Preferential flowpaths and fertilizer placement influence subsurface P transport across soil textures and seasonal conditions

by

Kirsten Grant

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

This thesis is structured in accordance with the manuscript option. Chapter 3 has been accepted for publication, and Chapter 4 has been submitted for publication in a peer-reviewed journal. As such, final published papers may differ from the chapters presented here based on comments from the peer review process. Due to the nature of the manuscript style thesis, some background information and abbreviations may be repeated.

Kirsten Grant planned and carried out the fieldwork and laboratory work, and wrote and edited this thesis. Dr. Merrin Macrae and Dr. Fereidoun Rezanezhad advised on methodology and provided editorial comments on Chapter 3. W.V. Lam assisted with laboratory work and provided editorial comments on Chapter 3. As such, Dr. Macrae, Dr. Rezanezhad, and W.V. Lam are listed as co-authors on the published version of Chapter 3. Dr. Merrin Macrae and Dr. Genevieve Ali advised on methodology and provided editorial comments on Chapter 4 of this thesis, and are listed as co-authors for the submission of this chapter to a peer-reviewed journal.

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Abstract

Agricultural tile drains are a source of phosphorus (P) contributing to eutrophication. Preferential flowpaths can rapidly transport P to tile drains, but their activation in different soil textures and under variable seasonal conditions (antecedent moisture conditions and presence of soil frost) is not well understood. Subsurface placement of fertilizer has been proposed as a management practice to reduce P loss, compared to surface applications. However, how subsurface placement reduces P loss is not well understood. The goal of this thesis is to relate subsurface flowpaths and fertilizer placement to identify source and transport mechanisms controlling P movement to tile drains, across soil textures and seasonal conditions. A lab experiment was done on intact soil monoliths (clay, silt loam) to investigate interactions between fertilizer placement, subsurface flowpaths, and soil frost. Conservative water tracers (Br^-, Cl^- and D_2O) applied through successive events identified matrix flow as the dominant flowpath in unfrozen silt loam, while preferential flow dominated in unfrozen clay and in both soil types under partially frozen conditions. Subsurface placement of fertilizer reduced dissolved reactive P losses by 60% in silt loam and 64% in clay over the simulated non-growing season compared to surface broadcast applications. A field study used blue dye as a tracer to investigate subsurface flowpaths in clay and silt loam plots under wet and dry conditions. Dye stain patterns were analyzed to determine the relative importance of matrix and macropore flow. Soil samples were collected to determine soil P distribution post-fertilization. Preferential flow occurred under all soil texture and moisture conditions. Dry clay soil showed the deepest staining (92 ± 7.6 cm), followed by wet clay (77 ± 4.7 cm). In silt loam soil, depth of staining did not differ between wet (56 ± 7.2 cm) and dry (50 ± 6.6 cm) conditions. Soil water-extractable P distribution varied with fertilizer application in the top 10 cm of the soil profile, but did not differ at depth. Together, the results of this research suggest subsurface placement is a suitable practice for minimizing subsurface nutrient loss, by reducing contact between the nutrient supply and preferential flowpaths, particularly in clay soils prone to preferential flow. This work provides an improved understanding of subsurface flowpaths carrying P to tile drains, and more broadly, solute transport through preferential flowpaths.

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Dedication

This thesis is dedicated in loving memory of Theodore (Ted) Van Dreumel, a farmer, storyteller, and family man. Thank you for teaching me the value of perseverance and hard work, for this thesis would not be possible without them.

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Chapter 1

Introduction and Problem Statement

The eutrophication of surface water is a global water quality concern caused by excess nutrient loading, resulting in increased productivity and oxygen depletion (Schindler, 2006). Excessive eutrophication can negatively impact aquatic ecosystem function by causing nuisance and harmful algal blooms, shifting species composition, and causing biodiversity loss (Anderson et al., 2002; Carpenter et al., 1998; Correll, 1998; Scavia et al., 2014; Smith et al., 1999). Eutrophication can also result in economic, social, and human health impacts including the loss of economically important fish (Smith et al., 1999), inhibited tourism and recreational activities (Carmichael and Boyer, 2016; Hudnell, 2010), and loss of potable drinking water due to toxins from cyanobacteria (Carmichael and Boyer, 2016; Hudnell, 2010; Jetoo et al., 2015). Excess phosphorus (P) loading from human impacts, primarily agricultural production and wastewater treatment, contribute to eutrophication (Carpenter et al., 1998; Schindler et al., 2012), as P is a limiting nutrient in freshwater systems (Schindler, 1977). Within the Great Lakes region, the eutrophication of Lake Erie continues to be a major concern causing governments to set targets to reduce P loading to the lake by 40% of 2008 levels (Annex 4 Objectives and Targets Task Team, 2015).

Within agricultural landscapes, P is also an important nutrient to crop growth and is commonly added to fields in conventional systems. As concern over eutrophication issues rises, farmers are faced with pressure to mitigate losses of P from their operations. There is a need to find a balance between supplying adequate P for crop growth and limiting P loss to water bodies, to maintain crop yields while also achieving water quality targets. Farmers and land managers can adopt beneficial management practices (BMPs) to reduce nutrient losses from their fields. However, there is no ‘one-size-fits-all’ approach to management (Gitau et al., 2004; Sharpley et al., 2000). There is a growing need to understand soils and management systems that may be at the greatest risk of P loss (Sharpley, 1995). As research calls for more site-specific management recommendations, there is an ongoing need to understand how management practices interact with each other and how they perform over time under various soils, seasonal conditions, and site characteristics.

One BMP that has been broadly recommended to farmers to reduce soil erosion is to switch from conventional tillage practices to no-till (Derpsch et al., 2010). While no-till is effective at reducing soil erosion, some have questioned the role of no-till in P management, suggesting that increased P stratification and macropore development under no-till can exacerbate subsurface P losses (Bertol et al., 2007; Jarvie et al., 2017; Kleinman et al., 2009). Further, preferential flowpaths and surface inlets can quickly transport P from the soil surface to surface waters through tile drains (King et al., 2015), bypassing retention opportunities within the soil (Djodjic et al., 1999). Under no-till management, some work has shown increased dissolved reactive P (DRP) loss through tile drains (Kleinman et al., 2009; Williams et al., 2016), particularly when fertilizer is broadcast over the soil surface (Kleinman et al., 2009; Smith et al., 2016). However, Lam et al. (2016) found that tillage practice did not influence P loss in tile drains when fertilizer was applied in subsurface bands. Therefore, the combination of tillage practice and fertilizer application method may influence P losses to tile drains, more than either on their own. Further, the effectiveness of management practice combinations may differ with seasonal changes and site conditions.

Studies that have observed elevated P loads to tile drains have found that these elevated losses are driven by P transport through preferential flowpaths in the vadose zone. Thus, understanding preferential flowpaths in the vadose zone is critical for managing P movement to tile drains (King et al., 2015), and for understanding the transport of other solutes to tiles or groundwater resources (Beven and Germann, 2013). However, the activation of preferential flowpaths is not well understood and is challenging to quantify as the relative contribution of preferential flow can differ with soil texture, antecedent moisture conditions, the presence of soil frost, management practices (Allaire et al., 2009), and season (King et al., 2016). There is a need to understand when and where preferential flowpaths are activated, and how this may vary across soil textures and seasonal climatic conditions. As the non-growing season (NGS) is a critical time for P loss from agricultural systems in cold temperate regions (Van Esbroeck et al., 2016), there is a need to understand how preferential flowpaths respond under both frozen and unfrozen conditions, and if and how this relates to P transport. In addition, understanding preferential flowpath activation in both wet and dry soil conditions can provide insight into optimal timing of fertilizer application to minimize transport, as part of a 4R nutrient stewardship strategy (Bruulsema, 2018).

To understand when and where the risk of P loss to tile drains is greatest, there is a need to investigate the interaction between fertilizer placement and subsurface flowpaths in no-till soil, across different soil textures, antecedent moisture conditions, and soil frost conditions. This can ultimately enable policy makers and influencers to make more informed, site-specific, and seasonal BMP recommendations to farmers to aid in reducing P loss from agricultural landscapes.

Chapter 2
Review of Literature

P loss from agricultural lands is a function of both available P supply and transport pathways. From this perspective, understanding both supply and transport components are critical for mitigating P loss from agricultural landscapes. This literature review will first describe the terrestrial P cycle, including sources and forms of P in soil, then discuss pathways for P transport and factors influencing preferential transport pathways in space and time. Next, on-farm nutrient management will be highlighted, with a focus on how and why fertilizer placement may be an optimal BMP from a source and transport perspective. Nitrate is briefly considered in Chapter 3, but is not the primary focus of this thesis and therefore is not discussed within this review or in Chapter 4. Finally, this review will conclude with the overall objectives of this thesis.

2.1 Terrestrial P Cycling

2.1.1 Overview

P is an essential nutrient required for life (Compton et al., 2000), as it is needed to perform many biological functions including photosynthesis, metabolism, and the development of cell structures (Filippelli, 2008). In particular, hydrozylapatite is necessary for the formation of bones and teeth, adenosine triphosphate (ATP) is required for photosynthesis, and phosphate ester bridges are essential for creating DNA (Filippelli, 2008). P cycles through the environment via geochemical and biological reactions (Ruttenberg, 1976). In terrestrial environments, P cycles primarily between bedrock, soils, and living organisms (Ruttenberg, 1976), as P does not occur in a gaseous phase (Filippelli, 2008).

P enters natural systems through the weathering of apatite, a primary mineral that occurs in bedrock (Rodríguez and Fraga, 1999; Ruttenberg, 1976). Apatite is the most abundant primary mineral containing P and is the dominant source of P in soil during soil development (Rodríguez and Fraga, 1999; Ruttenberg, 1976). Apatite refers to a group of phosphate minerals which include hydroxylapatite, fluorapatite and chloropatite, often written as $Ca_{10}(PO_4)_6(OH,F,Cl)_2$ (Hinsinger, 2001; Rodríguez and Fraga, 1999). Once weathered from bedrock, P in terrestrial systems cycles between soils and living things, or is lost from the system.

As soils establish overtime, primary minerals containing P weather and P occurs in soil, in both organic and inorganic forms (Compton et al., 2000; Ruttenberg, 1976). Inorganic forms of P include those bound to cations, metal oxides, and clay particles (Filippelli, 2008; Sharpley, 1995). Inorganic P can vary in its availability, depending on how it is adsorbed to other particles (Holtan et al., 1988; Sharpley, 1995). P can be tightly held if it is incorporated into the bulk of other compounds (Holtan et al., 1988; Tiessen et al., 1984). Alternatively, P adsorbed to the surface of other compounds is more loosely bound and can be more easily removed (Holtan et al., 1988; Tiessen et al., 1984). Organic P includes readily available forms, such as phospholipids, and more stable forms such as those found in humus (Sharpley, 1995). Microbial communities living in soil can mineralize organic forms of P, and cycle P between organic and inorganic forms (Sharpley, 1995).

Within water, P exists as organic or inorganic compounds that are either in ‘dissolved’ (<0.45 µm) or ‘particulate’ (>0.45 µm) form (Compton et al., 2000; Haygarth and Jarvis, 1999). For practical purposes, the terms ‘dissolved’ and ‘particulate’ are used to refer to these pools of P, however the size distribution more accurately describes these pools as P can be associated with colloids that are <0.45 µm (Haygarth and Jarvis, 1999). As there are many ways P can exist in the soil and in solution, there are many ways to measure it (Tiessen et al., 1984). In this thesis, dissolved reactive P (DRP) represents the available P pool that is <0.45 µm and total P (TP) represents P in both dissolved and particulate forms.

P within the soil solution can either be taken up by plants and cycled through organic matter, or carried out of the system by water (Sharpley, 1995). P can be carried in dissolved or particulate form through surface runoff, lost to surface waters through tile drains, or leached to groundwater (Haygarth and Jarvis, 1999). To estimate P in a soil at risk for transport by leaching or runoff, water extractable P (WEP) has been shown to be the most representative, as it measures P that is loosely bound and easily extracted by water (Mcdowell and Sharpley, 2001; Pote et al., 1996). As P is removed or added to the system, a new equilibrium state is established (Hinsinger, 2001; Özgül et al., 2012). Therefore, the amount of available P in a system is a balance between adsorption and desorption of P, and precipitation and dissolution of P (Hinsinger, 2001; Özgül et al., 2012). This equilibrium between sources of P and transport mechanisms ultimately controls both the bioavailability and chemical mobility of P in the soil (Hinsinger, 2001; Sharpley, 1995).

2.1.2 Forms of P in soil

Sources of inorganic P within soil include P bound to calcium, metal oxides, and clay particles. First, calcium (Ca), and to a lesser extent magnesium (Mg), can bind with P through a precipitation reaction (Hinsinger, 2001). Calcium-bound P makes up a large portion of the soil-P pool in neutral and alkaline soils, such as those that occur in southern Ontario (Wang et al., 2010). In these environments, P will commonly precipitate with calcium cations to form calcium phosphate (Hinsinger, 2001; Rodríguez and Fraga, 1999; Tiessen et al., 1984). P can also be bound to metal oxides including iron (Fe) and aluminum (Al) oxides, as these compounds are positively charged across a wide pH range (Goldberg and Sposito, 1984; Hinsinger, 2001). These metal oxides undergo similar reactions with P, where P is adsorbed via a substitution reaction on the surface of Fe or Al oxides, although adsorption rates are highly dependent on pH (Goldberg and Sposito, 1984; Rodríguez and Fraga, 1999; Ziadi et al., 2013). Fe and Al oxides primarily exist as small crystals with a relatively large specific surface area, therefore making them efficient at sorbing phosphates in soil (Hinsinger, 2001). P bound to Fe and Al oxides are most common in acidic soils (Hinsinger, 2001; Rodríguez and Fraga, 1999). Finally, the occurrence of clay particles is also important for P cycling within soils. Clay particles are negatively charged, and have a larger surface area for chemical reactions than other soil particles (Fontes and Weed, 1996). Therefore, P can be sorbed to the surface of clay particles through ligand exchange, similar to the reaction that occurs with Fe and Al oxides (Fontes and Weed, 1996; Ruttenberg, 1976). Since clay is able to sorb P, soil texture is also able to influence the capacity of a soil to adsorb and store P (Andersson et al., 2013; Glaesner et al., 2011a).

Lastly, P can also exist in soils as organic P. Organic P commonly occurs as complex compounds that vary in mobility in soil (Haygarth and Jarvis, 1999). Many forms of organic P need to be mineralized by microorganisms to become part of the plant-available P pool (Rodríguez and Fraga, 1999). Microbial communities within a soil dictate the availability of organic P

(Rodríguez and Fraga, 1999). Within agricultural systems, the organic P pool can be replenished by crop and cover crop residues, and root matter.

2.1.3 P in soil solution

In terrestrial systems, P exists in an equilibrium state between soil and soil solution (Hinsinger, 2001; Özgül et al., 2012). Therefore, P existing in soil solution represents a pool of P readily available for uptake or transport. Concentrations of P in soil solution are often low in natural systems due to the many P retention mechanisms within the soil (Ruttenberg, 1976). In agricultural systems, this equilibrium between soil P and soil solution P is often elevated due to ongoing P application (Ruttenberg, 1976). P in soil solution primarily consists of orthophosphate (PO_4^{3-}), and some forms of organic P (Hinsinger, 2001). Orthophosphate is the most bioavailable form of P and can be readily taken up by plants (Ruttenberg, 1976) and algae (Correll, 1998). P can also exist as negatively charged, positively charged, or neutral ions in the soil solution, depending on pH and concentrations of other cations in solution (Hinsinger, 2001). However, most P species found in solution are negatively charged (Hinsinger, 2001).

2.1.4 P in agricultural systems

Agricultural landscapes are open systems with respect to P cycling as P is removed from the system with crop harvest, and must be replaced to continue agricultural production (Haygarth and Jarvis, 1999; Sharpley, 1995). Therefore, agricultural soils often receive added P as manure or synthetic fertilizers along with other major nutrients such as nitrogen and potassium (Sharpley, 1995). Manure is often added to fields to meet N requirements, resulting in the over-application of P (Sharpley, 1995). Fields receiving manure have been shown to have greater DRP and TP losses than those receiving synthetic fertilizer applications *(e.g.*, Macrae et al., 2007a). With respect to synthetic fertilizers, P is often supplied in the form of PO_4^{3-}, which can be dissolved into mobile forms including $H_2PO_4^-$ and HPO_4^{2-} which are available for plant uptake (Rodríguez and Fraga, 1999). Incidental losses of P can occur following application of manure or synthetic fertilizer, when rainfall carries newly applied nutrients off of the field before they have an opportunity to bind to the soil (Ball Coelho et al., 2012; Haygarth and Jarvis, 1999). Incidental losses are short-term but can be particularly high if there is minimal time between fertilizer application and a rainfall event (Ball Coelho et al., 2012; Haygarth and Jarvis, 1999).

Application of fertilizer and manure have been common practice within conventional agricultural systems for decades (Ruttenberg, 1976; Sharpley, 1995). These ongoing applications of P to agricultural soils have resulted in the stratification of P with depth, particularly in soils under no-till or conservation tillage, with the highest P concentrations in the soil surface posing the greatest risk for being lost (Simard et al., 2000; Zhao et al., 2001). Such historic applications of nutrients influence the long-term soil P status within a field, and can be considered legacy sources of P (Haygarth and Jarvis, 1999; Kleinman et al., 2011). These historic pools can be released from fields slowly over long periods of time, continuing to contribute to water quality problems (Haygarth and Jarvis, 1999; Kleinman et al., 2011). Changes in land management do not result in immediate changes in water quality at the watershed scale due to legacy P and time-lags along the system (Bennett et al., 2001; Haygarth et al., 2005). This remains an ongoing challenge for reaching water quality targets.

2.2 P transport pathways

2.2.1 Transport of P to surface waters

In agricultural fields P can be transported to surface waters via surface runoff, tile flow and subsurface flow both above and below the groundwater table (Holman et al. 2008, Kleinman et al., 2011; Simard et al., 2000). P is commonly measured in surface runoff and tile flow in agricultural systems (*e.g.* Smith et al. 2015), however little is known about P movement in subsurface flow as this pathway is often overlooked (Holman et al. 2008). Surface runoff has been shown to transport water with greater concentrations of P than tile drains (Van Esbroeck et al., 2017). Surface runoff occurs following heavy rainfall or snowmelt events, and can be a key pathway for the movement of particulate P (Daniel et al., 1994). Runoff generation mechanism also influences nutrient transport, with greater P loss in saturation excess runoff compared to infiltration excess runoff (Kleinman et al. 2006). Where areas of high transport potential overlap with areas of high supply, large quantities of nutrients can be rapidly transported to surface waters via runoff (Kleinman et al. 2006). Particulate P losses in surface runoff increase as the proportion of precipitation that arrives as rainfall increases, and when rainfall occurs over unfrozen bare soils (Van Esbroeck et al., 2016). BMPs that aim to reduce soil erosion, such as cover cropping, often also reduce the loss of particulate P during surface runoff events (Daniel et al., 1994), as soil remains covered.

In artificially drained systems, tile drains are an important pathway for P transport from fields to surface water (King et al., 2015; Macrae et al., 2007a; Smith et al., 2015). Tile drains are perforated pipes installed into the soil subsurface to artificially lower the water table in poorly drained soils, reducing crop water stress and allowing farm machinery onto the field earlier in the spring, extending the growing season (King et al., 2015). The presence of tile drains results in reduced surface runoff and an increased proportion of water moving through the subsurface to tile drains (*e.g.,* Macrae et al., 2007a). Historically, P losses from tile drains were assumed to be negligible (Logan et al., 1980). However, more recent work has identified tile drains as an important pathway for P movement from agricultural landscapes, particularly under no-till conditions (King et al., 2015; Sims et al., 1998). Although concentrations of P in tile drains are often lower than found in surface runoff (Van Esbroeck et al., 2017), tile drains can contribute the majority of annual flow from agricultural fields (Van Esbroeck et al., 2016). Flow through tile drains has been shown to transport P, particularly during large events (*e.g.,* Gelbrecht et al., 2005; Macrae et al., 2007b; Vidon and Cuadra, 2011) and over the NGS (*e.g.,* King et al., 2016; Van Esbroeck et al., 2017). Therefore, mitigating transport of P through this tile drains is necessary for reducing overall P losses from agricultural landscapes.

2.2.2 Subsurface flowpaths in the vadose zone

Within the soil profile, water carrying P can reach tile drains through matrix or preferential flow (Haygarth and Jarvis, 1999; Vidon and Cuadra, 2011; Williams et al., 2016). Throughout this thesis, the term hydrologic connectivity is used to describe vertical pathways for water to flow from the surface to the subsurface. This can include both matrix and preferential flow, but where connectivity is enhanced or more direct it refers to a greater portion of water moving through preferential flowpaths. Matrix flow occurs as water travels through small pores in the soil matrix (Haygarth and Jarvis, 1999). This pathway is slow and offers a high degree of contact between water and the soil matrix, providing more opportunity for P retention (Geohring et al., 2001;

Simard et al., 2000; Williams et al., 2016). Despite increased contact, matrix flow can still transport P to tile drains in soils with low P sorption capacity (Smith et al., 2015).

