Edge of Field Vegetated Buffers as a Potential Source of Dissolved Phosphorus over the Non-Growing Season in Cold Climates

by

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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, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Phosphorus (P) rich runoff from agricultural landscapes are a major contributor to freshwater eutrophication issues. To intercept this runoff before it reaches waterways, vegetated buffer strips (VBS) are often employed at field edges. Over time, sediment and nutrients accumulate at these unmanaged field edges and can become legacy sources of P, representing a source of dissolved P to waterways. In addition, typical non-growing season (NGS) conditions experienced in cold climates favour the release of P from vegetation within VBS, further adding to the potential for these features to contribute to P loads of waterways. Although these sites represent potential sources of P to waterways, it is unclear if the risk of release differs across different regions, or with riparian zone shape/topography or vegetation type. Thus, the aim of this thesis is to measure the variability of P concentrations in VBS soil and vegetation samples across several sites to determine the effects that topography, freezing temperatures, period of inundation, and soil P level have on mechanisms of P retention, mobilization, and transport over the NGS in typical Canadian VBS.

Soil and vegetation samples were collected at various topographic locations (up, mid, low slope) from 4 Ontario (moderate winter) and 4 Manitoba (severe winter) VBS sites at the beginning and end of the NGS (Fall of 2020 and Spring of 2021) to measure their water extractable P and plant-available P contents. This analysis was supplemented with in-field hydrologic and temperature data at most sites. Results demonstrate that topography can drive soil P levels but has no effect on vegetation P or on the change of soil or vegetation P concentrations over the NGS due to greater periods of inundation. While the severity of freezing impacted the extractability of vegetation P, it was found that the temperatures applied in the lab were more severe than those experienced in the field due to the presence of snow cover accumulating in ditches. Further analysis on the effects of vegetation management were conducted on frozen soil/vegetation columns extracted from one Ontario site. Those results indicate the efficacy of vegetation harvesting as a means of reducing P losses from runoff through VBS, with the potential to reduce SRP loads by 3 and 10 kg/ha (for lower and upper zones, respectively). To investigate the relationship between vegetation and soil P concentrations more thoroughly and determine if vegetation growing in P-rich soils exhibits greater risk for winter P loss, samples were collected from 2 additional sites with highly elevated soil P due to bunker silo runoff, as part of a pilot study. Results indicate that vegetation P concentrations are independent of

soil P concentrations and do not exhibit evidence of luxury P uptake and storage, though further investigation is recommended.

This thesis provides an initial investigation into the importance of VBS vegetation to NGS P losses. Future work should design experiments based on the recommendations and lessons learned to further enhance the understanding of vegetation management as a potential VBS best practice for P loss reduction, and to better understand the complex biogeochemical relationships in these systems.

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Chapter 1
Introduction and Problem Statement

The transport of nutrients into surface water bodies and their subsequent accumulation are causing water-quality impairment globally (Mateo-Sagasta, Zadeh, & Turral, 2018; Verhamme et al., 2016). Agricultural runoff, which consists of non-point sources such as diffuse runoff from agricultural cropped fields, as well as point sources such as effluent drainage from livestock operations, is seen as a major source for these excessive nutrient loads. Phosphorus (P) and nitrogen (N) released from these sources can have significant downstream environmental effects (Dosskey et al., 2010; Kronvang et al., 2005). Phosphorus acts as the limiting nutrient in most aquatic freshwater systems, and excessive loads of P result in an imbalance in these ecosystems, leading to nuisance and harmful algal blooms (Schindler, 2012). Therefore, P is of particular concern and the need for a reduction of P inputs drives much of the research reviewed as a part of this thesis.

To mitigate diffuse non-point sources of agricultural nutrient loading, catchment scale practices must be employed to reduce nutrient inputs (primary), decrease the supply of nutrients to runoff using conservation practices (secondary), and finally, to interrupt nutrient pathways before they reach surface water resources (Macrae et al., 2021; Osborne & Kovacic, 1993; Tomer et al., 2013). Vegetated buffer strips (VBS) are a commonly applied beneficial management practices (BMP) located at the edge-of-field and extend to the waters edge that are used across many regions to mitigate agricultural nutrient loading to surface water by trapping and treating the runoff water. While VBS can also be referred to by other names such as riparian buffers, vegetated filter strips, or agricultural buffers, in this thesis they are defined as thin strips (typically in the range of 5 to 10 meters) of non-producing land located between watercourses and agricultural fields growing vegetation for the purposes of intercepting sediment, nutrients, and pesticides from the producing agricultural field (Haddaway et al., 2018; Stutter, Kronvang, Ó hUallacháin, & Rozemeijer, 2019).

Due to their functional characteristics related to vegetation, VBS are most effective during the warmer growing season (X. Liu, Zhang, & Zhang, 2008; Roberts, Stutter, & Haygarth, 2012) and are typically less effective in cold agricultural regions (Kieta, Owens, Lobb, Vanrobaeys, & Flaten, 2018). Indeed, there are many agricultural areas within cold climate regions, such as in North America and Northern Europe, in which the non-growing season hydrology (frozen soils, decreased infiltration), seasonal discharge fluctuations (i.e. dramatic snowmelt discharges), reduced growing season, (i.e., nutrient uptake) and nutrient leaching from frozen vegetation affect VBS efficacy (Kieta et al., 2018). Due to the neutralization of runoff retention mechanisms during colder weather (Kieta et al., 2018), or due to increased soil P solubility in buffer soils (Stutter, Langan, & Lumsdon, 2009), VBS can increase P losses from the landscape, indicating that they are acting as a net source of P rather than a net sink (Roberts, Stutter, & Haygarth, 2012). As a result, the prescription of VBS as a BMP for agricultural runoff has come into question as a way to reduce P loading to surface waters. Indeed, although such landscape features are important for biodiversity and wildlife corridors, they may be problematic for P management in runoff.

Although the potential contribution of VBS to P release in winter has been observed and described, the extent of this spatially is less clear. It is unclear if P release is consistent across VBS (i.e. with topography and proximity to fields and/or adjacent streams). Moreover, the release of P by plants following frost has been found to differ with vegetation species (Cober, Macrae, & Van Eerd, 2018), frost magnitude (Cober et al., 2018) and the degree of contact with water (Lozier & Macrae, 2017), all of which could potentially differ with topography. Moreover, some vegetation grown in P-rich soils can take up Luxury P, increasing plant P content (T Ericsson, 1994; Kröger, Holland, Moore, & Cooper, 2007). This may make vegetation grown in constructed treatment wetlands especially vulnerable to winter P loss. An improved understanding of how the amount of P released from vegetation following freezing may differ with different types of VBS is needed.

