P) is an essential plant nutrient, but it can cause detrimental effects when in excess on surface water bodies by promoting algal growth and eutrophication. The input of P fertilizer or manure into agricultural lands can enhance P loading to water bodies (Schindler et al., 2012). In the Canadian prairies, the geomorphological features, such as the flat landscapes and impermeable clay soils, lead to temporary flooding during the spring snowmelt period. Spring snowmelt accounts for 80% of the runoff volume of Lake Winnipeg (Dibike et al., 2012; Liu et al., 2019), making it the primary mode of P transport from agricultural lands to the lake (Rattan et al., 2017; Kokulan et al., 2019). The dominant form of P in the snowmelt runoff is dissolved P (Liu et al., 2013; Casson et al., 2019). Prolonged flooding of soils induces anaerobic conditions and decreases redox potentials (Eh), thus resulting in P release (Ajmone-Marsan et al., 2006; Amarawansa et al., 2015; Scalenghe et al., 2012; Hoffman et al., 2009) through a microbial-mediated reductive dissolution of iron (Fe) and manganese (Mn) compounds (Amarawansa et al., 2015; Scalenghe et al., 2012; An et al., 2000). Even though P release is temperature dependent, significant P releases have been reported from previous studies of soils with simulated snowmelt flooding even under cold temperatures (Concepcion et al., 2021; Weerasekara et al., 2021).

The expansion of agriculture in Manitoba has increased livestock production, generating a large volume of livestock manure. Applying swine manure to agricultural lands became a cost-effective management practice as it is an excellent nutrient source and facilitates waste recycling (Khaleel et al., 1980; Choudhary et al., 1996). However, the usage of swine manure for crop production has become a threat to surface water quality, as manure is usually a rich source of P (Karmakar et al., 2013; Riemersma et al., 2006). In addition, livestock manure contains metals and metalloids (Olatuyi et al., 2014; Nicholson et al., 1999) since some are naturally present in livestock feed

while some are added as supplements (An et al., 2020). These metals are not fully absorbed during digestion, and the remaining amounts are released through urine and feces (Feng et al., 2018). With long-term manure applications, P and metals accumulate in soils, increasing the risk of losses to waterways via different pathways (Allen and Mallarino, 2008; Ceretta et al., 2010; Legros et al., 2013; L'Herroux et al., 1997; Oliveira Filho et al., 2020). Phosphorus and metal losses from manured lands via rain-driven runoff and leaching have been extensively studied (Coelho et al., 2012; He et al., 2004; Kang et al., 2011; Nelson et al., 2005), but studies on snowmelt transport of excess nutrients and contaminants are lacking. In a recent field study, Lasisi et al. (2023) observed higher concentrations of dissolved reactive P (DRP), calcium (Ca), magnesium (Mg), manganese (Mn), and iron (Fe) in snowmelt runoff from a manured field than from an unmanured field. For long-term manured soils, Eghball et al. (2002) reported that manure application just before simulated rainfall resulted in significantly greater dissolved P loss compared to the un-manure control, suggesting that recently added manure resulted in more runoff P loss than previous manure applications.

There is increasing evidence that nutrient runoff loss from soils is reduced when manure is injected or incorporated compared to the surface application without incorporation (Jokela et al., 2016; Eghball and Power, 1999; Tabbara, 2003). However, the benefits of injection or incorporation may not be realized when there is a significant time gap between rainfall events and manure application. For example, a delay of approximately 15 days in a simulated rain event after liquid swine manure application sharply reduced DRP in runoff compared to the rainfall event simulated soon after manure application, with the effect being greater for the manure surface applied treatments. In the same study, a 6-month delay in rainfall simulation substantially reduced DRP concentrations and loads in runoff in manured treatments to levels similar to unmanured control (Allen and Mallarino,



2008). These results suggest that the benefits of incorporating swine manure into soils are reduced when the time gap between manure application and rainfall events increases. To our knowledge, no studies have been conducted to investigate the effect of manure application methods on P and metal release with snowmelt flooding. Therefore, the objectives of this study were to (a) determine the release of P and metal(loids) [Ca, Mg, Fe, Mn, selenium (Se), nickel (Ni), copper (Cu), Zn, and As] to floodwater under simulated snowmelt flooding from a long-term manured soil with and without recent application of liquid swine manure and (b) investigate the effect of manure application methods (surface application versus injection) on P and metal(loids) release from soils. We hypothesized that the release of P and metal(loid)s from soil to floodwater under simulated snowmelt flooding would be (a) greater with recent manure applications than without, (b) greater with prolonged flooding, and (c) lower when liquid swine manure was injected compared to surface application.

## **2.3 Materials and methods**

### **2.3.1 Site location and soil description.**

The selected experimental site was a farmer's field in Randolph, Manitoba (49°32'47.3" N 96°51'53.3" W). The field is located in an agricultural area of the Red River Basin that is prone to flooding (McCullough et al., 2012) and identified as a high-risk area for P transport into Lake Winnipeg (Lake Winnipeg Foundation, <https://doi.org/10.25976/hxqe-py39>), where livestock manure is frequently being used in cropping practices. The selected site has a history of swine manure application where the field has received manure every 2-3 years for >30 years, with the last application in the Fall of 2020. The field was cropped with corn in 2021. The soil of the site belongs to the Osborne series, which is classified as Gleyed Rego Black Chernozem (MAFRI 2010). The soil had a Clay texture with a pH of 7.9 (measured by 1:2 soil-water) and available P concentration determined as Olsen-P (Olsen et al., 1954) of 99 mg kg<sup>-1</sup>. The organic matter content

measured by loss-on-ignition (Dean,1974) was 7.1%. Other nutrient and metal concentrations in the soil are listed in supplemental Table S1. The soil characterization was done at the Farmers Edge Laboratories Inc.

### **2.3.2 Experimental design and sample collection.**

The experimental plots were set up in the fall of 2021, following the same design described in Soto et al. (2023). The three treatments, including no recent manure addition (control), liquid swine manure injected, and liquid swine manure surface-applied, were arranged in a randomized complete block design with four replicates, resulting in a total of twelve plots. Each plot had an area of 1.2 x 1.2 m and was separated from each other using a 0.6 m alley. Liquid swine manure (1.87% solid content and total P content of 540 mg kg<sup>-1</sup>, fresh weight basis) was applied at a rate of 170,000 L ha<sup>-1</sup> to match the application rate used by the farmer in previous years. Total Kjeldahl nitrogen (TKN) and total P in the manure used for the study were within the range reported for typical liquid swine manure in Manitoba (TKN range was 6 to 68 lb/1000 gal and total P range was 1 to 32 lb/1000 gal) (Government of Manitoba, 2009). For the surface application, manure was spread on the surface of the plot using small pails to evenly distribute the manure, to ensure the accuracy of the manure rate for manure surface applied treatment. For the injection treatment, three trenches (0.15 m deep) were manually made using a pickaxe to apply manure to the subsurface, which were then backfilled with soil.

Two weeks after manure application, intact soil columns (15 cm in depth) from random spots in each plot were collected into cylindrical polyvinyl chloride (PVC) tubes (height = 30 cm and diameter = 10 cm) by pushing PVC tubes into the soil using a sledgexhammer against a wooden plank. PVC tubes were carefully removed, and the bottoms were capped using PVC caps to retain the soil. The collected soil columns were transported immediately to the laboratory and stored at

4 ±1 °C. In addition to soil columns, soil samples (0-15 cm) from each plot were collected using a Dutch auger, transported back to the laboratory, and stored in the cooler (4 ±1 °C) for analysis of available P and metal(loid)s.

The laboratory-simulated snowmelt flooding experiment was conducted approximately 4 weeks after manure application (2 weeks after the collection of soil columns), using the same procedure as Vitharana et al. (2021) and Kumaragamage et al. (2022). To extract soil porewater, two Rhizon-MOM samplers (Rhizosphere research products; 0.15 µm pore size, 2.5 mm diameter, and 10 cm length) were horizontally inserted through pre-drilled holes on each PVC pipe at 5 cm depth from the soil surface and sealed with silicone to prevent leaking. The spring snowmelt flooding conditions were simulated by flooding the columns with deionized water (Milli-Q – 18 MΩ cm) and incubating at 4±1 °C. A water level of 10 cm was consistently maintained above the soil surface throughout the incubation period. To measure soil redox potential (Eh), Pt redox probes were installed at 5 cm depth from the soil surface in each soil column after flooding. Sampling for both porewater and floodwater was conducted on days 0, 3, 7, 10, 14, 17, 21, 28, 35, 42, and 49 after flooding. The Eh data for day 0 could not be collected due to some leaking in the soil columns. Porewater was collected by suction through the Rhizon-MOM samplers using syringes (20.0 mL). An additional set of syringes was used to extract floodwater samples from the surface, and the floodwater samples were syringe filtered (0.45 µm).

### **2.3.3 Analysis of water samples**

The DRP concentrations in both floodwater and porewater samples were immediately analyzed using the molybdate blue method (Murphy and Riley, 1962) and measuring the absorbance at 882 nm using an ultraviolet-visible spectrophotometer (Ultrospec 500 pro). The pH of porewater and floodwater samples was measured using the Fisher Accumet AB15 pH meter. A subset of

porewater and floodwater samples was acidified with 20  $\mu$ L of concentrated nitric acid and analyzed for total P, Ca, Mg, Fe, Mn, Se, Ni, Cu, Zn, and As using the inductively coupled plasma-optical emission spectrometry (ICP-OES; iCAP 6500, Thermo Scientific). These metals were selected for this study based on our previous research findings and reported literature (Concepcion et al., 2021; Olatuyi et al., 2014). Redox potential in the soil columns was measured using the pre-installed Pt electrodes at 5 cm depth coupled with an Ag-AgCl reference electrode with KCl electrolyte, which was inserted into the floodwater surface at the time of obtaining the readings. The total dissolved P concentrations measured using ICP-OES were only slightly higher than the DRP concentrations, with DRP accounting for >98% of total dissolved P. Therefore, our analysis and discussion will focus only on DRP concentrations, which is considered as the bioavailable form of P.

The sampled soil from field plots was air-dried, ground, and sieved using a 2-mm mesh. Labile P in the soils was extracted using the Olsen- P method (Olsen et al., 1954) and the DRP concentration in the extracts was analyzed using the molybdate blue color method (Murphy and Riley, 1962).

#### **2.3.4 Statistical analysis**

Analysis of variance (ANOVA) was performed using the mixed procedure for repeated measures (PROC GLIMMIX) to assess the impact of manure treatment and the time of flooding on DRP, pH, Eh, and metal concentrations of the collected porewater and floodwater samples. The manure treatment was considered a fixed effect, and blocks (replicates) were treated as the random effect and days after flooding (time) as the repeated measure. Where treatment effect was significant, means were compared using the Tukey's or Tukey-Kramer significant difference method. Compound-symmetry (CS) was used to structure covariance matrices in repeated measures ANOVA. Data that were not normally distributed were log-transformed to fulfill the distributional

assumptions of the statistical tests. Two outliers in the porewater and floodwater pH data, distributed beyond the range of 3 interquartile, were excluded from the analysis. One-way ANOVA was performed for the concentrations of Olsen P, where manure treatment was considered a fixed effect, and blocks (replicates) were treated as the random effect. A paired t-test was carried out to compare DRP concentrations between porewater and floodwater samples. All statistical analyses were performed in SAS OnDemand for Academics online software (SAS Institute, 2014) at a significance level of  $\alpha = 0.05$ .

## **2.4 Results and discussion**

### **2.4.1 Dissolved reactive phosphorus concentrations in porewater and floodwater.**

The mean DRP concentration ( $2.3 \pm 0.61 \text{ mg L}^{-1}$ ) in the porewater was significantly ( $P < 0.0001$ ) higher than those in the floodwater ( $0.7 \pm 0.33 \text{ mg L}^{-1}$ ), which was consistent with other incubation studies (Concepcion et al., 2021; Vitharana et al., 2021; Weerasekara et al., 2021). The development of anaerobic conditions led to P release into the soil solution due to reductive dissolution reactions, increasing DRP concentrations in porewater, followed by gradual diffusion to overlying floodwater over time (Amarawansa et al., 2015). This likely explains the higher DRP concentration in porewater than in floodwater at any given time.

Table 2-1. Dissolved reactive phosphorus (DRP) concentrations ( $\text{mg L}^{-1}$ ) and pH of the porewater and floodwater over the flooding period in manure-injected, surface-applied, and unamended (control) soil. Least square means are listed with associated standard errors in parentheses.

