Nutrient Leaching in Soil Affected by Fertilizer Application and Frozen Ground

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Agricultural runoff containing P and 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 explored interactions between nutrient supply and infiltrating water during a simulated nongrowing season using a laboratory experiment to understand how water and nutrients move through partially frozen and unfrozen soil and if fertilizer placement influences NO$_3^-$ and dissolved reactive P (DRP) leaching. Intact silt loam and clay soil monoliths (28 by 30 by 30 cm) were fertilized with P and N via subsurface placement or surface broadcast and subjected to simulated rainfall under unfrozen (10°C) and partially frozen (unfrozen) conditions. Conservative tracers (Br$^-$, Cl$^-$, and D$_2$O) applied to characterize subsurface flow paths throughout a subset of events indicated that matrix flow dominated in unfrozen silt loam soil. However, preferential flow paths 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$^{-1}$ [23%] in silt loam and 65.73 kg ha$^{-1}$ [61%] in clay) and DRP losses (by 2.33 kg ha$^{-1}$ [60%] in silt loam and 4.25 kg ha$^{-1}$ [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.

Abbreviations: DRP, dissolved reactive phosphorus; F1, first frozen event; F2, second frozen event; FTC, freeze–thaw cycle; KVL, Kingsville; NGS, nongrowing season; PT, pretreatment; S, final saturation event; STM, St. Marys; TP, total phosphorus; U1, first unfrozen event; U2, second unfrozen event; WEP, water-extractable phosphorus.

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 P and 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 with 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 be lost through tile drains, particularly as 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 flow paths, 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 (Jarvis, 2007; Shipitalo and Gibbs, 2000). Water tracers have been commonly used to investigate preferential flow pathways and solute transport in agricultural soils.

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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 to variability of flow paths over space and time (Haygarth and Jarvis, 1999; Jarvis, 2007). Quantifying the movement of adsorbing nutrients (e.g., P) through preferential flow paths is an additional challenge (Jarvis, 2007).

Tile drains are easily activated during the nongrowing season (NGS) because 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 to the 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 (FTCs) 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.

Flow paths 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., 2006). 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 on freezing (Stähli et al., 1996). In addition, water infiltrating into unsaturated frozen soil can refreeze and may result in the blocking of preferential flow paths (Stähli et al., 1996; Watanabe and Kugisaki, 2017). Infiltration and refreezing dynamics in preferential flow paths are related to temperature and moisture conditions of the soil and to heat transfer between infiltrating water and soil (Mohammed et al., 2018). However, how these conditions influence preferential flow paths through frozen soil remains unclear (Mohammed et al., 2018). An improved understanding of flow paths through frozen soils is necessary to enhance the understanding of nutrient transport under these conditions.

Because the NGS is a critical period for nutrient loss, it is essential that beneficial management practices 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 (Triticum aestivum L.) in a corn (Zea mays L.)–soybean [Glycine max (L.) Merr.]–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; Kalbic 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 with surface broadcast applications (Williams et al., 2018). Previous studies investigating manure and fertilizer placement and nutrient export have favored methods that incorporate nutrients into the soil over surface applications (Glasner et al., 2011b; King et al., 2017; Kleinman et al., 2009). Two primary mechanisms explain why subsurface placement can have advantages over surface broadcasting in no-till systems: (i) the physical retention of nutrients caused by fertilizer being placed away from active flow paths reduces the exposure of P to preferential flow paths (Glasner et al., 2011a; Jarvis, 2007), and (ii) the chemical retention of nutrients as subsurface placement provides more contact with the soil, leading to greater opportunity for adsorption to soil particles (Glasner et al., 2011b; Williams et al., 2018).

Although these retention mechanisms have been demonstrated with subsurface manure application (Glasner 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 was to characterize the movement of water through frozen and unfrozen soils and to determine if subsurface fertilizer placement can reduce the leaching of nutrients in the subsurface under NGS conditions. The main objectives of this study were (i) to characterize the movement of water and conservative tracers through preferential and matrix flow paths in soils under different soil frost conditions (partially frozen vs. unfrozen), (ii) to determine if subsurface flow pathways differ with soil texture (silt loam vs. clay), and (iii) to quantify the mobilization of NO3 − and dissolved reactive P (DRP) through the soil profile under surface broadcast and subsurface placement (banding) application strategies and relate this to differences in flow paths.