This thesis is organized into a literature review and two manuscripts that outline two distinct studies. The first manuscript examines how hydroclimatic and landscape factors affect potential non-growing season (NGS) P loss from eight VBS sites within two cold agricultural regions (Ontario and Manitoba, Canada). While both areas experience extended periods below freezing, the winters in Ontario tend to be milder and wetter than those in the Canadian prairies. Consistent trends across these regions could indicate likely systemic issues with VBS as a BMP in Canadian landscapes. The second manuscript investigates the relationship between soil P and vegetation P in VBS sites subjected to high nutrient loads. The goal of this manuscript is to determine if typical VBS grass vegetation P content is impacted by P content of the soil, or whether or not this increases the risk of winter P release from this vegetation. The results have implications on the potential management options of these systems.

Chapter 2
Review of Literature

Vegetated buffer strips were historically identified as landscape units that retained P; however, this understanding has changed and these landforms are now viewed as units that modify P, storing pools of P for finite periods of time to be released later and in different forms (Roberts et al., 2012). With this understanding arises the implication that proper soil and vegetation management of these systems might be needed for efficient and long-term P storage. Therefore, improved understanding of factors affecting P retention and release is needed to inform how management practices could be targeted. Such factors may impact specific physical, geochemical, and biological processes occurring within VBSs. This literature review focuses on summarizing the types of processes that occur within a VBS related to P dynamics, and the factors that affect those processes, to uncover gaps in the conceptual understanding of P dynamics of agricultural VBSs in cold climates.

2.1 Phosphorus in Agricultural Systems and Eutrophication

Surface water bodies throughout the world have been, and continue to be, impacted by the accumulation of Phosphorus (P) (Mateo-Sagasta et al., 2018; Verhamme et al., 2016). This abundance of P is known to cause eutrophication, impairs water quality, allows the proliferation of aquatic algae blooms, and depletes Oxygen levels (Environment and Climate Change Canada, 2018; Ludsin, Kershner, Blocksom, Knight, & Stein, 2001). Although industrial and municipal wastewater can contribute to this problem, agriculture is often seen as the predominant anthropogenic source of P causing eutrophication (Environment and Climate Change Canada, 2018; Schindler, 2012). There are initiatives underway to combat these issues in both Ontario (Environment and Climate Change Canada, 2018) and Manitoba (Environment and Climate Change Canada, 2021) which include focus on the retention of P within the agricultural landscape through the use of land use Best Management Practices (BMP). The implementation of Vegetated Buffer Strips (VBS) along watercourses adjacent to agricultural fields is one such BMP and these landscape units operate by intercepting overland runoff before it reaches watercourses.

Surface runoff from agricultural fields is generated through either infiltration excess or saturation excess flow from rainfall and wet conditions. Infiltration excess results from the rate of rainfall exceeding the soils capacity to absorb the rain, whereas saturation excess occurs when the water table rises above the soil surface and the soil is at maximum water storage capacity (Kleinman et al., 2006). This surface runoff is recognized as major transport pathway for terrestrial P to surrounding waterways (Sharpley et al., 2013).

Phosphorus in agricultural runoff often consists of particulate phosphorus (PP) bound to sediment and dissolved fractions of phosphorus: total dissolved P (TDP), where TDP can be separated into Non-reactive P (NRP) and soluble reactive P (SRP). The operational distinction between dissolved and particulate is based on a filter size of 0.45 µm, meaning P bound to particulates smaller than that size are designated as part of dissolved P pools (Haygarth & Sharpley, 2000). Dissolved reactive P is labile or readily available for uptake by microbes and plants in a solution, and is also referred to as Soluble Reactive P (SRP) or inorganic Phosphorus (Pi) and is typically represented as the proportion of orthophosphate ions in solution (Haygarth & Sharpley, 2000). Total Dissolved P (TDP) is operationally defined as the bioavailable P after a digestion procedure to loosen P bound to very fine grained organic and inorganic sediment. Non-Reactive P is the difference between SRP and TDP and is often referenced as dissolved organic P. Total P (TP) constitutes all forms of P and is often calculated as the sum of TDP and PP. The state (or speciation) of P is vital in determining the risk to downstream water sources from runoff generation, and the potential for biological utilization in soils. Part of the complexity inherent in soil P dynamics is the fluctuation of these specific P pools and how they each influence the other.

Water Extractable Phosphorus (WEP) is a typical experimentally defined metric in measuring P concentrations of agricultural soil and vegetation samples. While not specifically defined, it is the measure of P obtained from a sample when using water as an extractant. The concentration of WEP in soil and vegetation samples is often measured in P cycling studies to gauge the risk for P to be lost to the environment during runoff generation events. Whereas other measured biochemical fractionations (e.g., Olsen-P) of P require extractant solutions, WEP concentrations are typically more representative of conditions experienced in the field by using water as the extractant, and therefore are thought to better predict actual field scale losses.

2.2 Phosphorus Retention Processes in Vegetated Buffers

The transport of P from terrestrial to aquatic environments is highly complex due to its affinity for geochemical adsorption, mineral precipitation, and biogeochemical processing within soils (Dodd, Sharpley, & Berry, 2018; Roberts et al., 2012) as well as its role as a vital molecular building block for all biological functioning (Malhotra, Sharma, & Pandey, 2018). Structurally, a Vegetated Buffer Strip (VBS) in an agricultural setting can be as simple as a natural unmanaged zone of vegetation at the field edge, and as complex as a specifically constructed vegetated swale. VBSs are unique ecologically and environmentally as they represent this fringe zone between terrestrial and aquatic ecosystems. Such transitional ecotones within agricultural landscapes have been identified as important P storage sites (Neidhardt, Achten, Kern, Schwientek, & Oelmann, 2019). During natural runoff generation events, runoff water from surrounding agricultural areas is intercepted by these buffers resulting in the removal of P and sediment from runoff water and stored within the VBS (Mateo-Sagasta et al., 2018; Roberts et al., 2012). Within the relevant scientific literature, VBS have a clear effect of reducing TP loads from runoff into surface waters (Hoffmann, Kjaergaard, Uusi-Kämppä, Hansen, & Kronvang, 2009; Uusi-Kämppä & Jauhiainen, 2010). The majority of this reduction corresponds to retention of PP from diffuse pollution sources that are transported to the VBS by overland runoff (Hoffmann et al., 2009; Roberts et al., 2012).

In addition to nutrients from agricultural fields, runoff from manure and feed storage facilities for livestock operations can contribute nutrient loads to waterways as a point source of pollution (Mateo-Sagasta et al., 2018). While relatively smaller in area, these agriculturally intensive zones often contribute highly-concentrated inputs of nutrients to surface water bodies (Gebrehanna, Gordon, Madani, Vanderzaag, & Wood, 2014). For livestock operations adjacent to waterways, a VBS can be ineffective in reducing nutrient loading into surface water bodies (Price, Plach, Jarvie, & Macrae, 2021) as the nutrient loads in these 'end of pipe' runoff volumes are too concentrated to be effectively buffered. As a result specific, engineered buffers and wetlands are sometimes used to maximize the residence time of wastewater and provide a greater volume of soil and vegetation to uptake excess nutrients (Zak et al., 2019). Many manure management plans incorporate some sort of constructed wetland for this purpose, as it allows for rudimentary treatment of point-source agricultural waste water before discharge into the environment (Gottschall, Boutin, Crolla, Kinsley, & Champagne, 2007).