Manure Treatment	Porewater DRP	Floodwater DRP	Porewater pH	Floodwater pH
	$\text{mg L}^{-1}$			
Control	2.2(0.26)	0.8(0.12)	7.7(0.05)	7.6(0.14)
Injected	2.0(0.26)	0.6(0.12)	7.7(0.05)	7.5(0.14)
Surface-applied	2.6(0.26)	0.7(0.12)	7.7(0.05)	7.5(0.14)
<b>Day</b>				
0	1.7(0.20) <sup>C*</sup>	0.2(0.13) <sup>D</sup>	7.4(0.04) <sup>D</sup>	7.2(0.13) <sup>C</sup>
3	2.0(0.20) <sup>C</sup>	0.5(0.12) <sup>CD</sup>	7.6(0.04) <sup>BC</sup>	7.9(0.12) <sup>A</sup>
7	1.8(0.20) <sup>BC</sup>	0.6(0.12) <sup>BC</sup>	7.8(0.04) <sup>A</sup>	7.6(0.12) <sup>B</sup>
10	2.3(0.20) <sup>AB</sup>	0.8(0.12) <sup>AB</sup>	7.6(0.04) <sup>BC</sup>	7.4(0.12) <sup>BC</sup>
14	2.6(0.20) <sup>A</sup>	0.8(0.12) <sup>ABC</sup>	7.8(0.04) <sup>A</sup>	7.6(0.12) <sup>B</sup>
17	2.5(0.20) <sup>A</sup>	0.7(0.12) <sup>ABC</sup>	7.6(0.04) <sup>CD</sup>	7.4(0.12) <sup>BC</sup>
21	2.5(0.20) <sup>A</sup>	0.7(0.12) <sup>ABC</sup>	7.8(0.04) <sup>A</sup>	7.6(0.12) <sup>B</sup>
28	2.4(0.20) <sup>AB</sup>	0.7(0.12) <sup>ABC</sup>	7.7(0.04) <sup>A</sup>	7.5(0.12) <sup>B</sup>
35	2.5(0.20) <sup>A</sup>	0.8(0.12) <sup>ABC</sup>	7.7(0.04) <sup>A</sup>	7.6(0.12) <sup>B</sup>
42	2.5(0.20) <sup>A</sup>	0.8(0.12) <sup>AB</sup>	7.7(0.04) <sup>AB</sup>	7.5(0.12) <sup>B</sup>
49	2.4(0.20) <sup>A</sup>	0.9(0.12) <sup>A</sup>	7.7(0.04) <sup>A</sup>	7.5(0.12) <sup>B</sup>
	<b><i>P value</i></b>			
Treatment	0.23	0.48	0.62	0.44
Day	<.0001	<.0001	<.0001	<.0001
Treatment $\times$ Day	0.86	1.00	0.61	0.29

\*The different letters in columns indicate Tukey's significant difference at a significance level of  $\alpha = 0.05$ .

#### 2.4.2 The effect of flooding on DRP concentrations

Time of flooding significantly affected DRP concentrations in both porewater and floodwater (Table 2-1). At the beginning of flooding, the DRP concentrations of both floodwater and porewater were low ( $< 0.3$  and  $2.5 \text{ mg L}^{-1}$ , respectively), but by the end of the flooding period, the mean DRP concentrations of both floodwater and porewater increased, resulting in a 1.5-fold increase in mean porewater DRP concentration and a 5-fold increase in mean floodwater DRP concentration from day 0 to day 49 (Figure 2-1; Table 2-1). The effect of treatment or interaction between treatment  $\times$  day was not significant; the DRP increased over time regardless of the manure application method.

We observed that the porewater DRP concentrations remained relatively stable after day 35, similar to previous studies (Amarawansa et al., 2015; Kumaragamage et al., 2019; Vitharana et al., 2021; Weerasekara et al., 2021) where the stable (or declining) concentrations after an initial increase have been attributed to the resorption of released P over time (Shober and Sims, 2009) or metabolic activities by microorganisms that may consume the P released into the soil solution (Pant and Reddy, 2001). Previous studies conducted on P release under room temperature flooding conditions ( $\approx 20$  °C) have also shown an increase in DRP with flooding time, but with a greater magnitude of DRP concentrations in porewater and floodwater (up to 17-fold increase) in both manured and unmanured soils (Amarawansa et al., 2015; Jayarathne et al., 2016; Kumaragamage et al., 2019), with flooding at higher temperatures releasing more P from soils than at colder temperatures (Weerasekara et al., 2021).

### **2.4.3 The effect of manure application on DRP concentrations**

The manure amendment effect was not significant, and DRP concentrations in porewater and floodwater were similar in manured and control treatments in the current study (Table 2-1). Flooding-induced P release is reported to be consistently higher in manured compared to unmanured soils (Amarawansa et al., 2015; Concepcion et al., 2021; Lasisi et al., 2023); however, we did not observe similarly, which could be due to the long-term history of manure application in the study site. We also observed that there were no significant differences ( $P= 0.83$ ) in soil available P (Olsen P;  $\text{mg kg}^{-1}$ ) between manure injected ( $131.0 \pm 14.78$ ), surface-applied ( $134.3 \pm 14.78$ ), and control ( $122.6 \pm 14.78$ ) treatments. Likely, the effect of recent fresh manure application on P accumulation and P release was negligible in this field site, with an elevated soil P status (Olsen P of  $> 90 \text{ mg kg}^{-1}$ ) resulting from the long-term manure applications. However, even in long-term manured soils, Eghball et al. (2002) found that having recent manure

applications significantly increased DRP losses to runoff compared to the residual effect of previous manure applications, which was not observed in our research. The four-week gap between the manure application and the simulated flooding in the current study may have reduced the release of manure P, most likely due to P sorption, to the point that the effect of recent manure application was not significant in relation to floodwater or porewater DRP concentrations. While this has not been observed under snowmelt conditions before, in a simulated rainfall runoff study, Allen and Mallarino (2008) observed the ratio of DRP concentrations between non-incorporated and incorporated manure was 5.4 after 24 h simulated rain runoff, whereas it reduced to 3.1 with a 15-day delay between manure application and simulated rain runoff.

#### **2.4.4 The effect of the manure application method on DRP concentrations**

In this study, the mean DRP concentrations of porewater of the manure surface-applied treatment were numerically higher compared to the manure injected and control treatments, whereas the floodwater DRP concentrations were similar across treatments. Subsurface injection of manure has been established as the recommended method of application of liquid manure since research evidence has clearly shown that surface application of manure (unincorporated) increased nutrient losses, including P, into the rainfall-runoff compared to the injected manure application (Kleinman et al., 2002; Daverede et al., 2004; Joy et al., 2013). A decrease in nutrient loss is expected with manure injected treatment since added nutrients are retained and can form complexes with soil colloidal fraction (Dittmer et al., 2020), while with surface-applied manure, added nutrients are exposed and more vulnerable to erosion and runoff with rainfall and flooding effects. Daverede et al. (2004) compared P losses with rain runoff from incorporated and surface-applied liquid swine manure and P fertilizer and found that the injected application resulted in a 99% decrease in runoff DRP load and a 94% decrease in total P load compared to the surface application. In another study,



a reduction in DRP loss by 98%, 80%, and 53% was observed using strip-till injected, disc incorporation, and aerator band methods, respectively, compared to the broadcast-surface manure application (Jokela et al., 2016). This effect may depend on the time period/gap between manure application and hydrological transport; Allen and Mallarino (2008) observed that swine manure in non-incorporated plots significantly increased runoff P concentrations during both 24-hour and 10-16-day rainfall-runoff events compared to the incorporated plots, while a longer delay of 5 to 6 months in the rainfall simulation brought runoff P levels in both manure non-incorporated and incorporated plots close to those observed in control plots, indicating a substantial reduction in P loss with the extended time gap. Our results, therefore, suggest that the benefits of injecting manure over surface applications in reducing P loss to snowmelt may not always be seen when soils have excessive available P relative to the amount of P added with recurrent fresh manure applications and/or when manure is applied in the fall approximately 5 to 6 months prior to the snowmelt event. As an implication, land managers can consider the initial soil P and the probability of runoff caused by rain or snowmelt after manure application when evaluating the potential benefits of manure injection to reduce P loss.

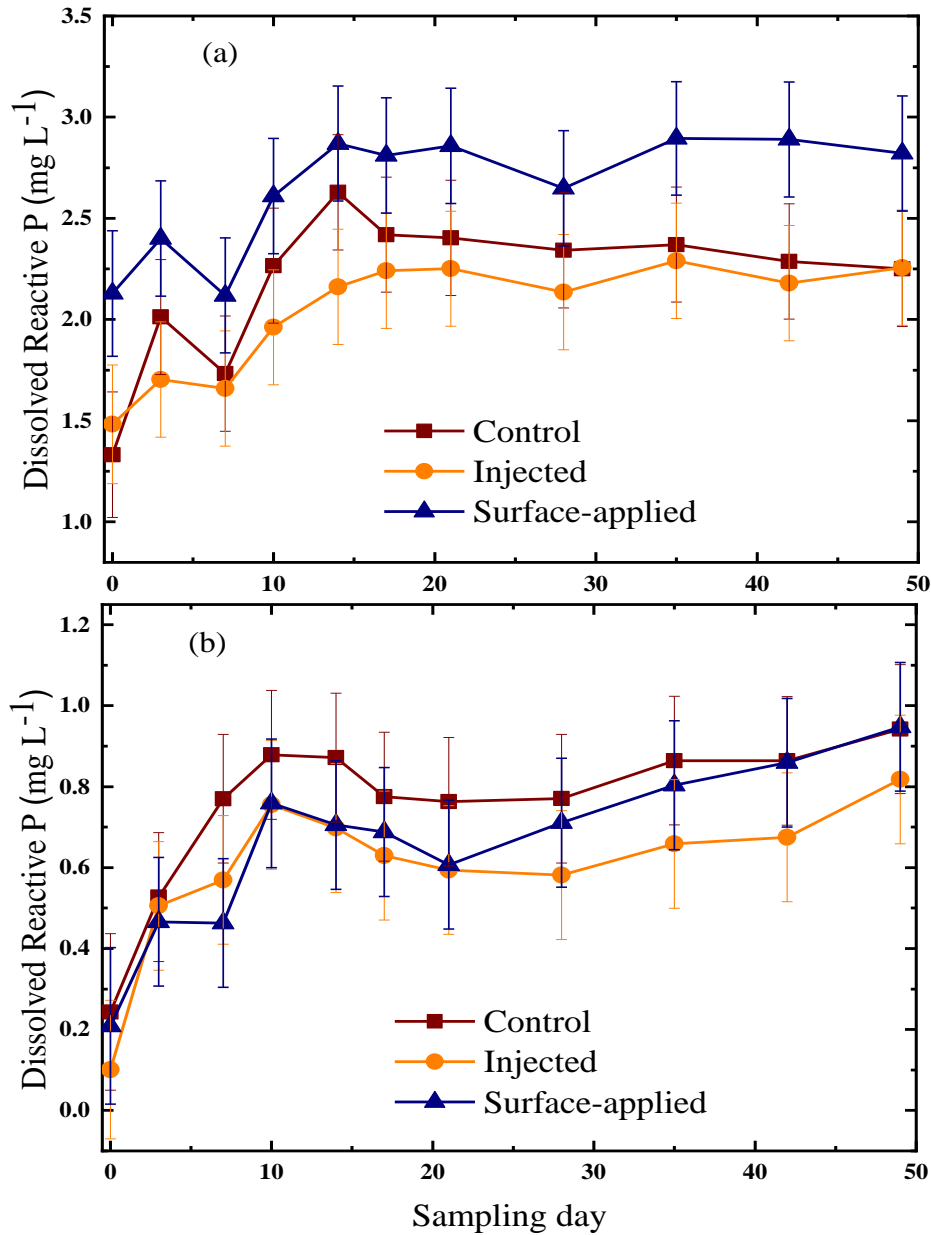


Figure 2-1. Changes in soil (a) porewater and (b) floodwater dissolved reactive P (DRP) concentrations over the 49 days of flooding in manure injected, surface-applied, and unamended (control) soil. The error bars represent standard errors of the mean DRP concentration values.

#### 2.4.5 The effect of the manure application method and day of flooding on Zn, Mn, Fe, Mg, Ca, and As concentrations of porewater and floodwater.

The concentrations of Fe, Mn, Se, Ni, Cu, Zn, and As in porewater and floodwater were measured in this study. Ni and Se concentrations were below the detection limit (0.012 mg L<sup>-1</sup>), and As

concentrations in most floodwater samples were also below the detection limit ( $0.015 \text{ mg L}^{-1}$ ). The effect of the manure application method on porewater Zn, Mn, Fe, Ca, and As concentrations (Table 2-2) and Mn, Fe, Mg, and Ca in floodwater (Table 2-3) was not significant.

There was a significant effect of day (time of flooding) for Zn, Mn, Fe, Ca, and As concentrations in porewater. However, only Mn and Fe had a day effect in floodwater. The Zn concentrations in porewater were low ranging from  $0.028\text{-}0.064 \text{ mg L}^{-1}$  (Figure 2-2a; Table 2-2). Floodwater Zn concentrations were significantly higher in the manure surface-applied treatment compared to the manure-injected and control treatments on day 7. Both manure-injected and surface-applied treatments had significantly higher Zn concentrations than the control on day 10 (Figure 2-2f; Table 2-3). For both porewater and floodwater Zn concentrations, after reaching a peak on day 10, concentrations slowly declined, possibly due to the precipitation reactions as sulphide (Bunquin et al., 2017).