Methods
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, soybean, and winter wheat. The field at KVL has been under no-till management for 20 yr, and the STM field has been under rotational conservational till for 25 yr with a shallow disk tillage.
every 3 yr 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 to 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- by 30- by 35-cm steel corer. The corer was sledge-hammered 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 by 30 by 30 cm) were extracted from the corer and gently placed into 28- by 30- by 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. After extraction, soil monoliths were stored in their tanks at 4°C prior to the start of the experiment. At the end of the experiment, additional soil samples from the undisturbed outer walls of each exposed pit were taken at depths of 0 to 10 cm, 10 to 20 cm, and 20 to 30 cm. 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.

**Chamber and Rainfall Setup**

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 (10°C) and partially frozen (~0°C) conditions, during a 35-d period for the silt loam monoliths and a 40-d period for clay (Fig. 1; Supplemental Fig. S1). Monolith soil temperature was recorded every 30 min during the experiment by two temperature sensors (no. DBSA720, DaqLink Fourier Systems Ltd.), 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.

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 (pretreatment [PT]). After this, two rainfall simulations on unfrozen soil were conducted (first unfrozen event [U1], second unfrozen event [U2]). All unfrozen events (PT, U1, U2) were conducted while the chamber was held at 10°C. After these events, the chamber temperature was decreased to −10°C and held for 5 d (freezing phase). The chamber temperature was subsequently increased from −10 to 5°C for 8 h before simulated rainfall was applied to the partially frozen soil; this was repeated twice (first frozen event [F1], second frozen event [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 (Supplemental Fig. S1); therefore, thawing probably 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 d for the silt loam monoliths and at 10°C for 10 d for the clay monoliths. The discrepancy in holding time between the two F simulations was due to human error but is unlikely to have affected the results. Although the shift from −10 to 5°C over an 8-h period is somewhat extreme and shifts of this magnitude are

![Fig. 1. Air temperature in the chamber and soil temperature at −5 cm and −25 cm over the simulated nongrowing 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 d at 10°C between partially frozen events (F1 and F2). F1, first frozen event; F2, second frozen event; PT, pretreatment; S, final saturation event; U1, first unfrozen event; U2, second unfrozen event.](image-url)
uncommon, they do occur in temperate climates such as Ontario (Environment and Climate Change Canada, 2018). 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, rainfall was applied at a rate of 4.4 mm h⁻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 with climate change are becoming more prevalent in cold regions (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 by 25 by 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 after the first event (PT) at a rate of 97.5 kg ha⁻¹ of P₂O₅ 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 was 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, because 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 the risk of seed damage associated with ammonia release from these fertilizers (Ontario Ministry of Agriculture Food and Rural Affairs, 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) (Ontario Ministry of Agriculture Food and Rural Affairs, 2017).

A rainfall simulator was designed using a polyethylene container (60 by 40 by 22 cm) with 25 needles (23G) evenly distributed over an area of 23 by 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 throughout each event to ensure a constant rainfall rate (4.4 mm h⁻¹). The artificial rainwater was prepared based on rainwater composition typical of southern Ontario (National Atmospheric Chemistry [NATChem] database) containing SO₄²⁻ (2.17 mg L⁻¹), NO₃⁻ (2.64 mg L⁻¹), Cl⁻ (0.19 mg L⁻¹), NH₄⁺ (0.81 mg L⁻¹), Na⁺ (0.10 mg L⁻¹), Ca²⁺ (0.48 mg L⁻¹), Mg²⁺ (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 and 255 mm, simulating NGS rainfall at the STM and KVL sites, respectively, was applied to the soil monoliths during the experiments, which is lower than the long-term (1981–2010) average of 561 mm for precipitation received between October and April for the region (Environment and Climate Change Canada, 2018). 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 the U₂ (100 mg L⁻¹ Br⁻ as KBr), F₁ (500 mg L⁻¹ Cl⁻ as NaCl), and F₂ (D₂O enriched to +100‰) events to identify breakthrough curves and to 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 (C₀).

We used four soil monoliths in our study, with one monolith of each soil type (silt loam or clay) subjected to each fertilizer application method (broadcast or subsurface placement). All soil monoliths were subjected to the same rainfall regimes and underwent the same experimental and sampling schedules for the duration of the experiment. Thus, there were two replicates to investigate the impacts of soil frost on hydrologic flow paths 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).