Preferential flow is the rapid transport of water through large pores in the subsurface (Cey et al., 2009; Smith et al., 2015; Vidon and Cuadra, 2011). Preferential flow often occurs through macropores, which can include desiccation cracks, earthworm and insect burrows, and root channels (Beven and Germann, 2013; Cey et al., 2009; Shipitalo and Gibbs, 2000; Simard et al., 2000). The rapid transport of P through preferential flowpaths is prominent in no-till systems, particularly in heavy clay soils where desiccation cracks can occur (Cey et al., 2009; King et al., 2015; Shipitalo and Gibbs, 2000; Simard et al., 2000; Smith et al., 2015). Over time, macropore walls can become saturated with P, while lower P concentrations exist in the soil matrix (Beven and Germann, 2013). P saturation along macropore walls, and little macropore-matrix interaction due to rapid transport, results in P bypassing retention opportunities in the soil and quickly being transported to the subsurface (Beven and Germann, 2013). Even if soils have the capacity to retain P in the soil matrix, preferential flowpaths bypass these retention opportunities resulting in subsurface P losses (Andersson et al., 2013; Haygarth and Jarvis, 1999). For this reason, P loss may be of particular concern following nutrient application on soils prone to preferential flow.

However, predicting when and where preferential flow will occur is complex (Allaire et al., 2009; Beven and Germann, 2013; Vereecken et al., 2016), making mitigating P losses through these flowpaths a challenge. While preferential flowpaths have long been understood to be a concern for solute transport (Beven and Germann, 1982), methods of studying preferential flowpaths remain limiting (Allaire et al., 2009; Beven and Germann, 2013). Conservative tracers provide insight into timing of flow patterns and solute transport, but are a 'black box' with respect to physical processes occurring within the soil and can range in ease of measurement (Allaire et al., 2009). Dyes and moulds are inexpensive and useful for visualizing flow patterns, but require destructive sampling and are not as precise as other methods (Allaire et al., 2009; Koch et al., 2016; Weiler and Naef, 2003). Newer technology, such as X-ray scanning and 3-D imaging, provides an opportunity for examining physical structures of soil in detail, but is expensive and ineffective at the landscape scale (Allaire et al., 2009; Koch et al., 2016). Overall, current methods have limitations with respect to quantifying preferential flow at the field scale, and for determining processes that influence preferential flow and solute transport in the field (Allaire et al., 2009).

2.3 Field conditions influencing preferential flow in the vadose zone

Environmental conditions and management practices can influence transport pathways in the vadose zone. Factors including soil texture, antecedent moisture conditions, soil frost, land use, and BMPs can influence the relative contributions of matrix and preferential flow (Allaire et al., 2009; Bachmair et al., 2009; Beven and Germann, 2013). While it is understood that preferential flow occurs across a wide range of conditions, there remains a lack of understanding of the physical processes controlling preferential flow (Allaire et al., 2009; Beven and Germann, 2013). This results in models that are unable to capture preferential flow and associated solute transport, because they rely over simplistic flow patterns that do not accurately represent field processes (Beven and Germann, 2013; Nimmo, 2012). For example, many models only consider preferential flow that occurs under near saturated conditions, when preferential flow has been shown to occur and be prevalent in unsaturated conditions (Nimmo, 2012). This can result in models inaccurately predicting low risk of contaminant transport under dry soil conditions (Nimmo, 2012). It is clear that research on basic hydrological processes is needed for improving model prediction (Vereecken et al., 2016), but this remains a challenge due to the limitations associated with methods of studying preferential flow (Allaire et al., 2009; Beven and Germann, 2013).

2.3.1 Variability in subsurface flowpaths with soil texture

First, soil texture can influence subsurface flowpaths. Increasing clay content in soils has been shown to increase preferential flow (Andersson et al., 2013; Glaesner et al., 2011a). In addition, macropores in fine-textured soils with more strongly developed soil structure may be more stable than similar macropores in coarse textured soils (Jarvis, 2007). Further, subsurface flowpaths may change along soil horizon boundaries (*e.g.*, Hardie et al., 2011), as changes in drainage occur due to differences in texture and structure. For these reasons, preferential flow is more likely to occur in fine-textured soils or horizons than more coarse textured soils.

2.3.2 Role of antecedent moisture conditions in subsurface flowpaths

Antecedent moisture conditions also influence the relative importance of preferential flow. However, the activation of preferential flow is not consistently related to moisture condition, making flow and transport difficult to predict. In dry soil conditions, desiccation cracks can form and exacerbate preferential flow (Hardie et al., 2011; Simard et al., 2000). When desiccation cracks are not present, matrix flow may be more common in dry soils or following low intensity rainfall when water has more time to infiltrate into the soil profile (Cey et al., 2009; Vidon and Cuadra, 2011). Under wet conditions, desiccation cracks can seal quickly resulting in reduced preferential flow (Hardie et al., 2011; Jarvis, 2007). In other cases, preferential flow can be particularly prominent under saturated soil conditions and during high flow events (Cey et al., 2009; Kung et al., 2000b; Macrae et al., 2007a; Stamm et al., 1998; Vidon and Cuadra, 2011), when the flow regime is decoupled from the water supply. The activation of preferential flowpaths is related to antecedent moisture condition, but also to the presence or absence of desiccation cracks. Thus, the effects of antecedent moisture condition on preferential flow may also be dependent on soil texture. As seasonal changes in soil moisture may influence efficacy of management practices, there is a need to understand how antecedent moisture conditions influence preferential flowpaths across soil textures. Furthering this understanding has relevance for solute transport to tile drains and groundwater resources across soil textures and moisture conditions. In particular, this knowledge may be useful in identifying BMPs that are suitable for specific seasonal moisture conditions (*e.g.*, dry fall vs wet spring).

2.3.3 Influence of soil frost on subsurface flowpaths

Soil frost can also influence the prevalence of preferential flow, however flowpaths through frozen soil remain poorly understood (Allaire et al., 2009; Mohammed et al., 2018). Preferential flow through frozen soils is of particular importance in understanding flow during thawing and snowmelt periods (Allaire et al., 2009; Mohammed et al., 2018). Flow through frozen soil can range from rapid preferential flow to impeded flow (Kane and Stein, 1983; Stähli et al., 1996). Under unsaturated conditions, preferential flow can occur in frozen soils, as macropores and large pore spaces remain air-filled upon freezing (Espeby, 1990; Stähli et al., 1996; Watanabe and Kugisaki, 2017). Preferential flow through pores that remained air-filled upon freezing is more likely to occur in soils that were drier at the time of freezing (Stadler et al., 2000). However, if antecedent moisture contents are near saturation at the time of freezing, ice formed in pore space can reduce infiltration rates in frozen soil (Kane and Stein, 1983; Stadler et al., 2000). Preferential flow can also occur through desiccation cracks formed upon freezing (Weigert and Schmidt, 2005). In other cases, infiltrating water has been shown to re-freeze and inhibit flow through frozen soil (Stähli et al., 1996; Watanabe and Kugisaki, 2017). Thus, flow dynamics through frozen ground are highly variable and dependent on moisture conditions, temperature regimes, and heat transfer between infiltrating water and the surrounding soil matrix (Granger et al., 1984; Mohammed et al., 2018). These confounding factors add to the complexity of understanding processes behind preferential flow through frozen soils, and create challenges for modelling and predicting flow through frozen ground (Mohammed et al., 2018).

Following freezing periods, thawed soils may also exhibit enhanced preferential flow. Swelling, caused by the formation of ice lenses, can create new macropores upon thawing (Asare et al., 1999; Djodjic et al., 2002). Multiple freeze-thaw cycles have been shown to result in the creation of larger pores, and more small and disconnected pores (Ding et al., 2019). This change in pore structure can result in an increased saturated hydraulic conductivity in thawed soils after consecutive freeze-thaw cycles (Ding et al., 2019). We do not yet have a full understanding of preferential flow under unfrozen soil conditions (Beven and Germann, 2013), nor frozen soil conditions (Mohammed et al., 2018). Understanding flowpaths, solute transport, and soil physical processes during transition periods between unfrozen and frozen soil remains an emerging area of research (Mohammed et al., 2018).

There is also a need for research to understand interactions between macropore flow and physical processes of soil freeze-thaw (Mohammed et al., 2018) in order to understand flow and transport processes in the vadose zone under winter conditions. Limited understanding of flow processes through frozen ground provides a complex challenge in predicting when and where preferential flow may occur through frozen or partially frozen soils (Allaire et al., 2009). As preferential flow through frozen soils is poorly understood, solute transport processes through these flowpaths remains even more unknown (Brouchkov, 2000). Improving our understanding of preferential flow and solute transport through frozen soil is an important area of emerging research, as it is necessary to understand and manage the migration of pollutants through the vadose zone during the NGS and snowmelt periods (Allaire et al., 2009). Of particular relevance to this thesis, understanding preferential flowpaths and P transport through seasonally frozen ground is important because these conditions exist over the NGS in cold temperate regions such as southern Ontario (*e.g.,* Van Esbroeck et al., 2016). In these regions, the NGS is a critical time for P loss from agricultural landscapes (King et al., 2016, Van Esbroeck et al., 2016) and tile drains are often active during this time (Lam et al., 2016). Further, climate change is expected to result in more precipitation as rain in Southern Ontario (Colombo et al., 2007), reducing the insulating snowpack and potentially exposing bare ground to more freeze-thaw cycles. Therefore, understanding nutrient transport and flow dynamics under frozen conditions is of increasing importance in a changing climate.

2.3.4 Management practices impact on subsurface flowpaths

Finally, management practices and land use can also influence transport pathways through the soil subsurface. Flowpaths through agricultural landscapes can be influenced by tillage practices, fertilizer application methods, crop root development, compaction and traffic, and drainage systems (Jarvis, 2007). Of interest to this thesis are practices surrounding tillage and fertilizer application methods. In the absence of tillage disrupting soil aggregates, macropores can develop in no-till systems via increased earthworm activity or cracking in dry soils (Djodjic et al., 2000; Geohring et al., 2001; Simard et al., 2000). Increased DRP transport to tile drains has been attributed to increased preferential transport through macropores in no-till soils (Kleinman et al., 2009; Williams et al., 2016). However, some have found no-till soils to have shallower infiltration and more matrix flow than tilled soils (Bachmair et al., 2009). In contrast, others have found that conventional tillage can break up macropores in the top soil and promote matrix flow (Jarvis, 2007). Bachmair et al. (2009) found land use and land cover to have more influence over subsurface flowpaths than soil textural characteristics, as land use strongly influences soil structure. While differences in preferential flowpaths have been observed between tillage methods, and types of land cover, effects are inconsistent and often are confounded with other influences on preferential flow.

2.4 Nutrient management decision making

In order to reduce P loss from their operations, farmers can adopt a variety of BMPs. These BMPs can include conservation/no-till, cover crops, buffer strips, and 4R nutrient management. The 4Rs is a nutrient management strategy that encourages farmers to adopt the right source, right place, right time, and right rate of fertilizer for their operation (Johnston and Bruulsema, 2014). This thesis focuses on fertilizer placement methods, specifically surface broadcast and subsurface placement (banding), as management practices.

In Ontario, it is recommended that farmers make nutrient management decisions and apply fertilizer based on soil test P in their fields (OMAFRA, 2017). Soil test P is based on an agronomic test that estimates the amount of P within a soil that is plant available (Delgado and Scalenghe, 2008; Haygarth and Jarvis, 1999; Ziadi et al., 2013). Methods for determining soil test P vary regionally based on soil type (Torbert et al., 2002). For calcareous soils, such as those in southern Ontario, Olsen P is the primary method for determining plant available P (Olsen et al., 1954). In Ontario, OMAFRA suggests optimal soil test P levels to be 12-18 mg kg^{-1} and fields with soil test P levels exceeding this threshold should not receive additional fertilizer (OMAFRA, 2017).

While farmers are encouraged to make P management decisions based on soil test P and crop removal rates (OMAFRA, 2017), other factors may also influence on-farm decision making (Baumgart-getz et al., 2012; Knowler and Bradshaw, 2007). Social and economic factors including access to information, financial capacity, and connection to local farmer networks have been shown to influence adoption of BMPs (Baumgart-getz et al., 2012). Other factors relating to individual farmer characteristics and farm biophysical characteristics have also been found to influence on-farm conservation decisions (Knowler and Bradshaw, 2007). Due to the complex nature of on-farm decision-making, recommended BMPs need to be both effective at reducing P losses under a particular farm's unique site conditions, and be economically viable, in order to be considered.

2.5 Fertilizer placement and 4Rs as BMPs

Right fertilizer placement is one of the 4Rs for nutrient management (Johnston and Bruulsema, 2014). Different types of nutrient placement include surface broadcast, injection, broadcast with incorporation, and subsurface placement (banding). Subsurface placement has been suggested as an application strategy with the potential to reduce P losses (Gildow et al., 2016; Glaesner et al., 2011b; Kalcic et al., 2016). Further, there is a need for BMPs that are effective over the NGS, a critical time period for nutrient loss when many BMPs may be ineffective (Tiessen et al., 2010). Subsurface placement may have potential to be an effective BMP during this important time. Recent work has shown subsurface placement can reduce P loss in surface runoff (Smith et al., 2016), as well as in subsurface flow (Williams et al., 2018). In addition to environmental benefits, subsurface placement of nutrients has also been shown to be agronomically viable (Khatiwada et al., 2012; Nkebiwe et al., 2016). Subsurface placement of fertilizer is also often associated with reduced application rates (OMAFRA, 2017), reducing fertilizer costs. While evidence suggests subsurface placement of fertilizer reduces P transport (Smith et al., 2016; Williams et al., 2018), the mechanisms behind this reduced transport remain unclear. From a supply and transport perspective, subsurface placement of fertilizer has the potential to limit contact between the nutrient supply and preferential flowpaths where they exist, and enhance retention within the soil by increasing contact between applied nutrients and the soil matrix (Glaesner et al., 2011b; Williams et al., 2018). Enhancing our understanding of these potential mechanisms could enable us to explain why subsurface placement may limit leaching of P to tile drains.

In order to make site-specific recommendations about fertilizer placement, there is a need to understand interactions between supply of nutrients and transport pathways over space and time. In particular, we must understand if and how the relationship between fertilizer and preferential flowpaths changes with soil texture, the presence of soil frost, and antecedent moisture conditions. This improved understanding will enable farmers to make more informed decisions about fertilizer placement on their land, and limit nutrient losses through tile drains to surface waters.

2.6 Thesis Objectives

The specific objectives of this thesis are to:

1) characterize the movement of water and conservative tracers through preferential and matrix flowpaths in soils under different antecedent temperature conditions (partially frozen vs unfrozen)
2) determine if runoff pathways differ with soil texture (silt loam, clay)

3) quantify the mobilization of dissolved reactive P (DRP) and nitrate (NO_3^-) through the soil profile under surface broadcast and subsurface placement (banding) application strategies, and relate this to differences in flowpaths

4) investigate interactions between soil texture, antecedent moisture conditions, and the relative contributions of matrix and preferential flow

5) determine the associated P movement through the soil profile when fertilizers were applied to the surface or placed in subsurface bands.

Objectives 1, 2 and 3 are addressed in Chapter 3 of this thesis ‘Nutrient leaching in soil affected by fertilizer application and frozen ground’ and objectives 4 and 5 are addressed in Chapter 4 of this thesis ‘Differences in preferential flow with antecedent moisture conditions and soil texture: implications for subsurface P transport’.

Chapter 3

Nutrient leaching in soil affected by fertilizer application and frozen ground

3.1 Abstract

Agricultural runoff containing phosphorus (P) and nitrogen (N) from drainage tiles contributes to nutrient loading in waterways, leading to downstream eutrophication. Recent studies suggest that nutrient losses through tile drains can be reduced if nutrients are applied in the subsurface. This study explores interactions between nutrient supply and infiltrating water over a simulated non-growing season (NGS) using a laboratory experiment to understand how water and nutrients move through partially frozen and unfrozen soil, and if fertilizer placement influences nitrate (NO_3^-) and dissolved reactive P (DRP) leaching. Intact silt loam and clay soil monoliths (28×30×30 cm) were fertilized with P and N via subsurface placement or surface broadcast and subsequently subjected to simulated rainfall under unfrozen (+10ºC) and partially frozen (~0ºC) conditions. Conservative tracers (Br^-, Cl^- and D_2O) applied to characterize subsurface flowpaths throughout a subset of events indicated that matrix flow dominated in unfrozen silt loam soil. However, preferential flowpaths dominated in unfrozen clay and in both soil types under partially frozen conditions, transporting applied nutrients while minimizing contact with the soil matrix. The subsurface placement of inorganic fertilizer relative to surface broadcast reduced both NO_3^- (by 26.85 kg ha^{-1} or 23% in silt loam, 65.73 kg ha^{-1} or 61% in clay) and DRP losses (by 2.33 kg ha^{-1} or 60% in silt loam, 4.25 kg ha^{-1} or 64% in clay). This study demonstrates the advantage of subsurface placement of fertilizer in the reduction of nutrient leaching by limiting the interaction of the nutrient supply with preferential flow pathways.

3.2 Introduction

The eutrophication and hypoxia of surface water bodies and coastal regions are global concerns leading to economic and environmental impacts (Bennett et al., 2001; Dai et al., 2011; Howarth et al., 2011; Michalak et al., 2013). Agricultural runoff, rich in phosphorus (P) and nitrogen (N), contributes to these water quality concerns (Bennett et al., 2001; Dai et al., 2011; Michalak et al., 2013). Within the Great Lakes region, P management has become an international priority with a target of 40% reduction in P loading to Lake Erie compared to 2008 levels, to help manage harmful algal blooms (Annex 4 Objectives and Targets Task Team, 2015). In coastal regions, including the Gulf of Mexico, N is the primary limiting nutrient and therefore agricultural N management is also important (Howarth et al., 2011). Although surface runoff is often assumed to be the primary pathway for P to leave agricultural fields, tile drains have been shown to play an important role in nutrient loss in artificially drained landscapes (King et al., 2015; Smith et al., 2015; Van Esbroeck et al., 2016). Similarly, N can also be lost through tile drains, particularly as nitrate (NO_3^-) due to its mobility (Drury et al., 2014; Nangia et al., 2010). Understanding solute transport and the supply of nutrients to tile drains is essential for mitigating nutrient export through this pathway.

Preferential flowpaths, particularly in reduced or no-till systems, can transport nutrients to tile drains (Sims et al., 1998). Reduced tillage systems limit soil erosion, but can facilitate preferential transport to tile drains through the development and retention of macropores (Bertol et al., 2007; Jarvis, 2007; Shipitalo and Gibbs, 2000). Water tracers have been commonly used to investigate preferential flow pathways and solute transport in agricultural soils in both field (Frey et al., 2012; Granger et al., 2010; Kung et al., 2000a) and laboratory (Akhtar et al., 2003; Tallon et al., 2007) conditions. Macropores can facilitate rapid delivery of nutrients to tile drains (Wang et al., 2013). However, quantifying preferential flow rates and pathways can be challenging due to the heterogeneity of macropores, and variability of flowpaths over space and time (Haygarth and Jarvis 1999; Jarvis, 2007). Quantifying the movement of adsorbing nutrients (*e.g.,* P) through preferential flowpaths is an additional challenge (Jarvis, 2007).

Tile drains are easily activated during the non-growing season (NGS) as soils are often near field capacity (Lam et al., 2016). However, nutrient transport processes during this time are difficult to predict due to climatic variability within and between years, and limited understanding of transport through frozen or partially frozen soils (Brouchkov, 2000). Temperature increases due to climate change are expected to modify the timing and duration of snow-cover in cold regions, which will expose soils to colder temperatures and increase the frequency of freeze-thaw cycles (FTC) during the winter (Kværnø and Øygarden, 2006; Sinha et al., 2010). Changes in FTC can influence both subsurface hydrology (Kane, 1980) and soil biogeochemical processes (Williams et al., 2011) in agricultural systems.

