Release of Phosphorus from Crop Residue and Cover Crops to Runoff Over the Non-growing Season in Southwestern Ontario

by

Tatianna M. Lozier

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Abstract

Maintaining crop residue or cover crops on fields during winter is a recommended Best Management Practice (BMP) in temperate regions. However, losses of phosphorus (P) to runoff have been attributed to vegetation following freeze-thaw cycles (FTC). Much of the existing knowledge on P loss from vegetation following FTC has been obtained under severe frost conditions (either simulated or natural). In cool temperate climates, such as Southwestern Ontario, air temperatures are more moderate. Consequently, crop residue and cover crops may be less severely impacted by FTC. An improved understanding of the role of surface vegetation in P losses during the non-growing season (NGS) in cool temperate climate zones is needed to determine if the use of cover crops is suitable for these regions. This thesis addresses two major objectives: (1) to better understand the potential role of hydroclimatic conditions (FTC and hydrological event type) in mobilizing P from crop residue, *Triticum aestivum L.* (winter wheat), as well as *Trifolium pretense L.* (red clover) and *Avena sativa L.* (oat) as cover crops, using laboratory experimentation; and (2) to quantify the release of P from vegetation and soil over the NGS in a field setting, and, determine if changes in water extractable phosphorus (WEP) in vegetation or soil were reflected in loads of dissolved reactive phosphorus (DRP) or total phosphorus (TP) in surface runoff and tile drain effluent. Results from this study revealed that the patterns observed in the laboratory were reflected in the field, where cover crops released more P than winter wheat residue. Oat cover crop was impacted by FTC whereas red clover was not, likely because it had been terminated in early fall using a herbicide. The laboratory and field experiments also demonstrated that potential losses of P from cover crops do not necessarily translate to losses of P in runoff because the mobilization of P in runoff is impacted by both supply and transport processes. Phosphorus leaching and loss from fields are hampered if crops

are not inundated/flooded or if surface runoff is limited, but enhanced when vegetation is subjected to prolonged contact with runoff water. The field study demonstrated that although P appeared to have been mobilized from both vegetation and soil pools during the NGS, loads of DRP P and TP leaving the fields were small in comparison, suggesting that much of the P released was retained within the field rather than lost in runoff. This study provides insight into the timing and magnitude of P release from vegetation throughout the NGS in regions with a cool temperate climate and provides an improved understanding of the contribution of cover crops to winter P losses.

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Table of Contents

List of Tables

List of Figures

List of Abbreviations

Abbreviation	Full Meaning
BMP	Best management practice(s)
C	Control
CC	Cover crop(s)
DRP	Dissolved reactive phosphorus
F	Frozen
FTC	Freeze-thaw cycle
FTL	Freeze-thaw leach
FWMC	Flow weighted mean concentration
IP	Inorganic phosphorus
NGS	Non-growing season
O	Oat
OP	Organic phosphorus
P	Phosphorus
PP	Particulate phosphorus
RC	Red clover
STP	Soil test phosphorus
TP	Total phosphorus
WEP	Water extractable phosphorus
WR	Winter wheat residue (stubble and straw)

1.0 Chapter One: Introduction and Problem Statement

Phosphorus (P) loading into the Great Lakes is a major environmental concern due to eutrophication, caused by the accelerated growth of algae and other aquatic plants. Eutrophication reduces ecosystem health and water quality (Carpenter et al., 1998), which restricts the use of that water for fisheries and other industry, as well as recreation and human consumption (Sharpley et al., 2001).

Phosphorus loading into the Great Lakes originates from point and non-point sources. Overall, there has been a reduction in P from point sources, such as the effluent from sewage treatment plants (Sharpley et al., 2001); however, due to the difficulty in the identification of non-point sources, they are challenging to control (Sharpley and Rekolainen, 1997). Agricultural fields have been recognized as an important non-point source of P loading to water bodies (Sharpley et al. 2015), as P is an essential nutrient for crop and animal production (Carpenter et al., 1998; Sharpley, 2000). As a result, controlling the loss (or export) of P from agricultural fields is essential to the protection of surface waterbodies from eutrophication (Withers et al., 2000). Incidentally, agricultural best management practices (BMPs) have been implemented to reduce nutrient, runoff and soil losses from agricultural fields.

Conservation tillage practices and the use of cover crops are promoted BMPs in Southwestern Ontario. They offer many benefits to a farm field including; reduced soil erosion (Gaynor and Findlay, 1995; Rousseau et al., 1987; Ulén et al., 2010) and particulate P export (Rousseau et al., 1987) by decreasing the volume of surface runoff (Gilliam et al., 1997). Roots enhance infiltration, soil porosity and aggregation (Sharpley and Smith, 1991). The use of cover crops also adds organic matter to the soil (Sharpley and Smith, 1991) and provides nutrients to the successive crop (Blanco-Canqui et al., 2015). However, there is uncertainty whether these

practices retain P during the non-growing season (NGS). Vegetation has been found to enhance dissolved reactive phosphorus (DRP) in runoff (Schrieber and McDowell, 1985; Schreiber, 1985; Sharpley, 1981; Wendt and Corey, 1980) and this can be enhanced under freeze-thaw conditions (Bechmann et al., 2005; Elliott, 2013; Liu et al., 2013a; Riddle and Bergström, 2013; Roberson et al., 2007; Timmons et al., 1970; White, 1973). Much of the existing knowledge on the contribution of vegetation to DRP losses in runoff exists from simulation studies in regions with colder winters than experienced in Southwestern Ontario, such as Western Canada (Elliott, 2013), the Midwestern United States (Roberson et al., 2007; Timmons et al., 1970) and Scandinavian countries (Liu et al., 2013a; Liu et al., 2014; Øgaard, 2015; Riddle and Bergström, 2013; Sturite et al., 2007). However, it is unclear whether the influence of FTC on vegetation P loss is as severe in cool temperate regions, and, subsequently, an improved understanding of the role of crop residue and cover crops in winter P losses in this climate is needed.

2.0 Chapter Two: Review of Literature

There are many interacting factors that control phosphorus (P) cycling within individual agricultural fields. To better understand the potential of cover crops to increase or mitigate P loss (transfer of P), it is essential to first review (2.1) P dynamics and supply in the terrestrial environment and how these are affected by agricultural practices; and (2.2) Dominant hydrologic pathways for P transfer from agricultural fields; (2.3, 2.4) How (2.1) and (2.2) vary in space and time, both naturally and with management practices, and, (2.5) If and how the use of conservation tillage practices and cover crops, as best management practices (BMPs), can mitigate these losses. These are described in the following sections.

2.1 Phosphorus dynamics and Supply in the Terrestrial Environment and the Influence of Agricultural Practices

Phosphorus cycling in agricultural systems is influenced by chemical, biological and physical processes, which interact amongst vegetation, soil and microorganisms (Figure 2.1; Pierzynski et al., 2005). Phosphorus availability is driven by weathering (Pierzynski et al., 2005) and the desorption, dissolution or extraction of P from soil and vegetation (McDowell et al., 2001), as well as the breakdown of organic matter (Schlesinger and Bernhardt, 2013).

2.1.1 Phosphorus in Soil and Factors Governing Phosphorus Availability in Runoff

Soil plays an important role in cycling P through the environment (Dorioz et al., 2006). The release of P into the environment occurs naturally through the weathering of primary phosphate minerals, mainly apatite (Shen et al., 2011). Weathering releases phosphate into solution, primarily as orthophosphate, which is available for plant uptake (McDowell et al.,

2001). Soil P exists in inorganic and organic forms (McDowell et al., 2001), which differ in behaviour and fate in the environment (Hansen et al., 2004). The inorganic P (IP) pool is generally of concern because the uptake of P from soil solution by plants occurs in the inorganic form (Damon et al., 2014). The size of the soil IP pool includes that P released from vegetation and microbial biomass, in addition to inputs from fertilizer and background native P in the soil (Damon et al., 2014). The concentration of P in soil solution is generally small, due to the low solubility of P minerals (Busman et al., 2002; McDowell et al., 2001; Schachtman et al., 1998). However, the supply of P to the soil-water solution and its potential loss in runoff is governed by a combination of abiotic and biotic processes.

2.1.1.1 Abiotic Reactions in Soil

Abiotic processes (adsorption–desorption and precipitation-dissolution) are the main processes that govern the balance of P between the soil particles and soil solution (Dorioz et al., 2006; Pierzynski et al., 2005). The concentration of P in solution governs the amount of adsorbed P (Frossard et al., 1995). This is controlled by the equilibrium between the soil adsorption system, soil solution and precipitated P compounds (Sample et al., 1980). The equilibrium P concentration represents an active reservoir between P source and sink (Özgül et al., 2012). Phosphorus in soil solution is replenished through the desorption of adsorbed P ions on the soil, dissolution of P compounds (Zaimes and Shultz, 2002) or the mineralization of OP (Condron et al. 2005).

4

(i) Adsorption-desorption Reactions Between Phosphorus and Soil Particles

Adsorption reactions involve the removal of P from solution, where P is held on active sites of soil particles (Holtan et al., 1988; Zaimes and Shultz, 2002) and is influenced by a number of soil properties (Frossard et al., 1995). Adsorption of P occurs greatest in soils containing clays, high iron (Fe) and aluminum (Al) oxides, calcium (Ca), magnesium and organic matter, as these are the main reactive soil phases (Djodijic et al., 2000; Dorioz et al., 2006; McDowell et al., 2001; Sharpley and Halvorson, 1994; Zaimes and Shultz, 2002), and have large surface areas to provide a greater number of adsorption sites (Shen et al., 2011). In addition, greater P adsorption occurs in acidic soils, as more Al and Fe exist in solution to form strong bonds with phosphate (Frossard et al., 1995; Pierzynski et al., 2000). Conversely, in soils with a greater pH, most P is in the form of calcium compounds.

Generally, the amount of P in soil solution is generally very low, as P is highly reactive (McDowell et al., 2001) and adsorbed at the surface of soil particles (Dorioz et al., 2006). When P is added to the soil, initial adsorption processes are easily reversible and added P is available for plant take up or leaching in runoff (Figure 2.1; Hansen et al., 2002; Pierzynski et al., 2005). Phosphorus removed from soil solution (via plant uptake or runoff) must be replenished via the solid soil phase (Figure 2.1; Condron et al. 2005; Hansen et al., 2002; McDowell et al., 2001). Phosphorus can re-enter soil solution via desorption processes, which is the release of P from the solid phase into the soil solution (Busman et al., 2002; Hinsinger, 2001; Pierzynski et al., 2005). A soil high adsorptive power will tend to release P slowly to the soil solution (McDowell et al., 2001); however, P desorption increases when oxides of Al and Fe are highly saturated with P (Uusitalo and Tuhkanen, 2000).

(ii) Precipitation-dissolution Reactions Between Phosphorus and Soil Particles

Precipitation reactions involve the removal of P from solution as P reacts with another compound to form a new solid mineral (Holtan et al., 1988). Over time, P can react and precipitate out of solution in soils containing Al, Ca and Fe to form insoluble compounds (Figure 2.1; Dorioz et al., 2006; Gburek et al., 2005; Frossard et al., 1995; Pierzynski et al., 2005; Reid et al., 2012; Schlesinger and Bernhardt, 2013). When a soil is supplied with P, the soils adsorbing constituents become increasingly saturated until a point is reached when precipitation of a sparingly soluble compound occurs (McDowell and Sharpley, 2002). Phosphorus retention is dominated by precipitation reactions in calcareous glacial soils such as those in Southwestern Ontario, due to high levels of Al, Ca and Fe (Reid, 2011). When the P concentration in soil solution is lowered, sparingly soluble P will dissolve until the adsorption complex has been saturated to a degree which corresponds to the solubility of the least stable P compound present (Larsen, 1967). The solubility of the least soluble P compound controls dissolution and therefore the concentration of P in solution (Frossard et al., 1995).
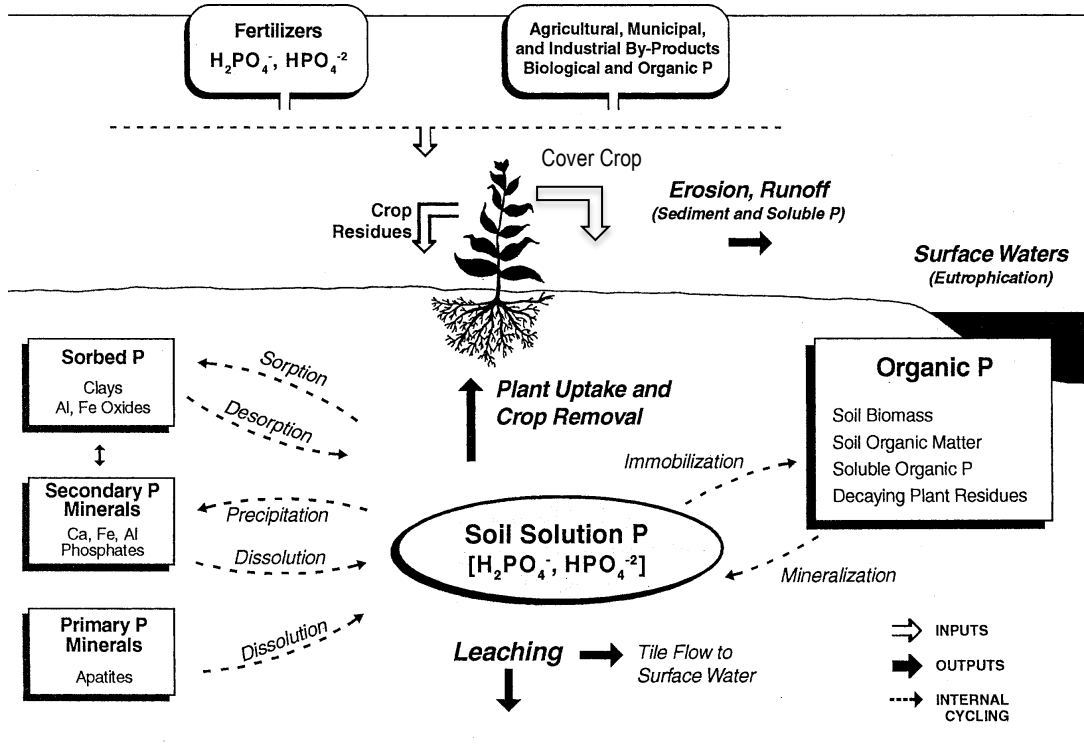
Figure 2.1: The terrestrial phosphorus cycle, including phosphorus inputs, outputs and internal cycling (modified from Pierzynski et al., 2000).

2.1.1.2 Biotic Phosphorus Cycling in Soil

Biotic processes influence the release of IP into solution through the turnover of P by microbial biomass and the mineralization of organic P (OP) (Figure 2.1; Frossard et al., 2000). Organic P is derived from plant residues and excreta from microorganisms (Haygarth and Jarvis, 1999). As a result, the internal cycling of P between the release of OP and the exchange to IP is an important process governing the availability of IP to plants, microbes and soil adsorption (Noack et al., 2012).

(i) Crop Phosphorus Uptake and Release

The uptake of P by vegetation is the primary method of P removal from the soil solution (Figure 2.1; Pierzynski et al., 2005), which is driven by the availability of IP (Schachtman et al., 1998). When crops take up IP from the soil it becomes incorporated into plant biomass as organic compounds, and as a result, plants provide a temporary storage of P (Dorioz et al., 2006). However, P is removed from agricultural systems when those crops are harvested. During senescence, remaining plant litter returns OP to the soil and through decomposition and mineralization processes by microbial biomass, OP is converted back into IP (Richardson and Simpson, 2011). The amount of nutrients released from vegetation will depend on the decomposition rate and nutrient concentration of the plant material (Lupwayi et al., 2003). Typically, OP of relatively fresh organic material is readily decomposed (Hansen et al., 2002) and P released through mineralization is available for plant uptake or can quickly react with soil constituents (Pierzynski et al., 2005). In addition, P may also leach from vegetation during senescence (Schreiber and McDowell, 1985; Sharpley, 1981), which is either returned to the soil or lost in runoff (White, 1973).

(ii) Microbial Biomass

Soil organisms play a major role in P immobilization-mineralization processes that control the transformations of P between inorganic and organic forms (Figure 2.1; Damon et al., 2014; Frossard et al., 2000). Microbial biomass may also compete with plants for orthophosphate and can represent a significant pool of immobilized P that is unavailable for plant uptake (Damon et al., 2014; Richardson and Simpson, 2011). The size of the microbial biomass in agricultural soil is stimulated upon addition of crop residues (Damon et al., 2014; McLaughlin and Alston, 1986; White and Ayoub, 1983), whereas the application of mineral P fertilizer causes little increase in the amount of P in the microbial biomass (Damon et al., 2014; McLaughlin and Alston, 1986).

2.1.2 External Addition of Phosphorus Through Agricultural Practices

Agricultural practices alter the rate and magnitude of P cycling through the landscape. The concentration of P in soil solution may not be sufficient to meet the requirements of agricultural crops (Shen et al., 2011) and the addition of P from manure and fertilizers is required to increase plant available P in soil solution (Figure 2.1; Hansen et al., 2002; Pierzynski et al., 2005). Over time P from applied fertilizers will be taken up by crops, react with soil constituents to form insoluble minerals or adsorb onto mineral and organic matter (Hansen et al., 2002).

2.2 Forms of Phosphorus and Transport Pathways in Agricultural Systems

2.2.1 Forms of Phosphorus in Runoff

Phosphorus cycled through the terrestrial environment is either dissolved in solution or attached to sediment (Hansen et al., 2002; Haygarth and Sharpley, 2000). A difference between

the speciation of P is commonly distinguished by filtration methods. Dissolved phosphorus (DP) is typically (and for the purposes of this thesis) defined as P that has been passed through a 0.45 μm filter (Haygarth and Sharpley, 2000), which primarily consists of orthophosphate, immediately available for biotic uptake (Busman et al., 2002; Sharpley et al., 1994). The loss of DP in runoff is dependent on the P content of the topsoil (Hansen et al., 2002; Sharpley et al., 2001). Particulate P (PP) is the P adsorbed to mineral and organic particles that is eroded during runoff (Heathwaite and Dils, 2000; Sharpley, 1995) and is retained on a 0.45 μm filter (Daniel et al., 1998). The ratio of DP to PP in runoff depends on the processes by which P is extracted from the source soil and the dynamics operating during transport (Dorioz et al., 2006).

2.2.2 Transport Pathways for the Loss of Phosphorus in Runoff

Agricultural runoff generally describes the lateral movement of water at/above the surface or below ground, mainly through tile drainage. Surface and tile runoff are important mechanisms in the removal P from agricultural systems (Figure 2.1). The importance of each of these pathways is described below.

2.2.2.1 Surface Runoff

Surface runoff describes water that exclusively flows over the soil surface (Zaimes and Shultz, 2002) generated either as infiltration excess or saturation excess flow. Infiltration excess runoff occurs when rainfall intensity exceeds the infiltration capacity of a soil (Kleinman et al., 2006) and typically occurs following high intensity or long duration rainfall events (Walter et al., 2000). Saturation excess runoff is generated when the water table rises to the soil surface and the water storage capacity is exceeded (Kleinman et al., 2006), which can occur during low rainfall

10

intensities (Walter et al., 2000). Surface runoff has been traditionally considered as the major transport pathway for P in agricultural landscapes (Sharpley et al., 1993).

2.2.2.2 Subsurface Runoff and Tile Drainage

Tile drains exist under many agricultural fields in Ontario, due to poor drainage (Reid, 2011). They significantly change the hydrology of the field by decreasing saturation excess surface runoff by lowering the water table (Gilliam et al., 1997; Reid, 2011; Sims et al., 1998), increasing hydraulic conductivity and available water storage of the soil (Bilotta et al., 2008). Subsurface P losses were originally considered nonexistent due to the soil adsorption capacity (Heathwaite and Dils, 2000). However, the transport of environmentally significant levels of P by subsurface flow is enhanced if the soil is artificially drained (Bottcher et al., 1981; Culley et al., 1983; Dils and Heathwaite, 1999; Heathwaite and Dils, 2000; Heckrath et al., 1995; McDowell et al., 2001; Sims et al., 1998; Stamm et al., 1998). Tile drains may be an effective conduit for P export from agricultural catchments, as they provide a direct path to transport water and solutes through the subsurface and increase the size of the catchment area in direct contact to the drainage network (Heathwaite and Dils, 2000). Whether significant amounts of P are transferred in tiles depends on whether water travels through the matrix or preferential pathways.

2.2.2.3 Importance of Vadose Zone Pathways on Subsurface Phosphorus Losses: Matrix Flow and Preferential Transport

Matrix flow refers to the slow movement of water through the soil medium (Jarvis, 2007). In general, P concentrations in water moving through the soil matrix are low, due to the adsorption capacity of subsoil (McDowell et al., 2001). However, P leaching through the soil

matrix can be significant for soils that have low P retention, such as sand (Eastman et al., 2010; Hansen et al., 2002). In some soil, the rapid transport of water and nutrients to tile drains can occur through preferential pathways, which are a network of subsoil conduits (Beven and German, 1982). These pathways are often referred to as macropores, as they are larger than the majority of pores in the soil matrix (Hendrickx and Flury, 2001; Wilson and Luxmoore, 1988). It has been documented that the presence of preferential pathways is favorable in the top portion of the soil profile (Hendrickx and Flury, 2001) and most commonly exist in well-structured soils (Beauchemin et al., 1998), as they are formed by earthworms, fissures, cracks (Beauchemin et al., 1998; Heppel et al., 2002) as well as plant roots (Beven and Germann, 1982). Enhanced P export can occur in tile drainage where soils contain preferential pathways, as water bypasses the adsorption capacity of the soil matrix and there is little opportunity for P to react with soil adsorption sites (Jarvis, 2007). Preferential flow has been the subject of debate in terms of the conditions needed to generate flow. Many studies suggest that preferential drainage networks develop during storms and seasonally wet conditions (Beven and Germann, 1982); however, some authors have suggested these pathways become active regardless of water content (Beven and Germann, 2013; Flury et al., 1994, Shapitalo and Edwards, 1996). Nevertheless, these pathways are often recognized as the dominant transport pathway for water, sediment and P to tile drains.

2.3 Factors Influencing Spatial Variability in Form and Rate of Phosphorus Loss

The loss of P from agricultural catchments is the result of a combination of P sources and hydrological transport pathways (McDowell et al., 2001). Phosphorus losses, independent of form, are highly correlated to hydrological events (Hansen et al., 2002). Large P losses from

agricultural fields occur when hydrologic and biogeochemical controls are integrated (Daniel et al., 1998). The quantity of P in the soil and the mechanisms to move that P within the landscape are influenced by soil type, topography, as well as farm management practices.

2.3.1 Effects of Soil Type on Phosphorus Losses

Phosphorus speciation can vary with soil texture (Ball Coelho et al. 2012). Particulate P has been found in high concentrations in fine textured soils as it is highly bound to clay particles (Beauchemin et al., 1998; Eastman et al., 2010; Gentry et al., 2007; Simard et al., 2000). Due to the favoured transport of fine clay material, the P content of eroded material is greater than that of the source soil (Sharpley, 1985). In addition, clay soils are subjected to drying and cracking during the summer, which enhances the detachment of sediment during summer storms (Beauchemin et al., 1998). Preferential flow paths may be extensive in clay soils, and is a probable mechanism of soil and PP loss in tile drainage (Beauchemin et al., 1998; Gaynor and Findlay, 1995; Heckrath et al., 1995). Characteristically, clay soils have a high P sorption capacity (McDowell et al., 2001) and as a result the concentrations of DP in water moving through the soil matrix is lower. However, in clay soils that contain high P content at the surface, subsoil adsorption capacities may not necessarily prevent P from leaching downwards (Beauchemin et al., 1996; Heckrath et al., 1995). Similarly, P leaching through the soil profile can be significant for soils that have very low P sorption capacity (Eastman et al., 2010; Hansen et al., 2002; McDowell et al., 2001).