### 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 cellulose acetate filter (FlipMate, Delta Scientific) for the analysis of DRP using colorimetric methods (Bran Luebbe AA3; Seal Analytical, 2005a) and analyses of NO₃⁻, Br⁻, and Cl⁻ using ion chromatography (Dionex ICS 3000, IonPac AS18 analytical column). Unfiltered subsample (50 mL) was acidified to 0.2% H₂SO₄ for total P (TP) analysis. The subsample was digested with acid persulfate in an autoclave (EPA/600/R-93/100, Method 365.1) and analyzed colorimetrically (Bran Luebbe AA3; Seal Analytical, 2005b). Sample preservation was completed within 24 h of sample collection. Filtered leachate samples collected from all events after D₂O tracer application (F2, S) were sealed with Parafilm to prevent fractionation.

In addition to the leachate water samples, pore water samples (5 mL) were collected separately from different depths (−5, −15, and −25 cm) to measure the PO₄³⁻, NO₃⁻, Br⁻, and Cl⁻ concentrations. These pore water samples were extracted by ceramic samplers, 5 cm in length and 2.5 mm in diameter (CSS5 MicroRhizon samplers, no. 19.21.23F), that were 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. Pore water samples were collected from all depths during saturated conditions (PT, S). Attempts to retrieve pore water 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 pore water samples were retrieved under frozen conditions. All outflow leachate and pore water samples were stored at 4°C prior to analysis. Leachate and pore water samples with PO₄³⁻ concentrations below Dionex ICS 3000 detection limit (0.75 mg L⁻¹ PO₄³⁻) were re-run on a Bran Luebbe AA3, along with soil WEP and soil NO₃⁻ (see below) (ammonium-molybdate ascorbic acid; Bran Luebbe AA3; Seal Analytical, 1999, 2005a). Leachate samples from F2 and S events were analyzed for δ²H using a liquid water isotope analyzer (Model L2130-I, Picarro) based on cavity ring-down spectroscopy technology at the University of Manitoba. Delta (δ) values were recorded in per mil (‰) deviations from the Vienna Standard Mean Ocean Water (Craig, 1961) with a precision of 0.1‰. Background concentrations of D₂O were subtracted from initial (C₀) and final (C) concentrations to allow comparisons with 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 nine locations at depths of 0 to 10 cm, 10 to 20 cm, and 20 to 30 cm (collected in an 8- by 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 h, and sieved to 2 mm. Dried soil samples from 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 h for WEP, and 2.5 g of dried soil extracted with 25 mL of 2 M KCl, shaken for 1 h for NO₃⁻). Extractants for WEP and NO₃⁻ were gravity filtered through a Whatman no. 42 filter. The WEP samples were also centrifuged for 5 min at 5000 rpm prior to filtering. Samples were stored at 4°C prior to analysis.

Results

Variability in Flow Paths between Soil Texture and Soil Frost

Variability between flow paths in unfrozen soil differed with soil texture, where preferential flow dominated in clay and matrix flow dominated in silt loam (Fig. 2). During U2, the breakthrough curve (C/C₀ vs. cumulative volume) of the Br⁻ tracer indicated the presence of preferential flow in clay monoliths (Fig. 2). In unfrozen clay, the C/C₀ 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 flow paths were activated (Fig. 2). In contrast, Br⁻ applied to silt loam soils during U2 was not found in the leachate samples during this event (Fig. 2). The lack of applied tracer in U2 leachate suggests that matrix flow was the dominant flow path through unfrozen silt loam because there was no direct connectivity between the surface and subsurface. Elevated C/C₀ of Br⁻ in leachate was found in subsequent events on silt loam (Fig. 2), also indicating the dominance of matrix flow.

In contrast, under partially frozen conditions, the observed patterns in the conservative tracers suggest that flow paths were...
similar among all monoliths (F1, F2) and indicate the presence of preferential flow paths (Fig. 2). 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\(_2\)O (F2) in both soil types (Fig. 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 as the \( C/C_0 \) of previously applied tracers increased (Fig. 2). The preferential flow pattern in partially frozen soils (high connectivity early in the 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 flow paths 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 (Fig. 2). Similar tracer responses among soil monoliths provide confidence that differences in leachate nutrient concentrations are due to differences in fertilizer application method and are not the result of potential variability in flow paths between soil monoliths despite only having one replicate of each soil type and fertilizer application method.