Flowpaths through frozen soil conditions have been shown to be variable, ranging from ice impeding flow to rapid preferential flow (Stähli et al., 1996; Watanabe and Kugisaki, 2017). Wet frozen soils can develop an ice-rich layer near the surface, reducing infiltration and hydraulic conductivity (Asare et al., 1999; Kane, 1980). However, ice lenses can facilitate flow by swelling in the soil and creating new macropores as ice lenses thaw (Asare et al., 1999; Djodjic et al., 2002). Soils frozen under unsaturated conditions can also demonstrate preferential flow (Stähli et al., 1996). As ice forms in the largest water-filled pore spaces, infiltrating water can preferentially flow through larger pores that remained air-filled upon freezing (Stähli et al., 1996). In addition, water infiltrating into unsaturated frozen soil can also refreeze, and may result in the blocking of preferential flowpaths (Stähli et al., 1996; Watanabe and Kugisaki, 2017). Infiltration and refreezing dynamics in preferential flowpaths are related to temperature and moisture conditions of the soil, and heat transfer between infiltrating water and soil (Mohammed et al., 2018). However, how these conditions influence preferential flowpaths through frozen soil remains unclear (Mohammed et al., 2018). An improved understanding of flowpaths through frozen soils is necessary to enhance the understanding of nutrient transport under these conditions.

As the NGS is a critical period for nutrient loss, it is essential that beneficial management practices (BMPs) are effective during this period. The application of fertilizer in the fall, prior to the NGS, is a common practice in cold temperate regions due to the narrow window of time for accessing fields in the spring. Snowmelt results in wet fields in spring that are often inaccessible to farm equipment and pose a risk of soil compaction. Fall fertilizer applications often coincide with the planting and harvest of winter-wheat in a corn-soy-wheat rotation. Changes to the application of fertilizer (rate, timing, and placement) on no-till fields may assist in limiting supply of nutrients to tile drains (Gildow et al., 2016; Jarvis, 2007; Plach et al., 2017). Subsurface placement of fertilizer has been proposed as a management practice that can reduce nutrient losses to the environment (Malhi et al., 2001; Smith et al., 2016) and have agronomic advantages (Khatiwada et al., 2012; Nkebiwe et al., 2016). Watershed models in the Great Lakes region have shown that subsurface placement of P can improve water quality at the watershed outlet (Gildow et al., 2016; Kalcic et al., 2016)(Gildow et al., 2016; Kalcic et al., 2016). Recent work at the plot scale has also shown subsurface placement of P to reduce concentrations of subsurface P leachate by 66%, compared to surface broadcast applications (Williams et al., 2018). Previous studies investigating manure and fertilizer placement and nutrient export have favoured methods that incorporate nutrients into the soil over surface applications (Glaesner et al., 2011b; King et al., 2017; Kleinman et al., 2009). Two primary mechanisms explain why subsurface placement can have an advantage over surface broadcasting in no-till systems: first, the physical retention of nutrients caused by fertilizer being placed away from active flowpaths reduces the exposure of P to preferential flowpaths (Glaesner et al., 2011a; Jarvis, 2007). Second, the chemical retention of nutrients as subsurface placement provides more contact with the soil leading to greater opportunity for adsorption to soil particles (Glaesner et al., 2011b; Williams et al., 2018). While these retention mechanisms have been demonstrated with subsurface manure application (Glaesner et al., 2011b), there is a need to quantify subsurface P losses among application strategies of inorganic fertilizers (Smith et al., 2016), and how losses may differ across soil types (Plach et al., 2017) and under both frozen and unfrozen soil conditions experienced over the NGS.

The goal of this study is to characterize the movement of water through frozen and unfrozen soils, and determine if subsurface fertilizer placement can reduce the leaching of nutrients in the subsurface under NGS conditions. The main objectives of this study are to: 1) characterize the movement of water and conservative tracers through preferential and matrix flowpaths in soils under different soil frost conditions (partially frozen vs unfrozen), 2) determine if subsurface flow pathways differ with soil texture (silt loam, clay), and 3) quantify the mobilization of nitrate (NO_3^-) and dissolved reactive P (DRP) through the soil profile under surface broadcast and subsurface placement (banding) application strategies, and relate this to differences in flowpaths.

3.3 Methods

3.3.1 Field site description and soil monolith extraction

Soil monoliths were extracted from two sites in Ontario, Canada located in Kingsville (KVL) and St. Marys (STM). Both fields were on active farms following a crop rotation containing corn, soybeans, and winter wheat. The field at KVL has been under no-till management for 20 years, and the STM field has been under rotational conservational till for 25 years with a shallow disc till every 3 years following wheat. At both sites, cover crops are planted in years with winter wheat, after harvest. Soil textures are characterized as Brookston Silt Loam at the STM site (Hoffman and Richards, 1952) and Brookston Clay at the KVL site (Richards et al., 1949). Both fields are tile drained, with tiles at depths of 75-100 cm, with ~15 m spacing. At each of the two sites, two intact soil monoliths were extracted in December 2016 using a custom-built 28×30×35 cm steel corer. The corer was sledgehammered into the soil using a wooden block to evenly distribute force and minimize compaction. A hole was dug around the steel corer and exposed monolith, and a steel plate was inserted underneath the monolith to extract it from the ground. In the field, soil monoliths (28×30×30 cm) were extracted from the corer and gently placed into 28×30×40 cm hard acrylic tanks. Tanks were designed with a 3 cm layer of rinsed pea gravel and two layers of fiberglass mesh window screening at the base prior to soil monolith installation. Following extraction, soil monoliths were stored in their tanks at 4°C prior to the start of the experiment. At the time the monoliths were collected, additional soil samples from the undisturbed outer walls of each exposed pit were taken at depths of 0-10, 10-20, and 20-30 cm and the samples were homogenized, dried (at 30°C for 24 h) and sieved to 2 mm grain size for the analysis of water-extractable P (WEP) concentrations.

3.3.2 Chamber and rainfall set up

Soil monoliths were placed in an environmental chamber (Percival I-41NL XC9) in which the air temperature was controlled. Soil monoliths were subject to six simulated NGS events with rainfall under unfrozen (+10ºC) and partially frozen (~0ºC) conditions, over a 35-day period for the silt loam monoliths, and 40 days for clay (Figure 3.1; Supplementary Figure A1). Monolith soil temperature was recorded every 30 minutes during the experiment by two temperature sensors (DaqLink Fourier Systems Ltd., #DBSA720), which were installed in one soil monolith of each soil type at depths of -5 and -25 cm relative to the soil surface. A third temperature sensor was placed in the chamber to monitor chamber air temperature.

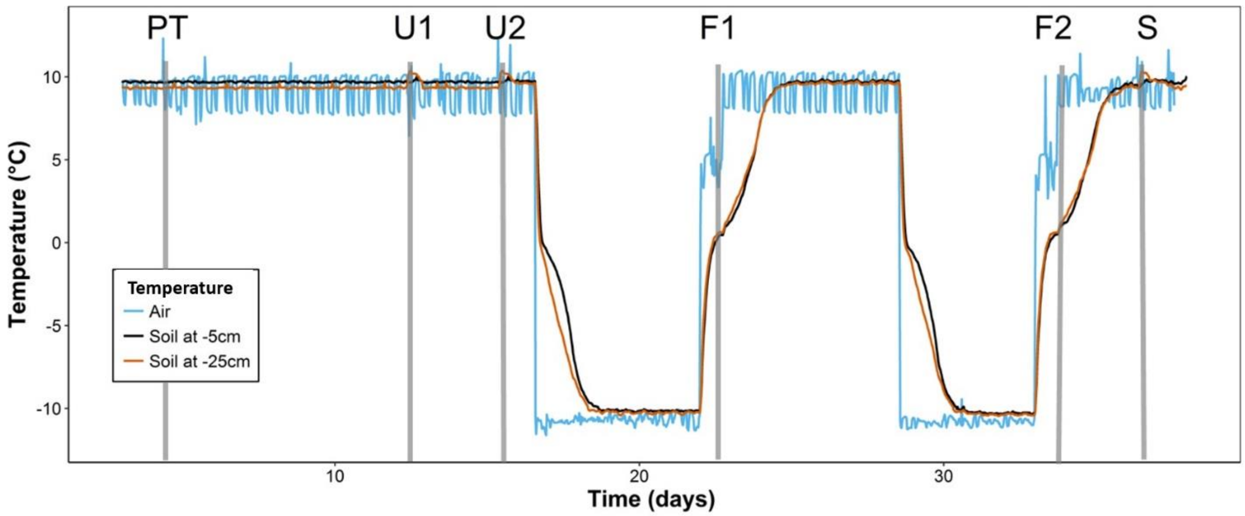

Figure 3.1 Air temperature in the chamber and soil temperature at -5 cm and -25 cm over the simulated non-growing season on silt loam monoliths. Rainfall simulations occurred while the soil monoliths were unfrozen (10°C) or partially frozen (~0°C). Temperatures during the simulations on the clay monoliths were similar with the exception of additional 5 days at 10°C between partially frozen events (F1 and F2).

The simulated NGS consisted of six events in which artificial rainwater (described below) was applied. Prior to the application of the fertilizer treatment, a single saturation event was conducted to provide baseline chemistry for each soil type and to characterize natural variability among the monoliths (pre-treatment, PT). Following this, two rainfall simulations on unfrozen (U) soil were conducted (U1, U2). All unfrozen events (PT, U1, U2) were conducted while the chamber was held at 10°C. Following these events, the chamber temperature was decreased to -10°C and held for 5 days (freezing phase). The chamber temperature was subsequently increased from -10 to 5°C for 8 hours before simulated rainfall was applied to the partially frozen (F) soil. This was repeated twice (F1, F2). Prior to both thawing phases, soils were frozen, but began to thaw as the events progressed. Soil monoliths were not insulated during this experiment (see Supplementary Figure A1), therefore thawing likely occurred from both top-down and lateral directions. Although a collar was used to prevent the short circuiting of flowing water, this may not have been effective against this process. Between the F1 and F2 simulations, the temperature was held at 10°C for 5 days for the silt loam monoliths and 10°C for 10 days for the clay monoliths. The discrepancy in holding time between the two F simulations was due to human error but is unlikely to have impacted the results. Although the shift from -10°C to 5°C over an 8-hour period is somewhat extreme and shifts of this magnitude are uncommon, they do occur in temperate climates such as Ontario (ECCC, 2018a). A final saturation (S) event was done on thawed monoliths, where the base of each tank was sealed and the applied rainfall caused the water table to reach the soil surface, simulating spring flooding. For each simulated event, rainwater was applied at a rate of 4.4 mm hr^{-1}, until 42 mm had been applied (U1, U2, F1, F2) or until soil reached saturation (PT, S). This experiment simulated rain-on-snow events. Such events are prevalent in temperate landscapes and are becoming more prevalent in cold regions with climate change (Leung et al., 2004; Ye et al., 2008). Soil was at field capacity for all post-fertilization events, including being frozen at field capacity.

In each monolith, an acrylic collar (23×25×9 cm) was inserted to a depth of 2 cm below the soil surface, to minimize potential preferential flow down the tank walls. Fertilizer and rainfall were applied to soil monoliths within bounds of the inner collar. Soil monoliths were fertilized following the first event (PT) at a rate of 97.5 kg ha^{-1} of P_2O_5 applied as mono-ammonium phosphate (MAP) and 185 kg ha^{-1} of N with 165 kg ha^{-1} applied as urea, and the remaining 20 kg ha^{-1} supplied from the applied MAP. One monolith of each soil type received the fertilizer prills via surface broadcast without incorporation and the other was fertilized in a single 3 cm wide band, 5 cm below the soil surface, to mimic how P is applied in agricultural fields. The same rate of N and P was applied in both treatments, irrespective of fertilization method as the purpose of this study was to investigate differences in transport between two application methods. However, it is recognized that this fertilizer rate is unrealistic for subsurface banded fertilizer application in working farm conditions due to risk of seed damage associated with ammonia release from these fertilizers (OMAFRA, 2017). Banding of urea directly with seed is not recommended, however, subsurface placement of urea at 5 cm beside and 5 cm below the seed row is safe if lower rates are applied (40 kg ha^{-1} of urea for corn, OMAFRA, 2017).

A rainfall simulator was designed using a 60×40×22 cm polyethylene container with 25 needles (23G) evenly distributed over an area of 23×35 cm, confining the uniform applied rainfall within the inner collar. A peristaltic pump was used to maintain a constant head for water in the rainfall simulator container over the course of each event, to ensure a constant rainfall rate (4.4 mm hr^{-1}). The artificial rainwater was prepared based on rainwater composition typical of southern

Ontario (National Atmospheric Chemistry (NATChem) Database) containing SO_4^{2-} (2.17 mg L^{-1}), NO_3^- (2.64 mg L^{-1}), Cl^- (0.19 mg L^{-1}), NH_4^+ (0.81 mg L^{-1}), Na^+ (0.10 mg L^{-1}), Ca^{2+} (0.48 mg L^{-1}), Mg^{2+} (0.08 mg L^{-1}) and K^+ (0.05 mg L^{-1}) and was adjusted to a pH of 5.15 ± 0.05. Total rainfall of 260 mm and 255 mm, simulating NGS rainfall at STM and KVL sites respectively, was applied to the soil monoliths over the course of the experiments, which is lower than long term (1981-2010) average of 561 mm for precipitation received between October and April for the region (ECCC, 2018a). However, typically a considerable amount of precipitation in the selected sites is received in the form of snow, which was not simulated in this experiment. Three types of conservative water tracers were applied during U2 (100 mg L^{-1} Br^- as KBr), F1 (500 mg L^{-1} Cl^- as NaCl) and F2 (D_2O enriched to +100 ‰) events to identify breakthrough curves and investigate differences in hydrologic connectivity and preferential flow between unfrozen and partially frozen conditions, and between successive partially frozen events. Comparisons between conservative tracers are made by comparing the ratio of the concentration of tracer found in leachate (C) to the initial concentration applied (C_0).

We used four soil monoliths in our study, with one monolith of each soil type (silt loam, clay) subjected to each fertilizer application method (broadcast, subsurface placement). All soil monoliths were subjected to the same rainfall regimes and underwent the same experimental and sampling schedules for the entire duration of the experiment. Thus, there were two replicates to investigate the impacts of soil frost on hydrologic flowpaths within each of the two soil textures. However, within each soil texture, only a single soil monolith was used to investigate the impacts of fertilizer application. Although replication is ideal, this was not logistically feasible due to equipment limitations. We attempted to address the issue of replication by using large soil monoliths (rather than small cores) and through repeated, successive events (n=6 events).

3.3.3 Sample collection and analyses

Leachate water samples (~125 mL) were collected from the base of all monoliths as monoliths drained and filtered through a 0.45 µm filter (Cellulose acetate filters, FlipMate, Delta Scientific) for the analysis of dissolved reactive phosphorus (DRP) using colorimetric methods (Bran Luebbe AA3, Seal Analytical, Method no. G-175-96 Rev. 13 for DRP) and analyses of NO_3^-, Br^- and Cl^- using ion chromatography (DIONEX ICS 3000, IonPac AS18 analytical column). 50 mL of unfiltered subsample was acidified to 0.2% H_2SO_4 for total phosphorus (TP) analysis. The subsample was digested with acid persulfate in an autoclave (EPA/600/R-93/100, Method 365.1), and subsequently analyzed colorimetrically (Bran Luebbe AA3, Seal Analytical, Method no. G-188-097 for TP). Sample preservation was completed within 24 hrs of sample collection. Filtered leachate samples collected from all events following D_2O tracer application (F2, S) were sealed with parafilm to prevent fractionation.

In addition to the leachate water samples, porewater samples (5 mL) were collected separately from different depths (-5, -15 and -25 cm) to measure the PO_4^{3-}, NO_3^-, Br^- and Cl^- concentrations. These porewater samples were extracted by ceramic samplers, 5 cm in length and 2.5 mm in diameter (CSS5 MicroRhizon™ samplers, Ejikelamp, Netherlands, #19.21.23F) installed horizontally into the soil matrix through ports in the tank wall, directly into the analysis vials through a needle delivering the sample in a septum-sealed vial. Porewater samples were collected from all depths during saturated conditions (PT, S). Attempts to retrieve porewater samples were made during all other events; however, our samplers had difficulty retrieving samples from unsaturated conditions. Few samples were obtained during unsaturated conditions and no porewater samples were retrieved under frozen conditions. All outflow leachate and porewater samples were stored at 4°C prior to analysis. Leachate and porewater samples with PO_4^{3-} concentrations below DIONEX ICS 3000 detection limit (0.75 mg L^{-1} PO_4^{3-}) were re-run on a Bran Luebbe AA3, along with soil water-extractable P (WEP) and soil NO_3^- (see below) (ammonium-molybdate ascorbic-acid, Bran Luebbe AA3, Seal Analytical: Method no. G-175-96 Rev. 13 for DRP, Seal Analytical: Method no. G-109-94 for NO_3^-). Leachate samples from F2 and S events were analyzed for δ_2H using a Picarro™ Liquid Water Isotope Analyzer (LWIA, model L2130-i) based on Cavity Ring-Down Spectroscopy (CRDS) technology at the University of Manitoba. Delta (δ) values were recorded in permil (‰) deviations from the Vienna Standard Mean Ocean Water (VSMOW) (Craig, 1961) with a precision of 0.1‰. Background concentrations of D_2O were subtracted from both initial (C_0) and final (C) concentrations, to allow for comparisons to other conservative tracers.

At the end of the experiment, soil monoliths were destructively sampled for the analyses of extractable nutrients. Soil samples were collected from 9 locations at each depth of 0-10, 10-20 and 20-30 cm (collected in a 8×9 cm grid while avoiding samples within 2 cm of the edge of the monolith). Soil samples were homogenized, dried at 30°C for 24 hrs, and sieved to 2 mm. Dried soil samples from both before and after the experiment were extracted using standard laboratory methods (5 g of dried soil extracted with 50 mL of deionized water, shaken for 1 hour for WEP, and 2.5 g of dried soil extracted with 25 mL of 2M KCl, shaken for 1 hour for NO_3^-). Extractants for both WEP and NO_3^- were gravity filtered through a Whatman no. 42 filter. The WEP samples were also centrifuged for 5 minutes at 5000 rpm prior to filtering. Samples were stored at 4°C prior to analysis.

3.4 Results

3.4.1 Variability in flowpaths between soil texture and soil frost

Variability between flowpaths in unfrozen soil differed with soil texture, where preferential flow dominated in clay and matrix flow dominated in silt loam (Figure 3.2). During U2, the breakthrough curve (C/C_0 vs cumulative volume) of Br^- tracer indicated the presence of preferential flow in clay monoliths (Figure 3.2). In unfrozen clay, C/C_0 of Br^- increased over the course of the event, indicating increased connectivity with the surface over time as the soil became more saturated and more preferential flowpaths were activated (Figure 3.2). In contrast, Br^- applied to silt loam soils during U2 was not found in the leachate samples during this event (Figure 3.2). The lack of applied tracer in U2 leachate suggests that matrix flow was the dominant flowpath through unfrozen silt loam, as there was no direct connectivity between the surface and subsurface. Elevated C/C_0 of Br^- in leachate were found in subsequent events on silt loam (Figure 3.2), also indicating the dominance of matrix flow.

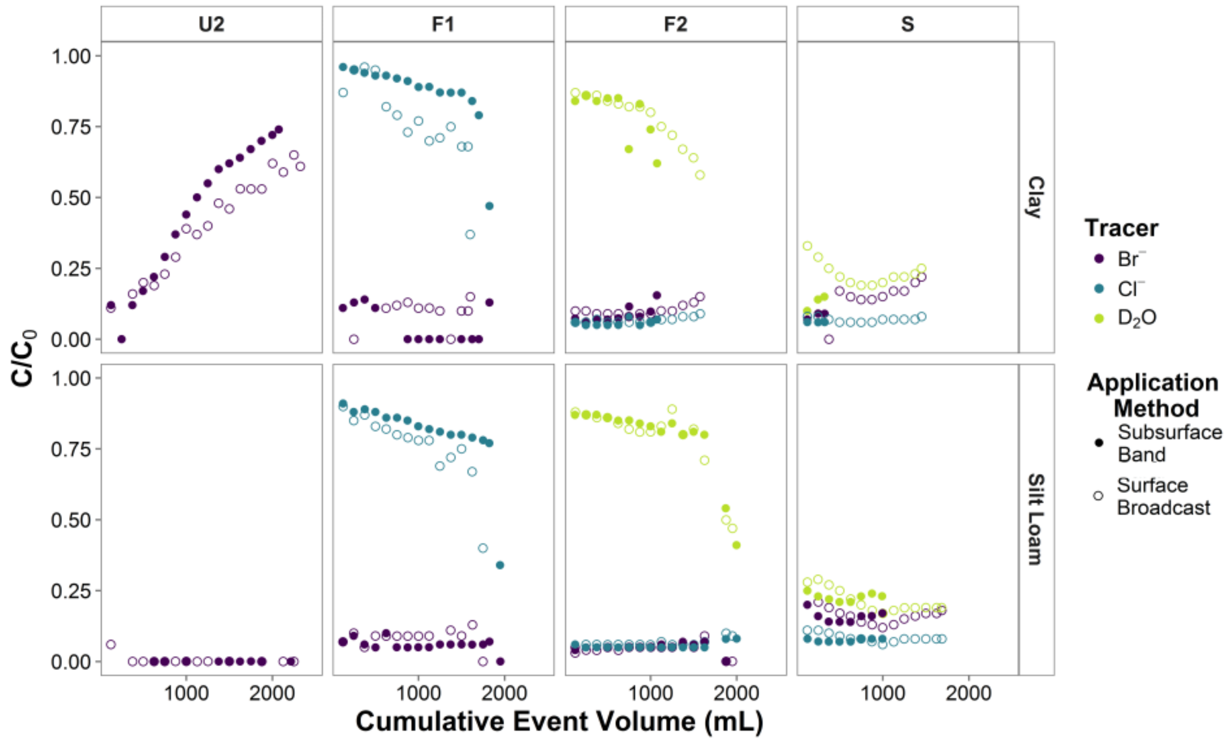

Figure 3.2 Tracer breakthrough curves (C/C_0) by cumulative volume over U2, F1, F2 and S events for the two soil types. For D_2O, C/C_0 represents sample concentrations over initial minus background concentrations.