2.3.2 Influence of Local Topography on Phosphorus Losses

The way in which water ponds and the generation of surface runoff is influenced by the spatial organization of the microtopography of the field (Appels et al. 2011; Djodjic and Villa, 2015; Gbuerk and Sharpley, 1998; McDowell et al., 2001). Generally, only the lower portions of a field experience surface ponding or generate runoff (Appels et al. 2011; Villa et al., 2015). Excess water ponding in and flowing through local microtopography increases the hydrological connectivity of fields (Appels et al. 2011; Needleman et al. 2004) as water-ponded conditions can induce preferential flow through the soil profile (Jarvis, 2007). As a result, field slope is an important driver of both soil erosion and nutrient export. Soil erosion generally increases with an increase in slope (Armstrong et al., 2011; Su et al., 2011), due to faster flow (Fox et al., 1997), which can result in enhanced losses of PP (Needleman et al., 2004; Su et al., 2011). In addition, Armstrong et al. (2011) found that higher slopes enhanced the loss of DP, due to enhanced P desorption with increased depth and velocity of flow (Ahuja et al., 1981). However, shallow slopes generally have greater surface connectivity, due to slower flow and deeper water ponding (Armstrong et al., 2011; Fox et al., 1997), which allows for an increased contact time between runoff and soil, allowing for the exchange of P (Ahuja et al., 1981). As a result, some areas of a particular field have a greater potential to mobilize P than others (Pionke et al., 1999).

2.3.3 Effects of Farm Management Practices on Phosphorus Losses

2.3.3.1 Type of Fertilizer Application

Agricultural soils low in readily available P require fertilization to achieve maximum crop yields (Hart et al., 2004). However, for many agricultural fields, the soil is the dominant source of P to runoff (Hanson et al., 2002; Hart et al., 2004; Sharpley et al., 1994). Several

studies have indicated that dissolved reactive phosphorus (DRP) and total phosphorus (TP) concentrations in runoff are correlated to soil test P (STP) values (Pote et al., 1999). Generally, concentrations of DRP and TP are greatest as STP levels increase (Pote et al., 1999; Sharpley et al., 1993). The fertilization of soils, generally exceeds the amount of P removed by crops and has been attributed to elevated STP levels in agricultural soils (Sharpley et al. 1994). High STP levels have been found in both fields with repeated manure applications (King et al. 1990) and the long-term use of commercial fertilizer (Sharpley et al., 1994). However, differences between the amounts of P lost from soil treated with inorganic P fertilizers compared with organic manures have been identified elsewhere. Hart et al. (2004) found that P released from fertilized soil was correlated to the amount of soluble P present in each type. Compared to inorganic fertilizer, manure has a large portion of organic P that requires mineralization to convert IP (Bundy, et al. 2005). Similarly, manure has lower nutrient content than inorganic fertilizers (Sharpley et al., 1994) and has been found to result in lower P concentrations in runoff (Eghball and Gilley, 1999). However, Eghball and Gilley (1999) found that manure had a longer legacy effect than inorganic fertilizer, as P concentrations in runoff were elevated in successive events following the application of manure. Overall, the loss of P relating to manure and fertilizer applications is influenced by the timing, rate, method and specific type of fertilizer or manure applied (McDowell et al., 2001), which is not discussed in this review of literature.

2.3.3.2 Conventional and Conservation Tillage Practices

Tillage practices can influence the form and pathway of P transport. There is often a tradeoff between DP and PP losses under conventional and conservation tillage (Addiscott and Thomas, 2000; Daniel et al., 1998; Reid, 2011; Schelde et al., 2006). Conventional tillage

encompasses methods of incorporating into the soil all crop residues that remain following harvest (ie: disking, plowing). These practices have been found to lower overall TP losses, compared to conservation tillage practices (Gaynor and Findlay, 1995; Geohring et al., 2001). Conservation tillage maintains a minimum of 30% crop residue on the field (Statistics Canada, 2015) and includes no till and minimal tillage methods (ie; strip, ridge). The mixing of surface and subsurface soil under conventional practices increases P adsorption (Geohring et al., 2001) and reduces the risk of DP losses in runoff following manure and fertilizers applications (Baker and Laflen, 1982; Reid, 2011). In addition, reduced subsurface P losses have been attributed to the ability of conventional tillage to destroy the preferential drainage network (Addiscott and Thomas, 2000; Geohring et al., 2001; Kleinman et al., 2009). The tradeoff from conventional tillage methods is greater PP losses are often reported (Gaynor and Findlay, 1995), mostly in surface runoff (Geohring et al., 2001). As a result, the increased loss of PP in some studies resulted in the increased overall TP losses under conventional tillage (Andraski et al. 1985).

Most P lost from agricultural fields is in the particulate form (McDowell et al., 2001). Uusitalo et al. (2001) reported up to 92% of the total P (TP) loss for both surface runoff and subsurface drainage were in particulate form. In order to minimize soil losses, many Ontario fields have implemented conservation tillage practices. Unlike conventional methods, there is minimal disturbance of conservation soils, which does not result in sufficient mixing of added P between surface soil and subsoil (Hansen et al., 2000 Shreiber, 1999), which can result in the build up of P at the soil surface (Bundy et al., 2001; Gaynor and Findlay, 1995; Gburek et al., 2005; Hansen et al., 2000; Hansen et al., 2002; Scheiner and Lavado, 1998; Sims et al., 2000). As discussed previously, an increase in STP increases the risk of P leaching in runoff (Hooda et al., 2000; Pote et al., 1996; Pote et al., 1999; Sharpley et al. 1996). The application of mineral

fertilizer and manure to conservation systems may dramatically increase P loss in subsurface

flow (Gaynor and Findlay, 1995; Sharpley et al., 2001; Stamm et al., 1998), due to the

preservation of preferential pathways (Djodjic et al., 2000; Ulén et al., 2010).

2.4 Factors Influencing Temporal Variability in Form and Amount of Phosphorus Loss

Seasonal differences in precipitation regimes (event drivers) play an important role in the

speciation of P and whether it is transported via surface runoff or tile drainage.

2.4.1 Effects of Event Driver: Rainfall and Snowmelt

Precipitation can influence the timing of P loss and the transport pathways. Elevated TP

concentrations have been found during summer months (Ball Coelho et al. 2012; Dils and

Heathwaite, 1999; Heathwaite and Dils, 2000; Macrae et al., 2007a), as dry surface soil may

increase the potential for erosion (Macrae et al., 2007a). Rainfall impact during convective

summer storms can result from both detachment of sediment and transport of PP in runoff (Ball

Coelho et al. 2012). Most P lost from agricultural fields is in the particulate form (McDowell et

al., 2001), both in surface runoff (Uusitalo et al., 2001) and tile drainage (Dils and Heathwaite,

1999; Gentry et al., 2007; Reid et al., 2012). Particulate P concentrations have been found to

increase in runoff as the rainfall intensity increases (Fraser et al., 1999), however PP

concentrations decrease quickly during a storm (Gentry et al., 2007). As the rainfall intensity

decreases, there is less force to move the soil (Gentry et al., 2007; Vidon et al., 2012). Rainfall

intensity has also been positively correlated to the loss of DRP in runoff (Kleinman et al., 2006).

Sharpley (1985) found that as rainfall intensity increased the depth of interaction between

rainfall and soil was enhanced, which resulted in the desorption of P. However, unlike PP, which

requires water to mobilize soil particles, DP concentrations are driven by the presence of a P source (Djodjic et al. 2000). Increased rainfall intensity can result in the dilution of DRP in runoff (Edwards and Daniel, 1993). Similarly, long duration rainfall events can result in the decline of DRP concentrations due to exhaustion of the P source (Vadas et al., 2004). This occurs either as the precipitation event continues or when successive precipitation events occur over a short period of time (Geohring et al., 2001; Kleinman et al., 2006).

In cold-climate regions, snowmelt is the dominant hydrological process and can exceed rainfall runoff during the course of a year (Hansen et al., 2000). During the spring freshet, an entire season's accumulation of moisture can be released over a few days, resulting in runoff from a large part of the landscape (Tiessen et al. 2010). The "first flush" of snowmelt runoff is considered to be the most critical event for nutrient export. Snowmelt tends to have higher proportions of DRP than rainfall-generated runoff (Little et al., 2007; Tiessen et al., 2010), as it extends over a longer period of time, which promotes soluble reactions between soil, water and vegetation (Tiessen et al., 2010). Liu et al. (2013b) found the volume of runoff, including snow water equivalent, flow rate, and runoff duration were the most important factors controlling nutrient concentrations and loads during snowmelt. However, despite the higher runoff levels during snowmelt (Hansen et al., 2000), it is typically less erosive than rainfall (Ginting et al., 1998; Ulén, 2003) due to lower kinetic energy and often occurs over soil that is frozen (Rekolainen et al., 1997) which reduces the detachment of soil particles (Hansen et al., 2000).

2.4.1.1 Influence of Antecedent Soil Moisture Conditions on Runoff Generation and Phosphorus Loss

Antecedent soil moisture content is an important factor in regulating soil responses to rainfall (Vidon et al., 2012) or snowmelt (Jamieson et al., 2004; Liu et al., 2013b). The greatest discharge and P in tile drains have been reported following storms where soils were saturated prior to the event (Heathwaite and Dils 2000; Stamm et al., 1998; Vidon et al., 2012), as the preferential movement of water and solutes increases with increasing antecedent soil moisture (Kung et al., 2000). In addition, Heathwaite and Dils (2000) found that DRP export increased as soil moisture increased through the winter. Similarly, higher antecedent moisture conditions during the NGS often result in surface runoff (Hirt, et al. 2011; Vidon et al., 2012). Fang and Pomeroy (2007) and Jamieson et al. (2003) reported the importance of antecedent soil moisture content in P losses in snowmelt runoff, where low antecedent soil moisture decreased snowmelt runoff. In contrast the volume of snowmelt runoff increased when soil moisture was high during the prior fall (Fang and Pomeroy, 2007; Jamieson et al., 2003; Suzuki et al., 2005).

2.5 Agricultural Best Management Practices to Reduce Phosphorus Losses

Agricultural BMP's are those farming practices meant to minimize sediment and nutrient loading to the environment without sacrificing economic productivity (Tiessen et al., 2010). These practices have been implemented in temperate and humid regions (Li et al., 2011), through managing P source and transport mechanisms. Practices aimed at the management P sources attempt to minimize the accumulation of P at the soil surface, whereas transport BMP's refer to any effort to control the loss of P in runoff by reducing the volume and velocity (Sharpley et al., 2001).

2.5.1 Managing Sources of Phosphorus

Techniques used to reduce the amount of P added to agricultural fields mostly involve altering the rate, method and timing of manure or inorganic fertilizer applications (McDowell et al., 2001; Sharpley et al., 2001). One of the greatest risks for the loss of P, both surface and subsurface, occurs when the timing of manure or fertilizer application overlaps with a period of intense rainfall (Daniel et al., 1998; Gburek et al., 2005; Heathwaite and Dils, 2000; Macrae et al., 2007a; Schelde et al., 2006; Sharpley and Halvorson, 1994). As the period of time between P application and precipitation increases the potential for the loss of P in runoff decreases, as it allows for adsorption reactions to occur (Kleinman et al., 2006; McDowell et al., 2001). In addition, fall or winter manure application represents a high potential for risk of P loss to runoff (Vadas et al., 2009), especially when P application occurs on frozen soils or atop the snowpack (Gentry et al., 2007). Phosphorus losses from fertilizer or manure can be minimized when applied during periods of low runoff risk (Geohring et al., 1998; Reid et al., 2012). In addition, the incorporation of applied P from fertilizer or manure can reduce the concentration of P in runoff, compared to broadcast application without incorporation (Bundy et al., 2001; Daverede et al., 2004; Hansen et al., 2002). Similarly, the injection of fertilizer or manures is a means of maintaining P below the soil surface to reduce the potential for DRP runoff (Daverede et al., 2004; Hansen et al., 2002; Reid, 2011).

2.5.2 Managing the Movement of Phosphorus

Managing the transport of P refers to efforts to control the movement of P from soils (Sharpley et al., 2001). Transport management practices include; conservation tillage, crop

residue management, cover crops, buffer strips, riparian zones, and impoundments (Sharpley et al., 2001). However, only crop residue management and cover crops are discussed further.

2.5.2.1 Crop Residue and Cover Crop Use as Agricultural Best Management Practices

In Southwestern Ontario, the use of conservation tillage practices is a promoted BMP. Conservation tillage maintains a minimum of 30% crop residue on the field following harvest (Statistics Canada, 2015). This BMP has been highly effective in decreasing the volume of surface runoff (Gilliam et al., 1997), lowering soil erosion (Gaynor and Findlay, 1995; Rousseau et al., 1987; Ulén et al., 2010) and reducing PP loss (Rousseau et al., 1987). Similarly, the use of cover crops has become a promoted BMP in Ontario. Cover crops also provide a physical mechanism to reduce soil erosion; however, they also enhance infiltration, soil porosity and aggregation, as well as increase soil organic matter (Sharpley and Smith, 1991). Cover crops are often used interchangeably with the term catch crop, which are predominantly used to reduce leaching of soluble nutrients, mainly Nitrogen (Bergström and Jokela, 2001; Blanco-Canqui et al., 2015; Dabney et al., 2001). Cover crops can also take up a considerable amount of P, depending on the species (Liu et al., 2014); however, little attention has been paid to the role of cover crops in P cycling.

Conservation tillage practices mainly target soil and P losses during the growing season, and have been found to be less effective in reducing runoff, soil and P during the winter, under snowmelt conditions (Hansen et al., 2000; Su et al., 2011; Tiessen et al., 2010). Generally, DRP is greatest during snowmelt in both surface runoff (Jamieson et al., 2003; Little et al., 2007; Su et al., 2011) and tile drainage (Jamieson et al., 2003; Lam et al., 2016; Macrae et al., 2007a; Van Esbroeck et al., 2016). Traditionally, DRP in runoff from conservation tillage systems has been

attributed to the build up of P in the soil surface due to the application of manure and fertilizer (Andraski and Bundy, 2003; Hansen et al., 2002; McDowell and Sharpley, 2002). However, there is increasing evidence in the literature to suggest that remaining crop residue on the surface over the winter may have adverse effects on P loss (Baker and Laflen, 1983; Bundy et al., 2001; Daverede et al., 2004; McDowell and McGregor, 1984; Sharpley and Smith, 1994; Zhao et al., 2001). Furthermore, cover crops have also been found to enhance DRP in runoff (Sharpley, 1981), especially during snowmelt (Bechmann et al., 2005; Elliott, 2013; Saleh, 2008; Tiessen et al., 2010). As a result, these BMPs developed to mitigate soil erosion and nutrient losses may solely be effective during the snow-free period (Su et al., 2011).

2.6 Effects of Frost on Vegetation and Soil Phosphorus

2.6.1 Vegetation as a Source of Phosphorus

The amount of nutrients released from crop residue depends on the decomposition rate and nutrient concentration of the residue (Lupwayi et al., 2003). For example; corn residues have been found to release more P than soybean and wheat stubble (Cermak et al., 2004; Gburek and Heald, 1974; Lupwayi et al., 2003), as they contain more P (Cermak et al., 2004) and have a higher biomass (Lupwayi et al., 2003). However, cover crops have been found to release greater P than crop residue , as they are less resistant to decomposition and generally have a higher nutrient content (Gburek and Heald, 1974; Elliott, 2013; Timmons et al., 1970). In addition, unlike crops, which represent a large removal of P from the soil, cover crops do not provide an output of P, unless also harvested. Therefore, all the P taken up by the plants has the potential to be returned to the soil as they decay (Sharpley, 1981). Overall, the amount of P assimilation

22

varies between plant species (Uusi-Kämppä, 2005), and therefore, P leaching also varies among species (Gburek and Heald, 1974).

2.6.2 Influence of Vegetation on Runoff and Phosphorus loss During the Non-growing Season

Remaining agricultural residues (crop residue and cover crop) have been increasingly acknowledged as a source of DRP in runoff during the winter, as vegetation is subjected to hydrological and climatic changes. The exposure of agricultural residues to freeze thaw cycles (FTC) has been found to enhance P leaching (Bechmann et al., 2005; Roberson et al., 2007; Timmons et al., 1970; Uusi-Kämppä, 2005). Freezing results in the disruption of plant cells due to the formation of ice crystals and causes the release of inter/ intra cellular soluble P (Jones et al., 1992; Liu et al., 2014). It is commonly acknowledged in the literature that as the number of freeze thaw events increases the amount of P leached also increases (Bechmann et al., 2005; Liu et al., 2013a; Messiga et al., 2010; Turner and Haygarth, 1999), as additional plant cells are ruptured (Bechmann et al., 2005; Messiga et al., 2010). However, the vulnerability of plants to release P during FTC may depend on several factors.

Many agricultural crop species are vulnerable to FTC damage, as most have a low frost tolerance (Sturite et al., 2007). Liu et al. (2013a) and Øgaard (2015) demonstrated that the difference in frost adaptation between species of crops resulted in differences in the amount of P leached, as annual species leached more P than perennial (Liu et al., 2013a; Øgaard, 2015). The lower P released from perennial crops was attributed to their adaptation to freezing stress (Øgaard, 2015). However, an effective reduction in P losses from perennial plants requires that growth has ceased before frost, as Elliott (2013) and White (1973) found that freezing actively

growing vegetation leached the highest concentrations of soluble P. Variations in the percentage of plant P released from different species suggest that plant characteristics control the concentration of P leached (Riddle and Bergström, 2013). Vegetation moisture content at the time of freezing can also alter P leaching (Elliott, 2013; Miller et al., 1994; White, 1973). White (1973) found vegetation located lower in the landscape released more DRP, as the result of higher plant cell rupture because vegetation was saturated at the time of freezing (White, 1973).

2.6.3 Influence of Soil Frost on Runoff Pathways and Phosphorus Loss

In cold climate regions a majority of runoff and P loss occurs during snowmelt (Ball-Coelho et al., 2012; Elliott, 2013; Gentry et al., 2007; Hansen et al., 2000; Hansen et al., 2002; Jamieson et al., 2003; Lam et al., 2016; Little et al., 2007; Macrae et al., 2007a; Macrae et al., 2007b; Rekolainen, 1989; Tiessen et al., 2010; Ulén, 2003; Van Esbroek et al., 2016), during which time the presence of soil frost is an important factor governing the flow of water, soil erosion and P loss (Liu et al., 2013b; Zuzel et al., 1982). The presence of a frozen soil will limit infiltration and promote surface runoff (Li et al., 2011; Little et al., 2007; Liu et al., 2013b; Su et al., 2011) from a greater proportion of the field (Little et al., 2007; McDowell et al. 2001). For example; in Western Canada, where surface snowmelt runoff dominates (Little et al., 2007; Liu et al., 2013b; Su et al., 2011; Tiessen et al., 2010), a majority of P lost in runoff occurs as DRP, as there is limited interaction between runoff and underlying soils (Little et al., 2007; Tiessen et al., 2010). In addition, prolonged saturated condition on the soil surface, encourage the release of dissolved nutrients (Bechmann et al., 2005; Little et al., 2007; Ontkean et al., 2005; Ulén et al., 2007). During snowmelt, DRP is difficult to reduce as most of the soil is frozen and there is little plant growth or nutrient uptake (Tiessen et al., 2010), Essentially, it is during this time the

contribution of vegetation to P losses in runoff may be larger than that from the soil (Saleh, 2008).

Zuzel et al. (1982) also reported that frozen soils were vulnerable to erosion when rainfall occurred. However, significant sediment and PP in both overland runoff and tile drainage has been found during snowmelt where the soil is not frozen (Ball Coelho et al., 2012; Tiessen et al., 2010). An unfrozen soil state allows water to infiltrate into the subsurface, which will reduce the volume of runoff, loss of soil and P (Liu et al., 2013b; Su et al., 2011). In Southwestern Ontario, soil temperatures frequently remain above freezing, as a deep snowpack often develops throughout the winter, which insulates the underlying soil to limit freezing (Su et al., 2011). As a result, in contrast to what has been observed in western Canada (Elliott, 2013), the Midwestern United States (Roberson et al., 2007; Timmons et al., 1970) and Scandinavian countries (Liu et al., 2013a; Liu et al., 2014; Øgaard, 2015; Riddle and Bergström, 2013; Sturite et al., 2007), snowmelt in Southwestern Ontario generally does not solely occur as surface runoff. Numerous studies have accounted for large losses of both runoff and P in tiles during the winter (Lam et al., 2016; Macrae et al., 2007a; Van Esbroek et al., 2016). When meltwater infiltrates into unfrozen soil, saturated soil conditions can result (Frey et al., 2012; Wade and Kilbride, 1998), which can increase connectivity between drainage tiles and surface soil and transport water and P through preferential pathways (Dils and Heathwaite, 1999; Frey et al., 2012; Jarvis, 2007; Kung et al., 2000; Stamm et al., 1998).

2.6.3.1 Influence of Freeze-thaw Cycles on Soil Phosphorus Cycling

Freeze-thaw cycles can impact the physical properties of soil, which may influence the cycling of P (Yu, 2012), as alterations in physical soil properties influence adsorption-desorption

processes. When soils freeze, the expansion of ice crystals in soil pores (Oztas and Fayetorbay 2003; Ron Vaz et al., 1994; Yu, 2012) disrupts particle bonds and breaks large aggregates into smaller ones (Lehrsch et al., 1991; Yu, 2012). The breakdown of soil aggregates during FTC has been found to both increase P adsorption (Özgül et al., 2012; Ron Vaz et al., 1994) and increase P availability (Hinman, 1970; Ron Vaz et al., 1994). It is more commonly reported that soils that undergo freeze-thaw cycles adsorb more P from solution than soils that do not (Edwards and Cresser, 1992; Özgül et al., 2012; Wang et al., 2007). This is because the buffering capacity of the soil increases as a result of freeze-thaw (Özgül et al., 2012; Wang et al., 2007), as the breakdown of soil aggregates exposes new reactive soil surfaces (Özgül et al., 2012; Ron Vaz et al., 1994), especially in soils with high clay content (Wang et al., 2007). In contrast, the exposure of new soil surfaces following freeze-thaw has also been reported to increase the desorption of P (Hinman, 1970; Ron Vaz et al., 1994), in mineral soils high in organic matter (Freppaz, 2007; Hinman, 1970; Ron Vaz et al., 1994) due to the solubilization of organic compounds (Ron Vaz et al., 1994) and the expansion of intercellular fluids from biomass (Ron Vaz et al., 1994).