**Phosphorus and Nitrogen in Subsurface Leachate**

During the entire simulated NGS, soils receiving fertilizer via subsurface placement had lower cumulative leachate DRP and NO\(_3^-\) losses compared with surface-broadcast applications on the same soil type (Fig. 3 and 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 with surface-applied fertilizer. Of the P fertilizer that was applied, broadcast treatments lost 15.9% (clay) and 9.0% (silt loam), whereas 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 with surface-broadcast applications. During 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, whereas surface broadcast applications on silt loam led to the highest cumulative NO\(_3^-\) losses.

Patterns in leachate DRP and NO\(_3^-\) varied 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 ± 0.5 mg L\(^{-1}\)) compared with STM silt loam (0.1 ± 0.0 mg L\(^{-1}\)). In contrast, PT mean NO\(_3^-\) losses from KVL clay soils were lower (0.1 ± 0.2 mg L\(^{-1}\)) than those from STM silt loam soils (60.9 ± 11.1 mg L\(^{-1}\)). Dissolved reactive P losses across both fertilizer placement methods and soil types were highest during U1 (i.e., the first event immediately after fertilization) compared with all other simulated events. In contrast, broadcast treatments lost marginally more NO\(_3^-\) in leachate during U1 than their banded counterparts (Fig. 4). In U2, differences in leachate

![Fig. 3. Cumulative dissolved reactive P (DRP; kg ha\(^{-1}\)) loss compared with cumulative leachate volume (mL) for all soil monoliths over all six non-growing season events. F1, first frozen event; F2, second frozen event; PT, pretreatment; S, final saturation event; U1, first unfrozen event; U2, second unfrozen event.](image)
NO\textsubscript{3}\textsuperscript{−} between application methods began to diverge as NO\textsubscript{3}\textsuperscript{−} from broadcast applications increased. Although actual differences in cumulative NO\textsubscript{3}\textsuperscript{−} loss in leachate differed between soils, the rates of NO\textsubscript{3}\textsuperscript{−} loss were similar among all monoliths during unfrozen events (Fig. 4). Higher cumulative NO\textsubscript{3}\textsuperscript{−} losses from silt loam soils were due, in part, to higher initial NO\textsubscript{3}\textsuperscript{−} in the silt loam soil. High DRP losses were observed immediately after fertilization in U1, whereas increases in NO\textsubscript{3}\textsuperscript{−} were less immediate.

Under partially frozen and saturated conditions, broadcast treatments continued to result in greater losses of DRP and NO\textsubscript{3}\textsuperscript{−} in leachate compared with banded treatments. Leachate DRP from broadcast treatments increased in both soil types during partially frozen events (F1, F2; Fig. 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. Although NO\textsubscript{3}\textsuperscript{−} losses from broadcast applications continued to be higher than those from subsurface banded applications, the rate of NO\textsubscript{3}\textsuperscript{−} loss declined in all soil monoliths during the first event on partially frozen soil (F1) compared with unfrozen events. In the second partially frozen event (F2), the rate of NO\textsubscript{3}\textsuperscript{−} loss in leachate differed between soil textures (Fig. 4). Through F2, the rate of NO\textsubscript{3}\textsuperscript{−} remained similar to F1 in the silt loam soil. However, the rate of NO\textsubscript{3}\textsuperscript{−} loss from clay soils increased dramatically from both application methods during F2 compared with all previous events. The final saturation event (S) showed similar rises in leachate DRP from broadcast treatments, whereas DRP from banded applications remained relatively steady for both soil types. The rate of NO\textsubscript{3}\textsuperscript{−} loss during saturated conditions remained high in clay soils and increased in silt loam soils compared with F2. Overall, through the entire simulated NGS, banded treatments retained more applied P and N than their broadcast counterparts in both soils.

**Phosphorus and Nitrogen Retention in Soil**

In general, fertilizer applied in subsurface bands resulted in more WEP and NO\textsubscript{3}\textsuperscript{−} available near initial band placement compared with the surrounding soil, whereas WEP and NO\textsubscript{3}\textsuperscript{−} from broadcast soils were more evenly distributed across the soil surface. Prior to fertilization, both soil types showed stratification of WEP with depth (Table 1), whereas only the clay soil showed stratification of NO\textsubscript{3}\textsuperscript{−} with depth (Table 2). The center of the clay band monolith was the only location where WEP after the experiment was higher than the control (Table 1). In contrast, fertilizer application increased soil NO\textsubscript{3}\textsuperscript{−} availability in the soil surface (0–10 cm) in both soil types and fertilizer application methods after the simulated NGS (Table 2). Fertilizer application method did not appear to influence NO\textsubscript{3}\textsuperscript{−} retention at depths of 10 to 20 cm and 20 to 30 cm. However, at depths of 10 to 20 cm and 20 to 30 cm, clay soils showed higher NO\textsubscript{3}\textsuperscript{−} retention under both fertilizer application methods, whereas NO\textsubscript{3}\textsuperscript{−} retention at these depths was not greater than the control in the silt loam monoliths (Table 2).