The effect of flooding day was significant for both porewater and floodwater Mn concentrations (Tables 2-2, 2-3). Mn concentrations in porewater showed a little increment up to day 14 and then declined until day 28 (Figure 2-2a). The decrease in porewater after 14 days coincided with the increase in floodwater concentrations from day 14 to day 28 (Figure 2-2b), suggesting the diffusion of Mn from porewater to floodwater may have reduced the porewater concentrations. An 8.6-fold and significant increase in floodwater Mn concentration was observed on day 21 relative to day zero. The decrease in floodwater Mn after day 21 is likely due to the conversion of  $\text{Mn}^{2+}$  to relatively insoluble  $\text{Mn}^{4+}$  when present in floodwater (Sparrow & Uren, 2014).

Both porewater and floodwater Fe concentrations were relatively high during the first week of flooding ( $>0.06 \text{ mg L}^{-1}$  for porewater and  $>0.20 \text{ mg L}^{-1}$  for floodwater) but decreased with time until about 28 days after flooding. A rapid increase in porewater concentrations was observed after

28 days of flooding when soils got progressively reduced. Similar results have been previously reported in flooded soils (Scalenghe et al., 2002; Shahandeh et al., 2003; Amarawansa et al., 2015). A corresponding increase in floodwater Fe was not observed, which is likely due to the conversion of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in floodwater and subsequent precipitation. The reason for the sudden drop in porewater Fe concentration at 49 days of flooding is unclear.

Dissolved porewater Ca and Mg concentrations were notably high compared to the other metal elements, as expected for calcareous soils (Table 2-2; Fig. 2c and 2e). Compared to floodwater, porewater Ca concentrations were much higher (often more than 10-fold) with a significant decrease over the flooding period. The porewater concentration of Mg of the control treatment was significantly lower compared to the manure injected and surface applied treatments on day 0; however, a significant difference between the three treatments was not observed for the rest of the sampling days. Overall, porewater concentrations of both Ca and Mg declined with time, possibly due to the precipitation with carbonates, as reported in previous studies (Dharmakeerthi et al., 2019; Amarawansa et al., 2015). In contrast, the floodwater Ca and Mg concentrations increased with flooding time, likely due to the diffusion of Ca and Mg from porewater to floodwater, and on the last day of sampling, concentrations were 1.7-fold greater than day zero. The increased floodwater Ca and Mg concentrations with the time of flooding have been reported in previous studies (Amarawansa et al., 2015; Jayarathne et al., 2016).

Table 2-2. Dissolved metal concentrations of the porewater over the flooding period in manure injected, surface-applied, and unamended (control) soil. Least square means are listed with associated standard errors in parentheses.

	Zn	Mn	Fe	Mg	Ca	As
	mg L <sup>-1</sup>					
<b>Manure Treatment</b>						
Control	0.035(0.0023)	0.006(0.0016)	0.07(0.008)	96(35)	170(49)	0.023(0.0011)
Injected	0.037(0.0023)	0.005(0.0016)	0.05(0.008)	139(44)	245(70)	0.022(0.0010)
Surface	0.035(0.0023)	0.006(0.0016)	0.05(0.008)	154(37)	284(82)	0.022(0.0011)
<b>Day</b>						
0	0.028(0.0063) <sup>B*</sup>	0.006(0.0030) <sup>AB</sup>	0.09(0.019) <sup>AB</sup>	370(106)	676(139) <sup>A</sup>	0.024(0.0027) <sup>ABCD</sup>
3	0.031(0.0047) <sup>B</sup>	0.007(0.0023) <sup>AB</sup>	0.08(0.014) <sup>AB</sup>	198(55)	351(65) <sup>B</sup>	0.024(0.0020) <sup>ABCD</sup>
7	0.038(0.0047) <sup>B</sup>	0.007(0.0023) <sup>AB</sup>	0.02(0.014) <sup>B</sup>	160(44)	285(53) <sup>BC</sup>	0.025(0.0020) <sup>ABC</sup>
10	0.064(0.0047) <sup>A</sup>	0.008(0.0023) <sup>AB</sup>	0.02(0.014) <sup>B</sup>	125(35)	221(41) <sup>CD</sup>	0.031(0.0020) <sup>AB</sup>
14	0.039(0.0047) <sup>B</sup>	0.011(0.0023) <sup>A</sup>	0.05(0.014) <sup>AB</sup>	113(31)	200(37) <sup>CD</sup>	0.029(0.0020) <sup>ABC</sup>
17	0.029(0.0047) <sup>B</sup>	0.009(0.0023) <sup>AB</sup>	0.04(0.014) <sup>B</sup>	90(25)	162(30) <sup>D</sup>	0.032(0.0020) <sup>A</sup>
21	0.038(0.0047) <sup>B</sup>	0.002(0.0023) <sup>AB</sup>	0.06(0.014) <sup>AB</sup>	82(23)	147(27) <sup>D</sup>	0.015(0.0020) <sup>DEF</sup>
28	0.034(0.0047) <sup>B</sup>	0.001(0.0023) <sup>B</sup>	0.01(0.014) <sup>B</sup>	109(30)	189(35) <sup>CD</sup>	0.011(0.0020) <sup>EF</sup>
35	0.030(0.0047) <sup>B</sup>	0.003(0.0023) <sup>AB</sup>	0.11(0.014) <sup>A</sup>	102(28)	177(33) <sup>D</sup>	0.022(0.0020) <sup>BCD</sup>
42	0.033(0.0047) <sup>B</sup>	0.004(0.0023) <sup>AB</sup>	0.12(0.014) <sup>A</sup>	106(29)	183(34) <sup>D</sup>	0.021(0.0020) <sup>CDE</sup>
49	0.030(0.0047) <sup>B</sup>	0.006(0.0023) <sup>AB</sup>	0.03(0.014) <sup>B</sup>	92(29)	157(29) <sup>D</sup>	0.010(0.0020) <sup>F</sup>
	<b><i>P value</i></b>					
Treatment	0.78	0.85	0.14	0.17	0.44	0.81
Day	<.0001	0.02	<.0001	<.0001	<.0001	<.0001
Treatment × Day	0.57	0.55	0.32	0.02	0.15	0.88

\*The different letters in columns indicate Tukey's significant difference at a significance level of  $\alpha = 0.05$ .

Table 2-3. Dissolved metal concentrations of the floodwater and soil redox potential over the flooding period in manure injected, surface-applied, and unamended (control) soil. Least square means are listed with associated standard errors in parentheses.

	Zn	Mn	Fe	Mg	Ca	Redox
	mg L <sup>-1</sup>			mV		
<b>Manure Treatment</b>						
Control	0.034(0.0014)	0.018(0.0063)	0.07(0.007)	5.6(2.3)	15(5.3)	298.3(17.66)
Injected	0.034(0.0014)	0.011(0.0063)	0.08(0.007)	12 (5.1)	31.(10)	299.5(17.76)
Surface	0.035(0.0014)	0.015(0.0063)	0.08(0.007)	8.8(3.6)	22.(7.9)	247.6(14.66)
<b>Day</b>						
0	0.027(0.0032)	0.005(0.0085) <sup>CD*</sup>	0.25(0.020) <sup>A</sup>	6.1(1.8)	15(3.7)	-
3	0.037(0.0024)	0.004(0.0067) <sup>CD</sup>	0.14(0.015) <sup>B</sup>	6.7(1.8)	16(3.8)	298.7(12.88)
7	0.039(0.0024)	0.003(0.0067) <sup>CD</sup>	0.07(0.015) <sup>CD</sup>	9.2(2.5)	24(5.5)	299.7(13.24)
10	0.051(0.0024)	0.003(0.0067) <sup>CD</sup>	0.12(0.015) <sup>BC</sup>	9.9(2.7)	24(5.6)	287.4(12.39)
14	0.030(0.0024)	0.006(0.0067) <sup>CD</sup>	0.19(0.015) <sup>AB</sup>	9.7(2.6)	25(5.7)	280.0(12.07)
17	0.034(0.0024)	0.028(0.0067) <sup>ABC</sup>	0.01(0.015) <sup>D</sup>	7.3(1.9)	19(4.4)	286.26(12.34)
21	0.036(0.0024)	0.043(0.0067) <sup>A</sup>	0.01(0.015) <sup>D</sup>	7.6(2.0)	20(4.7)	277.0(11.94)
28	0.033(0.0024)	0.040(0.0067) <sup>AB</sup>	0.03(0.015) <sup>D</sup>	7.4(1.9)	20(4.7)	279.2(12.04)
35	0.030(0.0024)	0.014(0.0067) <sup>BCD</sup>	0.02(0.015) <sup>D</sup>	8.2(2.2)	22(5.0)	271.7(11.71)
42	0.027(0.0024)	0.018(0.0067) <sup>ABCD</sup>	0.02(0.015) <sup>D</sup>	9.1(2.5)	23(5.3)	264.3(11.39)
49	0.034(0.0024)	0.001(0.0067) <sup>D</sup>	0.01(0.015) <sup>D</sup>	10.4(2.8)	25(5.8)	263.2(11.35)
	<b>P value</b>					
Treatment	0.91	0.74	0.58	0.36	0.38	0.08
Day	<.0001	<.0001	<.0001	0.23	0.06	0.01
Treatment × Day	0.04	0.95	1.00	0.97	0.95	0.04

\*The different letters in columns indicate Tukey's significant difference at a significance level of  $\alpha = 0.05$ .

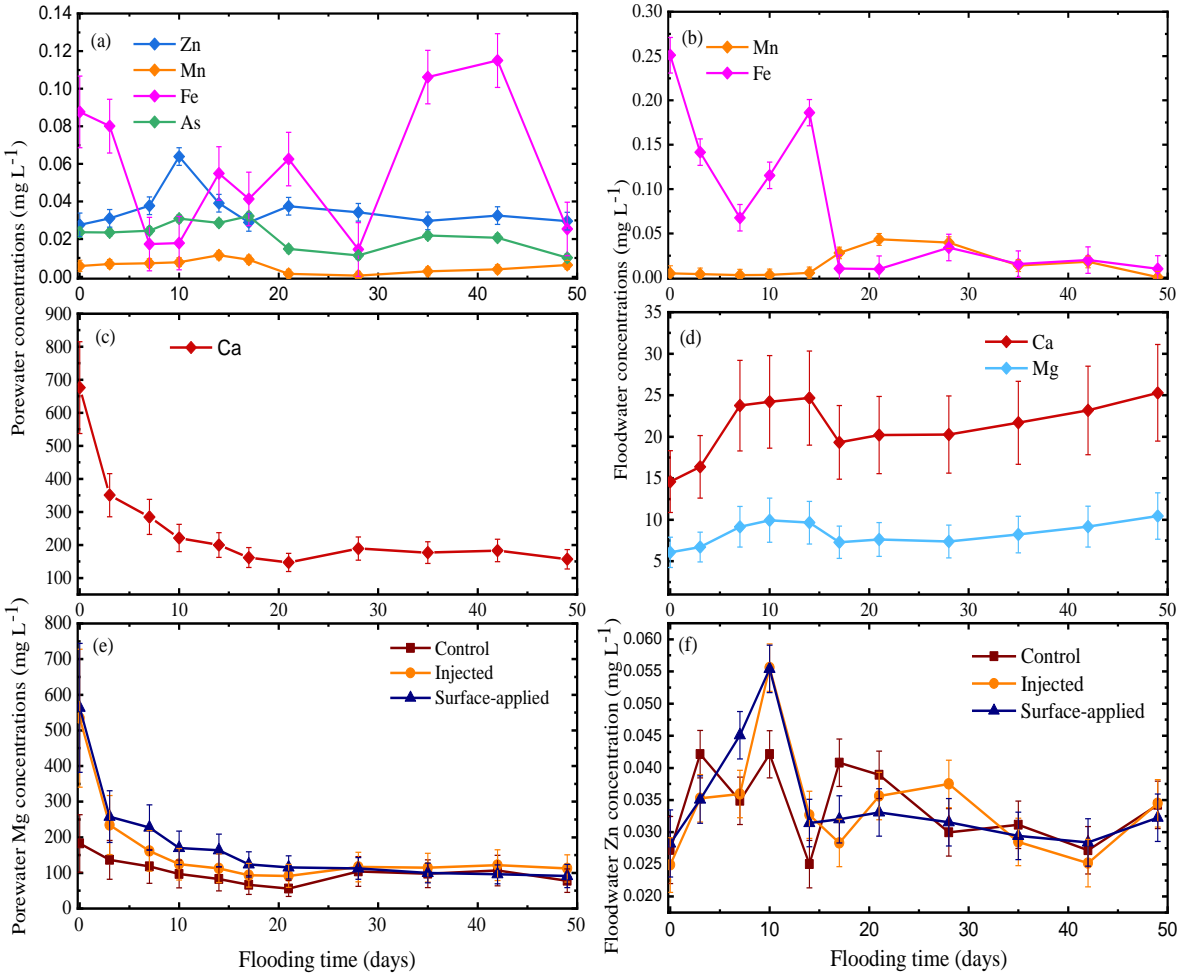


Figure 2-2. Mean concentrations (across Manure Treatments, when it is not significant, Tables 2-2 & 2-3) of (a) Zn, Mn, Fe, and As in pore water, (b) Mn and Fe in floodwater, (c) Ca in porewater, (d) Ca and Mg in floodwater. Mean concentrations for manure injected, surface-applied, and unmanured treatments of (e) Mg in porewater and (f) Zn in floodwater with flooding time (i.e., the metal(loid)s with significant Manure treatment  $\times$  Day interactions). Note: As concentrations in floodwater were below the detection limit (0.015 mg L<sup>-1</sup>).