2.6.4 The Contribution of Vegetation and Soil to Phosphorus Losses in Runoff

Researchers have quantified P concentrations in leachates from vegetation (Sharpley, 1981), including those exposed to FTC (Bechmann et al., 2005; Elliott, 2013; Øgaard, 2015; Riddle and Bergström, 2013; Roberson et al., 2007); however, the influence of the underlying soil on vegetative P leaching, is seldom considered. When the two components have been considered together, studies have found that the leaching of P from vegetation is lessened (Elliott, 2013; Riddle and Bergström, 2013); however, P leached from the vegetation exceeded that of the soil (Bechmann et al., 2005; Elliott, 2013; Roberson et al., 2007), even soil that had

26

received manure (Bechmann et al., 2005). Sharpley and Smith (1989) and Roberson et al. (2007) both reported that P leached from vegetation was highest when STP was also high, likely attributed to the enhanced P content of the vegetation (Miller et al., 1994). As a result, DRP losses in runoff during the NGS may come from vegetative sources (Bechmann et al., 2005; Elliott, 2013; Shreiber, 1999; Tiessen et al., 2010), as there is insufficient soil to adsorb the P released from plant residue (Schreiber, 1999). Even under conditions where FTC may enhance P adsorption by soils, Edwards and Cresser (1992) and Wang et al. (2007) found a decrease in soil P adsorption following FTC when P was added to soil solution, such as from vegetation. In addition, the literature often examines the leaching of P from vegetation solely under surface runoff conditions (Bechmann et al., 2005; Elliott, 2013; Miller et al., 1994; Roberson et al., 2007; Tiessen et al., 2010), often under frozen soil conditions (Tiessen et al., 2010). However, as it was previously discussed, soils are not typically frozen during snowmelt in Southwestern Ontario, and, it is important to consider how this influences the loss of P from vegetation. Similarly, P losses from crop residue and cover crops have not been explicitly studied in tile-drained fields, which may have implications for the interaction between vegetation, soil and solution, as well as the extraction of P. In addition, a majority of research on vegetative P loss has been conducted in climates, or under air temperatures, colder than experienced during a typical winter in Southwestern Ontario. As a result, it is important to understand the potential release of P from vegetation as temperature and precipitation regimes evolve over the NGS in a cool, temperate climate zone, such as Southwestern Ontario, in order to understand the timing of P loss from crop residue and cover crops and determine their contribution to runoff P losses.

2.7 Thesis Objectives:

(1) Quantify the change in P loss from winter wheat residue (WR), oat (O), red clover (RC) and surface soil due to variations in air temperatures and hydrologic source using laboratory experiments and a field setting

(2) To examine whether spatial differences (topographic) influence P concentrations in soil (S) and vegetation (WR, O and RC) over time in the field.

(3) To determine if observed changes in P from soil and vegetation (WR, O, RC) are reflected in surface runoff and tile drainage DRP loads.

(4) Compare and contrast patterns from experimental work in the laboratory with findings from the field setting

3.0 Chapter Three: Potential Phosphorus Mobilization from Above-soil Winter Vegetation Assessed from Laboratory Water Extractions Following Freeze-thaw Cycles

3.1 Abstract

Maintaining crop residue or cover crops on fields during winter is a recommended Best Management Practice (BMP). However, losses of phosphorus (P) to runoff have been attributed to vegetation following freeze-thaw cycles (FTC). Using a factorial design in the laboratory, this study investigated the potential influence of four FTC types at $-4^{o}C$ to $4^{o}C$ (frozen, frozen and thawed 1x, frozen and thawed 5x, frozen and thawed 5x with leaching after each thaw) and one control (never frozen) on P loss from the residue of *Triticum aestivum* (winter wheat) and two cover crops,, *Trifolium pratense* (red clover) and *Avena sativa* (oat), following three different water extraction treatments (traditional laboratory determination of water extractable P (WEP), rainfall simulation, and, simulated surface ponding). Both cover crops released more P than winter wheat residue under all treatments. However, only oat experienced increased P loss following FTC treatments. More P was lost under ponding conditions than under simulated rainfall and most P was lost in the first leaching event when vegetation was subjected to successive freeze-thaw-leaching events. This study suggests that both cover crop species and placement in the landscape can be optimized to reduce P leaching from above-ground vegetation in winter. Oat was the more sensitive cover crop to FTC and may pose a greater risk of late autumn/winter P loss compared to species such as red clover, which are often terminated in early fall. The use of cover crops in sections of fields that are prone to flooding following large events such as snowmelt should be avoided. Further research in a field setting is needed to evaluate the timing of the potential and actual losses of P from above-ground vegetation in winter,

3.2 Introduction

Crop residues are a key component of internal P cycling in agricultural fields. Crops take up P from the soil water system and store it in their biomass; however, this P is subsequently returned to the soil from decaying plants and roots (Liu et al., 2013a, Liu et al., 2014; Sharpley, 1981). Cover crops and conservation tillage (which leaves vegetation residues on the surface) are BMPs that have the potential to reduce dissolved reactive phosphorus (DRP) and sediment losses in agricultural runoff. This may be accomplished through the assimilation of excess P from soils following P application (Liu et al., 2015), and/or by slowing the velocity of surface runoff and facilitating the adsorption of DRP and deposition of particulate P (PP) (Sharpley and Smith, 1989). Cover crops may also reduce P losses indirectly by improving soil health and organic content, and consequently may also improve the infiltration of excess water and the water holding capacity of the soil (Blanco-Canqui et al., 2012). However, some studies have suggested that crop residues and cover crops may subsequently act as sources of P to runoff as plants decay, particularly following freezing (*e.g.* Timmons et al., 1970), which calls into question the efficiency of cover crops as a BMP for minimizing P losses. Indeed, the leaching of DRP from vegetation, and the consequent increases in DRP concentrations in runoff has been observed both in laboratory (Miller et al., 1994; Schrieber and McDowell, 1985; Schreiber, 1985) and field settings (Sharpley, 1981; Wendt and Corey, 1980). However, it is unclear how P release may vary in space and time, with different vegetation species, and under different types of hydro-meteorological conditions, and, how P derived from vegetation may interact with soil. An improved understanding of these factors and their interactions can assist scientists and managers with optimizing the use of vegetation for P management.

Crops subjected to FTC over the non-growing season can enhance the release of P (Bechmann et al., 2005; Elliott, 2013; Liu et al., 2013a; Riddle and Bergström, 2013; Roberson et al., 2007; White, 1973). During freezing, the disruption of plant cells, due to the formation of ice crystals, causes the release of inter/intracellular P (Bechmann et al., 2005; Jones, 1992; Liu et al., 2014). Should a runoff event occur, the supply of P from vegetation is vulnerable to transport in runoff. The release of P from vegetation following freezing (and therefore the potential *supply* to runoff) can vary, and may be influenced by the number of FTC events (Bechmann et al., 2005; Liu et al., 2013a), vegetation type (Riddle and Bergström, 2013) and plant P content (Miller et al., 1994; White, 1973).

The *transport* of P supplied by residues and cover crops can also vary with hydroclimatic conditions. Experimental studies have demonstrated the release of P from vegetation to runoff under rainfall simulations (*e.g.* Miller et al., 1994; Schreiber and McDowell, 1985; Sharpley, 1981), from freshly harvested wheat residues (*e.g.* Schreiber and McDowell, 1985; Schreiber, 1999) and cover crops exposed to FTC (*e.g.* Miller et al., 1994; Riddle and Bergström, 2013). These studies all concluded that vegetation had the potential to be a significant source of P to runoff. In addition, the intensity and quantity of rainfall have been shown to influence the rate of leaching from leaf-litter, where lower intensity rainfall (Miller et al., 1994; Schreiber and McDowell, 1985; Tukey, 1970; Wendt and Corey, 1980), or more frequent rainfall increase nutrient loss (Tukey, 1970) relative to higher intensity, less frequent rainfall. As a result, rainfall may be the main extractant for the removal of P from crops to runoff, at the time of senescence. However, this may be dependent on the crop species and climatic conditions. It is important to understand how rainfall influences P leaching from vegetation exposed to freezing, as rainfall

events can occur following frost but prior to snowfall, and/or throughout the winter during periodic thaw events in cool, temperate climates (*e.g.* Macrae et al., 2010).

The presence of standing water (flooding) in fields may also extract P from vegetation. Such conditions may present greater opportunity than rainfall for the mobilization and subsequent transport of P supplied by vegetation. Standing water on fields can occur in small surface depressions during runoff events (Brenneman and Laflen, 1982), and zones in fields where tile drain pipes are present may be submerged for 24 hour periods (ASAE Standards, 1998). For example; Ginting et al. (1998) found that the exposure of corn residue to surface ponding leached nutrients more effectively than rainfall exposure. However, the loss of P under ponding conditions has been mainly investigated using fresh material, whereas the potential release of P from previously frozen residue and cover crops under ponding conditions remains uncertain. Elliott (2013) previously reported that crops exposed to FTC under a simulated melting snowpack contributed nutrients to snowmelt runoff. Crops in northern climates with a significant snowpack are likely to be exposed to a combination of FTC and snowmelt-induced runoff. If vegetation presents a rich supply of P to runoff, it may in fact increase P loss from fields rather than reduce it. The potential release of P due to surface ponding conditions following FTC is important to understand as the spring freshet (major snowmelt event) is a critical period for the export of P from agricultural landscapes (Macrae et al., 2007a; Su et al., 2011), and winter thaws and snowmelt has been associated with standing water on fields (Macrae et al., 2010; Van Esbroeck et al., 2016). However, it remains unclear how surface ponding can influence vegetation P losses after exposure to FTC.

The potential P loss from residues and cover crops may vary spatially and temporally in response to antecedent hydroclimatic conditions (*i.e.* FTC) and event type/source (*i.e.* rainfall,

surface ponding), and, the vulnerability of vegetation to such losses may vary with species. However, this has not been studied in a controlled setting to investigate the effects of each of these drivers in isolation and when combined. This information can assist farmers, managers and scientists in the appropriate application of cover crops as a BMP in cool, temperate climates that experience a significant winter period. In this chapter, potential losses of P from winter wheat residue and cover crops were examined in a laboratory to address the following objectives:

(1) To determine the individual and combined effects of plant type and FTC treatment on P release using laboratory experiments

(2) Examine the influence of water extraction method on potential P leaching losses from those crops expose following exposure to different FTC treatments.

It was hypothesized that:

(1) The cover crops (red clover and oat) exposed to FTC would have a greater potential to release P than wheat residue, and this would increase with the number of FTC.

(2) Water extraction method in the form of ponding would result in greater leaching of P than water extraction in the form of rainfall.

3.3 Material & Methods

3.3.1 Experimental Approach

A factorial design experiment was conducted in a laboratory setting to test the effects of *vegetation species*: winter wheat residue (WR)*,* red clover (RC) and oat (O), *FTC treatment* and *water extraction treatment* (water extractable P, rain, surface ponding) on the leaching of DRP from vegetation (Table 3.2). The three factors were tested in triplicate.

3.3.2 Site Descriptions and Collection of Vegetation Samples

Vegetation material for the experiment was collected from two fields; Ilderton (*ILD*: UTM 17T 472219m E, 4767583m N) and Londesborough (*LON*: UTM 17T 466689m E, 4832203m N) in Ontario, Canada. Soil at the ILD consists of Thorndale Silt Loam and Embro Silt Loam of the Gleyed Brunisolic Grey Brown Luvisol and Gleyed Melanic Brunisol groups (Hagerty and Kingston 1992) with 15 ± 5 mg Olsen-P kg^{-1} in the top 15 cm of the soil profile. The LON site has Perth Clay Loam soil of the dark grey Gleysolic group (Hoffman et al., 1952) with 12 ± 2 mg Olsen-P kg^{-1} P in the top 15 cm of the soil profile. Both fields are under corn-soybean-winter wheat crop rotations, and were cropped with winter wheat in 2014 (planted October 2013).

At sites, nutrient management (based on soil P and crop removal rates over a 3-year rotation) and reduced tillage strategies are used (either shallow vertical tillage/harrowing or strip tillage, done generally every third year). Cover crops are used following wheat harvest at both sites (*i.e.* once every three years), concurrent with the time fertilizer for the 3-year rotation is added. Hardier species such as red clover are often terminated using herbicide in mid-October to avoid complications with planting and growth the following spring. Less hardy species, such as oat, are generally not terminated by herbicide, as they are typically killed by frost. At the ILD site, liquid poultry manure (90 kg P ha^{-1}) was surface broadcast on August 20th, 2014, following the harvest of winter wheat, and oat was surface seeded immediately. Approximately one week later, 38 kg P/ha (granular monoammonium phosphate) was surface broadcast in strips and blended throughout the strip to a depth of ~15 cm (strips were 25 cm wide at surface, 10 cm wide at the base of the incorporation layer). At the LON site, red clover was surface seeded into winter wheat in April 2014. The red clover was terminated with glyphosate on October 9, 2014. On

October 15th, 2014, 76 kg P ha^{-1} (granular) was surface broadcast and incorporated to a depth of ~6 cm using vertical tillage at the LON site.

Wheat residue was collected from the ILD site on August 7th 2014, 13 days following harvest (but prior to manure or fertilizer application). Wheat residue from the LON site was not used in the lab experiment. Cover crop samples were collected from the ILD site on November 5th 2014, and from the LON site on October 20th 2014. Both cover crops were in the vegetative state at the time of collection and did not become reproductive. Vegetation was collected from four randomly selected 5x5 m areas within each field and was cut at the soil surface using a serrated field knife. No roots were included with vegetation samples. Vegetation was stored in polyethylene bags in cool conditions (~4°C) and transported to the laboratory at the University of Waterloo. Samples were processed within 24 hours of collection.

Table 3.1: Description of site management. Sowing, sampling and P applications dates as (day/month/year), amount of P added in manure and mineral fertilizer, herbicide treatments as well as dates (day/month/year). Plant moisture content and total plant P (% of dry matter) are shown.

Site Management	Plant Type		
	Wheat Residue	**Oat**	**Red Clover**
Sowing date	10/2/13	20/8/14	7/4/14 (under sown)
Mineral P fertilization (kg ha^{-1}**)**	24 (27/9/13)	38 (26/8/14)	76 (15/10/14)
Manure P (kg ha^{-1}**)**	None	90 (20/8 2014)	None
Herbicide treatment	Glyphosate (5/11/14)	Glyphosate (5/11/14)	Glyphosate (9/10/14)
Sampling date	7/8/14	5/11/14	20/10/14
Moisture content (%)	15	85	85
Total Plant P (% dry matter)	0.087 ±0.008	0.49 ±0.05	0.36 ±0.10

3.3.3 Freeze-thaw Cycle Laboratory Treatment

In the laboratory, vegetation samples were homogenized and subsamples were removed for the various FTC treatments and water extraction simulations. Five FTC types (described in Table 3.2) were tested: unfrozen control (C), frozen (F), one freeze-thaw cycle (FTC1), five freeze-thaw cycles (FTC5), and five freeze-thaw-leach cycles (FTL). Samples were placed in freezer and held at a temperature of $-4^{o}C$ for four days, and thaws were conducted at $4^{o}C$ for 24 hours. This temperature range is smaller than what has been used in previous laboratory studies on FTC (*e.g.* $-18^{o}C$ to $10^{o}C$ in Bechmann et al., 2005 and $-18^{o}C$ to $20^{o}C$ in Riddle and Bergström, 2013), but is a more realistic representation of temperature fluctuations within and beneath the snowpack during FTC in regions with cool, temperate climate, such as the Great Lakes region of North America.

3.3.4 Water Extraction Laboratory Treatment

Each crop and FTC treatment was subject to three *water extraction treatments* (Table 3.2): (1) sample shaken with deionized (DI) water for 1 hour for the determination of water extractable P (*WEP*), an analytical method used to determine concentrations of P extracted in water, (2) water added to sample over 4.5 hours to simulate *rainfall*, and (3) sample submerged in water for 24 hours to simulate surface *ponding*. A unique subsample was used for each water extraction treatment. The determination of WEP in vegetation was conducted using traditional standard laboratory techniques, 5 g of field-moist vegetation was extracted in 50mL DI water and shaken for 1 hour at $23^{o}C$. The extractant was subsequently gravity filtered through a Whatman no.4 filter and immediately frozen until analysis. For the rainfall and ponding water extraction treatments, a 15 g subsample was placed in a 1.5 L clean, glass jar. For the *rainfall*

simulations, 40 mm of DI water (0.315 L) was manually applied to each jar using a custom-built drip system at a rate of 8.8 mm/hour for 4.5 hours. Samples were suspended on fiberglass screening in the jar to allow water to percolate through the sample and prevent vegetation from becoming submerged in the water (Figure 3.1). A 40 mm rain simulation event was chosen, as this is a typical magnitude for an autumn rain event in the study region (*M. Macrae, unpublished data*). The experiment was conducted under a low rainfall intensity that is typical of autumn rain events in the Great Lakes region, which tend to be cyclonic systems that produce low intensity rainfall. Subsamples subjected to *ponding* conditions were submerged in 0.315 L (40 mm rainfall equivalent) for 24 hours (Figure 3.1). Leachate following WEP analyses and ponding water extraction treatments were more tea coloured in comparison to the rainfall water extraction treatment. For each treatment, the entire 40 mm of leachate was poured off and filtered through a 0.45 μm filter and frozen until analysis.

Treatments were applied to field moist plant samples (provided in Table 3.1). However, dry weights were determined to permit the expression of nutrient contents per unit dry weight of plant material. A subsample (~3 g) of each treated sample was dried at 65°C for 48 hours and subsequently weighed. Those samples subjected to successive leaching events (FTL1 through FTL5) were weighed and recorded prior to each subsequent leaching event to account for small changes in extractant volume, and possible changes in the quantity of vegetation material. As samples could not be dried between leaching events, samples were dried in entirety after the final treatment (FTL5) and the dry weight for each leaching event was adjusted based on average mass loss (wet weight) between the 5 sequential leaching periods.

(a)

Extractant Reservoir

0.5m

Vegetation

Fiberglass Screen

Leachate

(b)

Vegetation

Extract Reservoir and Leachate
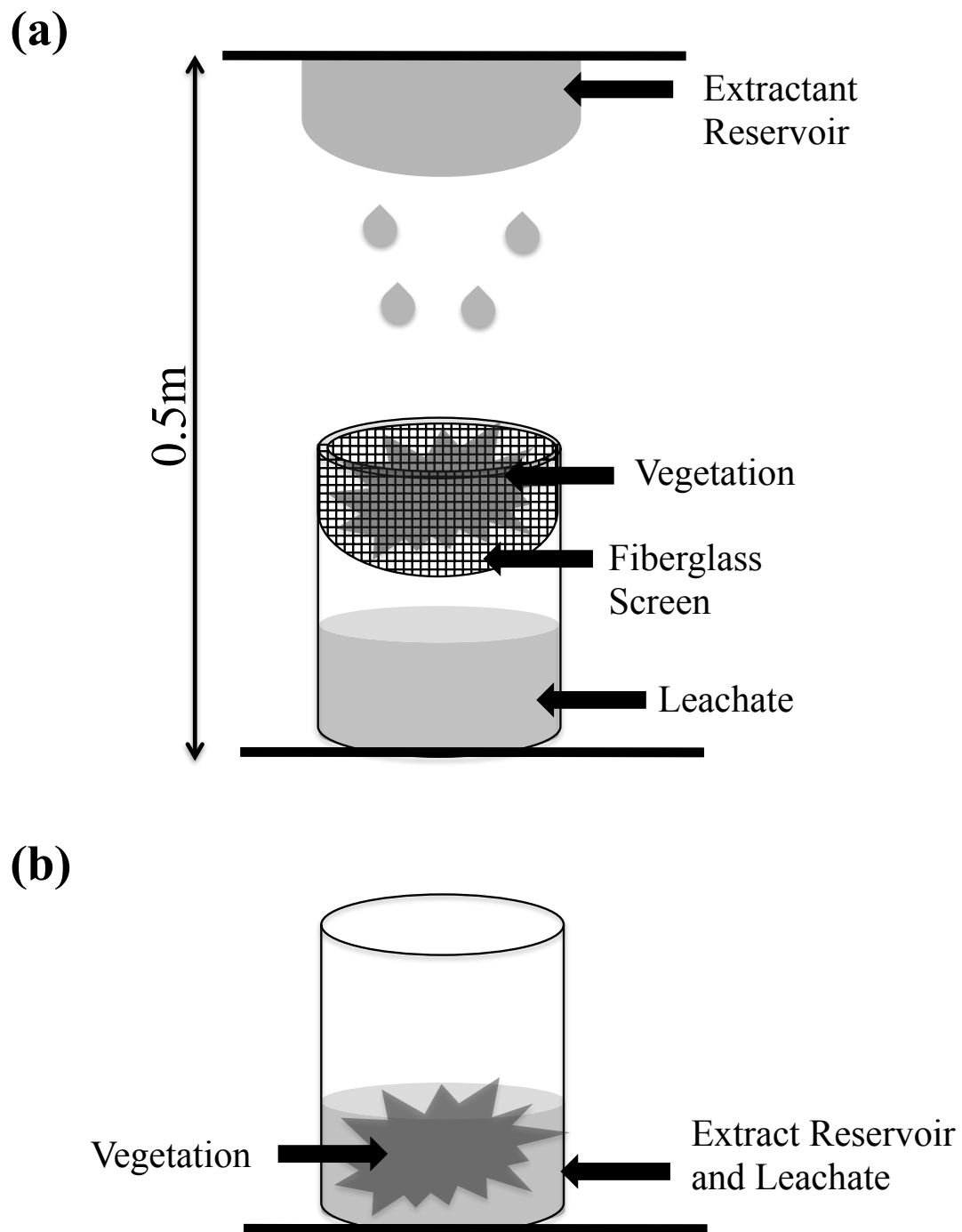
Figure 3.1: Schematic showing simulated rainfall and ponding extraction methods.

Table 3.2: Description of factorial design treatments on wheat residue, red clover and oat

FTC Treatment	Description
Control (**U**)	Never frozen sample; Vegetation extracted within 12 hours of collection
Frozen (**F**)	Vegetation frozen at -4° C immediately following collection and not thawed prior to extraction
Freeze Thaw (**FTC1**)	Vegetation frozen at -4° C within 12 hours of collection and thawed at 4° C for 24 hours prior to extraction
Freeze Thaw Repeat (**FTC5**)	Vegetation stored at -4° C within 12 hours of collection and thawed at 4° C for a 24 hour period, with cycle repeated 5 times. Vegetation was extracted once after the 5th thaw.
Freeze Thaw Leach (**FTLn**)	Vegetation frozen at -4° C within 12 hours of collection and thawed at 4°C for 24 hours prior to extraction. Vegetation was then extracted. Extracted vegetation was refrozen immediately following leaching and the freeze-thaw-leach pattern was repeated for a total of five cycles. (***FTL1, FTL2, FTL3, FTL4, FTL5***).
Water Extraction Treatment	
Water Extractable P	Vegetation was shaken with deionized water for 1 hour
Simulated Rainfall	Vegetation exposed to 40 mm of deionized water (0.315 L), which was manually applied at a rate of 8.8 mm/hour for 4.5 hours.
Simulated Ponding	Vegetation submerged in 40 mm of deionized water (0.315 L) for 24 hours.

3.3.5 Analytical Methods

All sample processing, experimentation and analyses were conducted in the Biogeochemistry Lab at the University of Waterloo. Dissolved reactive phosphorus (DRP) was determined colorimetrically using the ammonium-molybdate ascorbic-acid technique (Bran Luebbe AA3, Seal Analytical Ltd., Seattle, USA, Method G-103-93, detection limit 0.001 mg P L^{-1}). Five percent of all samples were analyzed in duplicate (12 duplicates in 216 samples) and found to be within 5% of reported values. Samples were analyzed for DRP but not total P (TP) as DRP is the form of P that has been most associated with winter P losses (Liu et al., 2013b, Liu et al., 2014; Timmons et al., 1970) and is the form most bioavailable to aquatic organisms. It was assumed that DRP would represent the dominant fraction of TP as particulate matter was not apparent in the leachate and a mass of material was not present on filter paper after samples were filtered. Following the final leaching of FTL5 and FTC5 (for WEP), remaining samples were dried at 80°C and sent to the Agriculture and Food Laboratories in Guelph Ontario for determination of total plant P (ICP-MS) following microwave digestion with nitric and hydrochloric acids (detection limit 0.01%).