In contrast, under partially frozen conditions, the observed patterns in the conservative tracers suggest that flowpaths were similar among all monoliths (F1, F2, Figure 3.2), and indicate the presence of preferential flowpaths. For example, early in F1 and F2, hydraulic connectivity between the surface and the subsurface was high, as demonstrated by the large ratios (C/C_0) of Cl^- (F1) and D_2O (F2) in both soil types (Figure 3.2). As soils thawed, the opportunity for matrix flow increased and more water from previous events entered the leachate. In F1 and F2, C/C_0 of applied tracer declined as tracers were diluted by soil water as the soil thawed, and the C/C_0 of previously applied tracers increased (Figure 3.2). The preferential flow pattern in partially frozen soils (high connectivity early in event) is different from the preferential flow patterns observed in unfrozen clay soil where connectivity was initially low and increased over the course of the event. There were no observed differences in flowpaths between the F1 and F2, or between soil textures during these events.

The results of conservative water tracers suggest that soil monoliths of the same soil texture are hydraulically similar within an event (Figure 3.2). Similar tracer responses among soil monoliths provides confidence that differences in leachate nutrient concentrations are due to differences in fertilizer application method and are not the result of potential variability in flowpaths between soil monoliths, despite only having one replicate of each soil type and fertilizer application method.

3.4.2 Phosphorus and Nitrogen in subsurface leachate

Over the entire simulated NGS, soils receiving fertilizer via subsurface placement had lower cumulative leachate DRP and NO_3^- losses compared to surface broadcast applications on the same soil type (Figure 3.3, Figure 3.4). Subsurface placement retained more DRP, exporting 4.25 kg ha^{-1} (64%) less in clay and 2.33 kg ha^{-1} (60%) less in silt loam soils, compared to surface applied fertilizer. Of the P fertilizer that was applied, broadcast treatments lost 15.9% (clay) and 9.0% (silt loam), while banded treatments lost 5.7% (clay) and 3.6% (silt loam). Similar patterns were observed for TP loss, where monoliths with subsurface fertilizer placement lost 3.06 kg TP ha^{-1} (60% less) compared with 7.43 kg ha^{-1} in the monolith with broadcast fertilizer in the clay soil, and 2.20 kg TP ha^{-1} (56% less) compared with 5.06 kg ha^{-1} in the monolith with broadcast fertilizer in the silt loam soil. Subsurface placement retained 65.73 kg ha^{-1} of N (61%) in clay and 26.85 kg ha^{-1} of N (23%) in silt loam, compared to surface broadcast applications. Over the simulated NGS, 57% (clay) and 60% (silt loam) of applied N was lost from broadcast applications, whereas under subsurface placement, only 22% (clay) and 45% (silt loam) of applied N was lost. Overall, surface broadcast on clay soils resulted in the highest cumulative DRP losses while surface broadcast applications on silt loam led to the highest cumulative NO_3^- losses.

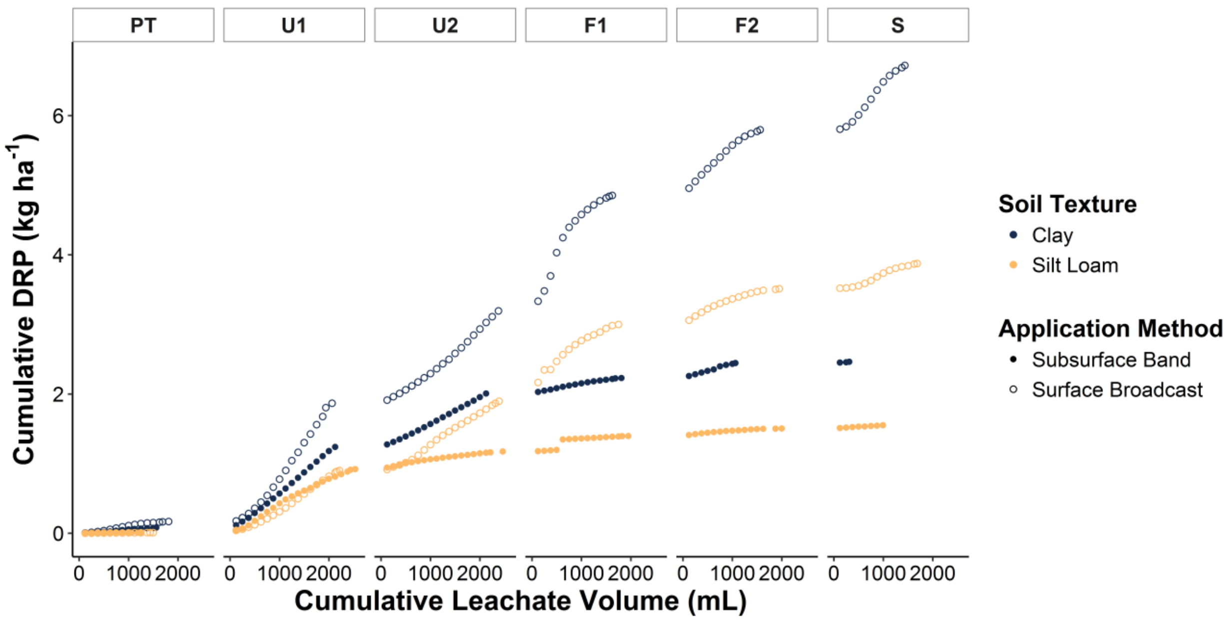

Figure 3.3 Cumulative DRP (kg ha^{-1}) loss over cumulative leachate volume (mL) for all soil monoliths over all 6 NGS events.

Patterns in leachate DRP and NO_3^- varied both throughout and among events during the simulated NGS. Initial nutrient concentrations from PT varied with soil type, where KVL clay soils had greater initial mean DRP concentrations in leachate (0.6 mg L^{-1} ± 0.5), compared to STM silt loam (0.1 mg L^{-1} ± 0.0). In contrast, PT mean NO_3^- losses from KVL clay soils were lower (0.1 mg L^{-1} ± 0.2) than those from STM silt loam soils (60.9 mg L^{-1} ± 11.1). DRP losses across both fertilizer placement methods and soil types were highest during U1, the first event immediately following fertilization, compared to all other simulated events. In contrast, broadcast treatments lost marginally more NO_3^- in leachate during U1 than their banded counterparts (Figure 3.4). In U2, differences leachate NO_3^- between application methods begin to diverge as NO_3^- from broadcast applications increased. Although actual differences in cumulative NO_3^- loss in leachate differed between soils, the rates of NO_3^- loss were similar among all monoliths during unfrozen events (Figure 3.4). Higher cumulative NO_3^- losses from silt loam soils were due, in part, to higher initial NO_3^- in the silt loam soil. High DRP losses were observed immediately following fertilization in U1, while increases in NO_3^- were less immediate.

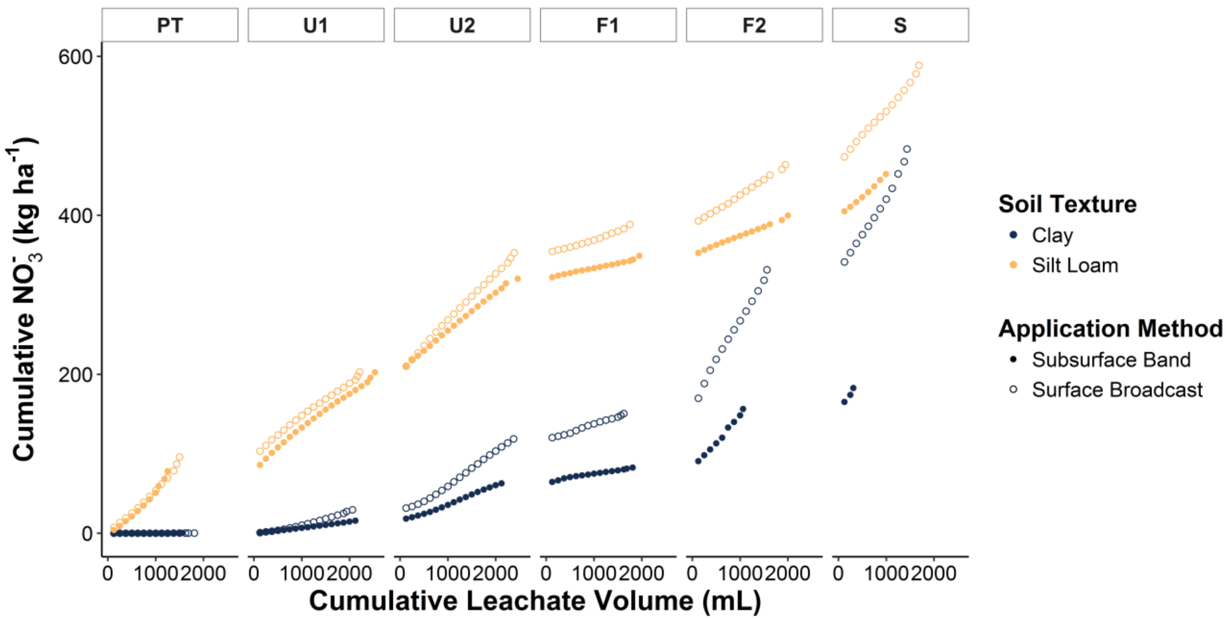

Figure 3.4 Cumulative NO_3^- (kg ha^{-1}) loss compared to cumulative leachate volume (mL) for all soil monoliths over all 6 NGS events.

Under partially frozen and saturated conditions, broadcast treatments continued to result in greater losses of DRP and NO_3^- in leachate compared to banded treatments. Leachate DRP from broadcast treatments increased in both soil types during partially frozen events (F1, F2, Figure 3.3). This increase in DRP was particularly apparent in the clay broadcast treatment during F1. In contrast, subsurface bands showed little increase in DRP in leachate over F1 and F2 in both soil types. While NO_3^- losses from broadcast applications continued to be higher than those from subsurface banded applications, the rate of NO_3^- loss declined in all soil monoliths during the first event on partially frozen soil (F1), compared to unfrozen events. In the second partially frozen event (F2), the rate of NO_3^- loss in leachate differed between soil textures (Figure 3.4). Through F2, the rate of NO_3^- remained similar to F1 in the silt loam soil. However, the rate of NO_3^- loss from clay soils increased dramatically from both application methods during F2, compared to all previous events. The final saturation event (S) showed similar rises in leachate DRP from broadcast treatments, while DRP from banded applications remained relatively steady for both soil types. The rate of NO_3^- loss during saturated conditions remained high in clay soils and increased in silt loam soils compared to F2. Overall, through the entire simulated NGS, banded treatments retained more applied P and N than their broadcast counterparts in both soils.

3.4.3 Phosphorus and Nitrogen retention in soil

In general, fertilizer applied in subsurface bands resulted in more WEP and NO_3^- available near initial band placement compared to surrounding soil, while WEP and NO_3^- from broadcast soils was more evenly distributed across the soil surface. Prior to fertilization, both soil types showed stratification of WEP with depth (Table 3.1), while only the clay soil showed stratification of NO_3^- with depth (Table 3.2). The centre of the clay band monolith was the only location where WEP after the experiment was higher than the control (Table 3.1). In contrast, fertilizer application increased soil NO_3^- availability in the soil surface (0-10 cm) in both soil types and fertilizer application methods following the simulated NGS (Table 3.2). Fertilizer application method did not appear to influence NO_3^- retention at depths of 10-20 and 20-30 cm. However, at depths of 10-20 and 20-30 cm, clay soils showed higher NO_3^- retention under both fertilizer application methods, whereas NO_3^- retention at these depths was not greater than the control in the silt loam monoliths (Table 3.2).

Table 3.1 Pre- and post-experiment soil water-extractable P (WEP) across soil depths for two soil texture and fertilizer placements. Values represent the mean and the values in ( ) are the standard deviation of three samples per depth.

			WEP (mg kg^{-1})		
Soil and Fertilizer	**Depth (cm)**	**Control**	**Post - Left**	**Post - Center**	**Post - Right**
Clay Band	0-10	8.71 (0.70)	4.62 (0.74)	13.97 (6.66)	4.29 (0.40)
	10-20	4.74 (0.16)	2.58 (0.36)	2.41 (0.51)	3.13 (0.47)
	20-30	4.46 (0.31)	2.92 (0.24)	2.11 (0.19)	3.24 (0.37)
Clay Broadcast	0-10	5.30 (1.10)	3.55 (0.51)	3.94 (0.67)	3.62 (0.47)
	10-20	2.38 (0.18)	0.97 (0.13)	1.39 (0.27)	1.72 (0.51)
	20-30	2.38 (0.36)	1.07 (0.28)	0.76 (0.19)	2.00 (0.71)
Silt Loam Band	0-10	3.97 (0.69)	0.24 (0.18)	1.85 (1.27)	0.30 (0.28)
	10-20	2.10 (0.26)	<0.01 (0.01)	0.23 (0.17)	0.12 (0.17)
	20-30	1.94 (0.25)	0.09 (0.11)	<0.01 (0.01)	<0.01 (0.01)
Silt Loam Broadcast	0-10	3.53 (0.59)	0.88 (0.55)	0.33 (0.08)	0.27 (0.38)
	10-20	1.93 (0.48)	0.23 (0.01)	0.29 (0.34)	0.49 (0.45)
	20-30	1.73 (0.44)	0.06 (0.07)	0.07 (0.08)	0.04 (0.03)

Table 3.2 Pre- and post-experiment NO_3^- across soil depths for two soil textures and fertilizer placements. Values represent the mean and the values in ( ) are the standard deviation of three samples per depth.

			NO_3^- (μg kg^{-1})		
Soil and Fertilizer	**Depth (cm)**	**Control**	**Post - Left**	**Post - Center**	**Post - Right**
Clay Band	0-10	12.60 (8.81)	32.90 (12.20)	306.00 (45.70)	43.40 (10.30)
	10-20	4.17 (0.79)	9.34 (0.74)	12.70 (2.92)	8.38 (1.19)
	20-30	4.19 (0.33)	13.10 (5.69)	13.40 (1.64)	10.10 (1.15)
Clay Broadcast	0-10	48.80 (33.40)	67.70 (6.41)	69.00 (6.92)	48.40 (17.60)
	10-20	4.34 (0.65)	7.01 (0.62)	12.50 (3.89)	7.74 (0.99)
	20-30	4.43 (0.85)	14.50 (10.50)	13.40 (1.88)	7.13 (1.16)
Silt Loam Band	0-10	30.40 (15.80)	22.90 (7.19)	346.00 (232.00)	30.30 (14.10)
	10-20	30.30 (7.90)	21.90 (15.10)	15.50 (0.79)	13.10 (2.14)
	20-30	22.80 (2.41)	13.70 (3.79)	16.10 (2.18)	12.10 (1.53)
Silt Loam Broadcast	0-10	29.60 (7.82)	110.00 (28.60)	78.20 (23.40)	68.40 (39.70)
	10-20	15.90 (15.90)	16.00 (3.67)	13.20 (3.65)	19.40 (8.06)
	20-30	21.50 (8.59)	20.20 (7.69)	21.90 (12.80)	14.80 (2.62)

3.5 Discussion

This research has demonstrated that nutrient transport in the subsurface is controlled by the connection of the nutrient source with active subsurface flowpaths. It has also shown that nutrient transport in agricultural soil is dependent on both dominant flow type and fertilizer placement. Flowpaths were shown to differ with both soil texture and the presence of soil frost. Fertilizer placement can result in differences in subsurface nutrient export, due to differing degrees of connectivity with flowpaths present under different texture and soil frost conditions. These results have implications for nutrient application strategies prior to the NGS.

3.5.1 Variability in flowpaths with texture and frost conditions

In this experiment, flowpaths differed with soil texture, and, the impacts of frost on flowpaths differed between the two textures. It was hypothesized that in unfrozen soil, matrix flow would dominate in the silt loam, whereas preferential flow would dominate in the clay. Leaching patterns for the conservative tracers used in the experimental rainfall additions supported this hypothesis. The differences in flowpaths with soil texture in unfrozen soils are unsurprising, as preferential flow is more common in fine-textured soil as the soil matrix is less permeable (Hendrickx and Flury, 2001). This work is also consistent with that of Glaesner et al. (2011a) who noted that the proportion of preferential flow increased with increasing clay content. It should be noted, however, that the silt loam soil also receives a shallow (5-8 cm) conservation till every 3 years, and tillage had occurred 3 years prior to monolith collection. As macropore networks can be slow to develop they may not have been fully formed at the time of monolith collection, and the rotational shallow till may have contributed to the prevalence of matrix flow in the surface of the unfrozen silt loam soil.

In this experiment, flowpaths differed under partially frozen conditions relative to unfrozen conditions; however, the effects of frost differed with soil texture. Preferential flow through frozen soil is known to occur (Stadler et al., 2000; Stähli et al., 1996), but can range from zero when water re-freezes upon entry (Watanabe and Kugisaki, 2017) to continuous macropore flow (Stadler et al. 2000). Knowledge of preferential flow through frozen ground remains poorly understood due to the challenges linking the interacting effects of preferential flow processes with soil freeze-thaw processes (Watanabe and Kugisaki, 2017, Mohammed et al., 2018). It was hypothesized that preferential flow would occur in partially frozen soils of both textures. Indeed, the experimental results indicate that preferential flow occurred in both silt loam and clay soils under partially frozen conditions. However, different mechanisms can result in the presence of preferential flowpaths among soils of different textures (Granger et al., 1984; Watanabe and Kugisaki, 2017). Macropores remaining air-filled upon freezing have been shown to result in preferential flow through frozen soils (Stadler et al., 2000), a mechanism that dominates in clay soils (Granger et al., 1984). Thus, it is likely that the preferential flowpaths present under unfrozen conditions in the clay soil remained active under partially frozen conditions (Figure 3.5). In contrast, the preferential flow observed in the partially frozen silt loam soil likely occurred as a result of the frost. When soil is frozen under unsaturated conditions, preferential flowpaths can develop as the smallest pores become blocked with ice (Stähli et al., 1996). Water entering this frozen soil must then flow through larger pores that remained air-filled upon freezing (Stähli et al., 1996), leading to the development of preferential flowpaths in frozen soils (Figure 3.5). Alternatively, desiccation cracks have also been shown to form during the freezing of loam soils (Weigert and Schmidt, 2005), providing another mechanism for the formation of preferential flowpaths through partially frozen loam soil.

It was also hypothesized that more preferential flow would occur during the second simulated rainfall on frozen soil, as ice expansion during multiple FTC can enhance preferential flow due to ice lens formation (Othman and Benson, 1993). However, this was not observed in the experiments in this study. Although the soil columns were at field capacity when frozen, it is possible that soils may need to be frozen at a higher antecedent moisture to promote the formation of ice lenses which could enhance preferential flow and transport. Total or liquid water content was not measured over the course of this experiment. Future work on flowpaths through partially frozen soil would benefit from moisture measurements, to further understand preferential flow under these conditions. Alternatively, soil may need to be exposed to multiple FTC to increase preferential flow (Ding et al., 2019).

The extent of preferential flow occurring throughout events also differed with frost conditions. For example, in unfrozen clay, contributions from preferential flow were initially low and increased over the course of the event, whereas preferential flow in partially frozen soils was initially high and then declined as the experimental event progressed. In this experiment, rainfall occurred on soils at field capacity. Given that more macropores and mesopores are activated as soils wet up (Kung et al., 2000b), it is likely that there was increased flow through macropores in the unfrozen clay as the soil approached saturation throughout the event. In contrast, in the partially frozen soil, infiltration was initially impeded, leading to surface ponding during the rainfall event, a phenomenon that has been observed by others (*e.g.*, Watanabe et al., 2012). Preferential flow is enhanced with increasing rainfall amount (Vidon and Cuadra, 2010) or when surface ponding is present (Watson and Luxmore, 1986) when the macropore flow capacity is not limited by water supply. As the soils thawed throughout the simulated event, the extent of surface ponding declined, decreasing preferential flow and transport.