The processes of phosphorus transport within the landscape are commonly split up into three distinct process types: physical, biological, and geochemical retention pathways (Kieta et al., 2018; Roberts et al., 2012). The transport of P in agricultural settings during the non-growing season is typically governed by physical processes, while in VBS physical, biological, and geochemical processes dictate P transport (Boomer & Bedford, 2008; Roberts et al., 2012). In the following sections, details of those processes relevant to VBSs is reviewed.

2.2.1 Phosphorus Retention Mechanisms in VBS

Physical retention of sediment within a VBS strip occur as a result of a reduction in flow velocity and increased rates of infiltration. The vegetation acts to slow water movement due to the hydraulic resistance provided by stems and roots present, which helps to trap sediment before they reach adjacent streams (Dosskey et al., 2010). This is an important physical retention function of buffers as P can easily adsorb to fine sediment within water, and slowing the flow allows these fines to settle out (X. Liu et al., 2008). The roots of the perennial vegetation cause an increase in soil infiltration rates in the VBS, further increasing physical retention mechanisms (Dosskey et al., 2010; X. Liu et al., 2008). Non-uniform, channelized flow decreases the effectiveness of VBS, and in work by (Tollner, Barfield, Haan, & Kao, 1976), they showed that the efficacy of VBS increased when subjected to a shallow and uniform overland flow. This increased the total area of the VBS engaged in filtering runoff, thereby increasing sediment trapping efficiencies.

Phosphorus within a VBS system can be used for biological processes by the VBS vegetation or microbial pools that are present within the soil and root structure of the plants. Phosphorus will cycle regularly between these plant, microbial, and soil pools depending on the needs of the biologic communities. For P incorporated into organic compounds, microbial communities can metabolize (i.e., mineralization) much of the organic P pools and make them available to plants as orthophosphate (Malhotra et al., 2018). In plants the uptake of P is mediated by active transport against the concentration gradient between soils and the vegetation tissue as the high affinity of P to bind to soil constituents decreases the presence of available orthophosphate in the soil matrix (Malhotra et al., 2018). Plants also have the ability to release root exudate compounds, which can change the surrounding soil geochemistry to promote bound P release and therefore biological uptake (Roberts et al., 2020). All of this occurs in order to transform labile forms of P in deposited sediment into organically incorporated non-labile forms (Hinsinger, 2001; Stutter et al., 2009). Plants add additional organic matter to the surrounding soils when they senesce, which adds Carbon to the soil and helps the microbial communities further decompose and uptake nutrients (Dosskey et al., 2010). In this way, nutrients that were initially present within hydraulic inputs to the VBS are then incorporated into biological tissues of microbes and vegetation. In a review of buffer functioning, it was found that microbial and plant bound P could account for up to 45% of total VBS soil P, indicating the importance of biological pools (Roberts et al., 2012).

There exists the potential for some vegetation to exhibit what is referred to as luxury P uptake when provided access to ample supplies of P. This is the process of vegetation incorporating more P than is necessary for growth into biomass, resulting in an increase in the concentration of P in vegetative tissues. In this way, it can be thought of as ‘superfluous’ or ‘emergency’ stores of P. It is hypothesized that this is an adaptation to survive through the sudden absence of P (Kröger et al., 2007) and in agronomy research, luxury P uptake by corn has been found to actually decrease economic yields (Heckman et al., 2003; Penn, Camberato, & Wiethorn, 2023). While there is some indication of luxury P uptake by wetland plants and trees (T Ericsson, 1994; Kröger et al., 2007) as well as by algae in aquatic environments (Solovchenko et al., 2019), this process has not been well researched for typical VBS type vegetation taking up excess soil P.

The soil of VBS can play a major role in geochemical nutrient retention, and has been found to be the dominant form of P retention in many buffers (Hoffmann et al., 2009). Phosphorus is mainly found in agricultural runoff as PP, which is adsorbed to the surface of particulates, often through available metal or organic cations of soil constituents (Alvarez, Evans, Milham, & Wilson, 2004; Boomer & Bedford, 2008; Surridge, Heathwaite, & Baird, 2007). Under aerobic conditions, common redox sensitive metal ions found in soils such as Manganese and Iron will remain in an insoluble oxidized state that readily binds phosphate molecules, which are anionic, thereby fixing the phosphorus in place (Patrick & Khalid, 1974). When the soils become saturated with water, the anoxic conditions causes the reduction of the metal ions (Hoffmann et al., 2009), and P that was bound to the metals will disassociate and enter solution as SRP (House, 2003; Roberts et al., 2012), particularly in organic soils typical of VBSs (Zak et al., 2019). These organic soils also contain abundant soil organic acids compared to mineral soils, and this is known to further inhibit the creation of stable calcium phosphates (Alvarez et al., 2004). Available phosphorus is then found in the soil solution in the form of negative orthophosphate ions (Hinsinger, 2001), the specific species being determined by the relative organic acid abundance and pH of the soils (Figure 2-1).

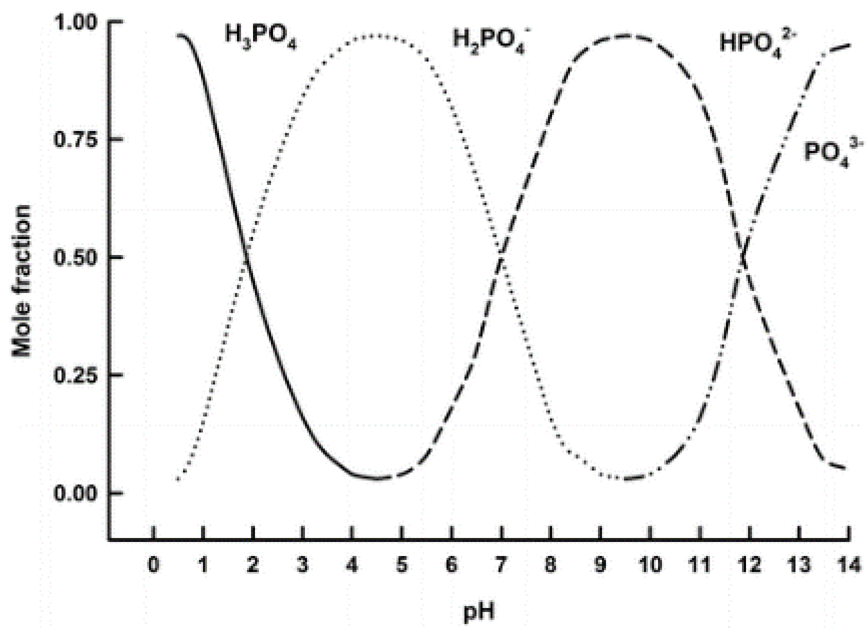


Figure 2-1: Ionic forms of phosphate depending on pH of solution. Taken from (Boyd, 2015)**.**