3.3.6 Statistical Analyses

Data were not normally distributed, and consequently, non-parametric analyses were used. A series of two-way non-parametric analysis of variance tests (ANOVA Sheirer-Ray-Hare, Dytham, 1999) were used to test the main effects and interactions of plant type, FTC treatment and water extraction treatment as factors. Where the ANOVAs revealed significant interactions between factors ($p<0.05$), factors were split and examined separately (Kruskal Wallis tests). For example, the effects of freezing (F, FTC1 and FTC5 data pooled but FTL data excluded) and

plant type were examined using a two-way ANOVA and Kruskal Wallis tests were subsequently run comparing the effects of plant type for control (unfrozen, C) and frozen (F, FTC1, FTC5) crops. A series of Mann-Whitney U tests were used to compare FTC treatments within and between plant types, water treatments within and between plant types, and water treatments between FTC for each crop. For each plant type and water extraction treatment, Mann-Whitney U tests were used to compare differences between FTL1 through FTL5, and, Mann-Whitney U tests were also used to compare differences between the various water extraction treatments for each of the FTL events (1 through 5) for each crop. A level of $p<0.05$ was accepted to be significant and the Bonferroni correction was used to adjust the p-value accounting for the number of comparisons completed. Statistics were conducted using SPSS v.22 statistical software.

3.4 Results

3.4.1 Concentration of Dissolved Reactive P Extracted Prior to and Following Freezing

The WEP from vegetation differed significantly with plant type in both control (C) samples (Chi-Square=7.20, p=0.027), and, in samples following a suite of FTC cycles (freezing: F, FTC1, FTC5 data pooled; FTL1-FTL5 excluded), (Chi-Square=22.06; p <0.001). In the C samples, WEP was greatest in red clover (Mdn=2403, range 1070-3368 $\mu g\ g^{-1}$), moderate in oat (Mdn=250, range 160-376 $\mu g\ g^{-1}$) and low in wheat residue (Mdn=33, range 10-34 $\mu g\ g^{-1}$).

In samples subjected to FTC cycles, WEP was greatest in the oat samples (Mdn=3106, range 1462-4062 $\mu g\ g^{-1}$) and lowest in the wheat residue (Mdn=75, range 22-208 $\mu g\ g^{-1}$), with red clover at an intermediate level (Mdn=1159, range 566-2560 $\mu g\ g^{-1}$). A two-way ANOVA with plant type and freezing (control versus F, FTC1, FTC5 pooled) as treatments yielded a

42

significant main effect of plant type (H=21.00, p<0.001), but no significant effect of freezing or interaction between plant type and freezing (p >0.05). When crops were considered independently, there was a significant difference in WEP between the C and frozen samples (F, FTC1, FTC5 pooled) for oat (U=0.00, p=0.013), but no difference for wheat residue or red clover (p >0.05). The greater WEP concentrations in the cover crop samples (O, RC) relative to wheat residue reflect the higher TP content in the cover crops (Table 3.1).

3.4.2 Differences in the Leaching of Phosphorus with Water Extraction Treatments

The quantity of P (μg g^{-1}) released from the three plant types generally increased in order of rain, which was less than WEP and ponding. There was a significant main effect of water extraction treatment (rain, WEP, ponding) on P loss from wheat residue (H=15.61, p=<0.001) and red clover (H= 20.89, p= <0.001), but no effect of water extraction type on P loss from the oat (H= 4.80, p =0.09). Post-hoc analyses revealed no significant differences between the WEP and Ponding treatments for each plant type (p>0.05); therefore, to minimize masking of effects due to similarities between WEP and ponding, P loss solely from rainfall and ponding were considered further. In all cases, the water extraction method of ponding resulted in greater DRP concentrations in leachate in comparison to P extracted by simulated rainfall (Figure 3.2).

For both wheat residue and red clover, clear effects of increased FTC under different water extraction techniques were not observed. For example, P losses from wheat residue subjected to rainfall increased with exposure to different kinds of FTC (Chi-Square = 8.23, p= 0.041), primarily driven by elevated losses following the FTC5 treatment, but there was no difference with FTC across the ponding treatment (Chi-Square = 2.59, p >0.05; Figure 3.2). In contrast, P loss from red clover among the different FTC treatments did not differ under

simulated rainfall (Chi-Square = 4.13, p>0.05), but differed under the simulated ponding treatment (Chi-Square = 9.05, p= 0.029; Figure 3.2c). Oat was the only crop where both rainfall and ponding losses both significantly increased with increasing exposure to FTC (Chi-Square = 9.97, p= 0.019 rainfall, Chi-Square = 9.15, p= 0.027 ponding; Figure 3.2b). Although P loss for each crop was influenced differently for each FTC and water extraction type, ponding consistently extracted more P than rainfall for wheat residue(U = 12.0, p = 0.001) and red clover (U = 1.0, p<0.001); however, only marginal differences were found from the oat (U = 39.00, p=0.057) when all FTC treatments considered together. When the various FTC were examined individually for oat, Mann-Whitney tests revealed that ponding extracted significantly more P than rainfall from vegetation subjected to freezing (p<0.05 for F, FTC1, FTC5). Overall, extraction method had the greatest influence on the quantity of P released from all three crops. The combination of FTC with ponding did not enhance P leaching from wheat residue or red clover in comparison to C (unfrozen) material. However, FTC combined with surface ponding substantially increased P leaching from the oat samples. These results suggest that oats are at especially high risk for P leaching following FTC in areas prone to flooding.

Table 3.3: Median (range) of phosphorus content in winter wheat residue, oat, and red clover extracted from water extractable P (WEP), and P leached by rainfall and ponding treatments are shown. Values beside brackets represent the amount of P leached in each treatment as a % of the median total P content in the control (C) samples. Extracted P is shown for the C and FTC5 treatments, and, the cumulative P lost across the 5 FTL treatments (ΣFTL1,FTL2,FTL3,FTL4,FTL5).

FTC Treatment	Water Extractable Phosphorus		
	Wheat Residue	**Oat**	**Red Clover**
C	33 (10-34,) 4%	250 (160-376), 5%	1477 (1001-1950), 42%
FTC5	43 (23-208), 5%	4062(3261-4801), 83%	944 (772-1221), 27%
FTL5	139 (120-146), 16%	3918 (2586-4932), 80%	2838 (2054-3793), 80%
	Rain		
C	6 (3-7), 1%	93 (78-303), 2 %	622 (578-919), 18%
FTC5	43 (18-399), 5%	1867 (1310-2032), 38%	545 (504-736), 15%
FTL5	36 (34-75), 4%	2366 (1862-2680), 48%	1736 (1718-1806), 49
	Pond		
C	89 (82-92), 10%	52 (33-319), 1%	2610 (2207-3220), 74%
FTC5	102 (84-299), 12%	3452 (3035-4011), 71%	1529 (1066-1904), 43%
FTL5	146 (144-148), 17%	4056 (3797-4598), 83%	2544 (2380-3133), 72%
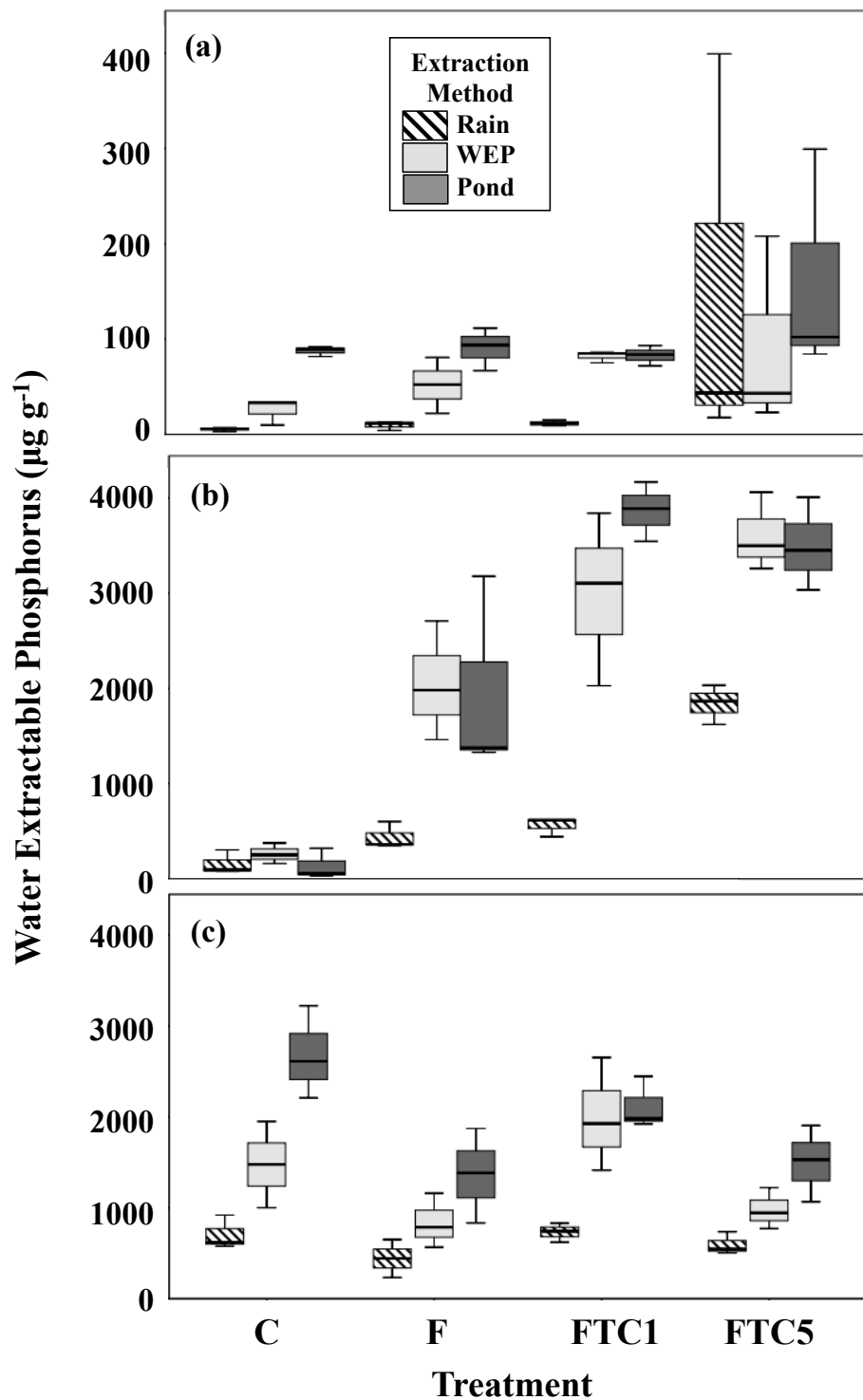
Figure 3.2: Box-whisker plots of P lost ($\mu g\ g^{-1}$) from (a) winter wheat residue, (b) oat and (c) red clover following different types of freeze-thaw cycles (described in Table 3.2) and following different water extraction treatments (rain = hatched; water extractable = light grey; ponding = dark grey). Boxes provide the 25th, 50th and 75th percentiles, and whiskers provide the 10th and 90th percentiles. *Note the scale on the Y-axis in (a) differs from (b) and (c).

3.4.3 Concentrations of Dissolved Reactive Phosphorus After Repeated Freeze Thaw Cycles Followed by Leaching

Crops subjected to FTL treatments (FTL1 – FTL5) were also extracted under rainfall and ponding scenarios (Figure 3.3). For each vegetation species, a two way ANOVA indicated a significant main effect of FTL event on P loss for wheat residue (H=29.29, p<0.05), oat (H=27.72, p<0.05) and red clover (H=35.07, p<0.05), but no significant effect of water extraction type (p>0.05) or interaction between the two factors (p>0.05). Post hoc analysis did not reveal a difference between the WEP and ponding treatments across the successive leaching events for all three crops (p>0.05), and therefore only rainfall and ponding were considered further. For each vegetation species, the rate and magnitude of P loss differed between the rainfall and water ponding treatments, with the ponding treatment extracting more P than rainfall (Figure 3.3).

As was observed for WEP (discussed above), the first FTL 'event' in the series of FTL simulations released the greatest P from all 3 vegetation species (Figure 3.3). This pattern was also observed for the rainfall and ponding simulations; however, the rate of P exhaustion differed between water extraction treatment and plant type. Overall, ponding caused a more rapid depletion of P from all vegetation compared to rainfall (Figure 3.3), where most P was lost during the first event (FTL1) and subsequent losses (FTL2-FTL5) were small. In contrast, P extractions by rainfall were generally smaller, and occurred over several events (*e.g.* FTL1-FTL3) rather than in the first event (FTL1). The first ponding event for each plant type (FTL1-ponding) extracted more P than cumulative rainfall across the five simulations (FTL5-rainfall, Table 3.3). When cumulative losses between rainfall and ponding were compared for all plant types together, ponding losses far exceeded losses under rainfall (p<0.001).

47
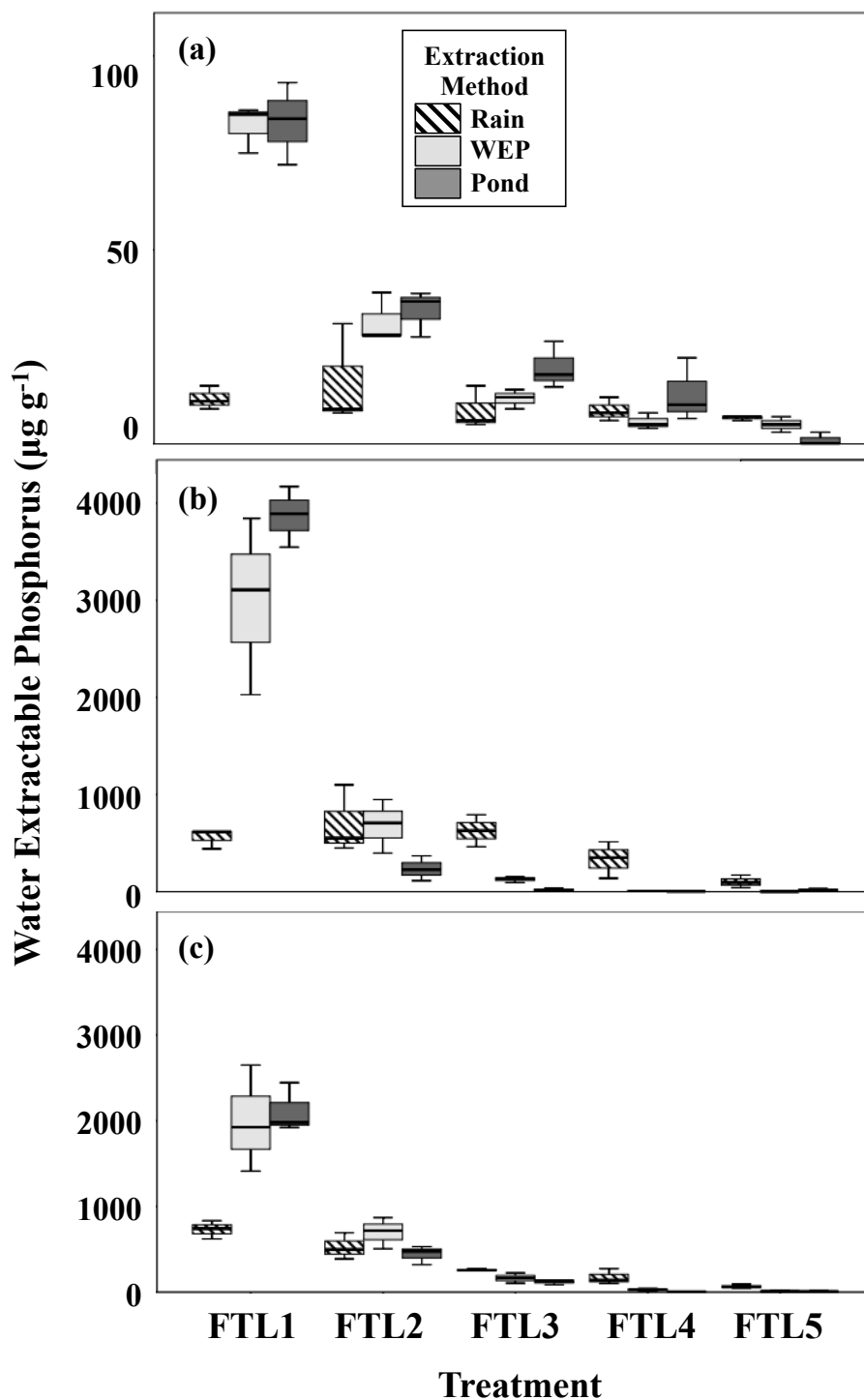
Figure 3.3: Box-whisker plots of P lost (μg g^{-1}) from (a) winter wheat residue, (b) oat and (c) red clover following different types of freeze-thaw cycles (described in Table 3.2) and following different water extraction treatments (rain = hatched; water extractable = light grey; ponding = dark grey). Boxes provide the 25th, 50th and 75th percentiles, and whiskers provide the 10th and 90th percentiles. *Note the scale on the Y-axis in (a) differs from (b) and (c).

48

Phosphorus losses following 5 FTC (FTC5) were compared to cumulative losses

following the 5 FTL cycles (the sum of FTL1 through FTL5, Table 3.3). There was no difference

for wheat residue and oat ($p>0.05$), but 5 FTL treatments mobilized more P from red clover than

5 FTC with a single leaching event at the end (FTC5, Table 3.3, $p<0.001$). This suggests that

hardier species such as red clover may not be affected by a single runoff event, but may be

affected by repeated FTC events that result in runoff. It also suggests that in species such as red

clover, the vegetation may be more impacted by the physical disturbance caused by

rainfall/runoff rather than FTC alone.

3.5 Discussion

3.5.1 Extracted Phosphorus from Different Plant Types

Plant type was an important factor influencing P loss. This was consistent across all FTC

and water extraction treatments. Wheat residue produced lower amounts of WEP in comparison

to the cover crops, oat and red clover. Our findings are consistent with the work of others who

have reported that crop residues release minimal amounts of P compared to cover crops (Gburek

and Heald, 1974; Lupwayi et al., 2003). Generally, vegetation with higher P content releases

larger quantities of P, and, more of the P is released as orthophosphate (White and Ayoub, 1983).

Indeed, the two cover crops in the current study had greater TP content than the wheat residues,

which may explain the low amounts of WEP .. However, red clover had higher WEP than oat

during the control, despite the fact that the TP content of the oat was higher. This may have been

the result of the application (surface broadcast) of glyphosate to the red clover several days prior

to its collection from the field. Glyphosate is rapidly adsorbed and translocated throughout the

plant (Segura et al., 1978) to effectively kill foliage and roots (Swanton et al., 1998), which can

enhance the release of nutrients (Tukey, 1970). Therefore, the high WEP from red clover in the control treatment is likely the result of the P released from decaying vegetation. Indeed, the red clover plant material was dead at the time of collection. The higher WEP and TP content in the cover crops relative to the wheat residue has implications for the management of fields over winter. Our results suggest that wheat residue left on the soil surface do not pose a substantial risk for P loss in runoff, irrespective of FTC or hydrologic conditions on the field (*i.e.* rain, ponding). However, cover crops should be used with caution (species, placement), as they can be a potential source of P to runoff.

3.5.2 Repeated Freezing and Thawing of Vegetation as a Phosphorus Source to Runoff

The three vegetation species used in this study responded differently to the suites of FTC that they were subjected to. Water-extractable P in the wheat residue was low in both unfrozen and frozen conditions, and was generally not affected by the type of FTC. This finding is consistent with the work of Elliott (2013) and Timmons et al. (1970) who also reported low P loss from cereal stubble compared to other plant material exposed to FTC, which was attributed this to the low TP content of wheat residue and low water content in the residue prior to freezing (Elliott, 2013).

Some cover crops are susceptible to injury following FTC due to low frost tolerance, which can result in cell damage (Bechmann et al., 2005; Miller et al., 1994; Sturite et al., 2007). Oat have a low frost tolerance and will typically die off following freezing, as compared to red clover and wheat, which have the capacity to overwinter. A minimum temperature of -4 C° was used in this study, which is smaller in magnitude than freezing used in other studies; however, temperatures of -4 C° are typical of conditions beneath the deep snowpack in the Great Lakes

50

region. The low frost tolerance of the oat may largely explain the increased loss of P when subjected to FTC disturbance (*e.g.* F, FTC1, FTC5). The result of P loss from oat following freezing has also been shown for alfalfa (Robertson et al., 2007), annual ryegrass (Bechmann et al., 2005; Øgaard, 2015) and bluegrass (Timmons et al., 1970). There are several additional factors that may explain the high P loss from oat following freezing. First, the oats were actively growing at the time of freezing, which can enhance P loss in response to FTC (Elliott, 2013; White, 1973). Further, the oats were likely tender as they were sown in late summer (not undersown). Second, the high moisture content of the oat while exposed to FTC treatments may have also enhanced P release, as there is greater cell rupture with high moisture content during freezing causing the release of nutrients (White, 1973) and P loss from plants has been correlated with their water content at the time of freezing (Elliott, 2013). Third, plant nutrient content is an important factor in plant P release, as species with greater plant P have been found to release more P (Elliott, 2013; Miller et al., 1994). Roberson et al. (2007) reported that increasing soil test P levels increased the amount of DRP released from frozen alfalfa. The oats used in this study were grown in soil that had received manure application, which may account for the higher P content, as plants are able to take up luxury P (White and Ayoub, 1983). The low frost tolerance, high moisture content and total plant P likely all contributed to the high P loss from the oats during the FTC treatments in the current study. In contrast, the subjection of the red clover to FTC treatments did not statistically increase the release of P when the treatments were pooled (F, FTC1, FTC5). This again may be because the red clover was killed before collection (with glyphosate), and, the P released from red clover may have been a combination of P released from senescing vegetation, rather than leaching due to exposure to FTC. Under conditions where the red clover was not terminated prior to FTC, it is likely the amount of P released following

exposure to FTC would remain lower than observed from the oat. Miller et al. (1994) reported that Red Clover released less P compared to annual cover crop species due to its lower total P content. In addition, Red Clover is a perennial species, which have been found to release lower concentrations of P when exposure to FTC due to their adaptation to freezing stress (Liu et al., 2013; Øgaard, 2015).

Increases in the number of FTC have also been linked to increases in P loss (Bechmann et al., 2005; Liu et al., 2013a; Robertson et al., 2007) due to the rupture of a greater number of plant cells (Bechmann et al., 2005). Results from the present study indicate that the number of FTC does not impact wheat residue or red clover (after termination). There was little difference in WEP in oat exposed to FTC1 or FTC5, although losses were greater than following F alone. This suggests that the pool of P released from the oat increased with FTC disturbance (*i.e.* F versus FTC), however, one FTC may be sufficient to release the WEP pool in the oat plants. Bechmann et al. (2005) observed the increase in P release with increasing FTC following relatively large temperature ranges (-18 C° to 10 C°). Under less severe freezing temperatures such as those used in the current study, the quantity of WEP in cover crops may not differ between single and multiple FTC, but may instead differ among plant species (*i.e.* more or less frost tolerant species). In the current study, a substantial portion of the initial plant TP in the oat was extracted as WEP following exposure to 5 consecutive FTC. This indicates that the temperature threshold of -4°C was sufficient to cause the release of most P from the oat. The fact that most TP in species such as oat was released under modest freezing temperatures, suggests that the potential P loss during a mild winter can be equally detrimental to P loss from frost intolerant cover crops as a severe cold winter. Although P leaching from red clover did not differ between 1 and 5 FTC, increased losses were observed following five FTC when each cycle was followed by leaching

(FTL). It is possible that the disturbance and breakdown of plant material from the repeated events made the red clover more susceptible to leaching and suggests that the P pool in hardier species can also be released with a sufficient number of runoff events.