**Discussion**

This research has demonstrated that nutrient transport in the subsurface is controlled by the connection of the nutrient source with active subsurface flow paths. It has also shown that nutrient transport in agricultural soil is dependent on both dominant flow type and fertilizer placement. Flow paths 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 flow paths present under different texture and soil frost conditions. These results have implications for nutrient application strategies prior to the nongrowing season.

### Variability in Flow Paths with Texture and Frost Conditions

In this experiment, flow paths differed with soil texture, and the impacts of frost on flow paths 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 flow paths with soil texture in unfrozen soils are unsurprising because preferential flow is more common in fine-textured soil because the soil matrix is less permeable (Hendrickx and Flury, 2001). This work is also consistent with that of Glæsner 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 yr, and tillage had occurred 3 yr prior to monolith collection. Because macropore networks can be

<table>
<thead>
<tr>
<th>Soil and fertilizer</th>
<th>Depth (cm)</th>
<th>Control</th>
<th>Post, left</th>
<th>Post, center</th>
<th>Post, right</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay, band</td>
<td>0–10</td>
<td>8.71 (0.70)†</td>
<td>4.62 (0.74)</td>
<td>13.97 (6.66)</td>
<td>4.29 (0.40)</td>
</tr>
<tr>
<td></td>
<td>10–20</td>
<td>4.74 (0.16)</td>
<td>2.58 (0.36)</td>
<td>2.41 (0.51)</td>
<td>3.13 (0.47)</td>
</tr>
<tr>
<td></td>
<td>20–30</td>
<td>4.46 (0.31)</td>
<td>2.92 (0.24)</td>
<td>2.11 (0.19)</td>
<td>3.24 (0.37)</td>
</tr>
<tr>
<td>Clay, broadcast</td>
<td>0–10</td>
<td>5.30 (1.10)</td>
<td>3.55 (0.51)</td>
<td>3.94 (0.67)</td>
<td>3.62 (0.47)</td>
</tr>
<tr>
<td></td>
<td>10–20</td>
<td>2.38 (0.18)</td>
<td>0.97 (0.13)</td>
<td>1.39 (0.27)</td>
<td>1.72 (0.51)</td>
</tr>
<tr>
<td></td>
<td>20–30</td>
<td>2.38 (0.36)</td>
<td>1.07 (0.28)</td>
<td>0.76 (0.19)</td>
<td>2.00 (0.71)</td>
</tr>
<tr>
<td>Silt loam, band</td>
<td>0–10</td>
<td>3.97 (0.69)</td>
<td>0.24 (0.18)</td>
<td>1.85 (1.27)</td>
<td>0.30 (0.28)</td>
</tr>
<tr>
<td></td>
<td>10–20</td>
<td>2.10 (0.26)</td>
<td>&lt;0.01 (0.01)</td>
<td>0.23 (0.17)</td>
<td>0.12 (0.17)</td>
</tr>
<tr>
<td></td>
<td>20–30</td>
<td>1.94 (0.25)</td>
<td>0.09 (0.11)</td>
<td>&lt;0.01 (0.01)</td>
<td>&lt;0.01 (0.01)</td>
</tr>
<tr>
<td>Silt loam, broadcast</td>
<td>0–10</td>
<td>3.53 (0.59)</td>
<td>0.88 (0.55)</td>
<td>0.33 (0.08)</td>
<td>0.27 (0.38)</td>
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<tr>
<td></td>
<td>10–20</td>
<td>1.93 (0.48)</td>
<td>0.23 (0.01)</td>
<td>0.29 (0.34)</td>
<td>0.49 (0.45)</td>
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<tr>
<td></td>
<td>20–30</td>
<td>1.73 (0.44)</td>
<td>0.06 (0.07)</td>
<td>0.07 (0.08)</td>
<td>0.04 (0.03)</td>
</tr>
</tbody>
</table>

† Means with SD of three samples per depth in parentheses.
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, flow paths 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 on 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 (Mohammed et al., 2018; Watanabe and Kugisaki, 2017). 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 flow paths among soils of different textures (Granger et al., 1984; Watanabe and Kugisaki, 2017). Macropores remaining air-filled on 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 flow paths present under unfrozen conditions in the clay soil remained active under partially frozen conditions (Fig. 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 flow paths 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 on freezing (Stähli et al., 1996), leading to the development of preferential flow paths in frozen soils (Fig. 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 flow paths through partially frozen loam soil.