Due to the propensity of phosphorus to bind to organic and inorganic particles, it has limited vertical translocation within a soil column (Hinsinger, 2001). Because of this, surface soil typically contain greater pools of P than subsurface soil (Jackson, 2000; Wilson, Elliott, Macrae, & Glenn, 2019) and most studies investigating soil P mobilization from the landscape focus on near surface soils (Roberts et al., 2012). Repeated cycling between anoxic and oxygenated conditions can cause a shift in soil P chemistry towards more labile forms of P (Ajmone-Marsan, Côté, & Simard, 2006). Therefore, highly fertilized soils that experience episodic flooding and drying throughout the year such as those within VBSs will have increased risks of P release (Scalenghe, Edwards, Barberis, & Ajmone-Marsan, 2014).

2.3 Factors Influencing Phosphorus Retention in VBS

Despite ongoing P reduction practices being employed in many agricultural jurisdictions, the issue of eutrophication remains. Whereas PP losses were initially identified as the primary driver, there is growing evidence that SRP is the cause of more recent eutrophication issues (International Joint Commission, 2014). The wide adoption of no-till versus conventional till as an agricultural practice is believed to have contributed to this through nutrient stratification in the soil column, as no-till increases the potential for SRP losses from the topsoil despite reducing PP losses (Cade-Menun, Carter, James, & Liu, 2010). With an increased emphasis on understanding the processes of P retention by VBS in recent years, there is a general consensus that VBS are inefficient in removing SRP from runoff and operate primarily through the reduction of PP (Vidon, Welsh, & Hassanzadeh, 2019), and that they do not permanently store P and typically only change the timing and speciation at release, as many of these VBS actually exhibit a net release of dissolved P species (Roberts et al., 2012). This net release can be caused by the increased biological activity in VBS, where plants and microorganisms uptake P from the soil and subsequently remobilize it (Roberts et al., 2012). There is additional speculation that VBS could 'leak' significant SRP through subsurface flow (Vidon et al., 2019). As SRP is considered of greater importance to current eutrophication issues (Environment and Climate Change Canada, 2018), it is important to ensure a complete understanding of the factors that contribute to VBS inefficiencies.

2.3.1 Altered Function of VBS in Cold Climates

Many studies investigating the mechanisms and function of VBS occur during the warmer growing season when they are at their most effective (X. Liu et al., 2008; Roberts et al., 2012). However, there are agriculture-intensive areas within cold climate regions, such as in North America and Northern

Europe. In these regions there is a dramatic impact during the NGS on hydrology (frozen soils, decreased infiltration), seasonal discharge fluctuations (dramatic snowmelt discharges), shorter growing season, and leaching of P from frozen vegetation (Kieta et al., 2018) that can all impact the P dynamics within a VBS.

In cold climates NGS runoff accounts for a large percentage of annual runoff volumes and nutrient loads (Liu et al., 2019) which can dramatically impact the effectiveness of VBS. In an analysis of nutrient loads in discharge from several Manitoba watersheds, 62% of annual TP loads occurred during a 12-18 day snowmelt period in 3 years of the study (Rattan et al., 2017). Similarly in a study conducted in southern Ontario by (Plach et al., 2019), the monitoring of nutrients in the annual outflow from several agriculture dominated watersheds showed that the vast majority of TP losses occurred during the NGS. Of these losses, the largest discharge events and nutrient loads in surface water was observed following major snowmelt periods in the early spring (Plach et al., 2019). Sub-watersheds in Alberta were similarly dominated by spring snowmelt discharge that accounted for 90% of the runoff volume during the years of a particular study (Little, Nolan, Casson, & Olson, 2007).

The particular species of P lost (dissolved fractions or particulate) in NGS runoff is also an important factor for VBS functioning in cold climates, as SRP and PP are retained through different mechanisms and PP in runoff is reduced by the frozen soils typical of the NGS (Stock et al., 2019). Snowmelt and rain on snow event driven runoff during the NGS typically produce a higher DRP:TP ratios than rain driven runoff as shown in a study by (Hoffman, Polebitski, Penn, & Busch, 2019). They saw hydrologic events driven by snowmelt or precipitation events near freezing temperatures to have 74% and 84% of TP in a dissolved form, compared to 39% for typical rain events throughout the rest of the year (Hoffman et al., 2019). This lack of PP and increase in TDP of NGS runoff is seen in another study examining NGS nutrient loads from several small Alberta sub-watersheds (Little et al., 2007). As noted previously, VBS have reduced abilities to filter out TDP, and inundation during high flows has the potential to release additional P stores from soils (Roberts et al., 2012). The combination of high flows, high nutrient loads, and increased TDP:TP ratios that occur during the NGS all contribute to the ineffectiveness of VBS functioning through the neutralization of the main buffering mechanisms that are optimized under shallow flow conditions and target predominantly PP species (X. Liu et al., 2008; Tollner et al., 1976).

During the large snowmelt induced runoff events of the NGS, the vegetation of a VBS is in a dormant stage with very little nutrient uptake (Kelly, Kovar, Sokolowsky, & Moorman, 2007), as are microbial soil pools (Blackwell et al., 2010). In addition to reduced VBS effectiveness linked to limited hydraulic retention abilities, the vegetation is also subjected to freeze-thaw cycles (FTC) which can induce the mobilization of vegetation bound P pools through the lysing of plant cells (Webb, Uemura, & Steponkus, 1994). There exists a strong ability for the release of SRP during freezing conditions by most vegetation, and research has attempted to quantify the extent of phosphorus release since the 1970s (Timmons, Holt, & Latterell, 1970). This FTC induced P release in agricultural residue (Roberson, Bundy, & Andraski, 2007) as well as cover crops (Cober et al., 2018; Lozier & Macrae, 2017) draws important conclusions regarding the species specific susceptibility to FTCs, with a variation in results between frost tolerant and intolerant species. Vegetation in Canada has been shown to have similar FTC susceptibilities between two common wetland plant species, Typha and Phragmites (Whitfield et al., 2019). Variation in P loss susceptibility for other VBS species, such as native grasses, is not as well studied.