#### 2.4.6 Soil geochemical changes and their influence on phosphorus and metal release.

Redox potential and pH are closely associated parameters in flooded soil and directly influence DRP and metal release. The day  $\times$  treatment interaction effect (Figure 2-3; Table 2-3) was significant for Eh changes. At the end of the flooding period, the manure surface applied treatment had the lowest soil Eh, while the manure injected treatment had the highest Eh. It has been well established that the addition of manure and other organic amendments causes soil Eh to decrease

more rapidly with flooding (Kashem & Singh, 2001; Gardiner & James, 2012) due to elevated organic carbon in the soil favouring microbial respiration through which the soil components get reduced.

Overall, the Eh values decreased over the period of flooding with some occasional fluctuations, similar to other studies with flooded soils (Amarawansa et al., 2015; Jayarathne et al., 2016). The rate of Eh decline was not as rapid in this study as has been observed in other studies (Shaheen et al., 2014; Vitharana et al., 2021), and this might be due to the frequent porewater sampling and addition of water after every sampling session. Another possible reason for the slower decrease of Eh could be due to the cold temperatures used (Dharmakeerthi et al., 2019; Weerasekara et al., 2021) since microbial activities are lower under cold temperatures (Stres et al., 2008; Jefferies et al., 2010). Even though the decrease in Eh was small in all three treatments, we observed a substantial increase in DRP concentrations in both porewater and floodwater. The mean soil redox potential (Eh) of all three manure treatments (manure surface applied, injected, and unmanured) ranged between 200 – 300 mV. The threshold value for the  $\text{Fe}^{3+}$  reduction is below 100 mV (Patrick et al., 2015), which might be the reason for not seeing a large increase in porewater concentrations of Fe with flooding time. However, slight but significant increases in porewater concentrations were observed for most metals (Fe, Mn, Zn) with flooding time, even though soils were not severely reduced.



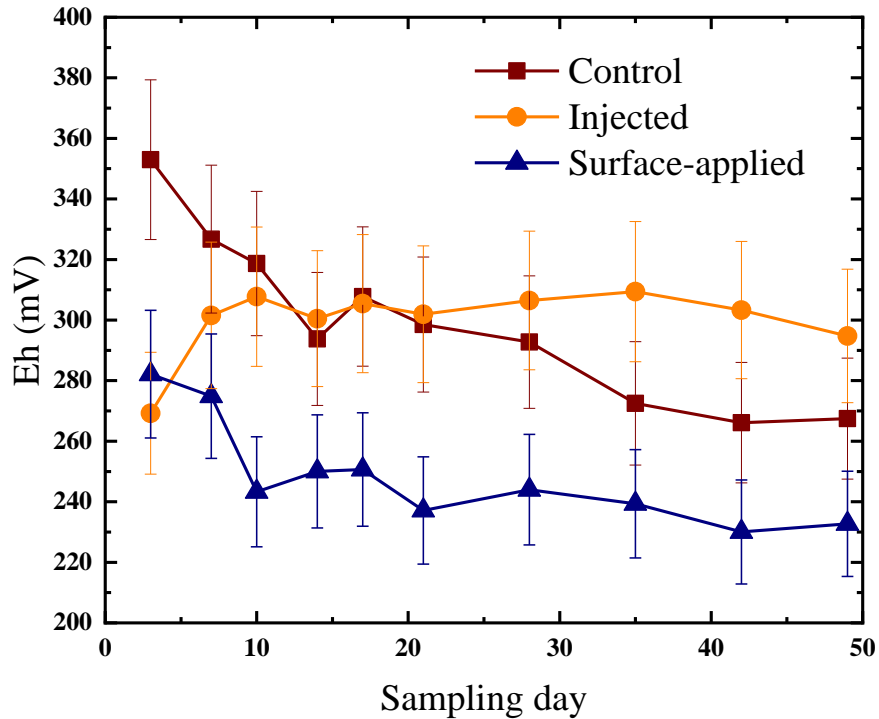


Figure 2-3. Changes in soil redox potential (Eh) over the 49 days of flooding in manure-injected, surface-applied, and unamended (control) soils. Standard errors of the mean redox values are represented by the error bars.

The porewater and floodwater pH values varied from 7 to 8. The effect of flooding day was significant (Table 2-1). The pH of both porewater and floodwater increased significantly from day 1 to day 3, and thereafter, porewater pH remained relatively stable while floodwater pH decreased slightly over time. The pH decrease over flooding in alkaline soils is a well-explained phenomenon and has been attributed to the formation of carbonic acid by the reaction of water and carbon dioxide accumulated under anoxic conditions (Ponnamperuma, 1972; Fageria et al., 2011). Previous studies with alkaline soils have shown a pH decrease over the flooding time, particularly in porewater, with a corresponding increase in Ca and Mg concentrations (Jayarathne et al., 2016; Concepcion et al., 2021). They attributed the increased Ca and Mg concentration to the enhanced dissolution of Ca and Mg minerals as a result of pH decrease and/or the addition of water (i.e., dilution effect). Even though we used alkaline soils in our study, highly reduced conditions were

not observed in the soils with flooding, which could be why porewater pH did not decrease during the flooding period. However, we still observed increased Mg and Ca concentrations in floodwater due to greater dissolution reactions with the addition of ultrapure water. In the current study, the release of P and metal(loid)s with flooding did not seem related to pH changes since pH remained relatively stable throughout the flooding period.

## 2.5 Conclusions

Prolonged flooding mobilized P and some metals, increasing their concentrations in porewater and floodwater with time, irrespective of manure application method. As a good management practice, promptly draining agricultural lands prone to temporary flooding is suggested. Application of manure and the method of manure application (injected vs. surface) did not significantly increase floodwater dissolved reactive P compared to the unamended control, which could be due to the high soil test P in this long-term manured field combined with the time gap of 4 weeks between the manure application and the flooding event that allowed time to sorb P onto the soil colloids reducing mobilization. Since snowmelt is a complex hydrological process in the natural environment, a field study would provide insight into how hydrological parameters such as temperature can impact the mobilization of P and metals. Furthermore, agricultural soils are a heterogeneous mixture of organic and inorganic materials, which further adds to the complexity of understanding the dynamics P and metal mobilization.

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### **3. COMPARISON OF MANURE APPLICATION METHODS ON NUTRIENT AND METAL LOSS WITH SNOWMELT FLOODING**

#### **3.1 Abstract**

Manure injection is well documented to reduce rain-driven nutrient losses, but the effect on snowmelt-driven losses is less studied. This study examined the surface application versus injection of liquid swine manure on phosphorus (P), nitrate-nitrogen (nitrate-N), zinc (Zn), manganese (Mn), iron (Fe), magnesium (Mg), and calcium (Ca) release from soils to snowmelt runoff. Manure was applied in the fall of 2021 to four replicated plots of surface-applied or injected treatments, and boxes were installed to collect snowmelt runoff in each plot, including four unmanured (control) plots. In the spring of 2022, the snowmelt was collected from each box for 10 days, volume was recorded, and analyzed for dissolved reactive P (DRP), nitrate-N, Zn, Mn, Fe, Mg, and Ca concentrations, and pH. The mean daily snowmelt volume ranged between 2.9 and 25.2 L, while the mean snowmelt DRP concentrations in runoff for manure injected, surface-applied, and control treatments were 0.66, 0.89, and 0.65 mg L<sup>-1</sup>, respectively. Snowmelt DRP concentrations increased ~4.2-fold over the sampling period compared to the beginning. Snowmelt DRP concentration was 26% (P= 0.07) lower with manure injection than when surface applied. The effect of the manure application method on nitrate-N (3.27 to 3.60 mg L<sup>-1</sup>) and metal concentrations in the snowmelt was not significant. Nitrate-N concentration increased by 44-fold on the last day of sampling relative to day 1. The cumulative loads (mean across application methods and sampling days in kg ha<sup>-1</sup>) of DRP (0.56), nitrate-N (4.03), and metals [Zn (0.11), Mn (0.01), Fe (0.18), Mg (8.03), Ca (21.70)] mobilized with snowmelt runoff did not significantly vary among the manure application methods and were primarily controlled by the snowmelt volume rather than their concentrations. Therefore, land management practices that reduce the

volume of snowmelt discharge could be more effective for reducing the P, nitrate-N, and metal loss from manured soils.

**Keywords:** snowmelt, liquid-swine-manure, dissolved reactive phosphorus, nitrate-N, metals.

### 3.2 Introduction

Phosphorus (P) is essential for plant growth and development as an important element in producing nucleic acids, phospholipids, and several metabolites (Ajmera et al., 2019), and therefore is often supplemented in the form of fertilizer or manure. However, P is accumulated in the soil when manure is applied exclusively to address the nitrogen (N) requirements (Liu et al., 2015). The transport of excessive P loads to surface water bodies from agricultural lands is a major source of water pollution (Kumaragamage and Akinremi, 2018; Reid et al., 2018). It promotes eutrophication, which is detrimental to water quality, aquatic life, and human consumption (Schindler et al., 2016).

Livestock manure is one of the main sources of N and P for crop growth in Canada. In Manitoba, the usage of swine waste as manure for crop production is a common management practice due to the abundant supply (Khaleel et al., 1980; Choudhary et al., 1996). In addition to N, P, and other major nutrients, heavy metals are found in livestock manure (Olatuyi et al., 2014; Nicholson et al., 1999) since they are naturally present in livestock feed or included as supplements (An et al., 2020). A study by Guo et al. (2018) reported that the long-term swine manure application resulted in zinc (Zn), copper (Cu), lead (Pb), chromium (Cr), and nickel (Ni) accumulation in the soil; among them, Zn and Cu were found as the most significant metal pollutants.

During the winter season in the Canadian prairies, the soil surface stays frozen for months due to temperatures below the freezing point. Due to the unique flat geographical features and the impermeable frozen clay soils, spring snowmelt flooding is a prominent hydrological event in the

region. Approximately 80% of the runoff volume that Lake Winnipeg receives is from snowmelt runoff (Dibike et al., 2012; Liu et al., 2019). Therefore, snowmelt is the dominant mechanism for mobilization of nutrients and contaminants from agricultural lands to the surface water bodies in the Canadian Prairies (Corriveau et al., 2011; Reid et al., 2018). Prolonged flooding during the spring snowmelt period induces anaerobic conditions and a series of redox reduction reactions which trigger microbial-driven reductive dissolution of iron (Fe) and manganese (Mn) compounds, that are often associated with P release (Ajmone-Marsan et al., 2006; Amarawansa et al., 2015; Scalenghe et al., 2012). In selected 11 sub-watersheds of the Red River Valley, Rattan et al. (2017) showed that 62% of the annual total P loads to Lake Winnipeg were received via snowmelt, implying the significant contribution of snowmelt in increasing P loads.

Different pathways for mobilization of contaminants and pollutants from manured soils are reported in literature (Allen and Mallarino, 2008; Ceretta et al., 2010; Legros et al., 2013). Even though there are ample studies (Coelho et al., 2012; Kang et al., 2011; Nelson et al., 2005) for the P and metal losses from manured lands via rain-driven runoff and leaching, studies on snowmelt runoff of excess contaminants and nutrients are limited. Greater losses of dissolved reactive P (DRP), calcium (Ca), magnesium (Mg), manganese (Mn), and iron (Fe) in snowmelt from a manured soil compared to an unmanured soil have been recently reported from a field snowmelt study (Lasisi et al., 2023).

Numerous research studies have reported a decrease in nutrient runoff losses from soils with injection of manure slurry compared to surface application (Jokela et al., 2016; Eghball and Power, 1999; Tabbara, 2003). Tabbara (2003) reported that the losses of DRP and total P were reduced to 30 to 60%, suggesting that the incorporation of manure is a best management practice to minimize surface water contamination. Even though most of these studies are carried out in a rain-runoff

setting, to our knowledge, there has been no research to investigate the P, N, and metal loss from soils under snowmelt flooding in field conditions with different manure application methods. This study aimed to determine the effect of liquid swine manure application method (injected and surface application of manure) on the P, nitrate N, and metal concentrations and loads in snowmelt runoff. Our hypotheses were (a) loss of P, nitrate, and metal is less with injected manure compared to surface-applied manure and (b) concentrations of P, nitrate-N, and metal concentrations in snowmelt will increase with the prolonged snowmelt flooding.