The variability in subsurface flowpaths with soil textures and under partially frozen or thawed conditions shown in this study provides an improved understanding of the potential for seasonal differences in nutrient transport into agricultural tile drains. Indeed, the influence of soil frost on preferential flow is critical for nutrient transport, as tile drains are most active during the

NGS (Macrae et al., 2007a) when frozen ground conditions are most likely to be experienced. The occurrence of FTC in agricultural soils in temperate cold regions is expected to increase under a changing climate, due to greater temperature fluctuations and reduced snowpack (Henry, 2008). Future work should investigate potential differences in preferential flowpaths on frozen ground following multiple FTC or changes in FTC magnitude. Furthermore, the influence of FTC on subsurface flowpaths may differ with the use of more natural top-down soil freezing processes.

3.5.2 Impacts of fertilizer placement and links to flowpaths

As part of the 4R Nutrient Management Strategy, the subsurface placement of nutrients is encouraged, particularly for farmers in no-till systems (Johnston and Bruulsema, 2014) given the potential for increased leaching of P into tile drains in no-till systems (Kleinman et al., 2015). In this experiment, it was hypothesized that the subsurface placement of fertilizer would reduce nutrient loss, as this has been observed at the field (Khatiwada et al., 2012) and plot scale (Williams et al., 2018). However, the mechanisms that cause reduced nutrient loss with subsurface placement are not well understood, and, it is not clear how subsurface placement performs in frozen soil. In a short duration, experimental study, Smith et al. (2016) showed that the subsurface banding of nutrients reduced surface nutrient losses by 98% when compared to surface fertilizer applications. Our work supports the work of Smith et al. (2016), and showed that reduced nutrient losses following the subsurface placement of fertilizers persisted in subsurface flow and throughout our simulated NGS. Although we did not have replicated monoliths for our fertilizer treatment within each soil texture, we observed a consistent difference between the two fertilizer treatments within the 6 simulated events, and, this reduction was observed in both the clay and silt loam soils. In our study, the subsurface placement of nutrients reduced DRP losses by 60% in silt loam and 64% in clay compared to when nutrients were surface broadcast (over the duration of our simulated NGS). These results are similar to those of Williams et al. (2018), who found that the subsurface placement of mono-ammonium phosphate fertilizer reduced subsurface DRP concentrations in leachate by 66% compared to surface broadcast fertilizer. Our work showed that NO_3^- losses to be reduced by 61% in the clay and 23% in the silt loam over the duration of our simulated NGS. This is consistent with others who have found increased N efficiency with subsurface placement (*e.g.*, Malhi and Nyborg, 1984). It has been shown that nitrification rates are reduced when N fertilizer is applied in subsurface bands due to higher pH associated with concentrated ammonia (Yadvinder-Singh et al., 1994). While benefits of banding were similar in both soil types for P, nitrate reduction in leachate from the silt loam soil monoliths were not as pronounced. This could be due to differences in microbial communities between the two soils, and differences in community response to FTC. Freezing has been shown to result in shifts in microbial communities, influencing nitrification and denitrification rates (Sharma et al., 2006). Alternatively, high initial nitrate concentrations in the silt loam soil before fertilizer application may have masked some of the differences in nitrate leaching due to fertilizer placement.

From a source and transport perspective, subsurface application results in reduced transport because fertilizer is placed in a concentrated area, limiting opportunity for the fertilizer to directly connect to preferential flowpaths (Figure 3.5). Subsurface placement of nutrients also increases contact between fertilizer and soil, an important factor in nutrient retention (Glaesner et al., 2011b; Williams et al., 2018). In many fields within the Great Lakes Region (*i.e.* silt and clay loams in Ontario, Van Esbroeck et al., 2016), surface runoff is the primary pathway for dissolved P, and surface runoff and tile drains contribute equal quantities of total P in runoff. However, in heavier clays within the Great Lakes Region, tile drains have been found to be the major pathway (*e.g.*, King et al., 2015). It is recognized that the subsurface placement of fertilizer results in the fertilizer being placed closer to the saturated zone, which could potentially increase subsurface leaching; however, in tile drained landscapes, the water table is maintained farther below the surface, outside of the top 5 cm, making this occurrence less likely. In contrast, nutrients in broadcast applications are spread across the soil surface and have a higher risk of connecting with a preferential flowpath and being rapidly transported through the soil profile (Figure 3.5). Furthermore, broadcast fertilizer may be exposed to surface ponding, which can result in inorganic fertilizers becoming dissolved and rapidly exported via preferential flowpaths to tile drains. Others have also attributed high subsurface DRP losses from broadcast applications to low fertilizer-soil contact, and increased risk of fertilizer in contact with ponded surface water (*e.g.*, Williams et al., 2018). Risk of subsurface nutrient transport is greatest when nutrients are broadcast over soils where preferential flowpaths dominate under both partially frozen and unfrozen conditions, as can occur in clays. Subsurface placement may be a viable management practice to reduce subsurface nutrient losses in no-till systems, and may be particularly effective for reducing P losses from clay soils. Further, subsurface placement may have particular relevance for fall fertilizer applications where nutrients are applied before the NGS and soils may experience freezing and potential for increased preferential flow.

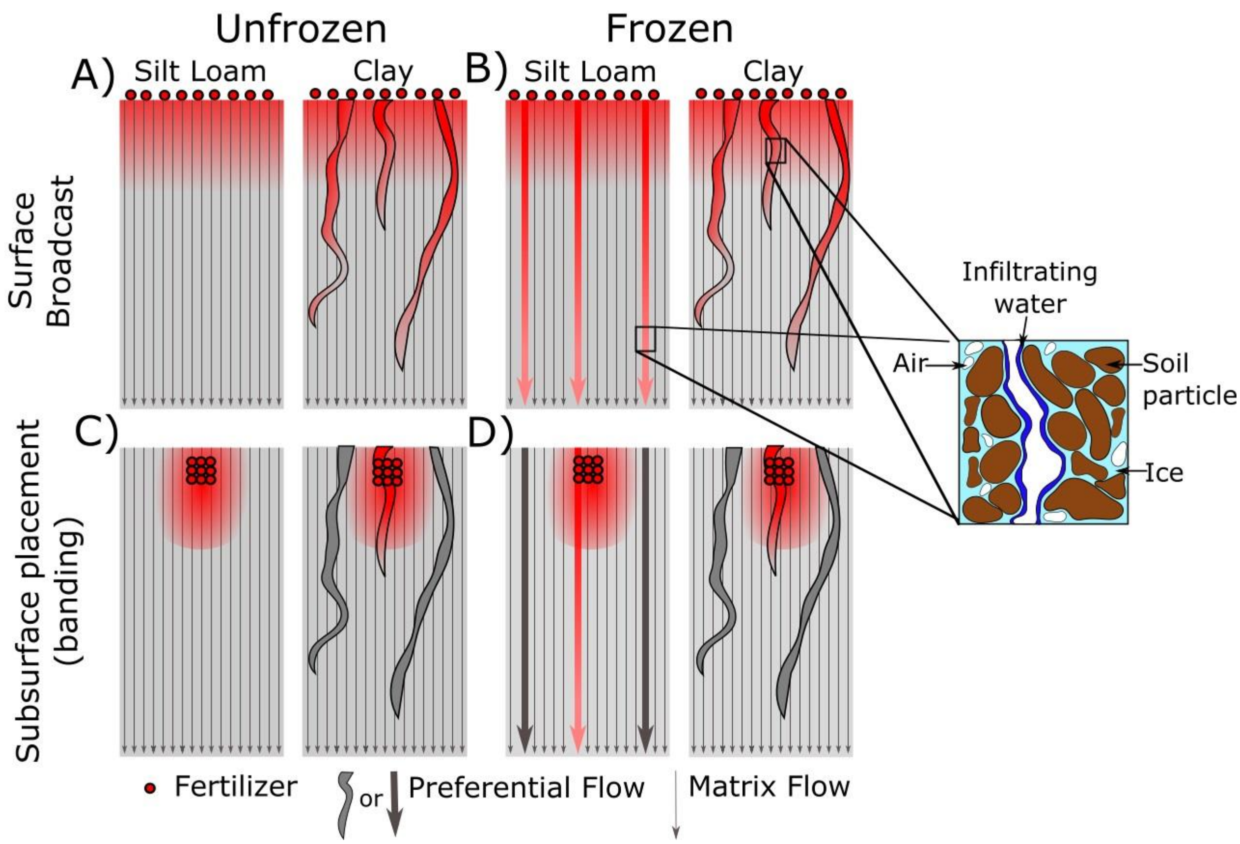

Figure 3.5 Conceptual diagram of interactions between flowpaths and fertilizer placement under different soil texture and antecedent temperature conditions. A) Surface broadcast nutrients over unfrozen soil infiltrate into the soil profile through matrix flow in silt loam, but are quickly transported deeper into the soil profile by preferential flowpaths in clay soil. B) Surface broadcast nutrients over partially frozen soils are quickly transported to the subsurface via preferential flowpaths. Macropores persist in partially frozen clays, while new preferential flowpaths are developed in partially frozen silt loam as larger pores remain air filled while smaller pores are blocked by ice in unsaturated partially frozen soil. Matrix flow begins to occur as soil thaws. C) Subsurface placement of fertilizer limits contact of nutrients with flowpaths, limiting the risk of transport via matrix and preferential flow in unfrozen soil. D) Subsurface placement limits contact of nutrients with preferential flowpaths in partially frozen soils, and can come into contact with matrix flow as soil thaws.

Finally, nutrient losses from tile drains on working farms are likely to be lower than the subsurface nutrient losses reported here. Subsurface nutrient losses are impacted by nutrient application, but are also a function of initial soil characteristics and biogeochemistry. Biogeochemical properties including soil test P, P sorption, P saturation, pH, redox conditions, P speciation, and microbial communities within the soil can all influence how added P fertilizer may be retained or lost from soil (Andersson et al., 2013; Ruttenberg, 1976; Haygarth and Jarvis 1999). Further, tile drains in many fields are deeper (75-100 cm) than the 30 cm soil monoliths considered in this study. Given that P sorption is typically greater with depth in the subsoil (Plach et al., 2018), DRP may have greater opportunity to be adsorbed by soil at lower depths if there is enough contact between soil and water (Andersson et al., 2013). As such, the importance of fertilizer application method may be less pronounced in soils where the capacity to sorb P is high and percolating water through matrix flow promotes contact between P-rich leachate and subsoil. Finally, nutrient losses from active farms using subsurface placement are expected to be lower than those reported here, as fertilizer applied via subsurface placement is associated with lower application rates to avoid seed damage (Court et al., 1962; OMAFRA, 2017). In the current study, nutrients were applied at the same rates to illustrate the significance of subsurface flowpaths and frost on nutrient transfer and demonstrate the mechanisms leading to reduced nutrient losses following subsurface placement. In a field setting where the same mechanisms are occurring but the nutrients have been applied at reduced rates, the benefits of subsurface placement are anticipated to be more pronounced. Field studies are needed to validate this hypothesis.

Although this work considers how flowpaths and fertilizer placement interact across soil frost and soil textures, other conditions may influence flowpaths and subsequent interactions with fertilizer. While this work investigated flowpaths through partially frozen soil, future work may consider similar experiments under alternative temperature regimes. In particular, holding soil monoliths at lower temperatures during rainfall or snowmelt simulations would provide an improved understanding of infiltration and potential refreezing in frozen soil and how this may influence preferential flow and transport. Future work should consider how flowpaths vary under differing antecedent moisture conditions as monitored by soil moisture sensors, and relate these to fertilizer placement methods. Investigating flowpaths under variable antecedent moisture conditions (*e.g.*, wet or dry) has particular relevance for spring fertilizer applications. Further, it will also be important to consider nutrient losses via both surface and subsurface flowpaths under various soil texture, temperature, and moisture conditions. Future studies should also investigate placement and application methods of other nutrient sources currently being used in agricultural fields in temperate cold regions, including injection and incorporation of manure, as well as applications that include a form of minimum tillage as it may break up preferential flow pathways and promote matrix flow and contact with the soil.

3.6 Conclusions

Our results indicate that differences in subsurface flowpaths in the vadose zone are related to differences in soil texture and soil frost. Preferential flow is prevalent in both clay and silt loam soil under partially frozen conditions, but is also prevalent in clay soil under unfrozen conditions. Our results demonstrate that the subsurface placement of fertilizer can reduce subsurface losses of N and P under NGS conditions in temperate cold regions when compared to surface broadcasts. The subsurface placement of fertilizer reduces subsurface nutrient losses because opportunities for applied fertilizer to interact with preferential flowpaths are reduced. Therefore, we conclude that subsurface placement is particularly advantageous for reducing nutrient losses in tile drainage when preferential flow is prevalent, such as in clay soils or in soils exposed to soil frost. For this reason, subsurface placement is recommended for clay soils and fall fertilizer applications, and should be used in conjunction with other BMPs including appropriate fertilizer application rate, source and timing (4R Nutrient Management Strategy).

Chapter 4

Differences in preferential flow with antecedent moisture conditions and soil texture: Implications for subsurface P transport

4.1 Abstract

Preferential flowpaths transport phosphorus (P) to agricultural tile drains. However, if and to what extent this may vary with soil texture, moisture conditions, and P placement is poorly understood. This study investigated (1) interactions between soil texture, antecedent moisture conditions, and the relative contributions of matrix and preferential flow and (2) associated P distributions through the soil profile when fertilizers were applied to the surface or subsurface. Brilliant blue dye was used to stain subsurface flowpaths in clay and silt loam plots during simulated rainfall events under wet and dry conditions. Fertilizer P was applied to the surface or via subsurface placement to plots of each soil texture and moisture condition. Photographs of dye stains were analyzed to classify flow patterns as matrix-dominated or macropore-dominated, and soils within plots were analyzed for their water extractable P (WEP) content. Preferential flow occurred under all soil texture and moisture conditions. Dye penetrated deeper into clay soils via macropores and had lower interaction with the soil matrix, compared to silt loam soil. Moisture conditions influenced preferential flowpaths in clay, with dry clay having deeper infiltration (92 ± 7.6 cm) and less dye-matrix interaction than wet clay (77 ± 4.7 cm). Depth of staining did not differ between wet (56 ± 7.2 cm) and dry (50 ± 6.6 cm) silt loam, nor did dominant flowpaths. WEP distribution in the top 10 cm of the soil profile differed with fertilizer placement, but no differences in soil WEP were observed at depth. These results demonstrate that large events following drought conditions in clay soil may be prone to rapid P transport to tile drains due to increased preferential flow, whereas flow in silt loams is less affected by antecedent moisture. Subsurface placement of fertilizer may minimize the risk of subsurface P transport, particularly in clay soil.

4.2 Introduction

Subsurface flowpaths are important for nutrient transport within agricultural landscapes, especially if they carry nutrients to tile drains, ultimately draining into surface waters (King et al., 2015). Agricultural runoff that is rich in nitrogen (N) and phosphorus (P) can contribute to water quality concerns (Bennett et al., 2001; Jarvie et al., 2017; Schindler et al., 2012). Excess P loading from agricultural lands can result in the eutrophication of freshwaters, negatively impacting drinking water quality, fisheries, tourism, and ecosystem health (Bennett et al., 2001; Correll, 1998). Understanding and subsequently managing P transport from agricultural landscapes is a critical component in combating global eutrophication problems.

Historically, P losses from tile drains were assumed to be negligible (Logan et al., 1980); however, it is now understood that tile drains can be an important pathway for transporting P (King et al., 2015; Sims et al., 1998). Water can move through the soil profile and into tile drains through two primary types of flowpaths: matrix and macropore (or preferential) flow. While P in matrix flow can be buffered by mineral subsoils, preferential flow via predominantly vertical soil macropores is important because it can rapidly transport water and nutrients from the surface to tile drains, bypassing opportunities for nutrient retention within the soil (Cey et al., 2009; Geohring et al., 2001; Smith et al., 2015). Recent research has examined the role of preferential flowpaths and associated P transport under no-till management (Smith et al., 2015; Williams et al., 2016), which has been widely promoted to reduce soil erosion (Derpsch et al., 2010). Such work has found that preferential flowpaths due to worm activity may be elevated in no-till systems (Djodjic et al., 2000; Geohring et al., 2001). It is generally thought that this increased macropore density, combined with P stratification in the soil profile associated with no-till, results in greater subsurface losses of P in tile drains (King et al., 2015). Although the existence of preferential flow is clear, the activation of these flowpaths in time and space is less well understood. The relative contributions of flowpaths can differ with soil texture, antecedent moisture conditions, seasonally frozen ground, and management practices (Allaire et al., 2009). An improved understanding of the activation of different pathways may assist land managers with the timing and placement of fertilizer P.

Dye staining is an established method to visualize subsurface water and study the relative importance – in terms of spatial extent – of different flowpaths (Forrer et al., 1999; Weiler and Flühler, 2004). This method is common in agricultural landscapes (Ali et al., 2018; Bachmair et al., 2009; Chyba et al., 2013; Kasteel et al., 2007; Yao et al., 2017) and other landscapes including grasslands (Bachmair et al., 2009; Weiler and Naef, 2003) and forests (Bachmair et al., 2009; Gimbel et al., 2015). Dye staining has also been used to compare dominant flowpaths under different regional and climatic factors, including soil texture (Bachmair et al., 2009; Gimbel et al., 2015), soil moisture conditions (Yao et al., 2017), and rainfall amounts (Bachmair et al., 2009). Within agricultural landscapes, this method has been used to study flowpaths under different management practices including tillage (Chyba et al., 2013; Kasteel et al., 2007; Wuest, 2009) and manure application (Ali et al., 2018). To date, few studies have investigated the link between subsurface flowpaths and fertilizer placement in no-till systems, particularly under different texture and moisture conditions.

The subsurface placement (banding) of fertilizer has been proposed as a beneficial management practice (BMP) that can play an important role in addressing the issue of nutrient loss from agricultural landscapes, particularly when compared to surface fertilizer applications over no-till soil (Smith et al., 2016). Although studies have reported increased P in tile drainage under no-till management (*e.g.*, Kleinman et al., 2009; Williams et al., 2016). Lam et al. (2016) found no difference in P losses through tile drains under different tillage practices when P was applied in the subsurface. This suggests the combination of tillage method and fertilizer application may be more important than either on their own. Additional work has shown that the subsurface placement of nutrients can reduce P loss in surface runoff (Smith et al., 2016) and subsurface drainage (Grant et al., 2018; Williams et al., 2018). The placement of nutrients in the subsurface may increase the interaction between applied nutrients and the soil, thereby increasing chemical retention of nutrients in the soil (Glaesner et al., 2011b; Williams et al., 2018), whereas nutrients broadcast over no-till soils have little contact with the soil and can easily be lost (Feyereisen et al., 2010; Kleinman et al., 2009). Further, it has been suggested that placement of nutrients in the subsurface reduces the risk of contact of applied nutrients with preferential flowpaths, therefore limiting nutrient leaching (Glaesner et al., 2011b). In the literature, the effects of subsurface fertilizer placement on subsurface P losses have been shown empirically (Glaesner et al., 2011b; Williams et al., 2018). However, studies to date have not directly investigated the relationship between subsurface flowpaths and fertilizer placement in no-till systems to understand why subsurface nutrient placement may result in reduced potential for nutrient leaching. Further, it is unclear how the link between dominant flowpaths and fertilizer placement may change with soil texture and antecedent moisture conditions. The present study aimed to examine detailed patterns of subsurface flowpaths and detailed profiles of P concentrations following fertilizer application in no-till agricultural soils and interpret them in terms of potential transport of applied P within the soil. This can be used to determine how and why subsurface placement of fertilizer may be a BMP for reducing subsurface nutrient losses in no-till systems. An improved understanding of if and how this varies under different soil texture and antecedent moisture conditions can assist land managers with optimized P application strategies. The specific objectives of this work were to investigate: (1) interactions between soil texture, antecedent moisture conditions, and the relative contributions of matrix and preferential flow, and (2) the associated P movement through the soil profile when fertilizers were applied to the surface or placed in subsurface bands.

4.3 Methods

4.3.1 Site description and plot establishment

Plots were established in September 2017 on two working farms in Kingsville (KVL) and St. Marys (STM), Ontario, post winter-wheat harvest. Both fields are under a corn-soy-wheat rotation and are tile drained. The field at KVL is a Brookston Clay (Richards et al., 1949) that has been under no-till management for 20 years, and the STM field is a Brookston Silt Loam (Hoffman and Richards, 1952) that has been under rotational conservational till for 25 years with a shallow disc till (5-8 cm) every three years following wheat. This experiment was conducted at STM prior to shallow disc tillage, and the field had not been tilled since 2014. Following winter wheat harvest (late July), soybeans were planted as a cover crop at the KVL site; however, emergent soybean plants within the plots at the KVL site were clipped prior to the experiment. Wheat stubble remained on the soil surface of all plots during the experiment.