The results of this study indicate that different cover crops are vulnerable to P release at different periods in time. Those cover crops that are terminated before the onset of frost will release the greatest P in the period following herbicide application such as the red clover in the current study, long before winter runoff events, and P release from these cover crops is not likely to increase with exposure to FTC. In contrast, frost intolerant cover crops such as the oat used in this study may release P to runoff, even following a mild frost. However, the loss of crop P in runoff or snowmelt will also depend on the processes that extract and transport P, which impact both the leaching of P from the plant material itself, but also the potential for the P to subsequently interact with the soil and be retained in the field.

3.5.3 Potential Phosphorus Losses from Wheat Residue and Cover Crops Following Different Water Extraction Treatments

The potential release of P from vegetation and the transport of that P in runoff can differ seasonally. Phosphorus loss in runoff under rainfall conditions has been attributed to vegetation on the surface (Sharpley, 1981), however, high DRP losses during snowmelt have been increasingly attributed to P supply from vegetation exposed to FTC during winter (Elliott 2013; Rekolainen, 1989; Saleh, 2008). In the current study, ponding enhanced P leaching from vegetation compared to rainfall. This is consistent with the work of Cermak et al. (2004) who reported the greatest P loss from unfrozen crops after submersion for 24 hours, and attributed this to the contact time between vegetation and solution. Similarly, Ginting et al. (1998) reported that

corn released nearly all P after 20 hours of surface ponding. Indeed, as the contact time between vegetation and solution increases, P leaching generally increases (Cermak et al., 2004). This has also been found under rainfall scenarios, as low intensity rainfall increases contact time between vegetation and solution and increases P losses compared to higher intensity rainfall (Miller et al., 1994; Schreiber and McDowell, 1985; Tukey, 1970). Similarly, Robson et al. (1994) found that the proportion of nutrients leached from vegetation is inversely related to the magnitude of the storm. Therefore, the amount of P lost during rainfall events in a field setting will differ with varying intensity and durations.

Overall, P loss from ponding and rainfall followed the same pattern for each plant type, suggesting that the effect of FTC on P supply (WEP) in plants was very important and governed the amount of P that could potentially be lost to runoff. However, the type of water extraction type (rain, ponding) influenced the magnitude of P leached following each FTC, suggesting that the type of runoff event can govern whether or not the P is lost to runoff. In general, the simulated ponding was more conducive to P loss compared to rainfall, and, the quantity of P lost during the ponding treatment closely reflected the amount of WEP in the samples. This may be especially important during snowmelt, as snowmelt is a gradual process that extends over a longer period of time compared to rainfall events (Tiessen et al., 2010), and tends to be associated with surface ponding (Van Esbroeck et al., 2016). This may be especially true in relatively flat agricultural landscapes due to slow water movement (Saleh, 2008). In the current study, DRP in leachate was extracted with deionized (DI) water to make the rainfall and ponding extraction treatments more directly comparable to traditional laboratory analyses of WEP, and, to be consistent with methods used in other studies (*e.g.* Timmons et al., 1970). However, in a field setting, leachate DRP concentrations may be greater given the weak salts found in rainwater and

surface runoff.

Over sequential extractions (both ponding and rainfall), DRP concentrations in leachate were greatest in the first "event" (FTL1) and declined in successive events. While this was observed for both ponding and rainfall, the rate of decline was greater for the ponded samples compared to those exposed to rainfall. Miller et al. (1994) found no decrease in P concentration after two successive rainfall extractions because vegetation was not fully exposed to rainfall water in the first leaching event, leaving more P available to leach in the subsequent rainfall extractions. Moreover, in the field, parts of the plant may be protected from rainfall (Tukey, 1970). Ginting et al. (1998) found that the first of three ponding events caused the greatest P loss from corn. These results are consistent with the patterns of P release under ponding from this study. In this study, the first ponding event lost more P than cumulative rainfall (Table 3.3, Figure 3.3), suggesting that the first field ponding event can potentially cause greater P losses than cumulative losses from intermittent rainfall over the non-growing season.

The current study included a laboratory experiment to investigate the potential losses of P from vegetation following FTC, and P interactions between plant material and soil were not investigated. It is important to note that P leached from vegetation may not necessarily be lost from the field in runoff due to the potential for the leached P to be adsorbed to soil. It is plausible that P extracted in rain events may pass vertically into the soil profile and be adsorbed by soil particles rather than be lost to runoff. Indeed, Elliott (2013) reported that the quantity of P in leachate was reduced by 40% when vegetation was in contact with the underlying soil. Similarly, Riddle and Bergström (2013) also reported a significant decrease in P released from cover crops when the underlying soil was considered. Despite this pattern, both Bechmann (2005) and Elliott (2013) reported that vegetation P concentrations were greater than soil concentrations. This

55

suggests that understanding the seasonality of the vegetation P pool may be important to determining the potential impact of vegetation to DRP loss in runoff, although soil conditions at the time of a hydrological event would ultimately determine the fate of the P released from vegetation. More field studies that directly investigate this are needed.

Sturite et al., (2007) proposed that P from frost-injured plant cells is preserved within plant tissue, and can be embedded under snow and ice and subsequently released during snowmelt. This may be especially critical under conditions where a majority of snowmelt occurs over frozen soil, such as in the Northern Great Plains of North America (Tiessen et al., 2010) and the first flush of snowmelt can be critical for nutrient export (Han et al., 2010). However, in cool temperate climates, such as the Great Lakes region of North America, rainfall events in late autumn (both prior to and following FTC) are common (Macrae et al., 2010). Given the fact that most P may be leached from oats following the first FTC, the potential for winter losses from cover crops such as oat may be reduced in the Great Lakes Region because much of the vegetation P pool may be washed into the soil by autumn rain events (following FTC but prior to the onset of the more severe winter, including snow cover). However, in the absence of autumn frost and rainfall or ponding events, frost intolerant cover crops preserved under the snowpack have the potential to release significant P during snowmelt, particularly when surface ponding occurs.

3.6 Management Implications and Conclusions

A laboratory experiment was used to investigate the effects of vegetation species, FTC type and water extraction treatment on DRP leaching from cover crops and residues. Maintaining crop residues on fields and growing cover crops offer many benefits including improved soil

health, storing some nutrients, and a reduction in surface erosion and runoff. These benefits may outweigh the potential for P leaching in winter. This study suggests that land managers can reduce the risk of winter P leaching by optimizing their choice of cover crop species and the way that the cover crops are managed over the non-growing season. This study found that the loss of P varied with vegetation species, where cover crops leached more P than wheat residue, which released little P, even following freeze-thaw cycles. This indicates that wheat residue on fields throughout the non-growing season likely will not significantly elevate P loss in runoff. Of the two cover crops studies, oat cover crop was affected by freeze-thaw cycles whereas red clover was not, likely because the red clover had been terminated prior to freezing. This suggests that the termination of crops (such as red clover) in autumn may be a strategy to gain some of the benefits of cover crops (soil health, some ground cover) without the risk of winter P leaching in runoff. In contrast, allowing tender crops such as oat to be killed by frost may increase risk for winter P losses in runoff. The type of precipitation event (rain versus ponding) that occurs in combination with the mobilization of P from crops is likely also important in determining the magnitude of P lost to runoff. In portions of the field prone to surface ponding, P losses from cover crops may be significant, especially following the first major surface ponding event. Rainfall events occurring throughout the non-growing season (including winter, such as during rain-on-snow events) can extract P from vegetation, but such events extract less P overall and over a longer time period. These results indicate that the use of cover crops in low-lying areas of fields prone to stagnant surface ponding should be avoided due to the increased potential for P leaching, particularly following FTC. This study has demonstrated that although P release may be a potential risk with planting frost intolerant species as cover crops over the non-growing season, such risks can be minimized through the appropriate selection of species, placement in

fields, and potentially terminating species before the onset of frost. Further research is needed to quantify P losses from crops in a field setting, where field ponding varies spatially and temperature changes vary temporally.

4.0 Chapter Four: Release of Phosphorus from Crop Residue and Cover Crops Over the Non-growing Season in a cool Temperate Region

4.1 Abstract

In northern climates, crop residue and cover crops exposed to freeze-thaw cycles (FTC) are potential sources of dissolved reactive phosphorus (DRP) to runoff; yet, there are limited field studies to quantify this. The objectives of this study were (1) to quantify changes in water extractable phosphorus (WEP) concentrations in the residues of *Triticum aestivum L.* (winter wheat)*, Trifolium pretense L.* (red clover) *and Avena sativa L.* (oat) cover crops as well as surface soil in a field setting over the non-growing season; and (2) to determine if changes in WEP in vegetation residue or soil were reflected in loads of DRP or total P (TP) in surface runoff and tile drain effluent. Concentrations of WEP in cover crops (Mdn=115.22, range 0-2971.66 µg g^{-1} oat, Mdn=79.36, range 0.91-2161.06 µg g^{-1} red clover) were larger than those in wheat residue (Mdn=13.17, range 0-224.71 µg g^{-1} ILD, Mdn=4.62, range 0-66.62 µg g^{-1} LON) and soil (Mdn=5.71, range 0-49.39 µg g^{-1} ILD, Mdn= 4.44, range 0-88.94 µg g^{-1} LON). As predicted, WEP concentrations in vegetation increased following FTC, and decreased following runoff events, particularly snowmelt, indicating that the plant WEP was mobilized in runoff. Differences in WEP concentrations were not observed with field topography, with the exception of the period following snowmelt when low-lying areas prone to surface inundation were depleted relative to more upland locations. Although WEP appeared to have been mobilized from both vegetation and soil pools, loads of DRP (0.165 kg ha^{-1} at ILD and 0.245 at LON) and TP (0.295 kg ha^{-1} at ILD and 0.360 kg ha^{-1} at LON) leaving the fields were small in comparison to P pools in cover crops (0.49, 0-12.21 kg ha^{-1} oat, 0.30, 0-8.39 kg ha^{-1} red clover), residues

(0.02, 0-0.41 kg ha^{-1} ILD, 0.01, 0-0.13 kg ha^{-1} LON) and soils (3.71, 0-32.10 kg ha^{-1} ILD, 2.67, 0-53.37 kg ha^{-1} LON), suggesting that much of the P released was retained within the field rather than lost in runoff. This study provides insight into the timing and magnitude of P release from vegetation throughout the non-growing season in Southwestern Ontario, with cool temperate climates, and provides an improved understanding of the contribution of cover crops to winter P losses.

4.2 Introduction

Agricultural best management practices (BMP) for environmental stewardship are designed to reduce soil and nutrient losses from fields. Conservation tillage practices and cover crops are two examples of BMPs that have been employed by some farmers to improve soil health and water quality. However, their effectiveness to provide these benefits during the NGS remains unclear, largely because surface vegetation may supply DRP to runoff as plant residues decay (Gburek and Heald, 1974; Sharpley, 1981) and/or are exposed to FTC (e.g. Bechmann et al., 2005; Elliott, 2013; Miller et al., 1994; Riddle and Bergström, 2013). Consequently, the use of conservation tillage or cover crops as BMPs is debatable in areas that experience significant winter periods. Much of the existing knowledge on DRP loss from vegetation following FTC has been obtained under severe frost conditions (either simulated or natural) and less is known about the vulnerability of crop residues and cover crops to DRP loss in more temperate regions such as Southwestern Ontario, that experience frost, but less severe winter conditions. In the Great Lakes region of North America, temperatures are moderated by the Great Lakes and both cover crops and crop residues are often covered by a thick snowpack that insulates them from frigid temperatures. Thus, an improved understanding of the role of surface vegetation in P losses

60

during the NGS in cool temperate climate zones is needed to determine if the use of cover crops is suitable for these regions.

Conservation tillage and cover crops have been shown to be effective BMPs for improving water quality. Conservation tillage is broadly defined as any tillage method that maintains at least 30% of crop residue on the soil surface (McDowell et al., 2001). This low disturbance BMP reduces the erosiveness of soil, leading to reduce the loss of sediment and particulate phosphorus (PP) in runoff (Sharpley and Smith, 1989; Ulén et al., 2010). Furthermore, maintaining crop residue on the soil surface increases infiltration and dissipates rainfall energy, thereby reducing runoff (McDowell et al., 2001) and facilitating the adsorption of DRP and deposition of PP (Sharpley and Smith, 1989). Cover crops may provide similar physical mechanisms as residues to reduce soil erosion and runoff and can also improve the water holding capacity of the soil through increased infiltration (Blanco-Canqui et al., 2012). In addition, cover crops can remove and store excess available nutrients from the soil, particularly nitrogen (Bergström and Jokela, 2001; Blanco-Canqui et al., 2015; Dabney et al., 2001; Liu et al., 2015). As a result of these combined benefits, managers have recommended that farmers leave at least 30% crop residue on the soil surface (McDowell et al., 2001), and use cover crops to reduce nutrient losses in runoff (Blanco-Canqui et al., 2012).

In cold climate regions, snowmelt runoff is an important period for P loss from agricultural systems (Ball-Coelho et al., 2012; Elliott, 2013; Gentry et al., 2007; Hansen et al.2000; Hansen et al., 2002; Jamieson et al., 2003; Macrae et al., 2007a; Macrae et al., 2007b; Rekolainen, 1989; Tiessen et al., 2010; Ulén, 2003) either through surface runoff or tile drainage (Jamieson et al., 2003; Macrae et al., 2007a; Van Esbroeck et al., 2016). The efficiency of residues and cover crops to reduce P in runoff during this period is uncertain. Generally, fields

61

under conservation tillage retain more snow, increasing snow water equivalents (Hansen et al., 2000) and therefore runoff (Hansen et al., 2002). Consequently, during snowmelt, the volume of water is often too large for residues to slow flow, and runoff is not decreased by the presence of surface vegetation (Elliott, 2013; Hansen et al., 2000). Furthermore, most vegetation freezes at the beginning of the winter period, and therefore is less able to protect the soil from water erosion (De Baetes et al., 2011). Indeed, Hansen et al. (2000) observed that crop residue did not limit runoff; however, a reduction in the concentration of sediments was observed during their study. Thus, although the role of surface vegetation for reducing PP may be dampened in winter, residues and cover crops may provide some protection against surface erosion during this critical period.

Numerous studies have reported that dissolved nutrient transport can be greater in surface runoff or ground water from conservation till or no-till systems than from conventional tillage systems (e.g., Baker and Laflen, 1983; Bundy et al., 2001; Daverede et al., 2004; Langdale et al., 1985; McDowell and McGregor, 1984; Sharpley and Smith, 1994; Zhao et al., 2001). Such increased losses have previously been attributed to the stratification of nutrients at the soil surface caused by reduced mixing of fertilizers or manures by tillage. However, the literature also suggests that the release of nutrients from plant residue that remains on the soil surface after harvest can also amplify P loss (McDowell and McGregor, 1984; Sharpley, 1981; Sharpley and Smith, 1989; Schrieber and McDowell, 1985; Wendt and Corey, 1980). Bechmann et al. (2005) and Sharpley (1981) reported greater P loss from plots containing cover crops and crops compared to plots with bare soil and soil applied with manure. This suggests that surface vegetation has the potential to be a significant DRP source to runoff. These findings have been observed in both laboratory (Miller et al., 1994; Schrieber and McDowell, 1985; Schreiber,

1985) and field settings (Sharpley, 1981; Sharpley and Smith, 1989; Wendt and Corey, 1980).

Freeze-thaw cycles during the winter period may amplify the potential for DRP loss from crop residues and cover crops. Indeed, DRP losses can be substantial during snowmelt (Ginting et al., 1998; Little et al., 2007), likely for several reasons. First, higher DRP losses have been reported from vegetation following exposure to freezing or FTC (Bechmann et al., 2005; Elliott, 2013; Liu et al., 2013a; Miller et al., 1994; Riddle and Bergström, 2013; Roberson et al., 2007; White, 1973). During freezing, the disruption of plant cells causes the release of inter/intra cellular P due to the formation of ice crystals (Bechmann et al., 2005; Jones, 1992; Liu et al., 2014). Second, snowmelt runoff often extends over longer time periods than rainfall-induced runoff events, providing ample time for increased reactions between soil, water and vegetation (Tiessen et al., 2010). However, such interactions may be restricted to areas within fields that experience surface inundation rather than areas that are higher topographically that do not experience significant contact with surface runoff. Given the significance of DRP as a highly bioavailable form of P, leaving residue and cover crops on fields (or low-lying sections of fields) throughout the winter may therefore not be a BMP for mitigating P losses.

Much of the existing knowledge on the role of crop residues and cover crops in P loss in regions subjected to freezing has been derived from controlled laboratory studies or has been conducted in regions that are much colder in winter than is experienced in the Great Lakes Region of North America such as western Canada (Elliott, 2013), the Midwestern United States (Roberson et al., 2007; Timmons et al., 1970) and various Scandinavian countries (Liu et al., 2013a; Liu et al., 2014; Øgaard, 2015; Riddle and Bergström, 2013; Sturite et al., 2007). Although air temperatures can reach lows in the range of -25°C in this region, temperatures beneath the thick snowpack are more moderate (often fluctuating between -4 to 0°C, Macrae,

unpublished data). Moreover, cool, temperate regions may experience numerous FTC throughout the NGS (beginning late in the autumn), prior to the onset of the spring freshet when most surface runoff typically occurs (Van Esbroeck et al., 2016). It is unclear when the majority of the vegetation pool is released over the NGS. It is possible that the pool of P in the crop residues and cover crops may be released vertically to soils following autumn FTC rather than mobilized during the snowmelt period.

Little field data exists that examines the role of crop residues and cover crops in runoff P during the NGS, and, it is unclear how P losses from vegetation compare to those from soils. Moreover, the contribution of vegetation to runoff has been examined in surface runoff but not subsurface (tile) drainage. At more southern locations within the Great Lakes region, tile drains often remain active during the winter period (Lam et al., 2016; Macrae et al., 2007a; Macrae et al., 2007b; Van Esbroeck et al., 2016). Therefore, P leaching from vegetation may contribute to both surface runoff and tile P losses, particularly where significant connectivity between the surface and tile drains through preferential pathways exists. However, the loss of DRP from the crop canopy, as well as senescent plant material must be considered along with the release and sorption of P by surface soil (Sharpley, 1981). In this chapter, potential losses of P from winter wheat residue, cover crops and surface soil were examined in a field setting and coupled with observations of P loss in surface and subsurface (tile) drainage to address the following objectives:

(1) To quantify water extractable P (WEP) concentrations in surface soil, winter wheat residue (WR) and cover crops (oat (O), red clover (RC)) throughout one non-growing season (August – April inclusive), and relate temporal differences to hydroclimatic conditions over the study period.

64

(2) To determine if WEP concentrations in soil and vegetation (WR, O and RC)

throughout the NGS differ topographically within a field between areas prone to

surface inundation in comparison to more dry, upland sections.

(3) To determine if observed changes in WEP over time in soil and vegetation (WR, O,

RC) are reflected in surface runoff and tile drainage phosphorus loads.

It was hypothesized that:

(1) Phosphorus concentrations in cover crops would initially increase as they began to

decompose, but would P concentrations in vegetation and soil would decrease

following successive runoff events.

(2) The reduction in WEP in vegetation between pre- and post-event collection periods

would be more apparent in low-lying areas exposed to surface flooding and less

significant in upslope locations.

(3) The mobilization of P from cover crops during thaw events would be reflected in

surface runoff but not tile drainage due to the adsorption of P by subsoils.

4.3 Site Descriptions

This study was conducted on two working farms Ilderton (*ILD*: UTM 17T 472219m E,

4767583m N) and Londesborough (*LON*: UTM 17T 466689m E, 4832203m N) in Ontario,

Canada (Figure 4.1a) between August 2014 and April 2015. Both sites are classified as having a

moderate humid continental climate, with hot summers and no dry season (*Dfa* under Köppen

Classification system). The sites are located approximately 75 km apart, and the ILD site (Figure

4.1c) is slightly warmer (8.2 ˚C mean annual temperature) than the LON site (7.2 ˚C mean

annual temperature), Figure 4.1b (London A and Wroxeter, Ontario sites, Environment Canada, 2016). Monthly temperatures demonstrate significant seasonality across the year, with cold winters (below freezing December – March, mean January temperature -5.6 ˚C at ILD and -7.0 ˚C at LON) and hot summers (mean July temperature 20.8 ˚C at ILD and 20.4˚C at LON). Mean annual precipitation is 1024 mm (17% as snow) at the ILD site and 1247 mm (30% as snow) at the LON site (Environment Canada, 2016). Precipitation distribution throughout the year are similar at the sites.

The ILD site has Thorndale Silt Loam and Embro Silt Loam soils of the Gleyed Brunisolic Grey Brown Luvisol and Gleyed Melanic Brunisol groups (Hagerty and Kingston 1992) with 15 ± 5 mg Olsen-P kg^{-1} in the top 15 cm of the soil profile. The LON site has Perth Clay Loam soil of the dark grey Gleysolic group (Hoffman et al., 1952) with 12 ± 2 mg Olsen-P kg^{-1} in the top 15 cm of the soil profile. Both fields are systematically tile drained using standard 100 mm diameter perforated plastic drainage tubing for the lateral lines, installed at approximately 0.75-0.9 m depth, spaced at 9 m (ILD) and 14 m (LON) apart. Surface runoff exits from one location in each field, facilitating the measurement of surface runoff at the edge of field (Figure 4.1b, Figure 4.1c). Any surface runoff or tile drainage from either field is restricted to the study field and no hydrologic inputs are received from adjacent areas.