The fate of vegetation released P due to FTCs is uncertain, as soils retain the ability to adsorb some P even during the NGS. In a study of cover crop nutrient release potential, field scale runoff losses of P were far less than potential cover crop P losses, indicating most vegetation derived P was adsorbed to surrounding soils (Lozier, Macrae, Brunke, & Van Eerd, 2017). Long term studies of runoff through VBSs in Finland indicate that FTCs cause vegetation to release P which is then geochemically adsorbed by the immediate VBS surface soils (Uusi-Kämppä & Jauhiainen, 2010), resulting in an increase in SRP in spring runoff when the saturated soils release the bound P. In a watershed level study, the finding that NGS SRP loads from agricultural watersheds were nearly identical to those from non-agricultural prairie grassland watersheds (Little et al., 2007) was attributed to the release of SRP from senesced vegetation during the snowmelt period, which presumes those soils are unable to buffer that pulse of P. Therefore, the risk of NGS vegetation P release to surface water in VBSs is still unclear. Seasonal differences in soil and vegetation P pools at the start and end of the NGS could inform the fate of vegetation P pools in Canadian VBSs.

2.3.2 Effect of Elevated Soil P Concentrations on P Dynamics in VBS

In contrast to the agricultural soils they border, VBS soils exhibit elevated levels of organic matter and SRP compared to adjacent field soils (Neidhardt et al., 2019; Stutter & Richards, 2012). The degree of phosphorus saturation (DPS) is also increased in agricultural VBS soils versus VBS in a more natural state indicating that VBS soils exposed to high P runoff in agricultural settings have some characteristics of P saturation (Neidhardt et al., 2019; Stutter et al., 2009). While the surplus of nutrients is useful for vegetation, the proximity of these buffers to surface water makes them particularly susceptible to having those nutrient stores be transported by runoff. As noted previously, the anoxic conditions in soils created by flooding and runoff causes additional geochemical release of bound P species into dissolved forms (House, 2003; Roberts et al., 2012). Due to high soil P levels, the geochemical buffering ability of these systems could be compromised over time and contributing to the ineffective retention of TDP (Dodd & Sharpley, 2016; Stutter et al., 2009).

A study focused on 13 buffer areas in Manitoba by (Satchithanantham, English, & Wilson, 2019) investigated the release of nutrients by VBS when exposed to simulated runoff. They observed a strong correlation between soil test P levels (Olsen-P) and SRP in simulated spring and summer runoff from these buffers, with high soil P soils lacking P uptake and releasing additional P to runoff. The seasonality did not affect the SRP concentrations in runoff, indicating primarily abiotic processes through soil adsorption/desorption reactions were the drivers of SRP loss. This relationship has been observed through other studies on runoff over agricultural soils (Aye, Nguyen, Bolan, & Hedley, 2006; McDowell, Nash, & Robertson, 2007; Roberson et al., 2007) resulting in some researchers using soil-test P levels as an indicator for the potential SRP losses in runoff (Amarawansha, Kumaragamage, Flaten, Zvomuya, & Tenuta, 2016).

It has been suggested that the implementation of vegetated swales or similar engineered buffers in place of VBSs would prove more effective at removing nutrients from agricultural runoff by increasing the contact time of runoff with buffering soils and targeting areas of concentrated runoff (Sheppard, Sheppard, Long, Sanipelli, & Tait, 2006). However, even wetlands and retention ponds have the potential to become sources of P as over time the geochemical saturation of the soils and sediment increases through the same processes that occur in agricultural buffers (White, Bayley, & Curtis, 2000). Therefore, both agricultural VBS and remediating wetlands have limited lifespans, as without management of soil P levels they will eventually become sources of P in the landscape.

While the short term mechanisms of P transport through VBSs are well understood, there remains speculation on the long term functionality of these systems as over time the buffers collect high P loaded sediment and become a net source of P loading to waterways (Baulch et al., 2019; Dodd & Sharpley, 2016; Dorioz, Wang, Poulenard, & Trévisan, 2006). Effective management of VBSs is identified as a critical area to research in order to address the long term efficacy of these systems (Haddaway et al., 2018).

2.3.3 Topography as a Driver of Dissolved Phosphorus Dynamics

Due to their inherent proximity to watercourses, VBSs are particularly susceptible to P losses compared to more terrestrial zones of accumulated soil P. During periods of high flow, including spring snowmelt, buffers are likely to be inundated, promoting the release of TDP to waters from the highly P saturated soils (Gu et al., 2017). Topography has been identified as the key driver to TDP losses from VBS due to the frequency of rewetting events after dry periods and duration of inundation which in turn drove the geochemical release of soil P (Gu et al., 2017). These flooded conditions are also likely to extract more nutrients from senesced VBS vegetation during the NGS, as was shown for cover crops under similar circumstances (Lozier & Macrae, 2017). Therefore, sections of the VBS that experience flooding are expected to have depleted soil and vegetation P pools when compared to non-flooded sections. Lower areas of the VBS are more likely to experience these fluctuating water levels, resulting in enhanced P mobilization compared to sections of the VBS further upland. Upper zones of a VBS are also more likely to have a higher P saturation than lower zones due to intercepting initial edge of field runoff and filtering sediment and nutrients out before they reach lower zones (Habibiandehkordi, Lobb, & Owens, 2019). Despite this, there is a lack of studies that specifically compare soil and vegetation P pools in VBS before and after these wet periods, at both wet lower zones and dry upper zones, to determine if any topographic stratification of soil P pools exist. In addition, there is little work investigating how the seasonality of cold climate regions may affect these hydrologic extractions. This information could prove valuable when addressing the possibility of management strategies to reduce excess P pools in VBS.

The larger scale topography of the region could also impact the P dynamics in VBS by altering the predominant hydrologic pressures experienced (Hoffmann et al., 2009). In the Canadian prairies, the low relief landscape leads to VBSs that have gentle slopes and so are susceptible to concentrated flow paths due to ponding which occurs at the field edge, resulting in a quicker and more complete P saturation of soils (Baulch et al., 2019). The prairies also have distinct wet and dry periods, with many ephemeral watercourses, and typically experience a severe wet period in the spring which hydrologically connects a large proportion of the landscape (Baulch et al., 2019; Habibiandehkordi, Lobb, & Owens, 2019). In contrast, the varied topography of much of Southern Ontario prevents large scale landscape hydrologic connection, though even this is variable throughout regions of Southern Ontario (Macrae et al., 2021). In these areas, P losses are more likely linked to NGS surface runoff rather than the inundation that is typical in the prairies (Plach et al., 2019), and more varied topography decreases the chances of concentrated flow paths through the VBS (Baulch et al., 2019). Therefore, a difference in NGS P losses is expected between these regions that can be attributed to major landscape drivers.