At each site, four 1 × 1 m plots were established along a transect, with 2 m between each plot. At the STM site, the transect had a slope of 1.6%. There was no slope gradient at the KVL site. Plots were established by installing 10 cm plastic edging around the plot perimeter to limit surface runoff out of the plot. Edging was installed without disturbing soil within the plot. Two plots at each site were wet up by applying 80 L (80 mm) of tap water over 2.5 hours (32 mm hr^{-1}). The remaining two plots received no additional treatment, as conditions prior to the experiment had been dry (14-day antecedent rainfall = 8.2 mm at KVL (ECCC, 2018b), 2 mm at STM (ECCC, 2018c)). Desiccation cracks were present in the KVL clay at the time of his study, but were not present in the STM silt loam. All plots were covered with tarp overnight to reduce evaporation from wet plots and protect dry plots against any potential rainfall.

Prior to the addition of P and the rainfall simulations, soil samples were collected surrounding each plot from depths of 0-2.5, 2.5-5, 5-15, 15-30 and 30-45 cm to determine the phosphorus sorption index (PSI). For each plot, one soil core was taken 1 m away from the middle of each plot edge and the four soil cores were homogenized into one sample for the plot, at each depth, for a total of 40 samples.

4.3.2 Fertilizer and dye application

Plots were fertilized one day after the wet-up at a rate of 97.5 kg ha^{-1} of P_2O_5, applied as mono-ammonium phosphate (MAP). At each site, one wet and one dry plot were broadcast with fertilizer, without incorporation. Similarly, fertilizer was applied to one wet and one dry plot at each site via a single subsurface band (5 cm wide x 5 cm deep) placed in the centre of the plot.

Following fertilizer application, 60 L (60 mm) of dye solution was applied to each plot over a 6-hour period (10 mm hr^{-1}), using a battery-powered sprayer. Dye solution was made by mixing 946 mL of highly concentrated Acid Blue #9 (Brilliant Blue FCF) with 19 L of tap water. Following dye application, all plots were covered with tarp overnight.

4.3.3 Plot excavation and soil sampling

At each site, plot excavation occurred one day after dye application. An initial 1 × 1 × 1 m pit was cleared in front of each plot. Within each plot, 8 vertical profiles were exposed with a shovel, 10-12 cm apart. Exposed soil profiles were perpendicular to applied fertilizer bands. Each profile was cleaned with a knife to remove any smeared soil or dye. If large stones were present they were left in the profile. Prior to photographing each profile, a meter stick and a gray card were placed into the frame for size and colour correction. In direct sunlight, a tarp was used to shade the plot and keep lighting consistent within the plot before taking photos. Photos were taken with a Canon DSLR camera on a tripod 1 m from each profile face. In total, 64 stained profiles were excavated and photographed over the 2 week study period.

Soil samples were taken from the 2nd and 6th exposed soil profiles, within each plot. All profiles were sampled by dividing the width of the plot into 3 equal sections (33 cm wide). Each section was then divided into depth layers of 0-2.5, 2.5-5, 5-15, 15-30 and 30-45 cm. Soil samples from clay profiles were also collected from the 45-75 cm depth layer. In total, 264 soil samples were taken from exposed soil profiles. Soil samples were collected uniformly from each subsection with a clean knife. Both dyed and non-dyed portions of the exposed soil profile were collected and homogenized into a single sample.

4.3.4 Soil analyses

All soil samples were dried at 30°C for 24 hours and sieved to 2 mm prior to analysis. A subset of 132 dried soil samples from the 2nd profile within each plot were processed for water-extractable phosphorus (WEP). For WEP analyses, standard laboratory methods were used, where 5 g of dried soil was extracted with 50 mL of de-ionized water and shaken for 1 hour. Samples were then centrifuged at 5000 rpm for 5 minutes. WEP provides an estimate of loosely bound P that could easily be lost in runoff or leachate from a particular soil (Pote et al., 1996).

PSI values were calculated for soils surrounding each plot following the method outlined by Sims (2009). The PSI can be used as an estimate for the maximum P sorption capacity of a soil (Sims, 2009), with a higher value indicating a greater potential capacity to adsorb P. Briefly, 1 g of dried soil (< 2 mm) was shaken with 20 mL of phosphorus sorption solution (80 mg P L^{-1}, made with KH_2PO_4) for 18 hours and subsequently centrifuged at 2000 rpm for 5 minutes. This solution concentration was selected based on previous work at the sites (or nearby sites) that found that P saturation was reached when soils were shaken with 75 mg P L^{-1} in sorption isotherms (Plach et al., 2018).

Extractants for both WEP and PSI were gravity-filtered through Whatman Grade 42 filters and stored at 4°C prior to analysis. Prior to WEP analysis, water samples containing blue dye were tested to determine if dye concentrations would interfere with colorimetric analysis of dissolved reactive P (DRP). The dye did not interfere with colorimetric analysis at 880 nm. WEP and PSI samples were analyzed on a Bran Luebbe AA3 (ammonium-molybdate ascorbic-acid, Bran Luebbe AA3, Seal Analytical: Method no. G-175-96 Rev. 13 for DRP) at the Biogeochemistry Lab at the University of Waterloo.

4.3.5 Image analysis

To identify dominant flowpaths from photographs of vertical profiles, photographs of 64 unique profiles underwent initial image processing. First, raw images were subsampled to a 1 × 1 m size using the metre stick that was present in the image. These square images were resampled to a 1000 × 1000 pixel resolution to be compatible with secondary processing. The preliminary classification of image areas was done using the maximum likelihood semi-supervised classification tool from the ENVI 5.4 suite. Six regions of interest were manually digitized for each image to be used as training data required for the classification tool. These regions of interest represented both stained and unstained areas found within the image. Unwanted objects, including stones and plant matter, were manually masked out of images to prevent potential inaccuracies in the classification process. The resulting output of this classification was a binary raster dataset which consisted of stained and unstained regions. Images were classified individually as a spectral library for all images could not be built due to variability in colours between sites and across time of day when photos were taken. A 3-by-3 pixel majority filter was applied to the resulting binary raster datasets post-classification to reduce artifacts or misclassified pixels. The product of this filtering was used in secondary processing.

Secondary processing of each image was completed using MATLAB R2017b to compare stain patterns across soil textures and antecedent moisture conditions. To do this, vertical volume density, depth of staining and stained path width were determined following methods from Weiler and Flühler (2004), based on 1 mm depth increments. Briefly, the volume density is the fraction of stained to unstained pixels at each depth (Weiler and Flühler, 2004). The depth of staining is mean stain depth across all 8 vertical profiles within a plot. Stained path widths are estimates of spatial extent of each stain within a vertical profile, calculated as the horizontal width of each stain at each depth (Weiler and Flühler, 2004). Within each plot, the mean and standard deviation of the volume density was determined based on all 8 vertical profiles.

Flowpaths were classified into one of six types: (1) homogeneous matrix flow, (2) heterogeneous matrix flow, (3) macropore flow with high interaction, (4) macropore flow with mixed interaction, (5) macropore flow with low interaction, and (6) macropore flow with very low interaction. Interaction is defined as the lateral water flow from a macropore into the surrounding soil matrix (Weiler and Naef, 2003). While classes 1 to 5 were defined by Weiler and Flühler (2004), a sixth class was developed for the present study to isolate macropore flow with "very low" interaction, which was previously grouped together under the class macropore flow with low interaction. Macropore flow with very low interaction was defined as having > 75% of stained path widths < 20 mm and < 20% of stained path widths > 200 mm. A sensitivity analysis was done to determine appropriate thresholds for this class. It should be noted that flowpath classifications were based on 5 mm depth increments, this to avoid outliers or menial changes in stain patterns occurring at 1 mm depth increments.

4.4 Results

4.4.1 Differences in stain patterns with soil texture and antecedent moisture conditions

Visual assessments of photographs indicate variability in stain patterns within plots, between soil textures, and between moisture conditions. Figure 4.1 highlights examples of contrasting raw photographs, binary stain patterns in processed images, and volume density plots in dry clay and dry silt loam. Examples of raw photographs and binary stain patterns from all soil moisture and texture conditions can be seen in Supplementary Figure A2. Additional examples of raw photographs from all soil texture and moisture conditions are included in Appendix B of this thesis.

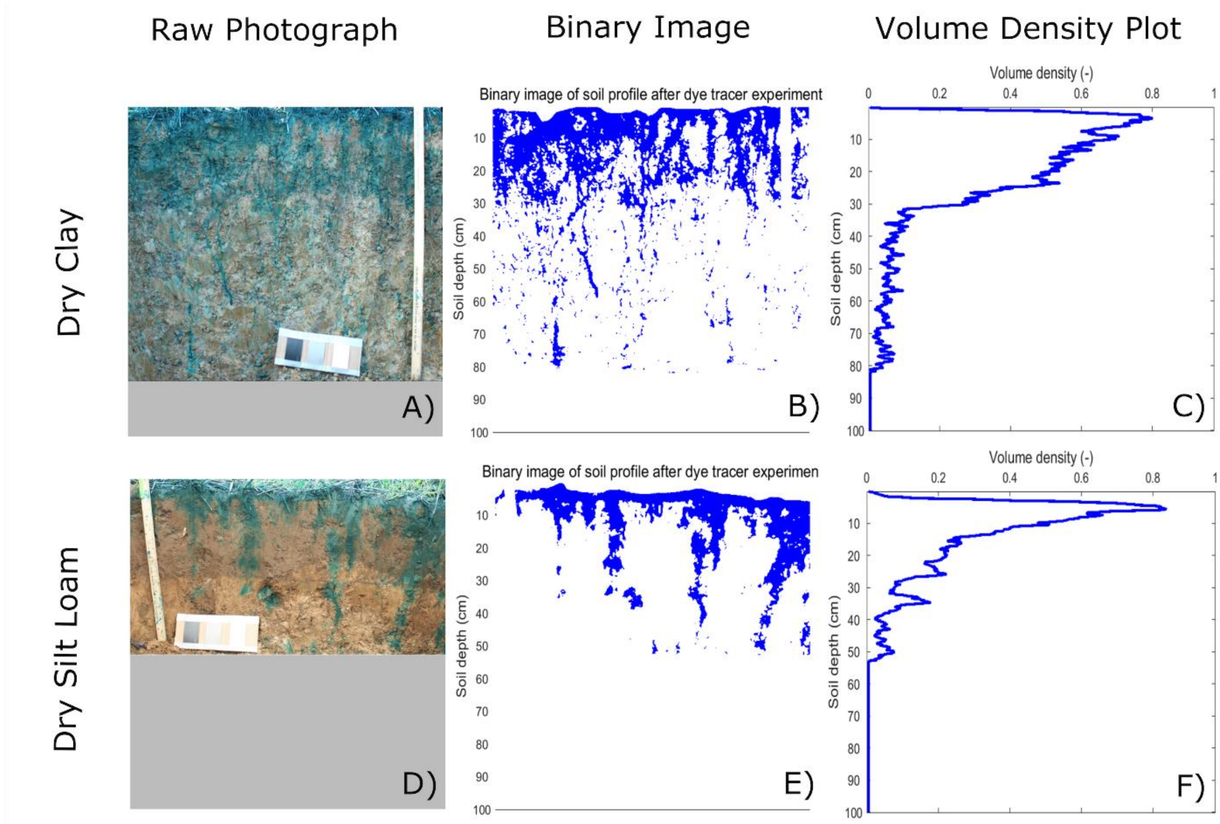

Figure 4.1 Examples of contrasted scaled profile photographs (A, D), binary images (B, E) and associated volume density (C, F) for two vertical profiles exposed in dry clay and dry silt loam. In binary images B) and E), blue represents stained and white represents unstained portions of the profile.

Overall, dye stain patterns varied between soil textures. Dye infiltrated deeper into clay soils, compared to silt loams (Figure 4.2). Although there was deeper dye infiltration, clay soils showed lower volume density beyond the wetting front (Figure 4.2). In contrast, dye staining in silt loam soils showed shallower dye infiltration, but greater volume density at depth (Figure 4.2). In some silt loam plots, areas of restricted flow were observed beyond the wetting front (Figure 4.2– E, G, H). Areas of restricted flow are indicated by an area of low volume density followed by an increase in volume density at greater depths. Such patterns were not observed in any clay plots. Areas of restricted flow were found in silt loam profiles as the volume of staining declined at depths of ~20 cm, and then increased at depths of ~30 cm (Figure 4.2 – E) or ~40 cm (Figure 4.2 – G, H).

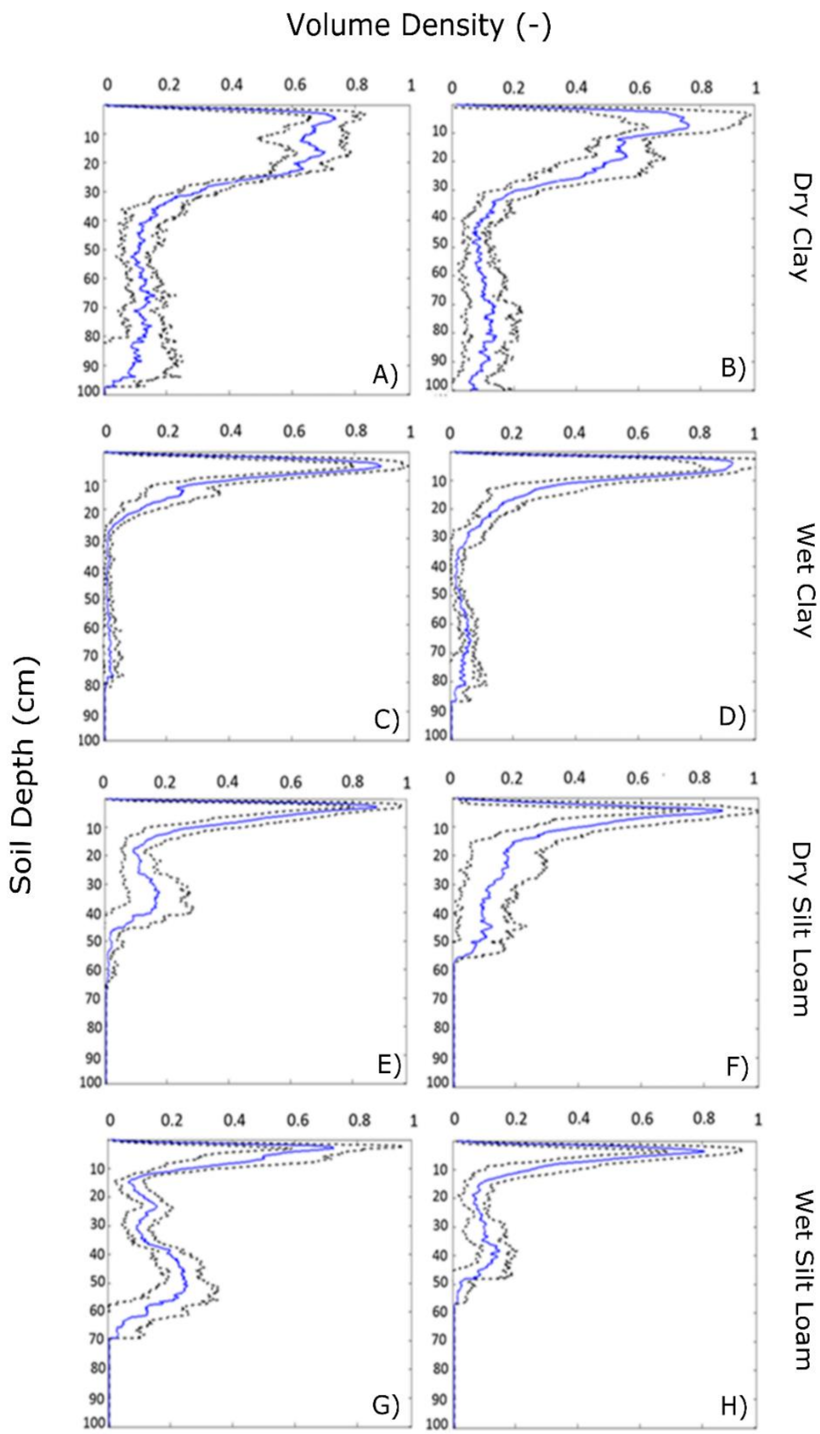

Figure 4.2 Mean volume density of soil stained at each depth (blue line) ± one standard deviation (dashed gray lines) for all vertical profiles within a plot (n = 8). Volume density values of 1 indicate complete matrix staining at a given depth, while low values signal a large bypassing of the soil matrix.

Within clay soil, antecedent moisture conditions influenced dye stain patterns. First, depth of staining in dry clay was the greatest out of all soil texture and moisture conditions in this study, with a mean stain depth of 92 ± 7.6 cm and a maximum recorded stain depth of 100 cm. In a few dry clay profiles, dye was observed beyond 100 cm but no image analysis or sampling occurred beyond this depth. In dry clay, a high volume of dye reaching depths of 30 cm (Figure 4.2 – A, B) suggests a deeper wetting front than found in other plots. However, dye in dry clay had the lowest mean volume density in the surface than any other plot type (Figure 4.2). Beyond the 30 cm depth, an average of 10% of the width of the profile was stained in dry clay plots (Figure 4.2). In comparison, dye infiltration in wet clay was not as deep as in dry clay. In wet clay, dye staining reached a mean depth of 77 ± 4.7 cm, with a maximum stain depth of 86 cm. Wet clay soils had a shallower wetting front (10 cm) with greater volume density than the surface of dry clay plots, with an average of 88% stain coverage in the wetting front across profiles (Figure 4.2 – C, D). However, the proportion of the profile that was stained beyond the wetting front was very low, at < 0.05 (Figure 4.2 – C, D). In summary, these results indicate that the deepest dye infiltration occurred in clay soil under dry conditions.

In contrast, dye stain patterns in silt loam soil appeared to be unaffected by antecedent moisture conditions. Mean depths of staining in silt loam soils were similar between wet (50 ± 6.6 cm) and dry (56 ± 7.2 cm) conditions. Wetting front progression appeared to be comparable across all silt loam plots, as stain patterns in the top 20 cm were similar. Beyond the wetting front, areas of restricted flow were observed in some plots (Figure 4.2– E, G, H); however, these patterns occurred under wet and dry conditions and are unlikely to be related to antecedent moisture condition.

4.4.2 Differences in classified flowpaths with soil texture and antecedent moisture conditions

Both matrix and preferential flow occurred in the clay and silt loam plots under wet and dry antecedent conditions. Matrix flow, when present, occurred in the top 10 cm of the soil profile and little matrix flow was observed below this in either soil texture. Flowpath classifications suggest that the wetting front in dry clay is deeper and with less macropore-matrix interaction than in wet clay (Figure 4.3 – A). The wetting front in silt loam soils consisted primarily of macropore flow with high interaction. Heterogeneous matrix flow with fingering was also found within the wetting front in silt loam soils, irrespective of moisture condition. Indeed, flowpaths with the greatest interaction with the soil were observed in all plots in the top 10 cm of the profile (Figure 4.3). Preferential flowpaths dominated in both soil textures, under wet and dry conditions. Macropore flow with very low interaction was most prevalent in clay soil under both antecedent moisture conditions. In silt loam soils, macropore flow beyond the wetting front had mixed, low, and very low interaction. Areas of very low interaction in silt loam profiles often corresponded with areas of restricted flow, particularly when macropore-matrix interaction increased to low or mixed at greater depths. Overall, these classified flowpaths highlight the prevalence of macropore flow with low and very low interaction across soil texture and moisture conditions.