The fields have a uniform cropping history (corn-soybean-winter wheat rotation, with winter wheat and cover crops in 2014). At both sites, landowners employ P conservation strategies including crop rotation, nutrient management and conservation tillage (strip till at ILD and vertical till to 5 cm at LON. Winter wheat was planted at both sites in October 2013. At the ILD site, liquid poultry manure (50-25-32; 90 kg P ha^{-1}) was surface broadcast on August 20th, 2014, following the harvest of winter wheat, and oats were immediately surface seeded. Approximately

one week later, 38 kg P ha^{-1} (granular monoammonium phosphate) was broadcast in strips (25 cm wide at surface, 10 cm wide at strip base) and blended throughout the strips to a depth of ~15 cm. Oats were terminated by frost at the ILD site on approximately October 25th, 2014; however, the landowner applied glyphosate on November 11th, 2014 to terminate biennial weeds and volunteer wheat. At the LON site, red clover was surface seeded on top of the winter wheat in April 2014. Winter wheat was harvested on August 7th, 2014. The red clover was sprayed with glyphosate on October 9, 2014, and, on October 15th, 2014, 76 kg P ha-1 (granular monoammonium phosphate) was surface broadcast and incorporated to a depth of ~5 cm using vertical tillage.
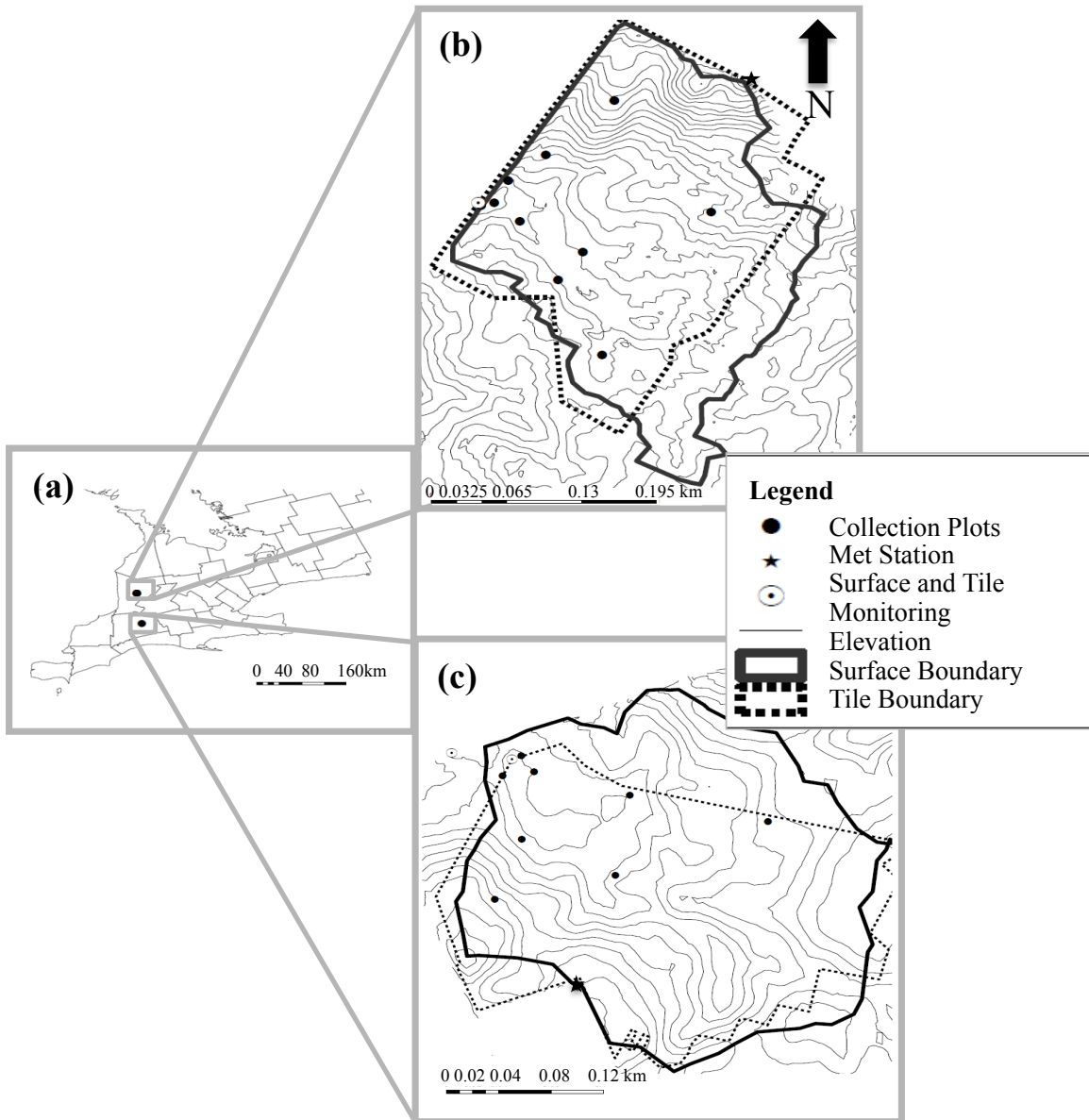
Figure 4.1: Map of study sites (b) LON and (c) ILD in the (a) Great Lakes region of Ontario. The location of vegetation and soil collection plots, as well as, surface and tile monitoring stations are shown.

4.4 Materials and Methods

4.4.1 Hydrometric Parameters and Collection of Samples for Water Quality

Meteorological conditions were recorded at 15-minute intervals (Hobo U30 GSM logger, Onset Corporation) using an automated weather station (HOBO Weather Station, Onset Corporation) equipped with a tipping bucket rain gauge (0.2mm Rainfall Smart Sensor - S-RGB-M002), an air temperature and relative humidity sensor (12-bit Temperature/RH Smart Sensor - S-THB-M002), and a soil temperature sensor (12-Bit Temp Smart Sensor - S-TMB-M002) installed at 10cm depth (Figure 4.1b, Figure 4.1c). Snow water equivalents (daily snowfall and estimates of snow on the ground) were quantified using data provided by nearby weather stations (Environment Canada, 2016), validated by periodic (2-3) manual field surveys at both sites. The Wroxeter Ontario Environment Canada weather station is located approximately 40 km northeast of LON and the London Ontario weather station is approximately 20km southeast of ILD.

Surface runoff and tile drainage were monitored at the edges of both fields (Figure 4.1b, Figure 4.1c). Surface runoff (velocity, volume and depth) was monitored continuously at 15-minute intervals (Hach Flo-Tote 3 sensors with FL900 data loggers, Hach Ltd.) installed in an aboveground culvert at LON (0.46 m diameter) and in a belowground, non-perforated pipe (0.20 m in diameter) connected to a surface inlet at the ILD site. Tile drainage (depth, velocity, flow) at both sites was monitored directly in the tile drain main outlet at field edges (Hach Flo-Tote 3 sensors with FL900 data loggers, Hach Ltd.), accessed from above using a riser pipe. Automated water samplers (Teledyne ISCO 6712, Lincoln, NE) were placed in the tile and surface flow monitoring station at each site and housed in enclosures to protect equipment from freezing. Automated water samplers were triggered by the occurrence of flow, and samples were collected at intervals of 0.5 to 6 hours in surface runoff, and 2-6 hours in tile drainage. Sampling intervals

were changed seasonally to adjust for differences in event duration and flow magnitude, ensuring that water samples were collected throughout entire events (n= ~6-24 samples per event). Phosphorus concentrations during baseflow periods were determined using periodic grab samples. All samples were retrieved within 24 hours (summer) to 72 hours (winter) of collection.

Water samples were frozen prior to analysis. In the Biogeochemistry Lab at the University of Waterloo, water samples were passed through 0.45 μm cellulose acetate filters, FlipMate, Delta Scientific) for the analysis of DRP. A separate 50 ml unfiltered sample was preserved with H_2SO_4 (0.2% H_2SO_4 final concentration) and digested in acid for the determination of Total Kjeldahl P (TP). Water samples were subsequently analyzed for their P concentrations using colorimetric analysis (ammonium-molybdate ascorbic-acid, Bran Luebbe AA3, Seal Analytical Ltd.: Method No. G-188-097 TP, detection limit 0.01 mg L^{-1}-P; G-175-96 Rev. 13 for DRP, detection limit 0.001 mg L^{-1}-P). Five percent of all samples were analyzed in duplicate and found to be within 5% of reported values.

Phosphorus concentrations in tile and surface flow for events occurring over the study period are presented in this paper as flow-weighted mean concentrations (FWMC), determined from discrete water samples and continuous flow data (see Williams et al., 2015). During the course of the study period, there were occasions where surface ponding occurred without leaving the field. Phosphorus concentrations in surface ponded water for these events are provided as arithmetic means of collected water samples and are noted in Figures.

4.4.2 Field Collection of Vegetation and Soil Samples

Nine plots were designated per field based on differences in topography (3 upslope, 3 midslope and 3 low slope) within the field (Figure 4.1b, Figure 4.1c). Vegetation was cut at the

soil surface using a serrated field knife within a 5x5 m area at each plot location. No roots were included with vegetation samples. Litterbags (20 x 20 cm) were custom-built using 1 mm fibreglass mesh. Twenty grams (+/- 0.1g) of fresh residue (winter wheat residue) and 100g (+/- 0.1g) of fresh cover crop clippings (oat and red clover) were loosely placed into litterbags and left on the soil surface until retrieval. To capture variability in WEP litterbags at each plot were assembled in triplicate for each vegetation type (wheat residue at both sites, oat at ILD and red clover at LON), and this was done for 7 time steps (Table 4.1). Thus, a total of 648 litterbags were placed in each field (triplicate samples x 4 crop types x 9 plots x 5 time steps + triplicate samples x 2 crop types x 9 plots x 2 time steps). Litterbag assembly and placement within fields was slightly offset between the two sites due to subtle differences in the timing of farming activities on fields. Litterbags containing wheat residue were assembled at the ILD site on August 7th 2014, 13 days following harvest and at the LON site on August 13th 2014, 4 days following harvest (prior to manure or fertilizer application at both sites). At LON, the residue consisted of the wheat straw, whereas at ILD the straw had been removed and only the stubble was collected. Cover crop samples were collected from the ILD site on November 5th 2014, and from the LON site on October 20th 2014. Both cover crops were in the vegetative state at the time of collection and did become reproductive.

At each plot, for each crop type (wheat residue, oat or red clover), triplicate litterbags were randomly selected and retrieved at discrete intervals throughout the study period (Table 4.1). The timing of litterbag retrieval were intended to reflect changes in temperature and precipitation that occurred throughout the NGS, which could reflect key periods for potential or actual P loss from vegetation and soil. Collection dates were also timed to capture the before and after effects of changes in hydroclimatic conditions on P loss from crops and soil (Table 4.1). At

71

each time that vegetation litterbags were retrieved, soil samples were also collected for comparison to vegetation pools of WEP. At each plot, 6 subsamples were randomly collected to a depth of 5cm and composited.

Soil bulk density was determined for each field as a field average using standard techniques (10 cm diameter, 10 cm deep soil cores collected in April, 2015) to permit the expression of WEP concentrations in soil in kg ha^{-1} in the top 5 cm. To express the vegetation WEP concentrations as the vegetation P pool (kg ha^{-1}), above ground biomass was determined for each vegetation type (WR, O, RC) by clipping three 1 x 1 m plots within each field.

Table 4.1: Time steps used for retrieval of litterbags of wheat residue (WR), oat (O), red clover (RC) and soil (S) throughout study period.

Sampling Campaign	Intended Condition Captured	Material Retrieved
August	Warm, immediately post harvest of winter wheat	S, WR
October	Living samples of cover crop clipped for extractions	S, O, RC
Early November	Following termination of cover crop. Light frosts had occurred (Air temperatures ranged from 0°C to -2°C)	S, WR, O, RC
Late November	Following a hard frost (-10°C) and brief thaw (8°C) with 26mm of rain at Lon and 44mm at ILD.	S, WR, O, RC
February	Following a hard frost (no thaws in the previous month and a half. Collected following air temperatures of -20 °C	WR, O, RC
Snowmelt	Following the major snowmelt event	S, WR, O, RC
April	Following a spring rain event on thawed soil (Air temperatures ranged between 5°C to 10°C)	S, WR, O, RC

4.4.3 Storage and Laboratory Analyses of Vegetation and Soil Samples

Upon retrieval, vegetation and soil samples were stored in polyethylene bags in an ice-packed cooler and transported to the Biogeochemistry Lab at the University of Waterloo. Samples were kept cool and processed within 12 hours of collection. Individual litterbags (or soil samples) were homogenized and 5 g was removed from each. Fifty mL of deionized (DI) water was added to 5 g of field-moist (vegetation or soil) material and shaken for 1 hour at 23°C. The extractant was subsequently gravity filtered through a Whatman no.4 filter followed by a 0.45 and transported to the Biogeochemistry Lab at the University of Waterloo. Samples were kept cool and processed within 12 hours och litterbag was dried at 65 °C for a minimum of 48 hours to determine the dry weight for each sample to allow the expression of water extractable P (WEP) per unit dry weight of material. Orthophosphate concentrations in soil and vegetation extracts were determined using the same colorimetric techniques as were used for water samples (noted above).

A separate 5g subsample of all crops from the first (August, October) and final (April) litterbag collections were dried at 85 °C and sent to the Agriculture and Food Laboratories at the University of Guelph (Guelph, Ontario, Canada) for the determination of total plant P. Dried plant material was microwave digested using a mixture of nitric and hydrochloric acid, which was diluted to volume with DI water. The solution was then analyzed (ICP-MS) and reported as percent of dry weight. The reporting limit for phosphorus was 0.01% (100 ppm).

4.4.4 Statistical Analysis

Data were not normally distributed, and consequently, non-parametric analyses were used. Mann-Whitney U tests were used to compare P release between crop types and soil samples at

various topographic positions and across sampling campaigns. A level of $p<0.05$ was accepted to be significant. The Bonferroni correction was used to adjust the p-value accounting for the number of comparisons completed. Statistics were conducted using SPSS v.22 statistical software.

4.5 Results

4.5.1 Variability in Meteorological Conditions Over the Study Period

Precipitation received at the sites was greater than normal for the region (e.g. 728 mm at ILD site compared to the long-term average of 582 mm, and 658 mm at LON site compared to the 30-year mean of 571 mm for the months of August to April (Environment Canada, 2016). Daily and seasonal mean air temperatures were similar between sites, ranging between a minimum of -24°C and a maximum temperature of 25°C over the course of the study period (Figure 4.2a). Between August and October 2014, daily mean air temperatures (~14.8 °C) were characteristic of the longterm 30-year climate normals (~14.7 °C) at both sites (Environment Canada, 2016); however, air temperatures between November 2014 and April 2015 (~ -2.9 °C) were colder than the 30-year longterm average (~ 0 °C) for the region (Environment Canada, 2016). In fact, air temperatures reached -29 °C at LON, which approaches the extreme minimum for this region observed between 1981-2010 (Environment Canada, 2016).

Throughout the study period (one NGS), a total of eight significant freeze-thaw cycles (FTC), varying in temperature range and duration were identified (Figure 4.2a). A single FTC was defined as the time from which daily air temperatures dropped below 0°C to when they rose back above 0°C. The magnitude of frost varied from light frost in November and December (e.g. ~ -5°C) to heavy frost from mid January to the beginning of March (e.g. ~ -20°C, Figure 4.2). A

75

thin snowpack formed over both sites for a brief period and was lost to thaw in November (Figure 4.3a; Figure 4.4a). A deep snowpack developed over both sites, which remained until the end of the major snowmelt period (Figure 4.3a; Figure 4.4a). The snowpack provided insulation and soil temperatures (10 cm depth) ranged between $-2°$ C and $5°$ C throughout the winter (Figure 4.2a). Snow surveys conducted prior to snowmelt determined a snow water equivalent of 83mm at ILD and 113mm at LON. Snowmelt occurred primarily as radiation-melt and sublimation at both sites, and runoff did not commence until a significant portion of the snowpack had disappeared. A considerable volume of runoff was generated during the single snowmelt runoff event at both sites (concurrent with the loss of the snowpack but no rainfall) that spanned several days (Figure 4.3b;c, Figure 4.4b;c). Rainfall (Figure 4.3a; Figure 4.4a) was received at both sites between the August and October sampling campaigns (October) and the Snowmelt and April campaigns, and, at the ILD site between the early November and late November campaigns, generating small volumes of runoff (Figure 4.3b;c, Figure 4.4b;c). Between October and April, the LON site lost a total of 105 mm in runoff and the ILD site lost 156 mm. The partitioning of this runoff between tile and surface runoff and P concentrations in runoff are discussed below (section 4.5.5).
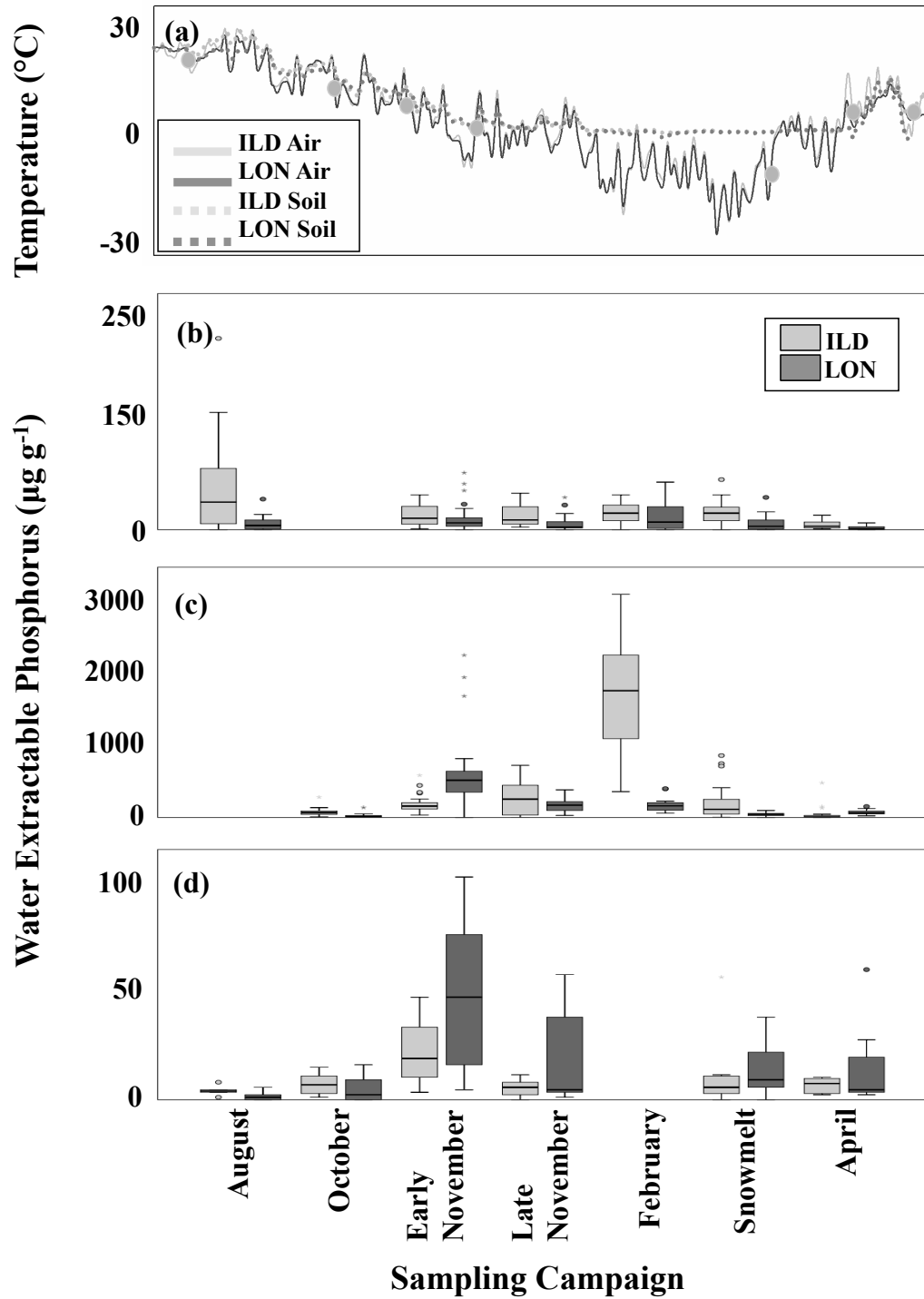
Figure 4.2: (a) Daily average air and soil temperature (10cm) from August 2014 to April 2015 at ILD (dark grey) and LON (light grey). Box-whisker plots of P lost ($\mu g \; g^{-1}$) from (b) wheat residue (c) cover crops and (d) soil across sampling campaigns. Boxes provide the 25th, 50th and 75th percentiles, and whiskers provide the 10th and 90th percentiles. *Note the difference in scales on the Y-axis.
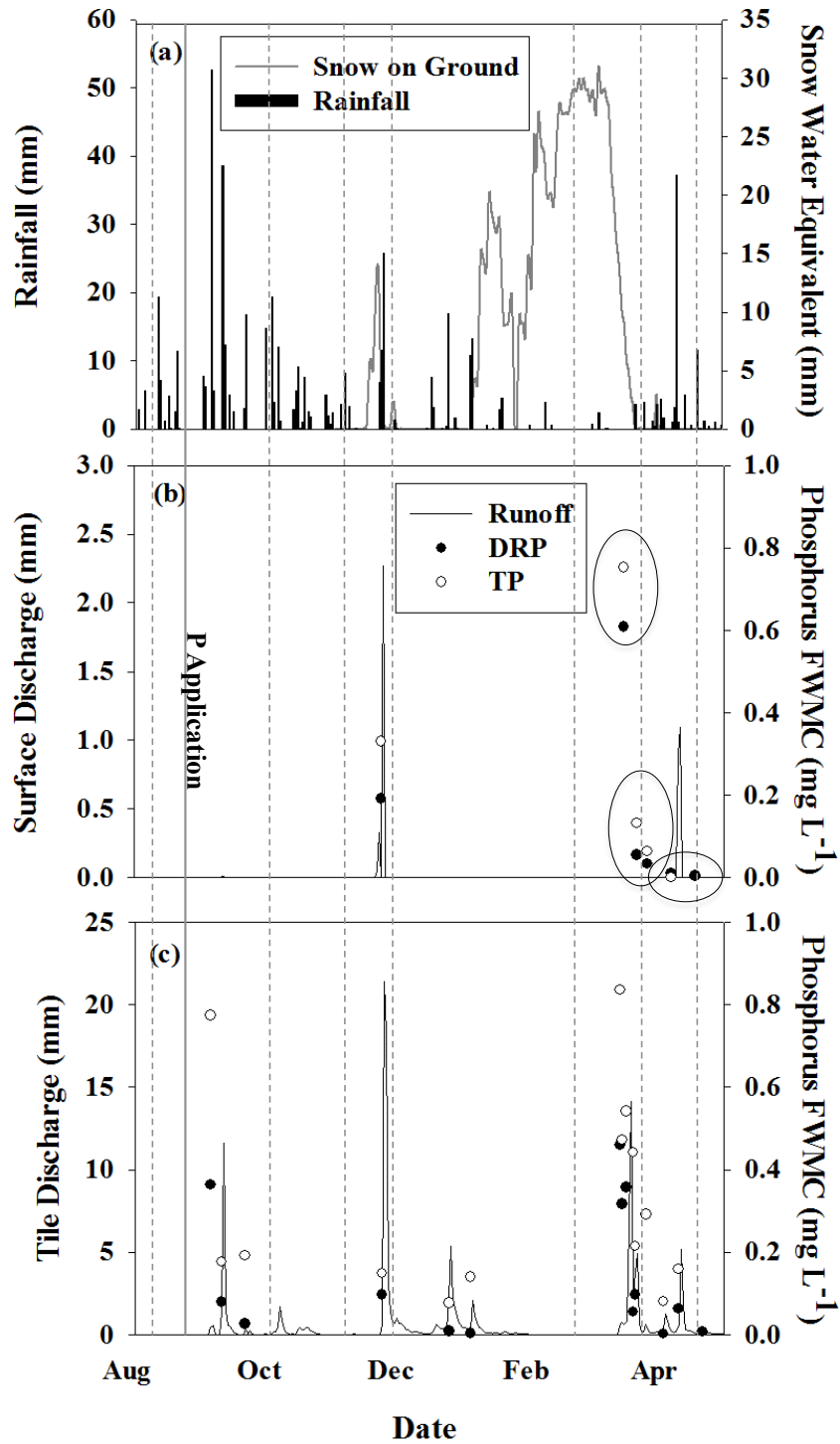
Figure 4.3: ILD (a) Daily total precipitation (rainfall = black bars; snow water equivalent = grey line). (b) Daily total surface discharge and (c) tile discharge with corresponding flow weighted mean concentrations of DRP (black circles) and TP (white circles). Sampling campaigns (dashed grey line) and P application (solid grey line) identified. *Note the difference in scales on the Y-axis. ** (b) average P concentration in surface ponds outlined with black circle.
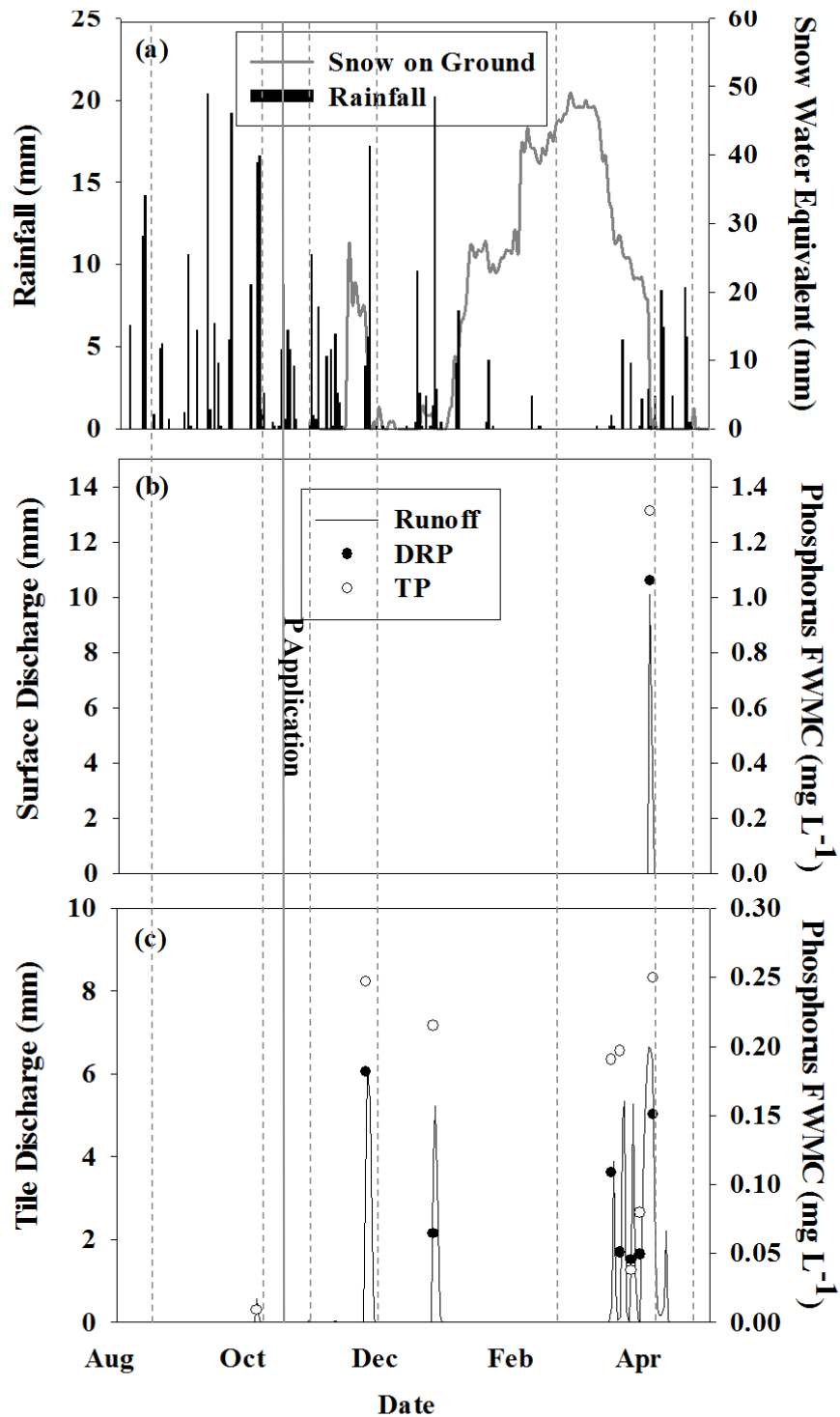
Figure 4.4: LON (a) Daily total precipitation (rainfall = black bars; snow water equivalent = grey line). (b) Daily total surface discharge and (c) tile discharge with corresponding flow weighted mean concentrations of DRP (black circles) and TP (white circles). Sampling campaigns (dashed grey line) and P application (solid grey line) identified. *Note the difference in scales on the Y-axis.