### **3.3 Materials and methods**

#### **3.3.1 Site location and soil characterization**

The experimental site was an agricultural field in the Red River Basin located in Randolph, South-East Winnipeg, Manitoba (49°32'47.3" N 96°51'53.3" W). This region is vulnerable to flooding during spring snowmelt (McCullough et al., 2012) and is also classified as a P hotspot that transports substantial amounts of P into Lake Winnipeg (Lake Winnipeg Foundation, <https://doi.org/10.25976/hxqe-py39>). The experimental site has a long history of manure application. The soil at this site is classified as a Rego Humic Gleysol under the Osborne Series (MAFRI 2010). The texture of the soil was clay, with a 7.1% content of organic matter, while the pH was 7.9 and the Olsen P concentration was 99 mg kg<sup>-1</sup>.

#### **3.3.2 Experimental design**

The three manure treatments used were liquid swine manure spread on the plot surface (surface-applied manure), liquid swine manure applied by injection (injected), and unamended (control). Treatments were arranged in a randomized complete block design with four replicates, resulting in a total of twelve plots (1.2 × 1.2 m) that were separated with an alley of 0.6 m between plots. The liquid swine manure had a 1.87% solid content and total P content of 540 mg kg<sup>-1</sup> (fresh weight basis) and was evenly applied using plastic pails at an approximate rate of 170,000 L ha<sup>-1</sup> to match

the rate used by the farmer in the remaining land. The plots for the injected treatment were created by manually digging three 0.15-m deep trenches using a pickaxe, applying manure into the subsurface soils, and then backfilling the trenches with soil. Manual manure application was practiced, increasing the precision of the manure application rate and methods. High-density polyethylene lined boxes (1.2 m x 0.9 m x 0.6 m) supported by wooden frames were installed 0.15 cm into the soil of each plot to collect the snow and snowmelt in the winter and spring of 2022.

### **3.3.3 Snowmelt collection in the spring of 2022**

Snowmelt samples were collected from March 20 to April 6, 2022, for 10 days between 12 pm –2 pm when the temperature was above 0 °C and liquid water (snowmelt) was present in the box. The weather data was collected from the Environment Canada daily climate database of Kleefeld station, Manitoba, the nearest weather station to the field site. The snowmelt was pumped out to 20.0 L pails with a Mastercraft 12 V DC water pump. All the snowmelt water was pumped out from each runoff box during each sampling day. The collected snowmelt samples were homogenized, and the volumes were recorded. Then, subsamples of snowmelt were collected into 200-mL plastic bottles and immediately transferred to the laboratory inside a cooler. A random snowmelt sample was also collected each day of sampling for quality assurance. The snowmelt samples were immediately filtered using syringe filters (0.45 µm) and then stored in scintillation vials (20.0 mL) in a cooler at 4 °C before analysis for P, pH, and metals. Another set of samples was stored in the freezer at  $-20 \pm 1$  °C for nitrate-N analysis.

### **3.3.4 Analysis of snowmelt**

The filtered snowmelt samples were analyzed within 24 hours after collection for DRP concentrations using the molybdate blue method (Murphy and Riley, 1962) measuring the absorbance at 882 nm using the ultraviolet-visible spectrophotometer (Ultrospec 500 pro), and pH

using the Fisher Accumet AB15 pH meter. The remaining portions of snowmelt samples were acidified with concentrated nitric acid (20  $\mu$ L) and were preserved at  $4 \pm 1$  °C. The preserved samples were later analyzed at a commercial laboratory (Farmers Edge Inc, Winnipeg) for total dissolved P, Ca, Mg, Fe, Mn, selenium (Se), Ni, Cu, and Zn using the ICP-OES (iCAP 6500, Thermo Scientific) while nitrate-N was analyzed using the automated colorimetry after reduction by hydrazine.

### **3.3.5 Analysis of soil samples**

Composite soil samples were collected soon after the snowmelt collection from each plot (4 cores/plot) at 0-15 cm depth using a Dutch auger and stored in the cooler at 4 °C until further analysis. The collected soil samples were air-dried and sieved using a 2 mm mesh after being ground. The soils were extracted for available P using the Olsen- P method (Olsen et al., 1954) and metal content using the Mehlich-3 extractable method (Mehlich, 1984). The extracts were analyzed for P concentration using the molybdate blue colour method (Murphy and Riley, 1962), while the metals were analyzed using the inductively coupled plasma-optical emission spectrometry (ICP-OES; iCAP 6500, Thermo Scientific).

### **3.3.6 Statistical analysis**

The daily DRP and metal loads were calculated as the product of daily concentrations and daily snowmelt volume. Cumulative loads were calculated as the sum of daily loads for all sampling days during the snowmelt. Volume-weighted concentrations for each plot were calculated by dividing the cumulative loads by the respective cumulative snowmelt volume. Analysis of variance (ANOVA) was performed for DRP, pH, nitrate-N, and metal concentrations of the snowmelt samples using the mixed procedure for repeated measures (PROC GLIMMIX) utilizing the SAS OnDemand for Academics online software (SAS Institute, 2014). We used a two-way ANOVA

where the fixed effect was manure treatment (application method), the random effect was the block (replicates), and the sampling day was the repeated factor. A one-way ANOVA was used for the cumulative loads, volume-weighted concentrations, and Mehlich-3 extractable P and metals, where the manure treatment was the fixed effect, and the block was the random effect. Compound-symmetry (CS) covariance structure was used after selection as the most fitting. The data that were not normally distributed were transformed using natural log transformation when needed. Pearson correlation coefficients and linear regressions were used to test the relationships between the snowmelt volume, DRP, pH, and the concentration of selected metallic elements. Mean comparison was conducted using the Tukey's or Tukey-Kramer method, and all statistical analyses were performed at a significance level of  $\alpha = 0.1$ .

### **3.4 Results**

#### **3.4.1 Air temperature during the snowmelt sampling period**

The maximum temperature recorded during the 10 days of field sampling was in the range of 1.3 - 9.4 °C (Figure 3-1). The total precipitation was 10.2 mm, including rain on days 3 and 7 during the sampling period. Sampling dates were not consecutive since the temperature dropped below freezing point after the first five sampling days starting from March 20. Sampling resumed on March 29th, April 1st, 4th, 5th, and 6th when the air temperature was above the freezing point and melt was available to collect.



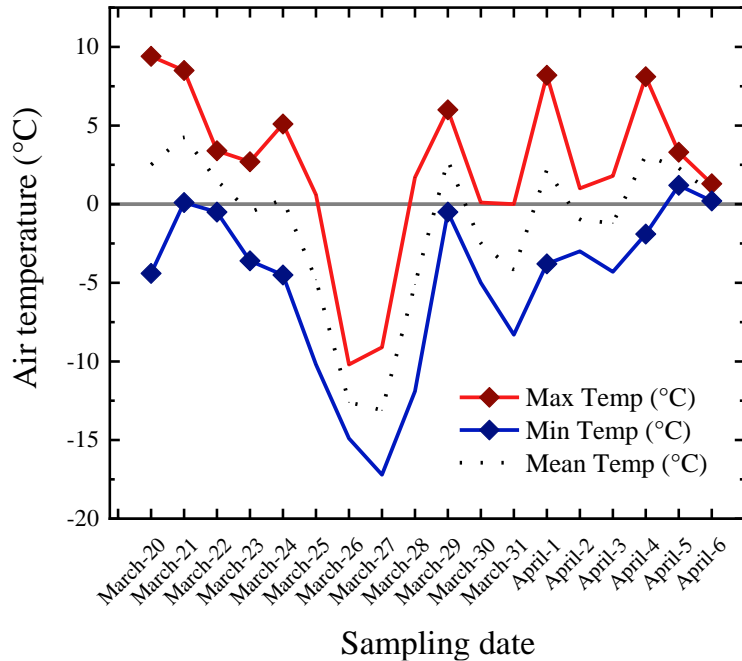


Figure 3-1. Changes in the maximum, minimum, and mean air temperature (°C) over the sampling period. Snowmelt sampling dates are represented by symbols.

### 3.4.2 Dissolved reactive phosphorus (DRP) concentrations, loads, and daily snowmelt volume.

The mean daily snowmelt volume ranged from  $2.9 \pm 0.47$  to  $25.2 \pm 4.15$  L throughout the sampling period of 10 days (Table 3-1). The effect of sampling day ( $P < 0.0001$ ) was significant (Table 3-1). The highest snowmelt volume was recorded on day 3 of sampling and was significantly larger than the daily snowmelt volume during days 6 to 10. In general, the volumes of the first half of the sampling period were higher than the latter half of the sampling period. The snowmelt volume on the last sampling day was significantly lower (approximately 50%) compared to day 1.

The mean DRP concentrations varied from  $0.31 \pm 0.070$  to  $1.30 \pm 0.093$  mg L<sup>-1</sup> (Table 3-1), while the mean concentrations of total dissolved P were in the range of  $0.34 \pm 0.083$  to  $1.24 \pm 0.111$  mg L<sup>-1</sup>. More than 90% of total dissolved P was present as DRP in snowmelt, which is also the bioavailable fraction. Therefore, our discussion will focus on DRP concentrations and loads. The day  $\times$  treatment effect was significant for DRP concentrations ( $P = 0.01$ ; Table 3-1). The mean DRP

concentration did not vary among the manure application methods for the first 5 days of sampling. However, it was significantly higher in the manure surface-applied, compared to manure injected and control treatments, from days 7 to 8 (Figure 3-2). The manure surface-applied treatment had the highest mean daily DRP concentration across days of sampling, which was 1.3-fold and 1.4-fold higher than the injected and control treatments, respectively (Table 3-1). Across the treatments, the DRP concentration increased over the sampling period (Figure 3-2). The peak DRP concentration was recorded on the last day of sampling and was 4.2-fold higher than the first day of sampling.

Table 3-1. Daily snowmelt volume dissolved reactive phosphorus (DRP) and nitrate-nitrogen concentrations of the snowmelt over the flooding period in manure injected, surface-applied, and unamended (control) soil. Least square means are presented with associated standard errors in parentheses. Mean comparison is shown only when the interaction is not significant. The different letters in columns indicate Tukey's or Tukey-Kramer's significant difference at a significance level of  $\alpha = 0.1$ .

	<b>Daily snowmelt volume</b>	<b>DRP</b>	<b>Nitrate-N</b>
	L		mg L <sup>-1</sup>
<b>Manure Treatment</b>			
Control	9.2(1.19)	0.65(0.074)	3.6(1.77)
Injected	10.0(1.28)	0.66(0.074)	3.6(1.80)
Surface-applied	6.8(0.88)	0.89(0.074)	3.2(1.63)
<b>Day</b>			
1	13.2(2.18) abc	0.31(0.070)	0.8(0.26) f
2	9.8(1.62) bcd	0.34(0.070)	1.0(0.34) f
3	25.2(4.15) a	0.33(0.070)	0.7(0.23) f
4	10.8(1.77) bcd	0.64(0.070)	1.6(0.53) ef
5	15.3(2.52) ab	0.49(0.070)	1.5(0.51) f
6	2.9(0.47) e	0.75(0.070)	4.9(1.65) cd
7	9.6(1.59) bcd	0.85(0.070)	3.8(1.26) de
8	5.7(0.93) de	1.17(0.070)	9.7(3.24) bc
9	4.4(0.84) e	1.15(0.078)	18.1(6.44) ab
10	6.1(1.43) cde	1.30(0.093)	34.9(13.85) a
<b>P value</b>			
<b>Treatment</b>	0.14	0.07	0.99
<b>Day</b>	<.0001	<.0001	<.0001
<b>Treatment × Day</b>	0.74	0.01	0.99

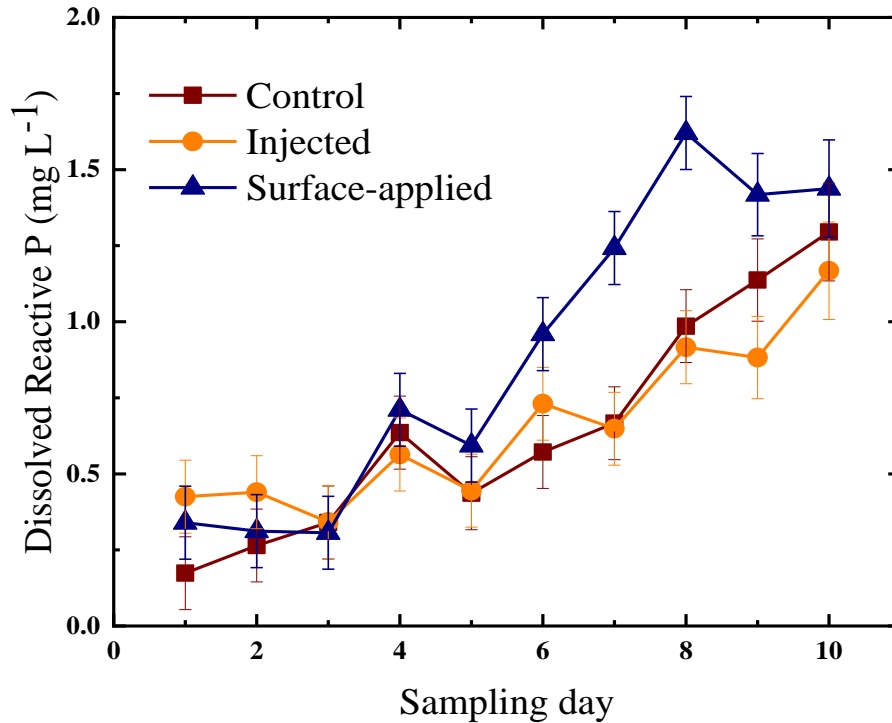


Figure 3-2. Changes in dissolved reactive P (DRP) concentrations over the 10 days of snowmelt period in manure injected, surface-applied, and unamended (control) soil. The error bars represent standard errors of the mean DRP concentration values.