2.4 Management of High Soil Phosphorus Through Vegetative Mining

The active management of VBS vegetation has been proposed as a solution to alleviate VBS P losses and to increase overall P buffering capabilities (Dorioz et al., 2006; Dosskey et al., 2010; Hénault-Ethier et al., 2019; Kelly et al., 2007; Walton et al., 2020). In an actively managed VBS, vegetation is cut and removed (harvested) from the buffer near the end of the growing season which reduces the potential NGS P losses through the removal of easily mobilized vegetation bound P pools (Uusi-

Kämppä & Jauhiainen, 2010). This harvesting of vegetation can also decrease overall soil P pools over time as the vegetation acts as soil nutrient pump to decrease VBS soil P through plant extraction (Salm, Chardon, Koopmans, Middelkoop, & Ehlert, 2009). This can be referred to as vegetative mining, as the vegetation serves as a method of nutrient extraction from the soils. Studies investigating the efficacy of vegetative mining on maintaining VBS functionality have been carried out in various regions of the world with mixed results (Brown et al., 2019; Dal Ferro et al., 2019; Hille et al., 2019; Räty, Uusi-Kämppä, Yli-Halla, Rasa, & Pietola, 2010). Although removal of vegetation biomass clearly removes the vegetation pools from leaching during the NGS, there is less evidence on the impacts vegetative mining can have on overall buffer functionality and in effectively reducing VBS soil P pools (Hille et al., 2019). There is also some uncertainty related to which vegetation species are best for vegetative mining purposes, which is compounded by the fact that even past vegetation can impact the nutrient loss susceptibility in VBSs (Dosskey et al., 2010).

In order to maximize VBS effectiveness during the growing season, the harvesting of buffer vegetation is typically conducted in the late fall. Ideally this will happen before the first frost, as there is a dramatic decrease in buffer plant nutrients (N and P) after the first autumn frost (Räty et al., 2010). This management through harvesting at the end of the growing season allows buffers to retain their nutrient and sediment trapping function throughout the year, while reducing the potential for nutrient release when the plants decay in the NGS (Uusi-Kämppä & Jauhiainen, 2010). Predictive models built to determine the change in VBS nutrient retention indicate that this end of growing season harvest of buffer vegetation may actually slightly improve the overall P reduction potential (Jiang, Preisendanz, Veith, Cibin, & Drohan, 2020).

The harvesting of buffer vegetation has also been shown to be useful from an ecological standpoint as low frequency harvesting (1-2 times a year) can shift the species composition of low diversity buffers to a higher diversity of species (Hille, 2018). While a higher vegetation diversity does not correlate to an increase or decrease in P retention capabilities (Kervroëdan, Armand, Saunier, & Faucon, 2019) the ecological advantages are important to consider.

Although the positive effects from vegetative mining on buffer nutrient losses are well documented, there remains a need for long term studies that evaluate the impact of buffer vegetation harvest over decades rather than years (Dorioz et al., 2006; Roberts et al., 2020). In addition to sediment and nutrient trapping, buffer vegetation impacts the biogeochemistry of these ecotones in other ways such as the build-up of vegetation detritus, which adds organic matter to the soil (Dosskey et al., 2010). The addition of organic matter and carbon from detritus is important for nutrient cycling in these buffers, and the long term effects of a reduction in organic matter additions to buffer soils is unclear (Stutter & Richards, 2012).

The effectiveness of vegetative mining will depend greatly on the specific climate, vegetation species, and topography of the locations in question. Understanding the potential impact of buffer management strategies on Canadian landscapes is an important step moving forward towards the effective usage of VBS. Questions remain as to what vegetation types are most effective in an actively managed VBS, as well as whether the nutrient content of natural buffer vegetation mimics the soil P content in which it grows.

2.5 Thesis Objectives

The overall objectives of this thesis are to determine:

1) Does topography affect P mobilization in vegetated buffer strips and does this differ with freezing severity and exposure to inundation?

2) Are vegetation P pools correlated to the soil P level in vegetated buffer strips both with and without freezing?

The thesis is structured according to these questions, in which Chapter 3 and Chapter 4 address the 1st and 2nd questions above, respectively. Each chapter examines these themes in more detail by addressing several more specific research questions. Research presented in Chapter 3 aims to answer the following: (1) do potential SRP losses from vegetation and soils differ between upslope and downslope regions of buffer strips; (2) do P concentrations in soil and vegetation differ between samples collected in fall and spring and are these changes impacted by the occurrence of flooding in the riparian zone; (3) if potential P losses from vegetation are impacted by frost severity; and (4) is there an observed decrease in P losses in simulated runoff following the harvesting of buffer vegetation. The research questions in Chapter 4 are: (1) Does quasi-natural vegetation (predominantly grasses) grown in soils with elevated P have greater P accumulation than vegetation grown in soils with smaller amounts of P; and (2) Are increases in water extractable P following freezing are greater in vegetation grown in P-rich soils?

Chapter 3
Spatial Differences in Potential Phosphorus Mobilization from Vegetated Buffer Strips

3.1 Overview

The mobilization and transport of agricultural sources of Phosphorus (P) is increasing the delivery of P to surface water bodies, contributing to a host of water quality impairments including eutrophication (Mateo-Sagasta et al., 2018; Schindler, 2012). Vegetated buffer strips (VBS) are important components of the landscape with respect to the nutrient transfer continuum, and consequently, their implementation in agricultural areas is often encouraged to trap P and alleviate the transfer of P from land to water. Through physical, geochemical, and biological processes within a VBS, both particulate P (PP) and dissolved P as either NRP or SRP loading into surface waters can be reduced (Roberts et al., 2012). However, recent work in landscapes with cold climates has called their efficacy into question (Kieta et al., 2018).

Many agricultural systems across the world are found in cold climates, which are defined in the Koppen-Geiger climate classification system as regions where the average temperature is greater than 10^0C during the hottest months and less than 0^0C during the coldest months (Peel, Finlayson, & McMahon, 2007). During the non-growing season in cold climates, many of the characteristics and processes that allow VBS to retain nutrients do not function effectively (Kieta et al., 2018). For example, the freezing and thawing of vegetative tissue accelerates the release of biological nutrient pools stored in vegetation (Øgaard, 2015; Whitfield et al., 2019), which can lead to elevated TDP losses during thaw events or snowmelt (Kieta et al., 2018). In addition, the slowing of runoff and associated deposition of PP or the buffering of TDP in the subsurface following infiltration are hampered under cold conditions due to the lack of living vegetation cover and the frozen soil. Indeed, concentrations and loads of P can be elevated during winter thaws and/or the spring snowmelt period in cold regions (Hoffman et al., 2019; Kokulan et al., 2019; Macrae, English, Schiff, & Stone, 2007a) and there is evidence that VBS may be a net source of this P loss (Kieta et al., 2018). However, the potential contribution of VBS to overall watershed P losses over this period are neither well understood nor quantified.

Studies have linked the concentrations of TDP in runoff through VBS to P concentrations in surface soils within the VBS (Wilson et al., 2019), which can be elevated due to the repeated physical deposition of high P sediment in runoff and the adsorption of P by soil constituents (Aye et al., 2006; Habibiandehkordi, Lobb, Owens, & Flaten, 2019). This loading can result in VBS soils reaching a high level of P saturation which greatly reduces their ability to geochemically adsorb any additional P (Stutter, Chardon, & Kronvang, 2012). If left unmanaged, this continued saturation of VBS soils causes the efficacy of VBS to diminish over time (Uusi-Kämppä & Jauhiainen, 2010). Due to these factors, VBS often exhibit net P release into adjacent surface waters, which is the inverse of their intended function (Baulch et al., 2019; Stutter et al., 2009).