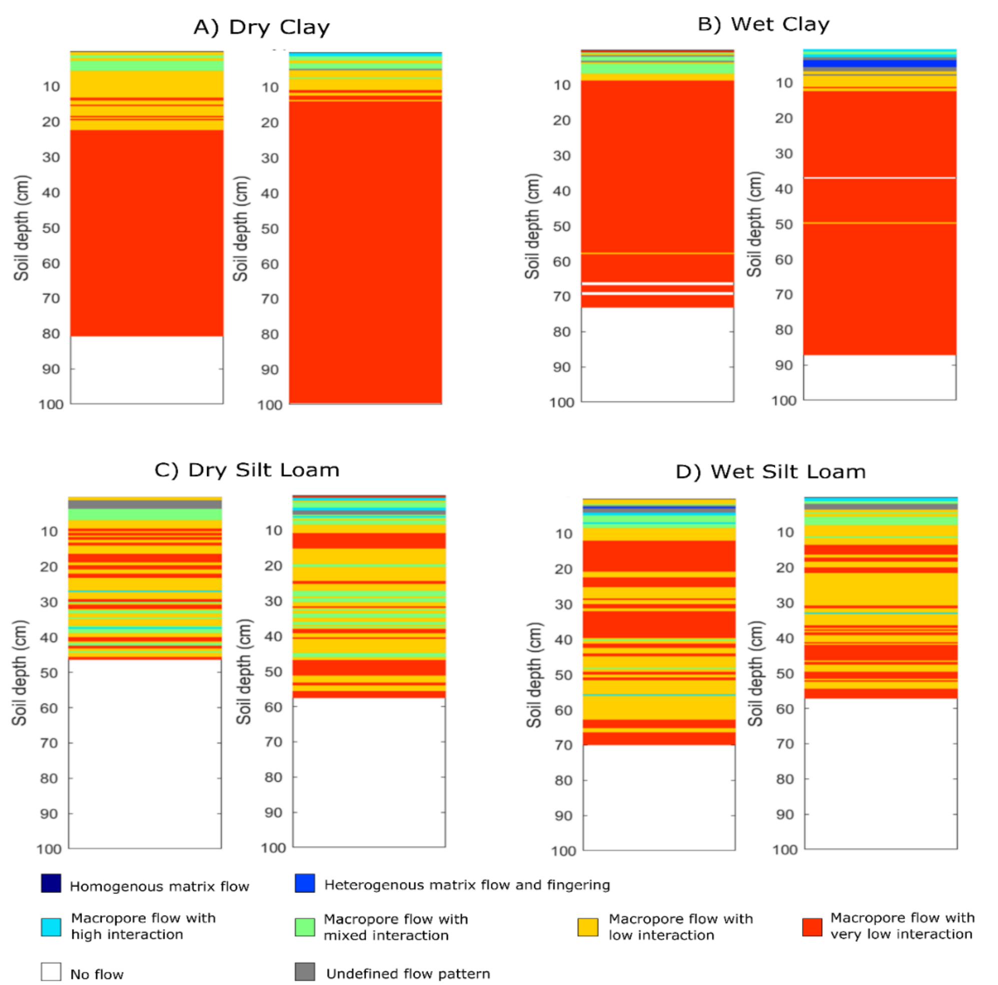

Figure 4.3 Classified flowpaths from each soil texture and antecedent moisture condition, represented by the second profile (~20 cm from edge of plot) within each of the 8 different plots.

4.4.3 Soil P distribution

Prior to fertilizer application, PSI values differed between the two soils, with the silt loam having a greater PSI (Supplementary Figure A3), suggesting more P can be bound within this soil. Following fertilizer application, soil WEP distributions also differed between the two soils. Although the same amount of fertilizer was applied to all plots, the clay plots showed a greater range of WEP with some soil P values over 20 mg kg^{-1} in the surface (Figure 4.4 – A). In contrast, silt loam soils had a lower range of WEP values, reaching up to 6 mg kg^{-1} in the centre of banded plots (Figure 4.4 – B).

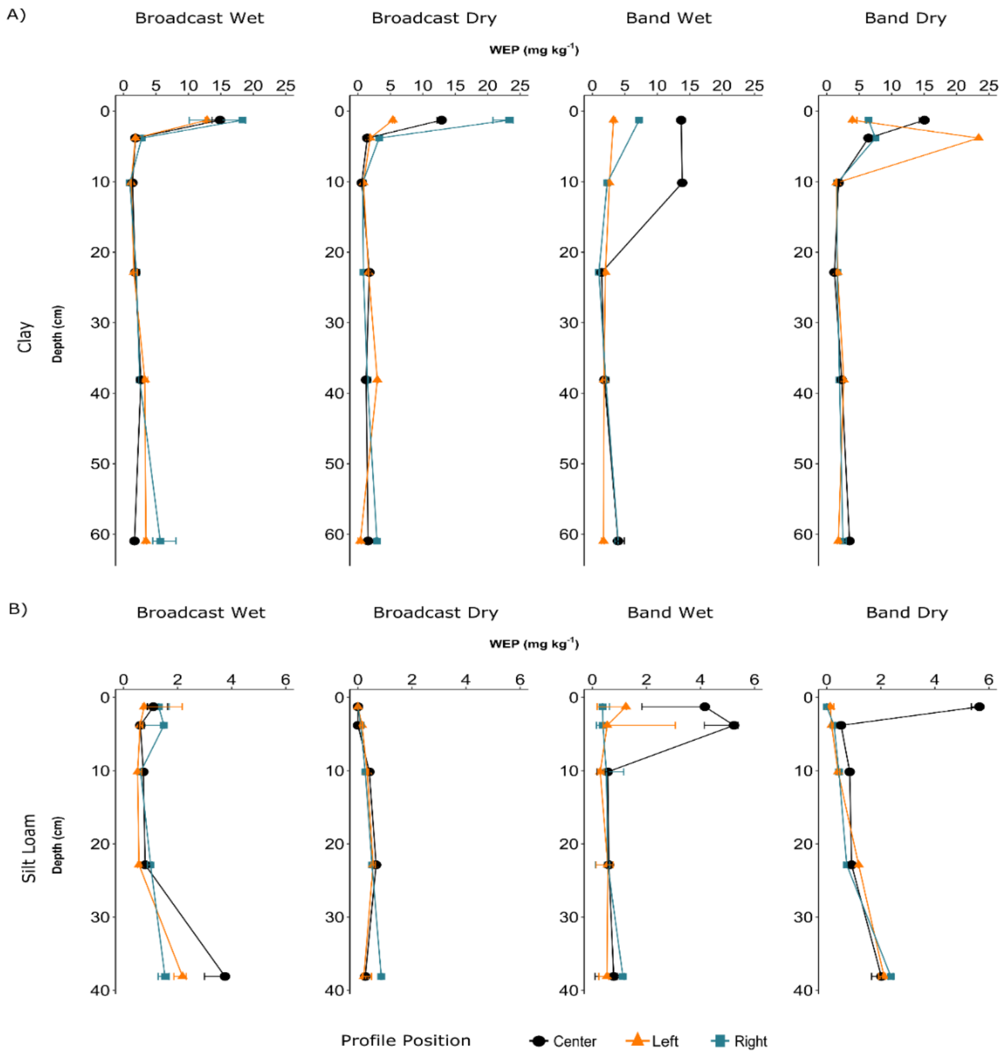

Figure 4.4 WEP (mg kg^{-1}) by depth (cm) for one profile representing each combination of antecedent moisture and fertilizer application method in A) clay and B) silt loam. Note that the x-axis scales for A) and B) are different.

In general, soil WEP distributions did not differ between moisture conditions within each soil texture, although there was more variability near the surface in the dry clays than in the wet clays (Figure 4.4). These more variable WEP distributions coincide with lesser amounts of homogeneous matrix flow at the surface in the dry clays (Figure 4.3). However, the differences in volume density between wet and dry clay in deeper portions of the soil (Figure 4.2) did not translate to differences in soil WEP distribution. Similarly, no change in WEP distribution in silt loam soils can be attributed to observed flowpaths.

Although soil WEP did not appear to differ with varying antecedent soil moisture, soil WEP distributions were related to differences in fertilizer placement. Subsurface placement of fertilizer (banding) resulted in the greatest accumulation of WEP in the top 5 cm, compared to surface broadcast applications (Figure 4.4); however, this was generally concentrated in the centre of the plots, where the P had been applied. In some cases, P applied in subsurface bands resulted in high WEP outside of the centre of the plot, indicating P was translocated laterally within the top 10 cm (Figure 4.4 – A, Band Dry). Broadcast fertilizer applications resulted in greater WEP in the top 2.5 cm in clay soil (Figure 4.4 – A). However, little change in surface soil WEP was observed in the silt loam soil following the broadcast fertilizer application and simulated storm event.

4.5 Discussion

4.5.1 Differences in preferential flowpaths across soil texture and moisture conditions

It was expected that preferential flow would dominate in clay soil while matrix flow would be more prevalent in silt loam, as macropores are more likely to persist in fine-textured and well-structured soils (Djodjic et al., 1999; Hendrickx and Flury, 2001). Due to the increased occurrence of macropores in clay soils, it was also expected that dye would infiltrate deeper into clay soils through these preferential flowpaths. Indeed, our results showed deep infiltration into clay soils through preferential flow with very low interaction. This is consistent with other literature that has shown preferential flow to increase in occurrence in soils with increasing clay content (Djodjic et al., 1999; Glaesner et al., 2011a). Grant et al. (2018) also found preferential flow to occur through clay soil, under both frozen and thawed conditions. Further, our results showed preferential flow to occur through silt loam soil, with mixed, low, and very low interaction. As this study simulated a large storm event (60 mm, 10 mm hr^{-1}), it is unsurprising that preferential flow occurred in all plots as others have found the contribution of preferential flow to total flow to increase with increasing rainfall amounts (Vidon and Cuadra, 2010). Identifying soil conditions prone to preferential flow is useful for determining when and where rapid solute transport to tile drains is more likely. This is important for targeting BMPs to certain soil and hydrologic conditions, based on potential for nutrient export.

It was also hypothesized that dye infiltration would be deeper in dry clay soils, compared to wet clay, due to the presence of desiccation cracks under dry conditions. Our results showed that dry conditions in clay soil resulted in the deepest depth of staining, deepest wetting front, and greater proportion of staining beyond the wetting front compared to wet clay. Deep dye staining in dry soils has been reported by others (Hardie et al., 2011; Yao et al., 2017). Antecedent moisture conditions influence the presence of desiccation cracks in clay soils, as cracks open under dry conditions (Simard et al., 2000). Others have found open cracks in clay soil to facilitate infiltration, but suggest that deep transport of solutes relies on connectivity between surface cracks and worm burrows deeper in the soil profile (Shipitalo et al., 2004). Therefore, the presence of a deep wetting front in dry clay due to desiccation cracks may result in more opportunities to connect with other types of preferential flowpaths (worm burrows, root channels) that exist deeper in the profile. Increasing connectivity to these other types of macropores existing in the subsurface can ultimately result in deeper overall transport, as was observed by the deep dye staining in dry clay in this study (see Figure 4.1 – B and Supplementary Figure A2 – C for examples). The deep transport of water through preferential flowpaths in dry clay suggests that this is a condition where rapid P transport to tile drains may be more prevalent. Others have also reported that storm events over dry conditions may be critical for subsurface P transport through preferential flowpaths (Simard et al., 2000). This has implications for subsurface nutrient transport during storms following drought conditions. Under future climate scenarios, such conditions may be of increasing concern, as changes to the timing and magnitude of precipitation events could result in both intense storm events and drought conditions (Jimenez Cisneros et al., 2014; Laporte et al., 2002).

Due to the lack of cracking in coarser-textured soils, we expected the wetting front in the silt loam soil to respond differently than the clay soil. Specifically, we anticipated that moisture conditions would influence fingering of the wetting front in silt loam soil, with greater finger flow and deeper infiltration in the wet silt loam. Other studies investigating flowpaths through loam-textured soils have reported wetter conditions leading to enhanced preferential flow (Jaynes et al., 2001; Kung et al., 2000b). Although some finger flow was observed in both wet and dry silt loam, we did not see a difference in depth of staining or in flowpath characteristics between moisture conditions. However, these results are in contrast to those observed in the clay soil, as anticipated.

Zones of restricted flow were seen in silt loam plots in both antecedent moisture conditions. This pattern of low volume density followed by greater volume density at depth suggests there is an area of the soil which water is bypassing, and then dye-matrix interaction increases beyond this layer deeper in the profile. This phenomenon has been observed elsewhere (*e.g*., Cey and Rudolph, 2009; Yao et al., 2017): studies have attributed increased interaction at depth to dye accumulating at the bottom of macropores being forced to laterally into the soil matrix (*e.g*., Cey et al., 2009), or restricted flow due to the presence of a plow layer (*e.g*., Shipitalo et al., 2004). In the current study, it is hypothesized that restricted flow occurred due to soil morphology of the Brookston Silt Loam. This poorly drained soil typically contains a brownish grey mottled layer from 18-28 cm, consisting of clay loam with a blocky structure and very hard consistency (Hoffman and Richards, 1952). Restricted flow with little dye-matrix interaction was observed at depths of ~20 cm coinciding with the presence of this hard clay layer. Therefore, we expect that soil morphology results in restricted flow in this case. While antecedent moisture conditions were important in clay soils, soil morphology may also play an important role in influencing subsurface flowpaths. This has implications for nutrient application and solute transport, as management practices and recommendations should not only be generalized across soil textures or moisture conditions and should also consider underlying soil morphology.

4.5.2 Implications of different flowpaths and P placement for subsurface P transport

In a laboratory study of soil monoliths, Grant et al. (2018) found increased P transport in leachate in both silt loam and clay soils (the same sites used in the current study). The greatest P transport occurred in clays, due to rapid transport through preferential flowpaths. Grant et al. (2018) found that subsurface placement of P reduced P leaching under both thawed and frozen conditions in wet soils, and this reduction occurred in both silt loam and clay soils. Reduced P transport following subsurface placement has been observed by others (*e.g.*, Glaesner et al., 2011b; Williams et al., 2018), due to increased contact with the soil matrix and reduced contact with preferential flowpaths.

In the current study in a field setting, it was expected that the movement of P through the soil profile would be related to both subsurface flowpaths and P placement. We did not measure P concentrations in subsurface leachate directly, to avoid the potential for field sampling instrumentation to create artificial preferential flowpaths in the soil. However, we hypothesized that increased contact with the soil matrix (*i.e.* homogeneous matrix flow) might lead to greater P adsorption, which would translate to an observable increase in soil WEP in the soil profile. In contrast, in situations where preferential flowpaths rapidly transported applied fertilizer through the subsurface, an increase in soil WEP would not be apparent. We expected the greatest movement of P to occur following broadcast fertilizer application over dry clay soil (*i.e.* least soil WEP present in subsurface), and the greatest P retention to occur in dry silt loam soils (*i.e.* greatest accumulation of soil WEP) as infiltrating water filled the soil matrix. Following subsurface placement, we expected to observe a concentrated pool of WEP in all plots near where the band was placed (~5 cm depth in the centre of the plot). We anticipated that this concentrated pool may migrate both deeper and more towards the sides of the plot (away from the P band) under matrix flow conditions, but would not migrate under preferential flow conditions unless directly in contact with a macropore.

As expected, we observed a concentrated pocket of elevated soil WEP in the plots in which P was placed in the subsurface, whereas P was more evenly distributed across the surface in plots where P was surface broadcast. In the plots in which subsurface P was applied, the P migrated deeper in the wet plots in comparison to the dry plots, and this was apparent in both the silt loam and clay soil. No differences in vertical distributions of P were apparent in the plots in which P was broadcast. Contrary to our expectations, distributions of soil P in this study were not clearly related to observed flowpaths, although some general patterns were apparent. As expected, we did not observe enhanced P retention deep in soil profiles where preferential flow occurred (*i.e.* clay soils). There was some evidence of increased WEP in the silt loam soils, where the restricted flow had occurred, but there were no clear trends in WEP distributions in deep soil under different soil moisture conditions or fertilizer placement methods. As noted above, Grant et al. (2018) reported differences in P concentrations in leachate between soil textures and fertilizer application methods; however, they did not find an observable change in soil WEP distributions in their study. Subsurface nutrient transport has been shown to be related to both fertilizer placement (nutrient supply) and subsurface flowpaths (transport) (Glaesner et al., 2011b) in other studies. Thus, it is expected that differences in P transport in leachate occurred in this study, but these may not have translated to a change in soil WEP distributions.

We propose three potential explanations for why soil P in this study may not be representative of P leachate patterns. First, when sampling soil within a plot, both stained and unstained areas of the soil profile were homogenized together into one sample. Isolating stained areas may better represent the movement of applied P as stained areas are the only parts of the soil in contact with incoming water, and potentially applied P. However, sampling only stained areas was not feasible due to the many small flowpaths following worm burrows and roots channels. Future studies linking soil characteristics to flowpaths should consider isolating soil that has interacted with such flowpaths when sampling.

Second, preferential flowpaths rapidly transport water and solutes from the surface to the subsurface. Preferential flowpaths offer little opportunity for adsorption of P to the soil because of short contact time between water and the walls of the macropores, particularly in cylindrically shaped macropores such as worm burrows (Cey et al., 2009). Further, the literature reports that walls of macropores in agricultural soils are often already saturated with P, limiting opportunity for adsorption through these pathways (Beven and Germann, 2013; Geohring et al., 2001): such was likely the case in the current study as well. It is also well understood that the greatest P export often occurs during the first event following P application (Gentry et al., 2007; Smith et al., 2007). Nutrient exports can be particularly high if the time between application and the first event is short (Smith et al., 2007), as was the case in this study. Therefore, it is possible that most of the applied P could have moved beyond the 1 m x 1 m profile during the simulated event, before the soil was sampled for WEP, particularly in clay soils with deep preferential flow.

Third, soil P distributions are also influenced by P sorption and partitioning within the soil. In this study, silt loam soil had higher PSI compared to the clay soil. A high PSI can contribute to lower P leaching, particularly in coarse-textured soils where more contact between applied P and the soil matrix can occur via matrix flow (Andersson et al., 2013). Plach et al. (2018) found P to be stored primarily in relatively stable acid-soluble form in silt loam soil from the STM site. In contrast, fine-textured soils from the region, similar to those found at KVL, had a greater fraction of P stored in loosely-moderately bound forms (Plach et al., 2018). This can explain why greater WEP values were found in the clay soil in this study, as more P is likely stored in more easily extractable forms. Future work should investigate water chemistry itself, and consider other methods of in-situ leachate collection such as the use of pan lysimeters (*e.g.*, Williams et al., 2018) or microrhizon samplers (*e.g.*, Ali et al., 2018).

Following the simulated rainfall event in this experiment, broadcast treatments showed very little available P in the soil surface, particularly in the silt loam. It is hypothesized that this applied P had either not been dissolved and made readily available, or had already been transported deeper into the plots, or was already bound tightly to the soil and therefore not easily extracted by water. From an agronomic perspective, subsurface placement of fertilizer is beneficial because it results in the greater availability of P in the soil near the root zone. Future work should continue to investigate subsurface fertilizer application on working farms, with year-round monitoring of surface and subsurface flow, to determine if this BMP continues to limit nutrient losses across seasonal conditions.

Continuing to understand conditions that may exacerbate preferential flow and interactions between infiltrating water and applied P is important to help identify situations that may result in enhanced nutrient leaching and subsequent export through tile drains. Preferential flowpaths should continue to be investigated under other soil textures, agricultural management practices, moisture conditions, and rainfall rates to better understand conditions at greatest risk for nutrient export. This work may help to target initial adoption of subsurface fertilizer placement as a BMP to areas which experience preferential flow, such as occurs in clay soils. In addition, improved understanding of flowpaths under varying antecedent moisture conditions shown in this study has particular relevance for transport of nutrients following spring fertilizer applications.

4.6 Conclusions

This study has shown that preferential flow with limited macropore-matrix interaction can occur across soil textures and moisture conditions; however, preferential flow is more prevalent in clays than silt loams. Dry antecedent moisture conditions increase the prevalence of preferential flow in clays, but not in silt loams. These findings have relevance to the transport of P through the vadose zone and into tile drains, particularly following fertilizer application. The staining patterns shown in this study suggest that the application of fertilizer in localized subsurface bands likely reduces the risk of subsurface leaching of nutrients by limiting contact between nutrient supply and transport pathways, particularly where preferential flow dominates. Clays appear to be at greater risk for P loss via preferential flow in comparison to silt loams, and this potential is greatest during storms that occur during dry periods as the enhanced preferential transport moves deep into the soil profile with little interaction with soil. The surface broadcast of P on dry clays is especially problematic as these conditions provide more opportunities for surface water to travel through the existing macropore network deeper in the soil profile. This study suggests that surface broadcast of P on clay soils may present the greatest risk for P transfer into tile drains by preferential flow. Farmers in clay-dominated landscapes may be able to reduce P transfer into tile drains by reducing the interaction of the P supply (fertilizer) with highly efficient transport pathways (preferential flow), by applying P in the subsurface.

Chapter 5
Major Conclusions of Thesis

P leaching from tile drains in no-till agricultural soils has been identified as a water quality concern (King et al., 2015). Previous research has suggested no-till management of tile drained fields to be one cause of this problem (Smith et al., 2015; Kleinman et al., 2015), as no-till management can result in enhanced macropore development and therefore rapid transport of P to tile drains (Geohring et al., 2001). However, Lam et al. (2016) found tillage practice did not influence P losses in tile drains when P was applied via subsurface placement. Therefore, this thesis set out to link fertilizer placement and vadose zone hydrology to identify mechanisms controlling P movement to tile drains in no-till agricultural soils, under different soil textures and seasonal conditions. This thesis has shown that both fertilizer placement and flowpaths in the vadose zone are critical for determining subsurface P losses.