### 3.4.3 Nitrate-nitrogen (nitrate-N) concentrations

The mean concentration of nitrate-N in snowmelt was in the range of  $0.7 \pm 0.23$  and  $34.9 \pm 13.85$  mg L<sup>-1</sup>. There was a significant day effect for the nitrate-N concentration (Table 3-1). Across the treatments, the nitrate-N concentrations increased with the sampling day. The highest concentration was recorded on the last day (day 10) of sampling, which was 44-fold higher than day 1.

### 3.4.4 Zn, Mn, Fe, Mg, and Ca concentrations of the snowmelt

A significant treatment effect or day  $\times$  treatment interaction effect was not found for any of the metal concentrations in the snowmelt (Table 3-2). The day effect was significant for all five metals tested. Zn concentrations were lower at the beginning of the sampling, the fluctuated and started to increase towards the latter phase of sampling. There was a significant and 3-fold increase in Zn

concentration on day 10 compared to day 1. The Mn concentrations were relatively lower compared to the other metals and fluctuated throughout the sampling period. The Fe concentrations were relatively high during the first 5 days of sampling compared to the last 5 days. The highest Fe concentration was detected on day 5, which was 7-fold larger than the day 10 concentration. A high spike in Mg concentration was observed from day 8 onwards, with the highest concentration on day 10, which was significantly and 18.4-fold higher than on day 1. The snowmelt Ca concentrations increased over time, with the highest Ca concentration on day 10, which was significantly and 9.4-fold greater than on day 1.

Table 3-2. Dissolved concentrations of Zn, Mn, Fe, Mg, and Ca of snowmelt in manure injected surface-applied, and unamended (control) soil. Values in parentheses are standard errors. The different letters in columns indicate Tukey's significant difference at a significance level of  $\alpha = 0.1$ .

	<b>Zn</b>	<b>Mn</b>	<b>Fe</b>	<b>Mg</b>	<b>Ca</b>	<b>pH</b>
<b>Manure Treatment</b>	<b>mg L<sup>-1</sup></b>					
Control	0.14(0.017)	0.010(0.0028)	0.17(0.013)	8.8(2.20)	25.6(5.51)	7.6(0.04)
Injected	0.12(0.014)	0.009(0.0026)	0.14(0.013)	8.5(2.12)	23.8(5.12)	7.6(0.04)
Surface	0.12(0.014)	0.010(0.0027)	0.16(0.013)	8.9(2.23)	25.6(5.50)	7.6(0.04)
<b>Day</b>						
1	0.09(0.014) d	0.018(0.0059) a	0.26(0.033) ab	3.3(0.58) e	12.7(1.94) de	7.6(0.04) c
2	0.11(0.017) dc	0.019(0.0062) a	0.20(0.033) abc	3.7(0.66) e	14.1(2.15) e	7.5(0.04) c
3	0.04(0.007) e	0.006(0.0022) a	0.13(0.033) bc	2.8(0.51) e	11.1(1.69) e	7.3(0.04) d
4	0.09(0.014) d	0.005(0.0018) a	0.25(0.033) ab	4.8(0.85) e	15.9(2.43) de	7.6(0.04) bc
5	0.08(0.013) de	0.006(0.0021) a	0.34(0.033) a	3.7(0.66) e	11.1(1.70) e	7.5(0.04) c
6	0.19(0.030) abc	0.007(0.0026) a	0.10(0.033) bc	11.0(1.96) c	26.9(4.11) c	7.5(0.04) c
7	0.16(0.026) abcd	0.007(0.0028) a	0.06(0.033) c	7.4(1.33) cd	18.6(2.84) cd	7.6(0.04) c
8	0.14(0.023) bcd	0.010(0.0038) a	0.05(0.033) c	20.4(3.64) b	47.8(7.29) b	7.9(0.04) ab
9	0.34(0.061) a	0.019(0.0069) a	0.10(0.038) bc	38.6(7.44) a	85.2(13.93) a	7.9(0.04) a
10	0.27(0.058) ab	0.013(0.0053) a	0.05(0.046) c	59.8(12.96) a	120.2(22.02) a	7.9(0.05) ab
	<b><i>P value</i></b>					
<b>Treatment</b>	0.56	0.99	0.28	0.99	0.96	0.79
<b>Day</b>	<.0001	0.02	<.0001	<.0001	<.0001	<.0001
<b>Treatment × Day</b>	0.69	0.88	0.93	0.89	0.87	0.96

### 3.4.5 Snowmelt pH

The mean pH values ranged from  $7.3 \pm 0.04$  to  $7.9 \pm 0.04$  across the treatments and the sampling days (Table 3-2). A significant effect of sampling day on pH was observed. The pH was significantly lower on day 3 compared to day 1. However, the pH again increased during the final stage of the sampling period, where the pH of day 10 was significantly higher than that of day 1.

### 3.4.6 Cumulative snowmelt volume, cumulative loads, and volume-weighted concentrations DRP and nitrate-nitrogen (nitrate-N).

The mean daily DRP loads ranged between  $0.7 \pm 0.39$  to  $2.0 \pm 2.07$  mg per plot ( $1.08 \text{ m}^2$ ). Manure treatment effect and day  $\times$  treatment interaction were not significant, while the effect of sampling day was significant ( $P < .0001$ ) for daily DRP loads. Daily DRP load fluctuated during the sampling period. The effect of manure treatment on the cumulative snowmelt volume and cumulative loads was not significant ( $P > 0.1$ ; Table 3-3). As with snowmelt concentrations, we observed higher cumulative loads for nitrate-N, Mg, and Ca compared to cumulative loads of DRP, Zn, Mn, and Fe coming onto snowmelt from the tested long-term manured land on calcareous parent material. The volume-weighted concentrations for DRP, nitrate-N, Zn, Mn, Mg, and Ca were not significantly different among the tested manure application methods/ treatments (data not shown). However, the volume-weighted concentrations ( $\text{mg L}^{-1}$ ) of Fe in the manure surface-applied treatment [0.21(0.011)] were significantly ( $P = 0.01$ ) higher than the manure-injected [0.15(0.011)] and unmanured [0.18(0.011)].

Table 3-3. Cumulative snowmelt volume and loads of dissolved reactive phosphorus (DRP), nitrate-nitrogen, and metal from manure injected, surface-applied, and unamended (control) treatments. Least square means are present with associated standard errors in parentheses.

Manure treatment	Cumulative volume	Cumulative loads							
	Snowmelt m <sup>3</sup> ha <sup>-1</sup>	DRP	Nitrate-N	Zn	Mn	Fe	Mg	Ca	
Control	1108(117.3)	0.53(0.109)	4.89(1.710)	0.14(0.019)	0.010(0.0036)	0.21(0.026)	10.2(2.33)	27.0(5.64)	
Injected	1122(117.3)	0.60(0.109)	3.85(1.710)	0.12(0.019)	0.012(0.0036)	0.18(0.026)	8.7(2.33)	23.9(5.64)	
Surface-applied	840(117.3)	0.53(0.109)	3.36(1.710)	0.09(0.019)	0.009(0.0036)	0.19(0.026)	7.2(2.33)	19.4(5.64)	
				<i>P value</i>					
Treatment	0.21	0.90	0.69	0.21	0.94	0.64	0.67	0.65	

### 3.4.7 Relationship between daily snowmelt DRP concentration, DRP load, pH, and snowmelt volume

The correlation between DRP concentration and pH was significant ( $P < 0.0001$ ) with a positive linear relationship ( $R^2 = 0.30$ ; Figure 3-3 a). There was a significant ( $P < 0.0001$ ) negative linear relationship ( $R^2 = 0.20$ ) between DRP concentration and snowmelt volume (Figure 3-3 b). The correlation between the DRP load and the snowmelt volume was significant ( $P < 0.0001$ ) and linear ( $R^2 = 0.30$ ; Figure 3-3 c), while the correlation between DRP concentration and DRP load was significant ( $P = 0.0038$ ) but with a weak linear relationship ( $R^2 = 0.07$ ).

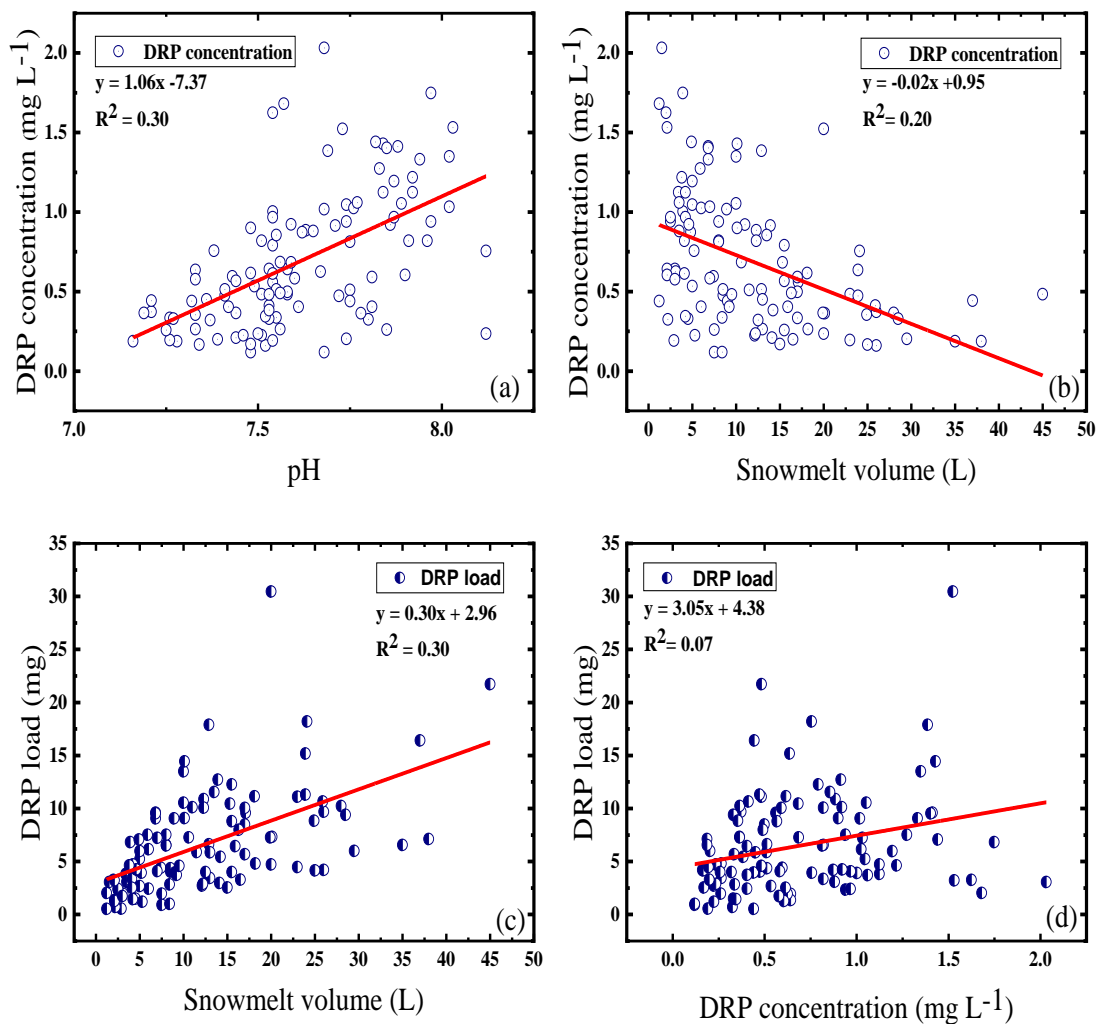




Figure 3-3. (a) Relationships between daily dissolved reactive P (DRP) concentration (mg L<sup>-1</sup>) with pH and (b) daily snowmelt volume (L). (c) Relationships between daily DRP load (mg) with daily snowmelt volume (L) and (d) daily DRP concentration.