The release of P from vegetation in VBS may differ regionally, within regions or even within a given VBS. Although vegetation in fields such as crop residues or cover crops have been shown to be a P source to runoff in cold regions (Elliott, 2013; J. Liu et al., 2019), it is not clear if this is also true of the perennial vegetation found in VBS. The quantity of P released from cover crops and residues increases with both frost magnitude (Cober et al., 2018) and contact time with water (Lozier & Macrae, 2017), and also differs with vegetation type (Cober et al., 2018; Elliott, 2013; Lozier & Macrae, 2017). However, P released by cover crops and crop residue following freeze-thaw cycles (FTCs) can also be rapidly adsorbed by soil in agricultural fields rather than transported in runoff

(Lozier & Macrae, 2017). It is unclear if, and to what extent, natural buffer vegetation may be as susceptible to nutrient loss following FTCs, and if this susceptibility changes with different vegetation species, different soil P concentrations or differences in freezing conditions (i.e., regions with different winter severity). Although the efficacy of VBS in the prairie region of Canada have been the subject of a variety of studies (Kieta, Owens, Vanrobaeys, & Lobb, 2022; Vanrobaeys, Owens, Lobb, Kieta, & Campbell, 2019) the drivers of VBS functionality have not been investigated as thoroughly in the Great Lakes basin region of Southern Ontario (Baulch et al., 2019; Kieta et al., 2018). Although this section of Ontario is still a cold climate region, the winters are typically milder with larger snowpacks than the Canadian prairie regions (Environment and Climate Change Canada, 2022). There is some reason to believe the frost susceptibility of VBS vegetation may differ between the regions (Whitfield et al., 2019), or that the increased snowpack and milder winter may impact P retention in VBS.

The susceptibility of VBS vegetation to release P in winter may also differ with topographic position within the VBS, and P may not be supplied equally across a given VBS. Elevated soil P levels are typically observed within the first two meters of the VBS due to the deposition of the majority of sediment and initial contact with nutrient rich runoff water (Habibiandehkordi, Lobb, & Owens, 2019; Uusi-Kämppä & Jauhiainen, 2010). Soils that are elevated in P are less capable of adsorbing TDP in runoff waters, and vegetation growing in soil with higher P content may in turn also take up more P, which could be released following FTC (Kröger et al., 2007). In contrast, sections of VBS closer to the water edge are more likely to experience anoxic conditions from flooding and/or high water table, which could aid in the release of geochemically bound soil P (Walton et al., 2020). As a result, there could be significant topographical trends in nutrient content in vegetation, and the potential for nutrient release for VBS systems. If so, this could affect the approach used to effectively manage these VBS and reduce their P loading.

The management of VBS vegetation through cutting and harvesting has been proposed by several studies as a means to reduce buffer soil P as well as remove P in vegetative biomass that would be mobilized over the NGS (Hille et al., 2019; Roberts et al., 2020; Stutter et al., 2009). The efficacy of this method to alleviate issues with VBS would depend on the ability of the vegetation to take up soil P, as well as soil P levels themselves. Some studies have indicated that the harvesting of buffer vegetation by itself results in an average reduction of soil P by about ~3% per year (Hille et al., 2019). While there are a variety of studies that investigate the P mining potential of buffer vegetation in other parts of the world (Dal Ferro et al., 2019; Räty et al., 2010; Sturite, Henriksen, & Breland, 2007), there is a lack of research on VBS management in cold regions, particularly Canadian landscapes. In addition, the potential topographic gradient of soil and/or vegetation P content might implicate the preferred harvesting of upper or lower zones of the VBS, which would leave portions of the vegetation in place for sediment and nutrient retention throughout the year.

For an improved understanding of spatial differences (topography, winter severity, soil P in upland fields) in potential P release from VBS in cold regions, an experiment was set up using a factorial design. Vegetation and soil samples were collected from different topographic positions from VBS and adjacent fields in both Ontario (moderate winter climate) and Manitoba (severe winter climate) during the Fall and analyzed for Water Extractable Phosphorus (WEP), TP, and Olsen P. A second round of samples was collected after the NGS during the Spring to compare changes in P pools. In the laboratory, Fall samples were subjected to different freezing treatments to examine the impacts of freezing severity. In the field, hydrologic and temperature conditions were monitored throughout the NGS with deployed field equipment.

The specific objectives addressed in this chapter are to determine if: (1) potential SRP losses from vegetation and soils differ between upslope and downslope regions of buffer strips; (2) P concentrations in soil and vegetation differ between samples collected in fall and spring and are these changes impacted by the occurrence of flooding in the riparian zone; (3) potential P losses from vegetation are impacted by frost severity; and (4) a decrease in P losses in simulated runoff is observed following the harvesting of buffer vegetation. It is hypothesized that both vegetation and soils near the field edge have elevated WEP relative to lower topographic positions due to their proximity to field runoff and less frequent exposure to surface flooding. It is also hypothesized that the vegetation will have greater WEP following severe freezing than moderate freezing, suggesting that VBS in colder regions may be more susceptible to winter P release from vegetation. Additionally, it is hypothesized that the harvesting and removal of vegetation cover will reduce P release from VBS following winter freezing.

3.2 Site Description and Methods

3.2.1 Study Site Selection

Eight VBS sites were selected for this study, four in Ontario and four in Manitoba (Table 3-1). A range of sites were chosen within each region to represent a variety of typical VBS types, and also based on ease and permission of access. All sites were located adjacent to agricultural land surrounding defined drainage ditches or water bodies. None of the sites had active management/ cutting of the VBS except for site STC, which had periodic cattle grazing during dry conditions.

The predominant soil textural class at the sites ranged from loam to clay (Table 3-1). Agricultural land use was for cash crop production with the exception of site MBFI which was pasture for cattle, although in the past it was used for cash crop production. Additional site details are provided in Table 3-1.

Table 3-1: Additional details of each site, or group of sites if in same geographic location. Predominant soil type gathered from Soil Survey of Canada (Agriculture and Agri-food Canada, 2022). Climate data represents climate normal for the years of 1980-2010 from nearest federal climate station (Environment and Climate Change Canada, 2022).