It was also hypothesized that more preferential flow would occur during the second simulated rainfall on frozen soil because ice expansion during multiple FTCs 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 flow paths 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 FTCs 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 Luxmoore, 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.

Fig. 5. Conceptual diagram of interactions between flow paths 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 flow paths in clay soil. (B) Surface broadcast nutrients over partially frozen soils are quickly transported to the subsurface via preferential flow paths. Macropores persist in partially frozen clays while new preferential flow paths 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 flow paths, limiting the risk of transport via matrix and preferential flow in unfrozen soil. (D) Subsurface placement limits contact of nutrients with preferential flow paths in partially frozen soils and can come into contact with matrix flow as soil thaws.
The variability in subsurface flow paths 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 because tile drains are most active during the NGS (Macrae et al., 2007) when frozen ground conditions are most likely to be experienced. The occurrence of FTCs 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 flow paths on frozen ground after multiple FTCs or changes in FTC magnitude. Furthermore, the influence of FTCs on subsurface flow paths may differ with the use of more natural top-down soil freezing processes.

Impacts of Fertilizer Placement and Links to Flow Paths

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 because 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 with surface fertilizer applications. Our work supports the work of Smith et al. (2016) and showed that reduced nutrient losses after 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 six 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 with 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 with surface broadcast fertilizer. Our work showed that NO₃⁻ losses were reduced by 61% in the clay and 23% in the silt loam over the duration of our simulated NGS. This is consistent with other studies that 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). Whereas 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 FTCs. Freezing has 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 flow paths (Fig. 5). Subsurface placement of nutrients also increases contact between fertilizer and soil, an important factor in nutrient retention (Glesner 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). 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 flow path and being rapidly transported through the soil profile (Fig. 5). Furthermore, broadcast fertilizer may be exposed to surface ponding, which can result in inorganic fertilizers becoming dissolved and rapidly exported via preferential flow paths to tile drains. Other researchers 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 flow paths 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.

Nutrient losses from tile drains on working farms are likely to be lower than the subsurface nutrient losses reported here. Subsurface nutrient losses are affected 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 influence how added P fertilizer
may be retained or lost from soil (Andersson et al., 2013; Haygarth and Jarvis, 1999; Ruttenberg, 1976). 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 because fertilizer applied via subsurface placement is associated with lower application rates to avoid seed damage (Court et al., 1962; Ontario Ministry of Agriculture Food and Rural Affairs, 2017). In the current study, nutrients were applied at the same rates to illustrate the significance of subsurface flow paths and frost on nutrient transfer and demonstrate the mechanisms leading to reduced nutrient losses after subsurface placement. In a field setting where the same mechanisms are occurring but where 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 flow paths and fertilizer placement interact across soil frost and soil textures, other conditions may influence flow paths and subsequent interactions with fertilizer. Although this work investigated flow paths 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 nutrient losses. Future work should consider how flow paths vary under differing antecedent moisture conditions as monitored by soil moisture sensors and relate these to fertilizer placement methods. Investigating flow paths under variable antecedent moisture conditions (e.g., wet or dry) has particular relevance for spring fertilizer applications. It will also be important to consider nutrient losses via both surface and subsurface flow paths 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 because it may break up preferential flow pathways and promote matrix flow and contact with the soil.

Our results indicate that differences in subsurface flow paths 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 with surface broadcasts. The subsurface placement of fertilizer reduces subsurface nutrient losses because opportunities for applied fertilizer to interact with preferential flow paths 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 beneficial management practices including appropriate fertilizer application rate, source, and timing (4R Nutrient Management Strategy).

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Annex 4 Objectives and Targets Task Team. 2015. Recommended phosphorus loading targets for Lake Erie. USEPA, Washington, DC.


Conclusions

Our results indicate that differences in subsurface flow paths 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