### 3.4.8 Relationship between snowmelt nitrate-nitrogen concentration, nitrate-nitrogen load, pH, and snowmelt volume

Significant correlations were observed for nitrate-N concentration with pH and snowmelt volume, even though the  $R^2$  values were low. The correlation between nitrate-N concentration and pH was significant ( $P=0.007$ ) with a positive linear relationship ( $R^2 = 0.06$ ; Figure 3-4 a). The correlation between the nitrate-N concentration and the snowmelt volume was significant ( $P < 0.0001$ ) with a negative linear relationship ( $R^2 = 0.16$ ; Figure 3-4 b), while there was no significant correlation ( $P=0.101$ ) found with the nitrate-N load with the snowmelt volume.

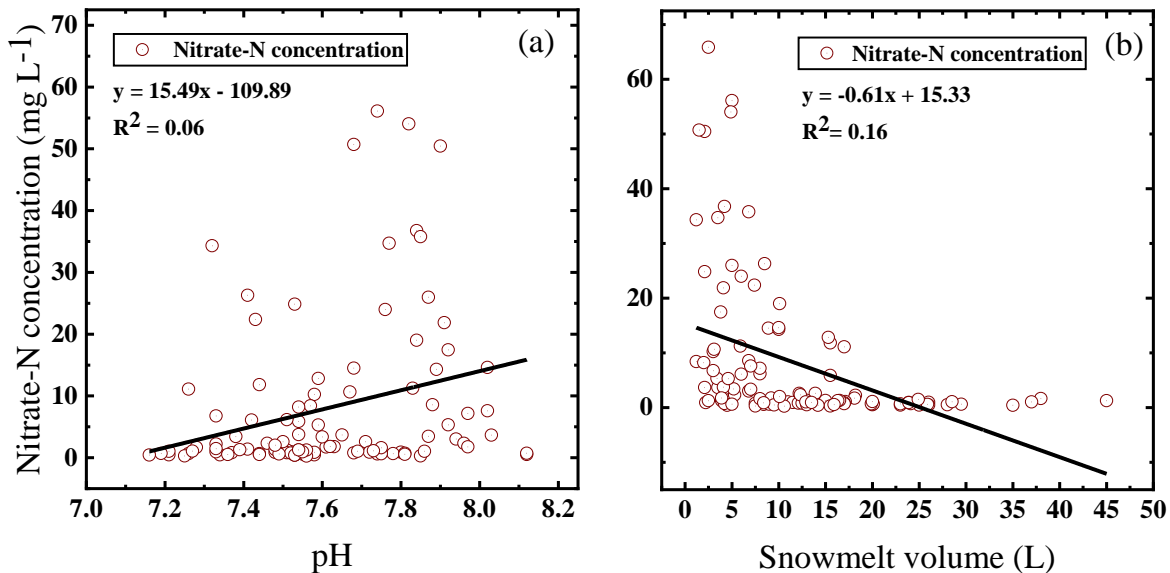


Figure 3-4. Relationships between (a) nitrate-nitrogen (nitrate-N) concentration (mg L<sup>-1</sup>) with pH and (b) snowmelt volume (L).

### 3.4.9 Relationship between metal concentrations, metal loads, and snowmelt volume in snowmelt

Significant correlations ( $P < 0.001$ ) and negative linear relationships were observed for concentrations of Zn ( $R^2 = 0.32$ ), Mg ( $R^2 = 0.15$ ), and Ca ( $R^2 = 0.15$ ) with snowmelt volume. The

correlations and linear relationships between the snowmelt volume and the metal loads of Zn ( $R^2=0.12$ ), Mn ( $R^2=0.41$ ), Fe ( $R^2=0.41$ ), and Ca ( $R^2=0.06$ ; Figure 3-5) were significant and positive, except for Mg load ( $P= 0.89$ ).

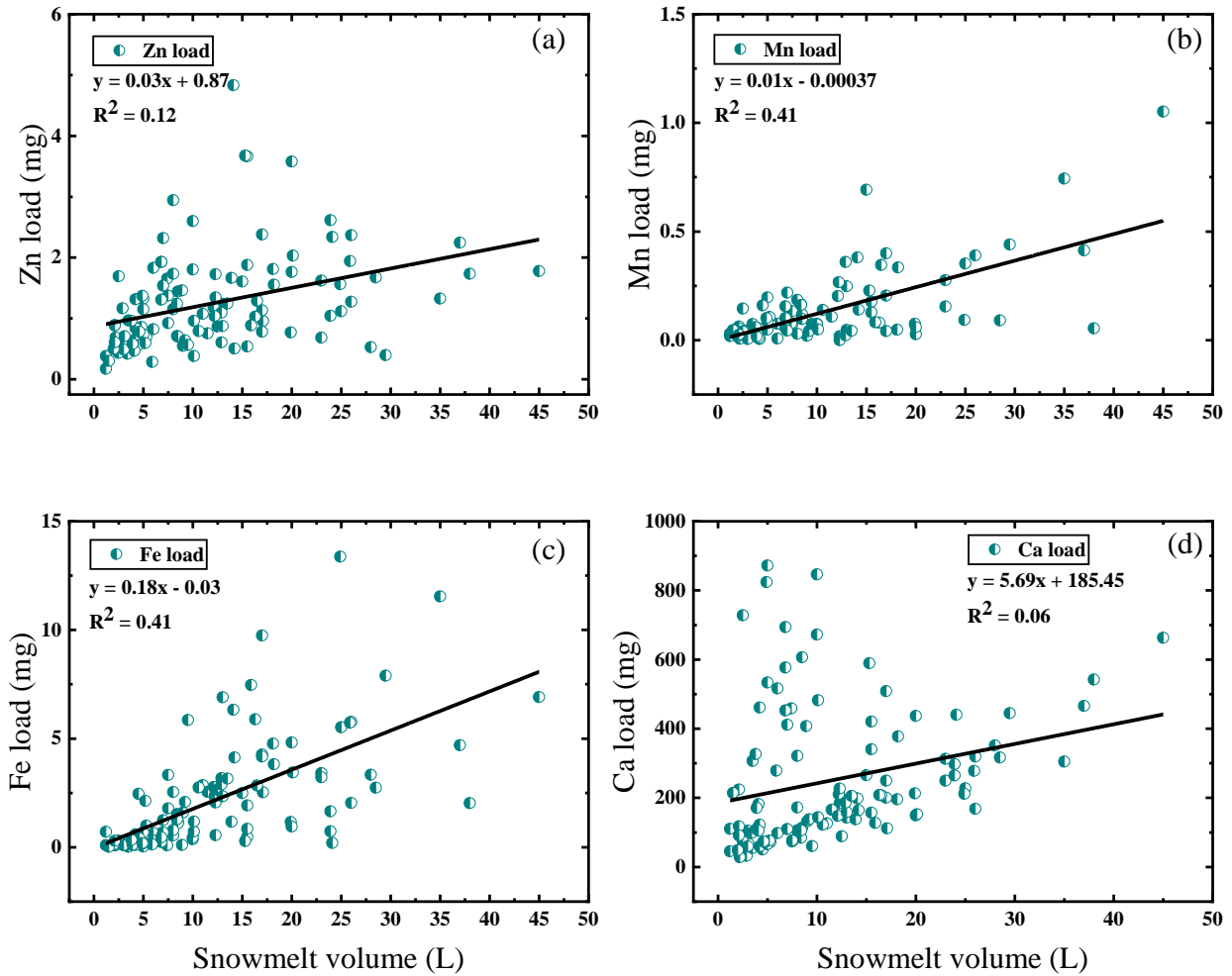


Figure 3-5. Relationships between (a) Zn, (b) Mn, (c) Fe, and (d) Ca loads (mg) in snowmelt water over a 10-day melt period with snowmelt volume (L).

### 3.4.10 Olsen P and Mehlich-3 extractable metal concentrations

The mean Olsen P values for manure injected, surface-applied, and control treatments were  $91.44 \pm 16.27$ ,  $105.07 \pm 16.27$ , and  $98.26 \pm 16.27$  mg kg<sup>-1</sup>, respectively. The treatment effect was not significant ( $P= 0.92$ ). Similarly, no treatment effect was found for any of the Mehlich-3 extractable metals (Supplemental Table S2).

## 3.5 Discussion

### 3.5.1 Snowmelt DRP concentrations

The snowmelt DRP concentrations were low ( $<0.5 \text{ mg L}^{-1}$ ) at the beginning of the snowmelt period, which is to be expected since the near-surface soils would remain frozen during the initial stage of snowmelt with limited interaction between soil and melting snow. Snowmelt from the manured and control plots had similar DRP concentrations, probably due to the residual P from the long-term manure application in the study site and limited mineralization processes in the frozen soils (Jarvis et al., 1996; Stres et al., 2008; Blackwell et al., 2010). As the soils thawed, snowmelt DRP concentrations increased with the duration of sampling due to the P release from soils, a process that could have been aggravated by the anaerobic conditions developed with the snowmelt flooding. Even though Eh was not measured in the field, a previous study showed reduced conditions in alkaline soils during the spring snowmelt period (Lasisi et al., 2023), which could enhance P release to overlying water (Vitharana et al., 2021; Van et al., 2022). Furthermore, the warming temperatures with the progressing spring could have increased the solubility of the phosphate compounds. The change in soil pH is another factor associated with DRP release, which was significantly correlated with DRP and was consistent with previous studies (Ni et al., 2020; Fortune et al., 2005; Wang et al., 2012).

The snowmelt DRP concentrations were greater in manure-treated plots than in the control. We expected lower DRP concentrations in the manure injected treatment as injection/incorporation of manure can form complexes with soil colloidal fraction and retain P (Kleinman et al., 2009). Previous research studies have shown higher nutrient and antimicrobial in rain runoffs associated with the surface application of manure compared to the sub-surface application (Daverede et al., 2004; Joy et al., 2013). Previous research studies conducted under rain runoff conditions have shown higher nutrient and antimicrobial in runoff. Our results, for the first time, show that the

manure injection is effective in reducing the DRP concentration of the overlaying snowmelt floodwater, compared to the surface application of manure and observed on days 7 and 8 of the flooding period.

### **3.5.2 Snowmelt Nitrate – N concentrations**

Manure surface-applied treatment had the numerically lowest mean nitrate-N concentration compared to the manure injected and control treatments. This could be due to the enhanced denitrification of nitrates that occurs on the soil surface under freeze-thaw cycles (Christianson & Cho, 1983; Phillips, 2008). We observed nitrate-N concentrations to increase across the sampling days in all treatments, with concentrations peaking in the last 3 days. Towards the end of the snowmelt period, the soil was exposed in most of the area within the box, and snow/ice cover was only present in small patches. This might have increased the rapid mineralization and nitrification with increasing temperature during the progression of spring, resulting in aerobic conditions favouring microbial activity. Furthermore, the microbial biomass in the soil immobilizes N within the cells (Brooks et al., 1998), and the collapse of the microbial biomass during the snowmelt period can also increase the release of N (Buckeridge et al., 2010; Isobe et al., 2018). Previous studies have shown elevated nitrate concentrations in the water discharge during snowmelt events (Corriveau et al., 2011; Townsend-Small et al., 2011).

### **3.5.3 Snowmelt metal concentrations**

Unlike DRP concentration, the manure application methods did not have any significant effect in reducing the metal concentrations in our study. However, relatively lower mean concentrations in snowmelt were observed for most metals (Mn, Fe, Mg, and Ca) for the manure-injected treatment compared to surface-applied and control treatments. A previous study by Lamba et al. (2019) reported a significant reduction ranging from 17% to 83% in mean flow-weighted concentrations

of copper, potassium, Mg, and Zn with subsurface-band application of boiler litter compared to surface application. Moreover, Kibet et al. (2013) showed a significant reduction of Zn concentration in surface runoff by subsurface application of broiler litter compared to surface application in a study using soil monolith lysimeters. The reasons for the lower metal concentrations in runoff with the subsurface application of manure can be attributed to the minimum interaction of manure metals with runoff water during a runoff event relative to the surface application of manure.

The initial concentrations of Zn, Mg, and Ca in the snowmelt were low but increased at the latter stage of sampling irrespective of the manure treatment, possibly due to the increased solubility with rising temperature when the spring progressed, as well as the temporal effect of snowmelt flooding. We observed higher Mg and Ca concentrations in snowmelt during the last three days, along with increased DRP concentrations, which is likely due to the dissolution of Mg and Ca phosphates when the soils have thawed. Previous studies have shown that flooding events can increase the concentrations of Zn, Mg, and Ca due to the development of anaerobic conditions (Kelly et al., 2020; Jayarathne et al., 2016; Dharmakeerthi et al., 2019). Fluctuations observed in Mn concentrations in the current study might have been caused by the development of anaerobic conditions and/or enhanced solubility with warming temperatures.  $Mn^{4+}$  acts as an alternative electron acceptor when oxygen is limited or under anaerobic conditions (Loeb et al., 2008; Unger et al., 2009). While previous studies have suggested the reductive dissolution of Mn-bound phosphate compounds under anaerobic conditions resulting in a simultaneous release of P and Mn (Patrick and Jugsujinda, 1992; Amarawansa et al., 2015), it is unlikely to happen in our study due to the short flooding duration and daily collection of snowmelt, preventing the development of severe reduced conditions. Contrary to previous research findings with flooded soils, we observe

a decrease in snowmelt Fe concentrations over time, which is possibly due to the re-oxidation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  over time when the soil became aerated in exposed areas, and precipitation as  $\text{Fe}(\text{OH})_3$  (Kuo and Mikkelsen, 1979; Patrick and Khalid, 1974; Young and Ross, 2001) and/or other insoluble Fe-compounds.