4.5.2 Water Extractable Phosphorus in Vegetation and Soil

Water extractable P (Figure 4.2) concentrations were greater in the cover crops (oat and red clover) than in wheat residue (U=1133.5, p= <0.001, comparing wheat residue from both sites against pooled oat and red clover for all sampled events). This pattern is consistent with the TP content of the two cover crop species, which were also considerably greater in the oat and red clover than wheat residue (Table 4.2). Water extractable P concentrations (data across the entire season pooled) did not differ between the two cover crops (p>0.05). The WEP concentrations in the two cover crop species were significantly greater than the WEP concentrations in surface soils (p<0.001), and this persisted throughout the study period (Figure 4.2c). In contrast, WEP concentrations in wheat residue exceeded that of the surface soil prior to the application of P in manure and/or fertilizer (Figure 4.2b,c; ILD U=36.00, p-=0.008; LON U=63.50, p=0.032); however, following the application of P, WEP concentrations in soil exceeded those in wheat residue at LON (U=42.50, p=0.003) whereas no difference was found at ILD (U=78.50, p >0.05). In addition, there were no further differences between wheat residue and soil at either site in the remaining sampling campaigns (p>0.05). Water extractable P concentrations in wheat residues differed slightly between the two sites. Overall, WEP concentrations were greater in the wheat residue from the ILD site compared to the LON site (U= p<0.001, Figure 4.2b), despite the two sites having similar soil test P concentrations prior to planting and P application (Table 4.2, p>0.05). Similarly, TP concentrations in the wheat residue were greater at the ILD site compared to the wheat residue at LON (Table 4.2). Although these subtle differences existed between the two sites, they were small in comparison to the differences between wheat residue and the two cover crops.

Collection Period	Total Vegetation P Pool (kg/ha)		WEP in Vegetation and Soil (kg/ha)			DRP Load in Runoff (kg/ha)		TP Load in Runoff (kg/ha)	
LON	WS	CC	WS	CC	Soil	Surface	Tile	Surface	Tile
PH	0.6 (0.1-1.3)	ND	0.01 (0.001-0.07)	ND	0.05 (0.001-2.2)	NF	NF	NF	NF
LC	ND	10.9 (9.5-16.6)	ND	0.04 (0.001-0.52)	1.1 (0.001-8.2)	NF	NF	NF	NF
BF			0.01 (0.001-0.13)	1.93 (0.75-8.39)	29.3 (2.3-53.4)	NF	0	NF	0
FF			0.01 (0.001-0.07)	0.63 (0.10-1.41)	6.7 (0.07-29.9)	NF	0.03	NF	0.04
BS			0.02 (0.001-0.11)	0.59 (0.22-1.46)	ND	NF	0.01	NF	0.03
FS			0.01 (0.001-0.07)	0.16 (0.06-0.35)	5.5 (0.001-20.0)	0.15	0.06	0.18	0.11
SR	1.0 (0.4-3.3)	9.1 (6.3-11.4)	0.00 (0.001-0.02)	0.22 (0.08-0.54)	3.9 (1.0-31.1)	NF	NF	NF	NF
Total			**0.03 (0.004-0.04)**	**1.70 (0.05- 5.74)**	**21.09 (1.39-51.69)**	**0.25**		**0.36**	
ILD									
PH	1.3 (0.5-4.1)	ND	0.06 (0.001-0.41)	ND	2.21 (0.35-4.41)	NF	NF	NF	NF
LC	ND	21.8 (16.0-36.6)	ND	0.3 (0.03-01.25)	3.91 (0.77-8.68)	NF	0.02	NF	0.03
BF			0.02 (0.001-0.08)	0.68 (0.14-2.51)	10.93 (2.27- 26.79)	0	0	0.01	0
FF			0.02 (0.01-0.08)	1.05 (0.01-2.98)	3.20 (0.09-6.57)	NF	0.04	NF	0.07
BS			0.04 (0.001-0.08)	6.93 (1.41-12.21)	ND	NF	0	NF	0.01
FS			0.04 (0.01-0.11)	0.42 (0.01-3.24)	3.36 (0.001-32.10)	NF	0.1	NF	0.16
SR	1.8 (1.1-3.1)	8.1 (5.0-15.5)	0.01(0.01-0.03)	0.03 (0.001-1.73)	4.04 (1.13-6.04)	NF	0	NF	0.01
Total			**0.06 (0.01-0.25)**	**7.70 (2.25-11.47)**	**5.87 (2.18-23.12)**	**0.17**		**0.3**	

Table 4.2: Total vegetation P (kg ha^{-1}) at the beginning and end of the study period is shown as median (range) values. Water extractable P (kg ha^{-1}) from vegetation and soil at each collection period is shown as median (range) values. Loads of DRP and TP in tile drainage and surface runoff events between sampling campaigns and total over study period. Total vegetation and soil P pools calculated as the sum of the change (decreases only) in P between sampling campaigns.*ND (no data collected). **NF (No flow occurred).

4.5.3 Temporal Variability in Water Extractable Phosphorus Contents in Vegetation and Soil Over the Non-growing Season

Temporal differences in WEP in vegetation and/or soil were observed over the NGS, and, these patterns differed among the wheat residue, cover crops and soil. Water extractable P concentrations in wheat residue did not change over the course of the study period, and P remained low at both sites throughout the duration of the NGS (Figure 4.2b, Figure 4.5b, Figure 4.6b). Similarly, the TP content of the wheat residues did not differ between the beginning and end of the study (p>0.05; Table 4.2).

Although there was no difference in WEP concentrations between oat and red clover when all sampling campaigns were pooled, splitting data into independent collection periods revealed differences in WEP from the cover crops throughout the NGS. While the cover crops were living (October sampling), WEP was greater from oat than red clover (U=63.50, p<0.001, Figure 4.2c, Table 4.2), reflecting the greater TP content of oat (U= 16.00, p<0.001, Table 4.2). Following the application of glyphosate ten days prior to the Early November sampling campaign, WEP concentrations increased in the red clover (U= 27.00, p<0.001, Figure 4.6c), and were greater than the concentration of WEP from oat (U=61.50, p<0.001, Figure 4.2c). During this period there was also increased WEP from oat as compared to the October sampling campaign (U=92.00, p<0.001, Figure 4.5c) but not to the same extent as was observed in the red clover after it had been terminated (Figure 4.6c). The light frost in early November sampling campaign) did not increase WEP concentrations in oat or red clover (p>0.05; Figure 4.2c) and WEP concentrations did not differ between the cover crops (p>0.05). However, during the Late February sampling campaign following the extended period of deep frost, WEP concentrations were greater than observed during the previous campaign for oat (U=10.0, p<0.001) but not red

clover (p>0.05; Figure 4.5c, Figure 4.6c). Following the main snowmelt event and April samplings WEP concentrations in both red clover and oat were depleted (Figure 4.5c, Figure 4.6c), and were comparable in magnitude to WEP concentrations in wheat residue. Overall, oat released more P than red clover throughout the snowmelt period, as there was a greater change in WEP concentrations (Figure 4.2c) and pools between the February and Snowmelt campaigns (Table 4.2). Between the start and end of the study period, the vegetation TP content (Table 4.2) declined for both oat (~54%, U=8.00, p<0.001) and red clover (~17%, U= 132.00, p<0.001). Although oat had a higher TP at the beginning of the study period (Table 4.2), the TP content in red clover remained significantly greater than oat (U= 227.00, p=0.043) by the end of the study period (April campaign), which also may be reflected in the greater WEP in red clover during the April sampling campaign (U=94.00, p<0.001).

Water-extractable P in soil at both sites followed a similar pattern over the NGS (Figure 4.2d). At both sites, soil WEP concentrations increased following P application (Figure 4.2d, Table 4.2, early November sampling). At the ILD site, soil WEP increased (U=10.0, p=0.021) following P application (surface broadcast manure and monoammonium phosphate broadcast and incorporated to 6" in strips) but returned to pre- P application concentrations before the subsequent collection campaign (late November) and did not differ for the remainder of the study period (p>0.05; Figure 4.5d). In contrast, WEP concentrations in soil at the LON site increased significantly (U=5.0, p=0.01) following P application (monoammonium phosphate surface broadcast and incorporated with vertical tillage to 5cm), and declined gradually throughout subsequent sampling campaigns (Figure 4.6d). Soil WEP concentrations did not return to pre fertilized levels by the following spring (April sampling campaign, U=12.5, p=0.011).

Although WEP concentrations in wheat residue and the two cover crops were greater

83

than WEP concentrations in soil, when the density of material (vegetation biomass, soil bulk density) is considered, the WEP pool in the top 5 cm of soil represented the largest P source at both sites (Table 4.2). The two cover crops also represented a considerably larger WEP pool than the wheat residues at both sites. Although these general patterns persisted, there were brief periods when the dominant P pool shifted between soil and plant material. For example, at the LON site, the peak period for P mobilization from red clover and soil were observed during the early November collection. During this time, there was a median of 1.93 kg ha^{-1} of WEP in red clover compared to 29.3 kg ha^{-1} of WEP within the top 5cm of the soil (Table 4.2). By the next sampling campaign (late November), the P pools had decreased to 0.63 kg ha^{-1} in red clover and 6.7 kg ha^{-1} in soil. Thus, between the early November and late November collection periods there was a decline of 1.3 kg ha^{-1} from red clover and 22.6 kg ha^{-1} of P from the soil. Therefore, the soil P pool had a greater potential to leach P to runoff in events following fertilizer application rather than the senescing vegetation. In contrast, a substantial quantity of P was leached from the oat between the February and Snowmelt sampling campaigns at the ILD site. Unfortunately, soil P was not determined due to frozen soil conditions, the small difference seen between the late November and April sampling campaigns suggest that soil P would have been similar during snowmelt (Snowmelt, Table 4.2). Thus, it is likely that the oat was the dominant source of DRP during this period (~6.51 kg ha^{-1} lost from oat).

4.5.4 Topographic Differences in Water Extractable Phosphorus Concentrations in Vegetation and Soil within Fields

Plots were compared across topographic positions within fields to determine if WEP concentrations in vegetation and soil prior to and following events differed with slope position

84

within the field (i.e. between topographic highs that do not experience surface flooding and low-lying areas prone to inundation). In general, concentrations of WEP in both vegetation and soil varied spatially within fields and clear topographic patterns were not observed (Figure 4.5, Figure 4.6) with the exception of the wheat residue at LON (Figure 4.6b), where the low slope constantly released greater P than wheat residue in the other two topographic positions. Overall, the low slope positions were infrequently inundated (late November and April at ILD, and Snowmelt at LON), whereas the mid-slope and upper slope positions did not experience surface inundation (i.e. water table above soil surface). Only following inundation during snowmelt did WEP concentrations of cover crops in the lower slope positions appeared to be smaller than at the other slope positions, whereas the opposite is true for wheat residue and soil (Figure 4.5c, Figure 4.6c).

4.5.5 Spatiotemporal Variability in Runoff and Phosphorus Concentrations in Surface Flow and Tile Discharge

Tile discharge and surface runoff events were episodic throughout the study period. Surface runoff was particularly rare during the study period, and was only observed on one occasion (snowmelt) at the LON site, generating a total of 14mm of runoff (Figure 4.4b), and, during two events at ILD (Figure 4.3b), which produced a combined total of 5mm of runoff. There were also a number of surface ponds that formed at ILD during and following snowmelt that did not generate flow. Overall, tile discharge was the dominant flow at both sites (Figure 4.3c, Figure 4.4c), accounting for 92 mm (87% of total flow) at LON and 152 mm (97%) of total flow at ILD.

Flow-weighted P concentrations were elevated during events compared to baseflow

conditions, which were low (<0.001 mg L^{-1} DRP, <0.01 mg L^{-1} TP). In addition, P concentrations were variable throughout individual events, often corresponding with discharge peaks, although flow-concentration relationships were poor (not shown). Across the events captured, FWMC of P were variable in tile drainage (0.03-0.84 mg L^{-1} TP; 0.01-0.46 mg L^{-1} DRP). P concentrations in tile drainage were most elevated during the first event (November) following P application and again during the main snowmelt event (Figure 4.3c, Figure 4.4c). At the ILD site, FWMC in surface runoff were 0.33 mg TP L^{-1} and 0.19 mg DRP L^{-1} (Figure 4.3b). In addition, surface ponds formed throughout the snowmelt period at the ILD site (although these did not appear to exit the field) and TP concentrations ranged from 0.01 mg L^{-1} to 0.75 mg L^{-1} and DRP from 0.001 mg L^{-1} to 0.61 mg L^{-1} (based on averages of samples collected throughout the duration of the melt event, Figure 4.3b). At the LON site, FWMC in surface runoff were 1.31 mg TP L^{-1} and 1.06 mg DRP L^{-1} (Figure 4.4b).

Observed loads of DRP and TP (kg ha^{-1}, Table 4.2) lost in surface runoff and tile drainage between each sampling period (late August through late April) were small in comparison to the available pools of WEP in vegetation and soil (Table 4.2). Loads of DRP and TP in surface runoff during the snowmelt event were an order of magnitude higher than observed losses of P in tile drainage (Table 4.2). However, the observed losses of both DRP and TP in surface runoff were lower than the observed WEP pools in vegetation and soils, and, small in comparison to the observed reduction in WEP in cover crops between the start and end of the snowmelt period. This suggests that not all of the WEP leached from vegetation (or soil) during snowmelt exited the field via runoff and may instead have been retained by the soil through adsorption.
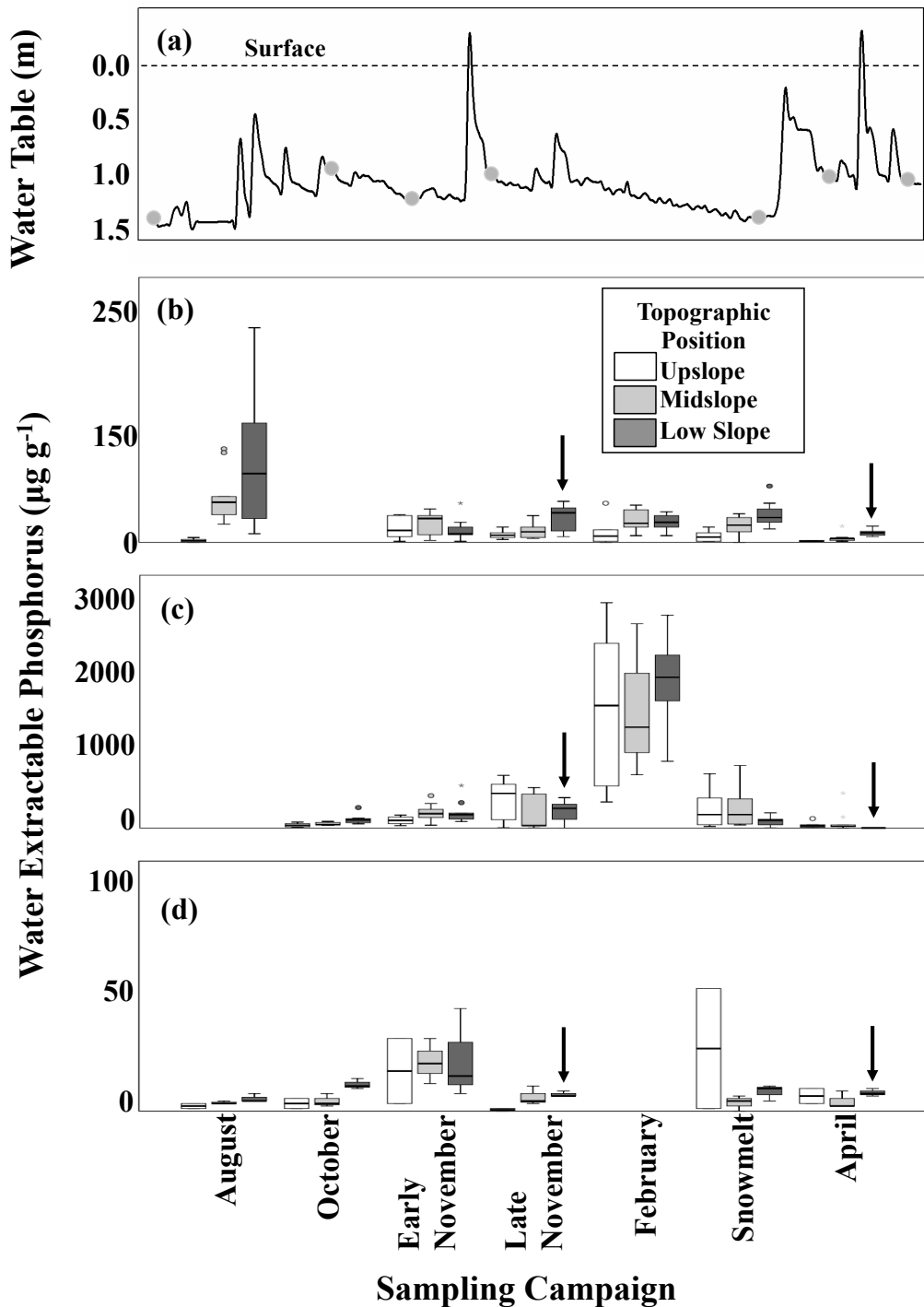
Figure 4.5: ILD: (a) Depth of water table relative to soil surface with vegetation and soil sampling campaigns identified (grey circle). Box-whisker plots of P lost ($\mu g\ g^{-1}$) from (b) wheat residue, (c) oat and (d) soil at the upslope (white), midslope (grey) and low slope (dark grey) topographic positions. Boxes provide the 25th, 50th and 75th percentiles, and whiskers provide the 10th and 90th percentiles. Period of inundation marked with downward arrow. *Note the difference in scales on the Y-axis.
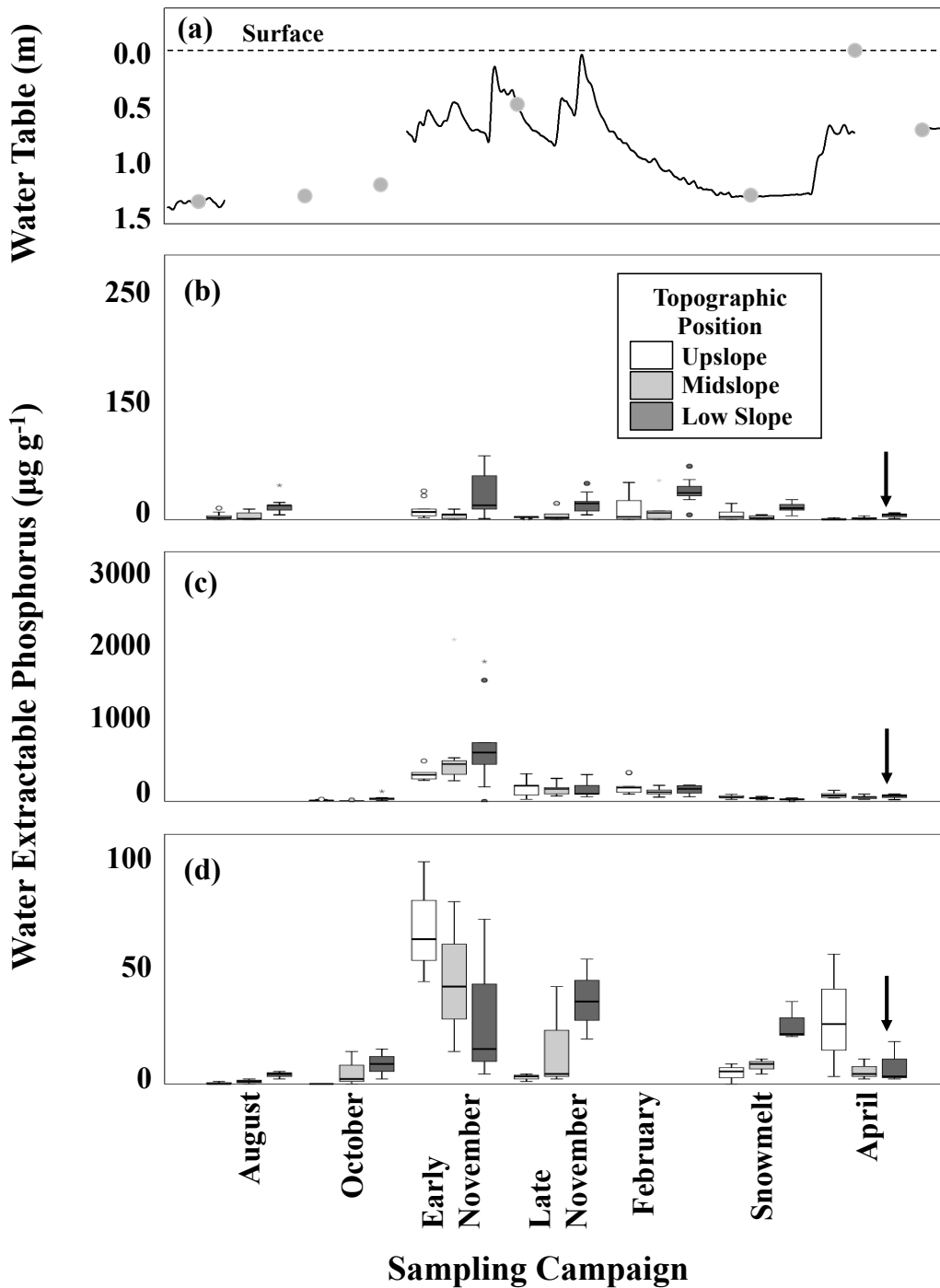
Figure 4.6: LON: (a) Depth of water table relative to soil surface with vegetation and soil sampling campaigns identified (grey circle). Box-whisker plots of P lost ($\mu g \ g^{-1}$) from (b) wheat residue, (c) red clover and (d) soil at the upslope (white), midslope (grey) and low slope (dark grey) topographic positions. Boxes provide the 25th, 50th and 75th percentiles, and whiskers provide the 10th and 90th percentiles. Period of inundation marked with downward arrow. *Note the difference in scales on the Y-axis. **(a) Water table estimated where data is missing.