This thesis has shown that preferential flow is prevalent across soil textures, antecedent moisture conditions, and the presence of seasonal frost (Figure 5.1). First, preferential flow was shown to be prevalent in clay soils, under both wet and dry, and unfrozen and partially frozen conditions. Conservative tracers used in Chapter 3 demonstrated the occurrence of preferential flow in clay soils under unfrozen and partially frozen conditions. These findings are consistent with others who have found macropores remain air-filled under frozen conditions, resulting in preferential flow (Granger et al., 1984; Stadler et al., 2000). In Chapter 4, dye patterns showed preferential flowpaths dominate in clay soil. These results are consistent with others who have found the prevalence of preferential flow to increase with increasing clay content in soils (Glaesner et al., 2011a; Djodjic et al., 1999). In particular, deep preferential flow (92 ± 7.6 cm) was observed in dry clay soils in Chapter 4, as desiccation cracks allowed dye to quickly bypass the top soil and provided more opportunity to connect with wormholes and root channels in the subsurface. Others have also reported deep preferential flow through dry clay soils due to the presence of desiccation cracks (Simard et al., 2000; Hardie et al., 2011). In summary, preferential flow was prevalent in clay soils in wet and dry conditions, and under unfrozen and partially frozen conditions.

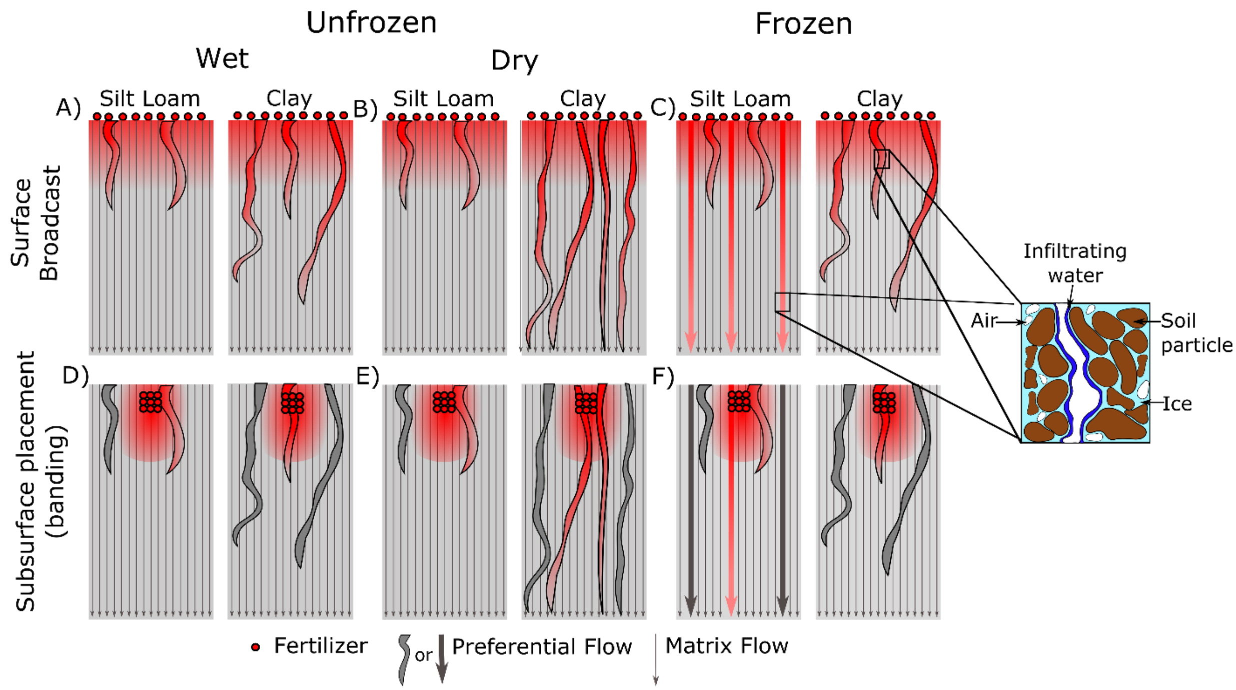

Figure 5.1 Conceptual diagram of interactions between flowpaths and fertilizer placement under different soil textures, antecedent moisture conditions, and the presence of soil frost. A and B) Surface broadcast nutrients over unfrozen silt loam (wet and dry) infiltrate through some shallow macropores. Broadcast nutrients are quickly transported via preferential flowpaths in unfrozen clay, with the deepest preferential flow occurring in dry clay due to desiccation cracks. C) Surface broadcast nutrients over partially frozen soils are quickly transported to the subsurface via preferential flowpaths. Macropores persist in partially frozen clays, while new preferential flowpaths are developed in partially frozen silt loam as larger pores remain air filled while smaller pores are blocked by ice in unsaturated partially frozen soil. Matrix flow begins to occur as soil thaws. D and E) Subsurface placement of fertilizer limits contact of nutrients with flowpaths, limiting the risk of transport via matrix and preferential flow. Subsurface placement is particularly effective where preferential flowpaths are most prevalent. F) Subsurface placement limits contact of nutrients with preferential flowpaths in partially frozen soils, and can come into contact with matrix flow as soil thaws.

This thesis has also identified that preferential flow can occur in silt loam soils, although it is not as prevalent as in clay soils (Figure 5.1). In Chapter 3, preferential flow occurred in silt loam soil under partially frozen conditions, but not under unfrozen conditions. Others have found preferential flow to occur in frozen loam soils as smaller pores become ice-filled upon freezing, leaving only large air-filled pores open as pathways for infiltrating water (Stähli et al., 1996). Movement of conservative tracers in Chapter 3 suggested matrix flow was the dominant flowpath type in unfrozen silt loam. Classification of dye patterns in Chapter 4 suggested that macropore flow was occurring in unfrozen silt loam soils, but this flow was more shallow and had greater macropore-matrix interaction than preferential flow observed in clay soil. Despite subtle differences in classification of flow type between Chapter 3 and 4, it is clear that flow through unfrozen silt loam has more contact with the soil matrix than in clay soils. Flowpath classifications in Chapter 4 found no differences in flowpaths between wet and dry silt loam. These results are similar to others who have found preferential flowpaths to be similar across moisture conditions (Tallon et al., 2007). However, some others have reported that wetter conditions contribute to greater preferential flow (Kung et al., 2000a; Jaynes et al., 2001). The prevalence of preferential flow across soil textures and seasonal conditions suggests that this is an important pathway for solute transport in agricultural soils, and further research is needed to understand underlying processes driving the activation of these preferential flowpaths.

In addition to subsurface flowpaths, this work also investigated fertilizer placement methods, as both source and transport are critical for understanding and managing P loss. This research has shown that subsurface placement (banding) of fertilizer can limit subsurface P leaching. Others have also shown subsurface placement to reduce P leaching in the subsurface (Glaesner et al., 2011b; Williams et al., 2018), and in surface runoff (Smith et al., 2016). The lab experiment described in Chapter 3 found subsurface placement of fertilizer to reduce subsurface P losses by 60% in silt loam and 64% in clay soil, compared to surface broadcast applications. These findings are consistent with those of Williams et al. (2018) who reported subsurface placement reduced subsurface P leaching by 66%. In Chapter 4, differences in fertilizer placement resulted in differences in soil WEP distributions in the top 10 cm of the soil profile, with greatest concentrations of WEP localized near placement of subsurface bands. In this thesis, subsurface placement of nutrients was shown to be most effective at limiting leaching in soils where preferential flow dominated the flow regime (*e.g.* clays).

Taken together, these results suggest that subsurface placement of nutrients limits the opportunity for applied fertilizer to come into contact with existing preferential flowpaths, thereby reducing rapid nutrient transport to subsurface drains through these pathways. As preferential flowpaths have been shown to be present across soil textures, antecedent moisture conditions, and the presence of soil frost, subsurface placement of fertilizer is a suitable BMP for managing subsurface P loss across a wide range of site conditions. Subsurface placement may be particularly effective in clay soils which are prone to preferential flow under the greatest range of conditions (Figure 5.1). In order to mitigate subsurface P losses from agricultural soils, subsurface placement of fertilizer is the preferred application method over surface broadcast, and is recommended as a BMP. As preferential flow was shown to occur under partially frozen conditions experienced over the NGS (Chapter 3) and through desiccation cracks that can occur in dry summer conditions (Chapter 4), subsurface placement of fertilizer is suitable for both fall and spring applications. However, future work is needed to quantify and compare the P export through preferential flowpaths following both fall and spring fertilizer applications to make further recommendations on timing of fertilizer application.

This work has also contributed to the understanding of the prevalence of preferential flowpaths in agricultural soils, with broad relevance to contaminant transport through these systems. Enhancing understanding of preferential flow processes across textural and seasonal conditions also has relevance for improving accuracy of preferential flow and associated solute transport in hydrological models. In particular, the results of this thesis showing the prevalence of preferential flow through dry and unsaturated conditions supports the calls of Nimmo (2012) for a need to include preferential flow through these conditions in hydrological modelling work and not rely on the overly simplified notion that preferential flow increases under wetter conditions. The work of this thesis can be used to help refine macropore flow parameters in hydrologic models, by modifying the relative importance of these flowpaths under different soil textures, antecedent moisture conditions, and under the presence of soil frost. Future work should continue to refine our understanding of processes activating preferential flow across a range of conditions, in order to improve model predictions of subsurface flow and solute transport. Future work should also continue to investigate flow and transport processes through frozen soils, as the NGS remains an important and understudied time period for P loss in agricultural systems. Understanding these baseline fundamental processes will be critical as winter soil processes shift under a changing climate. Finally, future research should continue to compare subsurface placement to other methods of fertilizer application, including incorporation of nutrients via tillage. The pillars of 4R nutrient management should continue to be investigated across site and seasonal conditions, in order to make appropriate site specific recommendations to landowners to mitigate losses of P from their fields.

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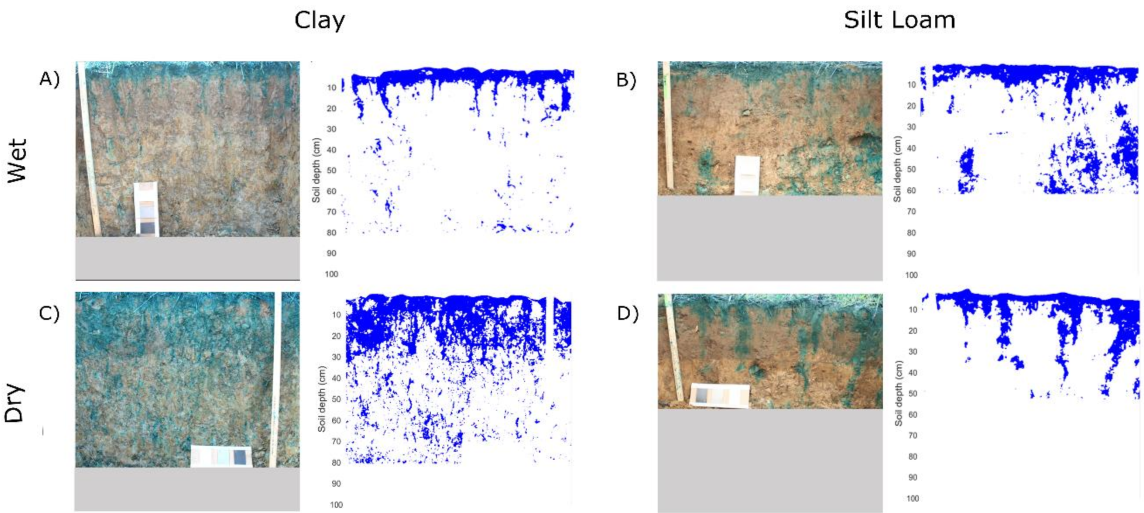
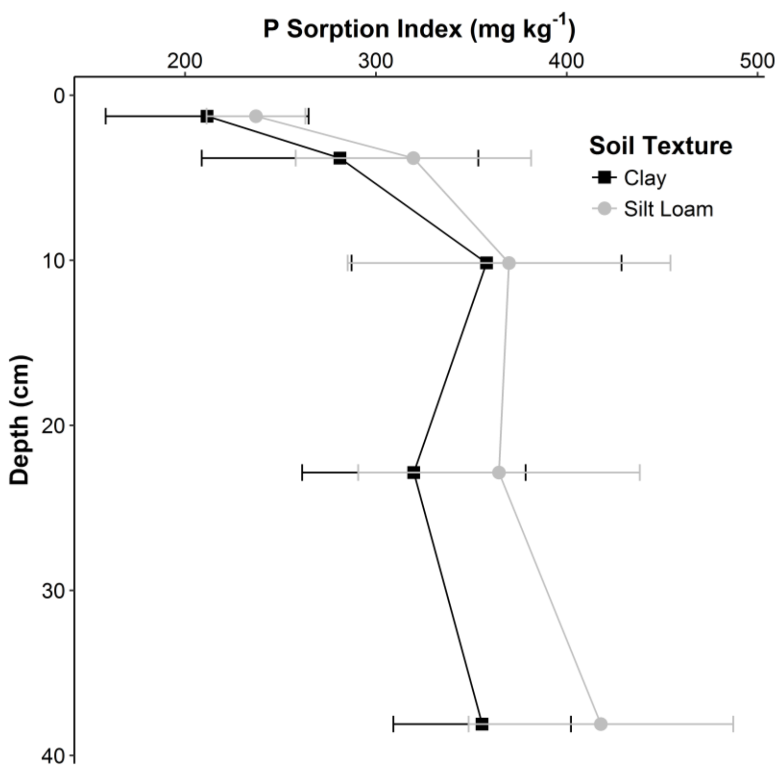
Appendix A

Supplementary Figures

Supplementary Figure A1 Photograph of experiment set up including soil monoliths inside temperature controlled chamber.



Supplementary Figure A2 Examples of raw photographs and binary images from each soil texture and moisture condition.



Supplementary Figure A3 Mean P Sorption Index (mg P kg^{-1}) ± one standard deviation (n=4) by depth for soils at each site.

Appendix B
Photographs of Dye Stained Soil Profiles

Below are examples of raw photographs of dye stain patterns from soil profiles under different antecedent moistures (wet vs dry) and soil textures (clay vs silt loam). These photographs have been scaled to represent a 1 x 1m profile.

Figure B1 Example of dye stained profile from a dry clay plot (Plot A - 1st profile).

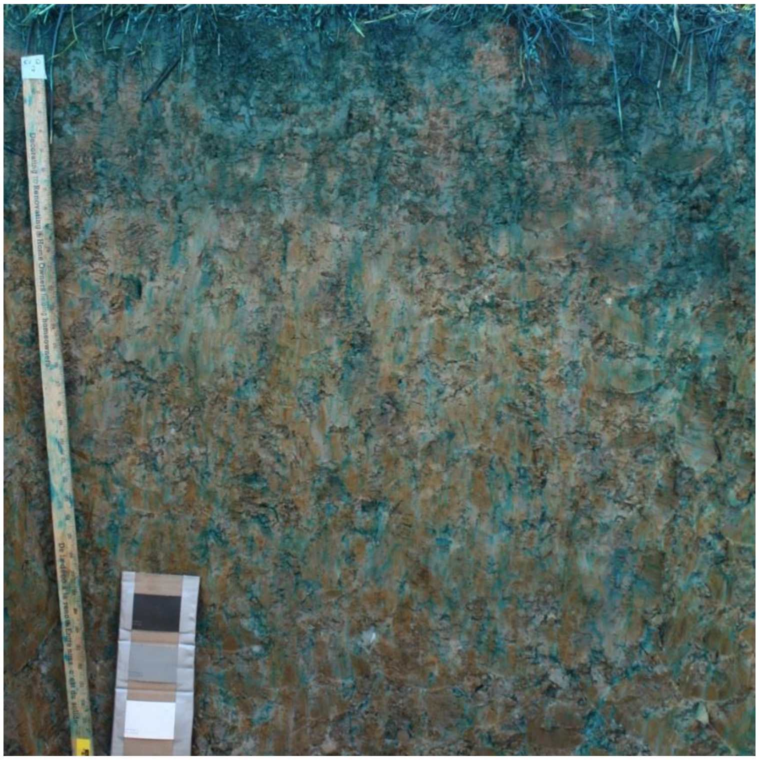


Figure B2 Example of dye stained profile from a dry clay plot (Plot D – 2nd profile).

Figure B3 Example of dye stained profile from a wet clay plot (Plot B - 3rd profile).

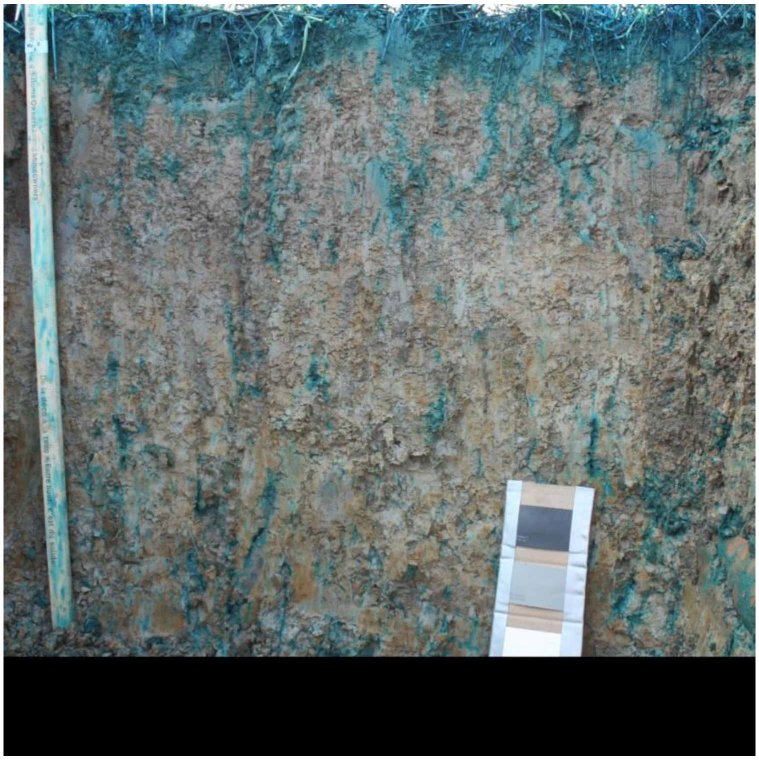


Figure B4 Example of dye stained profile from a wet clay plot (Plot C - 2nd profile).

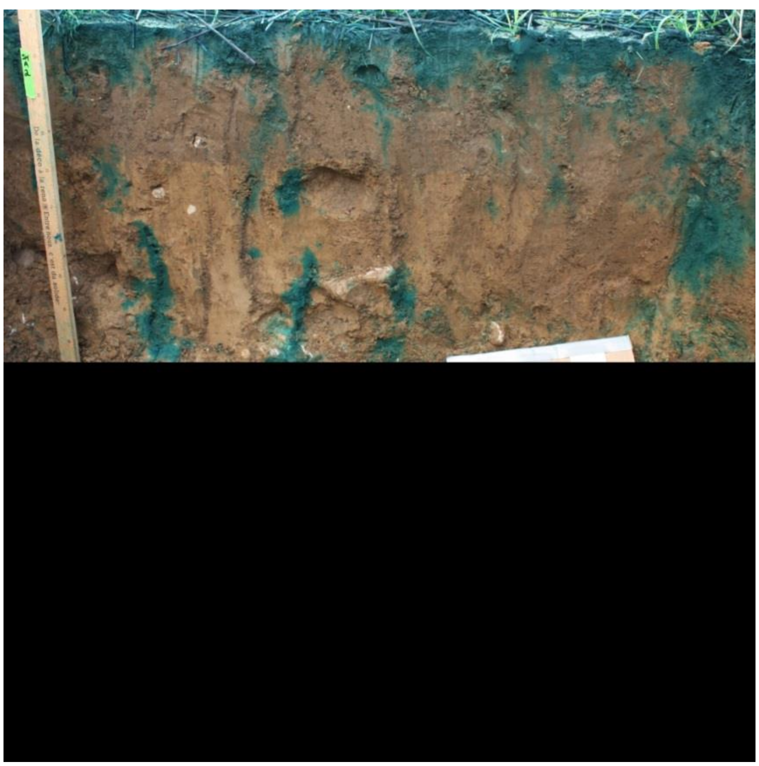


Figure B4 Example of dye stained profile from a dry silt loam plot (Plot A - 2nd profile).

Figure B6 Example of dye stained profile from a dry silt loam plot (Plot D - 3rd profile).

Figure B7 Example of dye stained profile from a wet silt loam plot (Plot B - 3rd profile).

Figure B8 Example of dye stained profile from a wet silt loam plot (Plot C - 4th profile).