#### **3.5.4 Snowmelt volume effect on nutrient and metal loads**

Even though the injection of liquid swine manure significantly reduced the DRP concentration during the latter part of the snowmelt period than the surface-applied treatment, the cumulative DRP load with snowmelt and volume-weighted concentrations of DRP in the snowmelt were not significantly different between the manure application methods. Similarly, cumulative loads and volume-weighted concentrations of nitrate-N or metals were not significantly different. The reason is the higher snowmelt volumes recorded from the manure-injected plots than in the surface-applied treatment.

Thus, the snowmelt volume was the main governing factor that determined the DRP, nitrate-N, and metal loads with snowmelt runoff. This is supported by the positive linear relationship between DRP load and snowmelt volume compared to the weak linear relationship between DRP load and DRP concentration. Previous studies conducted in cold climate regions have also reported similar linear relationships between snowmelt volume and DRP load (Tiessen et al., 2010; Baker et al., 2014; Lasisi et al., 2023). Similarly, the Zn, Mn, Fe, and Ca loads had significant correlations and positive linear relationships with the snowmelt volume, further implying the important role of the snowmelt volume during a snowmelt flooding event on nutrient and metal loss from soils.

### **3.6 Conclusions**

Concentrations of DRP, nitrate-N, Zn, Mn, Ca, and Mg increased in the snowmelt with time, suggesting that the longer the spring snowmelt flooding period, the greater their release to

snowmelt. In general, manure injection significantly reduced DRP concentrations compared to surfaced application, but not concentrations of nitrate-N and metals. Irrespective of the manure application method, the snowmelt volume was the controlling factor of the DRP, nitrate-N, and metal loads to snowmelt in this study. Therefore, reducing DRP concentration through manure injection alone will not result in a reduced load, and we suggest management practices focused on reducing the duration of the snowmelt flooding period and snowmelt runoff volumes (i.e., improving infiltration, increasing surface roughness, and proper drainage) to reduce the offsite transport of P, nitrate-N, and metals.

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## 4. OVERALL SYNTHESIS

### 4.1 Background, Findings, and Implications

The agriculture industry (crop and animal production) is one of the major industries in the province of Manitoba, which accounted for 5% (\$3.1 billion) of the provincial GDP in 2019 (Manitoba Analytics, 2020). Supplying sufficient quantities of macro and micro-nutrients is very important to maintain healthy crops and achieve higher harvests. Therefore, proper nutrient management is necessary, and manure is used in the province as a nutrient supplement alongside fertilizer. Since the Province of Manitoba is the major pork producer in the country (Government of Manitoba, 2022), a consistent supply of swine manure is available to be used as a nutrient supplement. Despite being a good nutrient source, liquid swine manure poses an increased risk of releasing pollutants and contaminants to the environment, threatening the surface water sources when applied to agricultural fields (Tabbara, 2003; Bakhsh et al., 2005; Thurston-Enriquez et al., 2005; Berenguer et al., 2008). These pollutants and contaminants could be in various forms, such as excess nutrients (P and N), metal(loid)s, antibiotics, pathogens, hormones, etc. Elevated P and nitrate-N concentrations could lead to high losses of P and N from soils to waterways with runoff and leaching and subsequent eutrophication in freshwater systems. Runoff and leaching losses of metals could increase metal concentrations in water bodies, which would result in bioaccumulation in freshwater organisms (Rubalingeswari et al., 2021) and harmful effects on human health. There are growing concerns regarding the environmental sustainability associated with swine manure applications and nutrient management. Therefore, evaluating the impacts of swine manure application methods is critical to reducing nutrient and metal(loid)s transport in prairie landscapes. Snowmelt runoff is a crucial hydrological process in the Canadian Prairies, including the Province of Manitoba. Due to the flat landscapes, lands get temporarily flooded during the snowmelt period, and the subsequent snowmelt runoff is the major pathway that mobilizes the excess nutrients from

agricultural lands to waterways. Manure injection has often been studied in previous research to reduce the flux of these pollutants and contaminants with rain-driven runoff losses (Ball Coelho et al., 2007; Aillery et al., 2014). However, the impact of manure injection in fall on nutrient and metal release to snowmelt runoff during the spring snowmelt period has not been studied. This research compared the surface and injected manure application methods on nutrient and metal release to snowmelt in the field and to overlying floodwater of intact soil columns from field plots with simulated snowmelt flooding in the laboratory. Therefore, two separate studies were conducted: a laboratory study with snowmelt simulation (Chapter 2) and a field study under spring snowmelt (Chapter 3). The laboratory study conducted under controlled conditions (e.g., constant temperature, constant water head of 10 cm throughout the study, ensuring prolonged flooding) allowed the continuous monitoring of changes in soil conditions (redox potential, pH) and soil solution (porewater) concentrations, which was not possible in a field study, facilitated the interpretation of data. On the other hand, the field study provided a more realistic situation with fluctuating temperatures, freeze-thaw conditions, infiltration of melted water, and other environmental conditions. Pumping out snowmelt daily in the field study prevented prolonged flooding conditions, unlike in the laboratory study. However, this would more or less mimic the natural situation of melted snow draining from field plots rather than being confined to a runoff box.

During the laboratory study (Chapter 2), the DRP concentrations in both porewater and floodwater increased with time in all three treatments (control, manure injection, surface-applied manure) with the flooding period. Floodwater DRP and most of the metal concentrations are lower than the porewater concentrations since these ions are first released into porewater with slow diffusion into the overlying flooding layer (Sallade & Sims, 1997; Amarawansa et al., 2015). In this study, a

significant decrease in soil redox potential with time was observed with flooding time. Anaerobic conditions developed due to the flooding increased the release of DRP and some metals from soils to the overlying flooding layer. The DRP and most metal(loid)s (Mn, Fe, Ca, As) concentrations in both porewater and floodwater were not significantly affected by the recent manure application in our study, possibly due to the increased residual P and metal(loid)s concentrations in the soil associated with the long-term manure application in this site. The freeze-thaw conditions were not present in the laboratory study increasing the interaction between soil porewater and floodwater and that might have also affected the observed no significance among the manure treatment methods in the laboratory study. Our results suggest that agricultural fields with a long history of manure application could have accumulated nutrients and metal contaminants at detectable levels.

Consistent with the laboratory simulations, increased nutrient concentrations and some of the metal (Zn, Mg, and Ca) concentrations were observed in the snowmelt, along with the sampling duration in the field study. More importantly and contrary to the laboratory findings, the manure application method significantly affected the DRP release to snowmelt in the field study, where the DRP concentrations of the manure-injected plots were significantly lower compared to surface-applied plots. The P release from the soil is dependent on several factors, namely, air temperature, snowpack depth, frozen soil surface, and interactions of multiple biogeochemical processes (Hoffman et al., 2019; Maranguit et al., 2017; Rakotoson et al., 2016). The distinctive conditions experienced in the field study such as the absence of prolonged flooding, as well as the fluctuating temperature and freeze-thaw conditions during the snowmelt period, may have contributed to the differences in findings between laboratory and field study. For example, in the field study, the reducing conditions in soils might not have been as severe as in the laboratory study since snowmelt water was removed daily. The freeze-thaw events that occurred during the snowmelt



period in the field may have influenced P dynamics, resulting in the release of more P from the surface application. The surface application of manure can result in more organic matter on the soil surface. Freeze-thaw cycles might increase the breakage of the manure particles as well as the competition between released ions for the charged surfaces of the soil colloidal fraction which could promote the release of P (Liao et al., 2019) along with the more aerobic conditions in the soil surface. Furthermore, the temperature in the field was constantly varying during day and night whereas in the lab simulation it was maintained at a constant temperature of +4 °C. Apart from that, the snow precipitation patterns are driven by the wind direction in the field, which is not seen in the laboratory study. Also, there are a number of processes associated with P release (i.e., mineralization of organic P, cell lysis of litter and microorganisms), which could be different between the laboratory and field conditions. Therefore, some of these factors might have changed the P dynamics in the field compared to the lab study with controlled environments, which resulted in significant differences in DRP concentrations in the snowmelt with different manure application methods.

The release of Mn and Fe from flooded soils to the overlaying flooding layer is associated with the reductive dissolution of Fe and Mn compounds. However, in both studies, an increase of Mn and Fe compounds was not clearly observed, which might be due to the absence of severe reducing conditions in the soil for reductive dissolution reactions to take place and/or the precipitation of released Fe and Mn cations after diffusing to floodwater or snowmelt. The observed elevated concentrations of Ca and Mg concentrations at the end of the sampling period of the field could be due to the increased dissolution rates with the increasing temperature, which was different in the laboratory setting as the temperature was constant. Apart from the elevated Ca and Mg, we observed very sharp increases in nitrate-nitrogen concentrations at the end of the field sampling,

which could be due to the accelerated nitrification rates associated with the increased temperature and oxidized conditions with snowmelt collection or snowmelt draining.

Any management practice that would result in a significant decrease in the cumulative loads of nutrients and metals per unit of land area would have a positive impact on the surface water quality. The cumulative loads of P and nitrate-nitrogen in the snowmelt flooding conditions showed significant correlations and strong linear relationships with snowmelt volume (rather than concentrations of P and nitrate in snowmelt), revealing that the snowmelt volume was the driving factor for the cumulative loads of the nutrients and metals. This implies that proper management of snowmelt runoff volume (i.e., drainage and infiltration) from agricultural lands is more important to reducing the nutrient and metal loads released to the surface water than reducing their concentrations in snowmelt.

#### **4.2 Recommendations**

Our research findings corroborate previous studies demonstrating the benefits of injection of liquid swine manure compared to surface application in reducing P loss from manured soils. However, losses of N and metals were not influenced by the manure application method. Our results clearly showed that the snowmelt volume is the major driving factor influencing the DRP and metal loads in a snowmelt flooding event. Therefore, parallel to reducing nutrient and metal concentrations in snowmelt through various manure management options, using efficient approaches to enhance the infiltration of snowmelt water that would reduce the snowmelt volume is important to reduce nutrient and metal loss to snowmelt effectively. Our laboratory study suggested that the duration of the flooding period is directly associated with increased nutrients and metal concentrations. Therefore, efficient draining of the flooded areas promptly in a snowmelt flooding situation would prevent waterlogging and the development of anaerobic conditions in the soils that would mitigate

P and metal release to the overlying water. More research is suggested to evaluate the effect of drainage on nutrient and metal concentrations. Developing more studies on releasing snowmelt runoff from multiple agricultural lands to a constructed wetland improved with phytoremediation expanded in watershed levels is suggested to control the nutrients, metals, and other contaminants in the snowmelt volume before releasing it to major freshwater sources. However, these recommendations and suggestions should be implemented according to the conditions specific to different regions, considering factors such as soil type and weather.

This study was conducted in one site for one snowmelt season. Even though it is complemented with a laboratory study under controlled conditions using intact soil columns from the same field plots, the external validity of findings is limited. Therefore, multiple years of research in multiple sites is needed to get a better understanding of the effectiveness of manure application methods in reducing nutrient and metal loss with snowmelt runoff. Expanding this research into other geographical areas with different soil types and topographies is important to get a broader understanding of the impact of manure application methods on nutrient and metal loss with snowmelt runoff events.

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## APPENDICES

### Appendix A: Supplementary tables

Supplemental Table S1. Nutrient and metal concentrations in soil.

Element	Concentration (mg kg <sup>-1</sup> )
Nitrate-N	170.0
Olsen P	99.0
Exchangeable K	480.0
Exchangeable Ca	7700.0
Exchangeable Mg	3900.0
DTPA-sorbitol extractable Cu	1.9
DTPA-sorbitol extractable Fe	16.0
DTPA- sorbitol extractable Mn	7.5
DTPA-sorbitol extractable Zn	5.0

Supplemental Table S1. Mehlich 3 extractable metal concentrations (mg kg<sup>-1</sup>) extracted from the soil samples collected soon after the snowmelt.

	<b>Zn</b>	<b>Mn</b>	<b>Fe</b>	<b>Mg</b>	<b>Ca</b>
<b>Manure Treatment</b>	mg kg <sup>-1</sup>				
Control	1.15(0.23)	7.91(0.48)	11.64(0.33)	329.75(6.09)	2995.45(88.56)
Injected	1.13(0.23)	7.72(0.48)	11.25(0.33)	327.18(6.09)	3146.72(88.56)
Surface	1.15(0.23)	7.85(0.48)	11.18(0.33)	341.57(6.09)	3203.42(88.56)
	<b>P value</b>				
Treatment	1.00	0.96	0.59	0.10	0.13