4.6 Discussion

4.6.1 The Evolution of Vegetation and Soil Phosphorus Throughout the Non-growing Season

Differences in WEP concentrations were observed among the potential P pools (wheat residue, oat, red clover and soil) and throughout the NGS in response to climatic drivers. Cover crops released significantly more P throughout the NGS than the wheat residue, which is consistent with what has been shown by others (Elliott, 2013; Gburek and Heald, 1974). At both sites, P losses from wheat residue were small and remained consistently low over the study period. Of the two cover crops, more P was leached from oat over time, although WEP concentrations varied between the cover crops across the sampling campaigns. The maximum WEP concentrations in oat were observed following exposure to an extended period of deep frost (February campaign). The impacts of freezing on P release from vegetation have been reported elsewhere (Bechmann et al., 2005; Robertson et al., 2007; Timmons et al., 1970), where the disruption of plant cells, due to the formation of ice crystals, causes the release of inter/intra cellular P (Bechmann et al., 2005; Jones, 1992; Liu et al., 2014; White, 1973). However, much of this research has shown that freezing of actively growing vegetation can cause the release of P (Elliott, 2013; White, 1973), whereas in northern climates, the exposure of biomass to freezing occurs slowly on senescing plant material. Timmons (1970) first reported that DRP losses increased as vegetation became dormant, and Uusi-Kämppä (2005) observed high P release from vegetation following the freezing of senesced plant material. Therefore, it is possible the exposure of sensing vegetative material to freezing may have enhanced P release from plant cells. In addition, as the waxy cuticle of the oat leaves break down, they became more easily wetted, which increases the potential for the plant to leach nutrients (Tukey, 1970). Noack et al.

(2012) found WEP represented the majority of TP in plant residues and suggested most of that

WEP had potential to be brought into solution after the first significant rainfall in the field.

However, the lack of change in WEP from the oat over time suggests that a majority of WEP

was not extracted by rainfall, but may have rather been preserved in plant material or embedded

in the snowpack until snowmelt (Sturite et al., 2007). This suggests that those cover crops

exposed to frost after senesce may also contribute to significant P losses in regions with

significant winter (snowmelt) conditions.

In contrast to the oat, WEP from red clover did not increase as the NGS progressed. This

is likely because the red clover was terminated before the early November collection period with

glyphosate. The WEP leached from the red clover may have been a result of P released from

quickly senescing vegetation as the sampling period occurred ten days following herbicide

application. Glyphosate is rapidly adsorbed and translocated throughout the plant (Segura et al.,

1978) to effectively kill foliage and roots (Swanton et al., 1998), which can enhance the release

of P (Tukey, 1970; Ulén et al., 2010). Phosphorus concentrations did not increase when the dead

red clover was frozen and instead slowly declined with successive events throughout the NGS. It

is possible that application of glyphosate caused much of the available P in the red clover to be

available for leaching in the fall, as observed with the high WEP concentrations observed during

the early November collection. However, the minimal leaching opportunities throughout the

NGS due to a paucity of runoff events permitted the red clover to have P available for leaching

during the spring melt. The fact that the greatest leaching losses from the red clover were

observed during the autumn months following termination suggests that farmers may be able to

reduce vegetation P losses during snowmelt by terminating vegetation in autumn. This allows the

leached P to travel vertically into the soil profile where it more likely to be retained, as surface

runoff events do not occur as frequently during autumn events than during winter thaw/snowmelt events (Lam et al., 2016; Macrae et al., 2007a; Macrae et al., 2007b; Van Esbroeck et al., 2016).

The limited generation of surface runoff at both sites may also explain the lack of difference in P leaching between topographic positions. The greatest decline of P appeared in the low slope position following snowmelt, and was likely due to the occurrence of ponded water, as Cermak et al. (2004) and Ginting et al. (1998) reported that nearly all P was leached from crop residue after 20+ hours of surface ponding. In this study, snowmelt was the only period on both fields where the low slope was inundated for more than one day, and therefore the greater contact time between melt water and vegetation likely lead to the extraction of greater amount of P. The reason for the greater P release from wheat residue at LON in the low slope position is unknown; it is possible that the wheat residue was subject to spray drift from neighboring fertilizer and herbicide applications, as the low slope positions were located closest to the neighbouring field. In addition, the greater WEP concentrations observed in the low slope position may be due to the transport of P from the more upslope portions of the field in runoff or P released from the vegetation material that was retained by the soil instead of exiting the field.

When crops were compared to the underlying soil, changes in WEP concentrations in vegetation exceeded the changes in soil WEP concentrations, suggesting that cover crops may have been a greater source of P than the soil (despite the fact that fertilizer and manure had recently been applied). This is consistent of the findings of Elliott (2013) and Bechmann et al. (2005) who found that P release from cover crops exceeded P release from soil (even when manure was applied). Although WEP concentrations in soil were considerably smaller than those in the cover crops, soil represented the greatest P pool at the sites (Table 4.2), which was a function of the soil bulk density.

At both sites, WEP concentrations in soil increased following P application, which is consistent with Kleinman et al. (2002) who reported increases in WEP following the application of manure and mineral fertilizer. However, at the ILD site, soil WEP returned to pre fertilized values before the next subsequent collection period and did not differ for the remainder of the study period (p>0.05). In contrast, at the LON site, soil WEP gradually declined over time following fertilizer application, and did not return to pre fertilization levels before the end of the study period. Relationships between soil WEP concentrations and runoff P concentrations are discussed in the subsequent section.

4.6.2 Spatiotemporal Variability in Discharge and Flow Weighted Phosphorus Concentrations

As noted above, runoff from the two sites was highly episodic, which is consistent with previous studies at these study sites (e.g. Van Esbroeck et al., 2016) and in the Great Lakes Region in general (e.g. Lam et al., 2016; Macrae et al., 2007a). Tile drainage was the dominant flow path during the study period, which is also in agreement with previous years at these sites (Van Esbroeck, et al., 2016) as well as other studies (Gaynor and Findlay, 1995; Eastman et al., 2010; Hirt, et al., 2011; Jamieson et al., 2003; Macrae et al., 2007a). Despite the fact that tile drainage was the dominant flow path, surface runoff represented approximately 50% of the TP and 60% of the DRP load at the LON site over the NGS. This is also consistent with what has been observed at this site in other years (Van Esbroeck et al., 2016). In contrast, nearly all of the losses from the ILD site were exported in tile drainage because so very little surface runoff occurred (<5mm).

Overall, total tile TP and DRP loads over the study period were greater than reported for

other years at both sites without fertilizer applications, but less in comparison to other years at the same sites that received the same fertilizer applications (Van Esbroeck et al., 2016). The high TP load in tile drain effluent during the September event at the ILD site coincided with the timing of strip tillage and inorganic P application and, this was the first event following the application of manure to the surface one week prior. Likewise, the high P load during the November 23th event at the LON site occurred during the first significant rainfall event following the surface application of inorganic fertilizer. This is consistent with others who have found that high P losses occur when the application of P coincides with rainfall (Haygarth and Jarvis, 1999; Sharpley et al., 1994; Withers, et al., 2003), often referred to as incidental P losses. This was also reflected in both the high soil WEP concentrations observed during the sampling campaign prior to this event (early November), and, the substantial reduction in soil WEP concentrations between the early November and late November events. The same November precipitation event also resulted in the largest tile discharge and the only event at ILD when surface runoff exited the field. The elevated loads in tile (and surface at ILD) are concurrent with the observed changes in soil WEP at both sites suggesting that the P lost during the autumn was driven by the recent P application rather than crop residue or cover crops.

Snowmelt was an important period for P export during the NGS, which is consistent with other studies (Hansen et al., 2000; Lam et al., 2016; Liu et al., 2014; Macrae et al., 2007a; Su et al., 2011; Van Esbroeck et al 2016). At ILD, snowmelt resulted in a greatest export of P to tile drainage, which accounted for 56% of total TP and 60% of DRP exported in tile drainage during the NGS. This is similar to what has been found in other regions of Southwestern Ontario, as 52% of annual tile DRP (Lam et al., 2016) and 50% of TP (Macrae et al., 2007a) was exported during snowmelt. During snowmelt, TP is primarily controlled by volume of runoff, which is

highly dependent on the snow water equivalent (of the snowpack (Liu et al., 2013b; Suzuki et al., 2005), antecedent soil moisture content (Jamieson et al., 2003; Liu et al., 2013b) and discharge (Fang and Pomeroy, 2007; Jamieson et al., 2003). These controls have largely been described for P lost via surface runoff; however, high P loss in tile drainage during snowmelt may result from enhanced hydrologic connectivity between surface soils and tile drainage, as preferential pathways in the subsurface become important under saturated soil conditions (Geohring et al., 1998; Kung et al., 2000). It is likely a combination of these factors that resulted in high tile P loss at ILD during snowmelt. Tile drainage represented 100% of the P load from the ILD site during the snowmelt period as no surface runoff occurred. In contrast, P export in tile drainage from the LON site during snowmelt was considerably lower than was observed at the ILD site due to elevated P losses observed in surface runoff at the LON site, where surface runoff accounted for 62% of TP export and 70% of DRP export. Higher surface runoff during snowmelt has been attributed to limited infiltration due to frozen surface soil (Li et al., 2011; Su et al., 2011), or, due to saturation of subsoils (Macrae et al., 2010).

The observed loads during the snowmelt period at both sites were considerably less than the pools in either cover crops or soil, or the changes in WEP concentrations between sampling campaigns, indicating, that despite the potential for DRP and TP loss from soil and plant pools, not all of the P may actually leave the field in runoff. The specific source of the P in the runoff that does exit the field is also unclear. The export of nutrients during snowmelt can originate from nutrients stored in snowpack, plant residues, and the surface soil (Liu et al., 2013b). During snowmelt, DRP concentrations can be enhanced due to a longer contact time with melt water (Macrae et al., 2007a), which encourages soluble reactions between soil, water and vegetation (Bechmann et al., 2005; Little et al., 2007; Liu et al., 2013b; Ontkean et al., 2005; Rekolainen,

1989; Tiessen et al., 2010; Ulén, et al., 2007). Snowmelt water, which is low in P, extracts the soil surface, which is high in P (Rekolainen, 1989). A similar principle can be applied to the extraction of P from vegetation. As P loading increased over the course of snowmelt at LON, it is likely the long duration of snowmelt caused P loss from both soil and red clover (reductions of ~1.2 kg ha^{-1} between late November and Snowmelt from soil and ~0.43 kg ha^{-1} from the red clover between the February and Snowmelt collections). However, snowmelt losses were not as substantial as had been observed following the November 23rd event that followed both the application of P and the spraying of red clover with glyphosate (reductions of ~2.7 kg ha^{-1} from soil and ~1.3 kg ha^{-1} from red clover between the early November and late November collections). Given the larger reduction in soil P values across the field, it is most likely the soil contributed a larger portion of P to runoff during the November event. The large nutrient pool in soil was likely also an important source of nutrients during snowmelt (Hansen et al., 2000; Liu et al., 2013b), through desorption (Rekolainen, 1989).

In contrast, at the ILD site, a greater reduction in WEP was observed in the oats rather than in the soil (Table 4.2), suggesting that the vegetation may have been a more important source of the DRP lost to surface water during the snowmelt period. Sturite et al. (2007) reported that P from frost-injured plants was preserved within the plant tissue or remained embedded in the snow until snowmelt. The melting of the snowpack likely caused the mobilization of P from oat following snowmelt, as a loss of 6.53 kg ha^{-1} from oat occurred during this period. This suggests that potentially all of the P supplied under the snowpack from oat could have been lost during snowmelt. Indeed, concentrations in the standing water on the field at this time were greater than what had been observed during the November event, even though the standing water did not exit the field during the snowmelt period (Figure 4.3b). Previous studies that have

attributed P loss to vegetation during snowmelt have only accounted for surface runoff over

frozen soil (Little et al., 2007; Tiessen et al., 2010). Although none of the ponded water on the

field actually left the field, tile drains flowed actively during the melt period. At this time,

concentrations and loads of P in tile drainage were highly elevated, and comparable in magnitude

to tile drain P losses during the November event that followed manure and mineral P application.

Standing water and partially frozen soil can induce preferential flow through the soil profile

(Jarvis, 2007). Van Esbroeck et al. (2016) observed a positive relationship between

concentrations of P in tile drainage and overland flow at the same sites (ILD and LON) and

reported that P concentrations were greatest during periods when overland flow was also

occurring. Thus, it is possible that at least some of the P extracted from the oat during snowmelt

passed through drainage tiles, and, that a significant source of the P in tile drain effluent was the

cover crop on the field. However, as noted above, P loads in surface or subsurface runoff from

both sites were considerably lower than the quantities of P leached from vegetation or soil

between the February and Snowmelt sampling campaigns. This suggests that the significant

potential pool of available P in surface vegetation and soil does not translate directly to observed

rates of P in runoff from farm fields.

4.7 Conclusions

This chapter has quantified changes in P in winter wheat residues, red clover, oats and

surface soil (5cm depth) over the NGS, and has compared these patterns with P losses in surface

runoff and tile drainage over the same period. Both cover crops and the surface soil are

significant pools of P on fields, although their relative contributions to runoff may vary

throughout the season. Although P concentrations were greatest in cover crops, the soil P pool

was greater due it is larger density per unit area. In addition, the concentration of P from eroded sediment is typically greater than the bulk soil due to the selective transport of fine textured material, such as clay particles (Hansen et al., 2002; Sharpley, 1985b). It is therefore plausible that a source of P from during the vegetation extractions was the result of P desorption from fine sediment that had settled on vegetation throughout the NGS. Results from this study suggest that cover crops such as oats have the potential to release substantial quantities of P during the NGS. However, future research is needed to quantify and observe the change in P release from frost intolerant cover crop species when let terminated by frost at the start of the NGS. The termination of crops in autumn may be a management strategy to lessen the potential for winter P losses. Indeed, the termination of the red clover at the LON site likely prevented elevated P losses from occurring during snowmelt because much of the P pool was released during autumn rain events. However, future research should compare the loss of P over the NGS from vegetation terminated with herbicide compared to those that are living at the time of the first frost. This study has also shown that although cover crops and soil are both significant pools of P on fields (whereas wheat residue is not), most of the P released from these pools is retained on site and P loads in surface and subsurface drainage are much lower. These findings have implications for the optimization of the use of cover crops as a BMP in cool, temperate climates, and, provide insight into the risks for P loss from vegetation in winter.

5.0 Chapter Five: Final Discussion and Thesis Conclusions

This thesis examined the potential for above-ground vegetation to release phosphorus (P) following freeze-thaw cycles (FTC) using laboratory experiments and quantified the release of P from that vegetation, as well as surface soil, in a field setting, to determine their contributions to P losses over the non growing season (NGS). This thesis has demonstrated that *P loss from vegetation following FTC varies with vegetation species*. Results from chapter three revealed that P leaching from vegetation varied between species; however, cover crops released greater P than wheat residue. Chapters three and four revealed that overall, P released from wheat residue was low and did not change over the NGS, which may be attributed to the low total plant P content (Elliott, 2013; Timmons et al., 1970) and therefore did not likely enhance P in surface runoff or tile drainage. Two cover crops were examined (Chapters three and four); oats released more P as the NGS progressed. The mechanism driving the enhanced release of P from oat over time is unclear, however it is possible that freezing the senescing vegetation caused P to become preserved within the plant until snowmelt.

This thesis has also revealed that *P loss from vegetation is also affected by hydrologic transport processes*. Experimental work in chapter three found that extraction method had the greatest influence on the quantity of P leached from vegetation, where ponding released more P than rainfall. The results from this chapter also revealed that the first ponding event was the most critical to P leaching from both cover crop species. From these findings it was hypothesized that those areas that experienced inundation during the NGS would leach a greater quantity of P faster. However, there was no difference in P found from vegetation (or soil) in the low-lying areas of the field, as compared to the upper portions, which may be the result of the limited surface runoff and inundation experienced at both sites in the study year. Results may differ in a

year with a greater number of thaw events. Indeed, P leaching can be enhanced when vegetation is subjected to prolonged contact with runoff water, as was seen in the significant decline in P from the oats following snowmelt.

In general, the patterns of vegetation P from the laboratory experiment were reflected in the field, although the magnitude of P leaching was reduced in the field. The differences between the lab and field results may have been related to the interaction between runoff and the soil (Elliott, 2013; Riddle and Bergström, 2013), where P released from vegetation was likely adsorbed by soil. Overall, P concentrations from cover crops remained elevated compared to the soil; however, when results were compared based on biomass and bulk density, the opposite occurred. Overall, the soil P pool was greater over the NGS, and therefore presented a greater source of P, likely due to the application of fertilizers. Thus, *this thesis has also shown the importance of coupling examinations of both vegetation and soil when assessing the efficacy of cover crops as a BMP*.

This thesis has also shown that *the relative contributions of soil and vegetation to field-scale P loss may vary throughout the NGS*. At both sites, there was a significant increase in soil WEP following P application, which was available to leach in runoff. This period of time was important for tile drainage and surface runoff P losses at both sites, which has also been reported by other studies (Haygarth and Jarvis, 1999; Sharpley et al., 1994; Withers et al., 2003). This time (Late October) also presented the greatest potential for the red clover to leach P to runoff, possibly due to the application of glyphosate. However, future research should compare the loss of P frost from a cover crop species when terminated with glyphosate or left living during the NGS. Under conditions experienced in autumn 2014, a majority of P leached from red clover likely moved vertically into the soil and concentrations of P in the vegetation pool decreased

99

over time. As a result, termination of cover crops, even frost intolerant species, may be a BMP to minimize their potential to contribute to winter P losses.

Snowmelt was also a critical period for P loss from both sites, which is consistent with other studies (Hansen et al., 2002; Lam et al., 2016; Liu et al., 2014; Macrae et al., 2007a, Van Esbroek et al., 2016). Phosphorus losses during snowmelt have mainly been attributed to the enhanced duration of melt water (Macrae et al., 2007a), which encourages soluble reactions between soil, water and vegetation (Bechmann et al., 2005; Ontkean et al., 2005; Little et al., 2007; Liu et al., 2013b; Rekolainen, 1989; Tiessen et al., 2010; Ulén, et al., 2007). Indeed, DRP loads during the snowmelt period have been increasingly attributed to vegetation (Bechmann et al., 2005; Elliott, 2013; Liu et al., 2013a; Riddle and Bergström, 2013; Roberson et al., 2007; Saleh, 2008; Tiessen et al., 2010; Timmons et al., 1970; White, 1973). However, results from chapters three and four revealed that the oats had the potential to release a large amount of P to runoff, whereas red clover and soil were less susceptible to enhanced losses following FTC.

Finally, this thesis has shown that *despite the potential for P release by vegetation in winter, this P may not exit fields*. Thus, the benefits of cover crops to agricultural systems may not be outweighed by winter leaching of DRP to runoff. It is possible that the dense cover crop aided in reducing surface runoff, and as a result, a large amount of P. If conditions were present to induce surface runoff, P losses from this field due to the presence of the cover crop may have been more consistent with the results of other studies (*e.g.* Bechmann et al., 2005; Elliott, 2013). However, it is also possible that the standing water triggered preferential flow through the soil profile (Jarvis, 2007) and therefore some of the P extracted from the oat passed through to drainage tiles. As a result, a significant source of the P in tile drain effluent may be from the oat cover crop. This is important given previous studies that have attributed P loss to vegetation

during snowmelt have only accounted for surface runoff over frozen soil (Little et al., 2007; Tiessen et al., 2010), which is not typical of farm fields in Southwestern Ontario (Macrae et al., 2007a, Van Esbroek et al., 2016). Irrespective of these losses, the observed edge-of-field losses of P were small in comparison to the P pool in the vegetation on fields. This finding is important for evaluations of cover crops as a BMP, as a majority of P taken up by a cover crop may be retained on the fields rather than exported in runoff.

In conclusion, this study provides insight into the timing and magnitude of P release from vegetation throughout the NGS in regions with cool temperate climates and provides an improved understanding of the contribution of cover crops to winter P losses. Cover crops can be optimized for use to allow managers to achieve the benefits (*e.g.* reduced erosion, improved soil health) without the risks for winter P losses. The laboratory study demonstrated the combination of hydroclimatic conditions required to mobilize P from vegetation. However, the field study demonstrated that although P appeared to have been mobilized from both vegetation and soil pools during the NGS, the observed loads of DRP and TP leaving the fields were considerably smaller, suggesting that much of the P released from vegetation and soil was retained within the field. It is important to consider the air temperatures during the NGS of 2014/2015 were colder than the long-term average, and, a deep snowpack existed for a majority of the study period, most of which was lost via sublimation. Future research should consider the implications of using a cover crop under conditions where a smaller snowpack develops and midwinter thaws exist, as this will alter both the extraction and transport of P from remaining vegetation as well as the underlying soil.

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