Site	MH1/MH2	ESS1/ESS2	STC	MBFI	ELM1/ELM2
Province	Ontario	Ontario	Manitoba	Manitoba	Manitoba
Field Use (2020)	Soybeans/Corn	Soybeans	Wheat	Pasture	Corn
Sample Dates	Sept 14th 2020 – April 13th 2021	Sept 21st 2020 – April 15th 2021	Sept 28th 2020 – April 1st 2021	Sept 29th 2020 – April 1st 2021	Oct 8th 2020 – March 29th 2021
Main Soil Type	Guelph (Loam)	Brookston (Silty-clay loam)	Dezwood (clay-loam)	Newdale (clay loam)	Thalberg (clay)
			Annual Meteorological Conditions		
Total Precipitation (mm)	916.5	882.3	545	474.2	578.3
Snowfall (cm)	159.7	79.2	100.3	117.8	113.9
Average Daily Temperature (^{0}C)	7	9.8	3.5	2.2	2.8
			Non-Growing Season Meteorological Conditions (Oct – Mar)		
Average Daily Temperature (^{0}C)	-0.9	+1.9	-7.2	-8.7	-8.0
Mean Minimum Daily Temperature (^{0}C)	-5.2	-1.7	-12.0	-14.0	-13.0

3.2.2 Experimental Design

Two experiments were conducted in this study, the first to examine the impacts of both topography and climate (freezing severity) on water extractable P release from vegetation in VBS, and the second to investigate the potential effects of vegetation management (unmanaged, mowed, harvested) on potential SRP release from vegetation following FTC and simulated runoff.

Experiment 1. Topography and Climate

Vegetation and soil samples were collected from three or four zones at each site across all eight sites (four Ontario, four Manitoba) and analyzed for WEP, TP (vegetation) and plant available soil P (Olsen P). Sampling was conducted twice, at the beginning and end of the 2020/2021 NGS to give an indication of seasonal changes in P content of soils and vegetation (Figure 3-1). Fall sampled vegetation was subjected to experimental temperature treatments: moderate (-4^{0}C, control) and severe freezing (-25^{0}C) to give an indication of the effects of freezing on vegetation WEP before the NGS. There was no 'unfrozen' treatment, so the moderate freeze typically expected from field conditions is the control for vegetation freezing effect analysis.

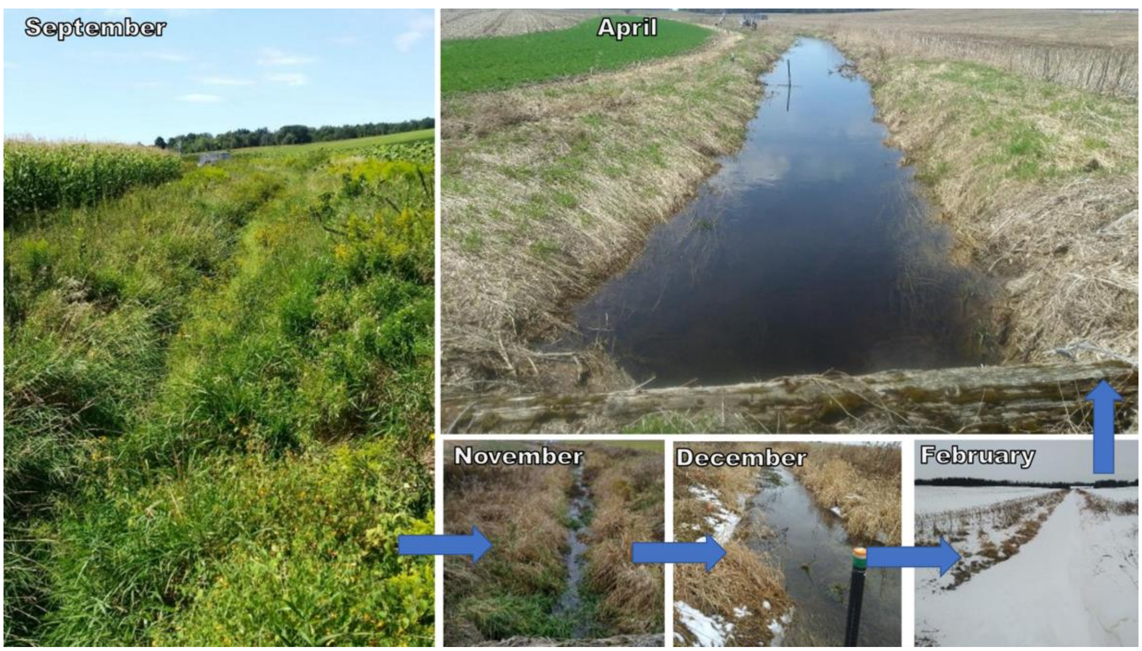


Figure 3-2: Pictures from site MH2 demonstrating the typical NGS conditions experienced at this site from the Fall to Spring sampling dates (September to April)

Experiment 2: Vegetation Management

Soil columns with intact (rooted) VBS grass from two topographic sampling zones (upper and lower) taken from site MH1 were subjected to one of three vegetation management techniques: intact (no treatment), cut, or harvest (Figure 3-2). Soil cores were subjected to severe freezing conditions (-25^{0}C) before ponding conditions were simulated. Resulting 'runoff' and remaining extracted vegetation residue was analyzed to determine vegetation management induced differences in P concentrations.

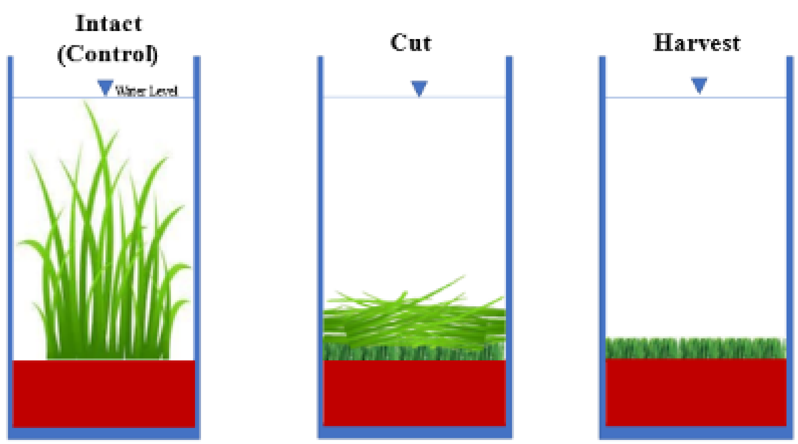


Figure 3-3: Diagram of intact soil/ vegetation mesocosms and the three applied treatments

3.2.3 Sample Collection and Field Instrumentation

Experiment 1: Topographic Experiment

Vegetation and soil samples were collected from the VBS sites at the beginning and end of the NGS. At each site, sampling zones were visually identified (by slope and proximity to field/ watercourse) to obtain samples from 3 distinct areas: Lower Zone, Upper Zone, and the Field (L, U, F). There was a 4th Transitional (T) sampling zone added between the Field and Upper Zone at sites ELM1 and ELM2 due to distinct vegetation differences, and at site STC due to an existing fence

(Figure 3-3), making a total of four sampling zones at each of these sites. All sampling areas were sampled for soil, while only the L, U, and T zones within the riparian area were sampled for vegetation. Field vegetation was not sampled as in most cases the field vegetation was harvested crops.

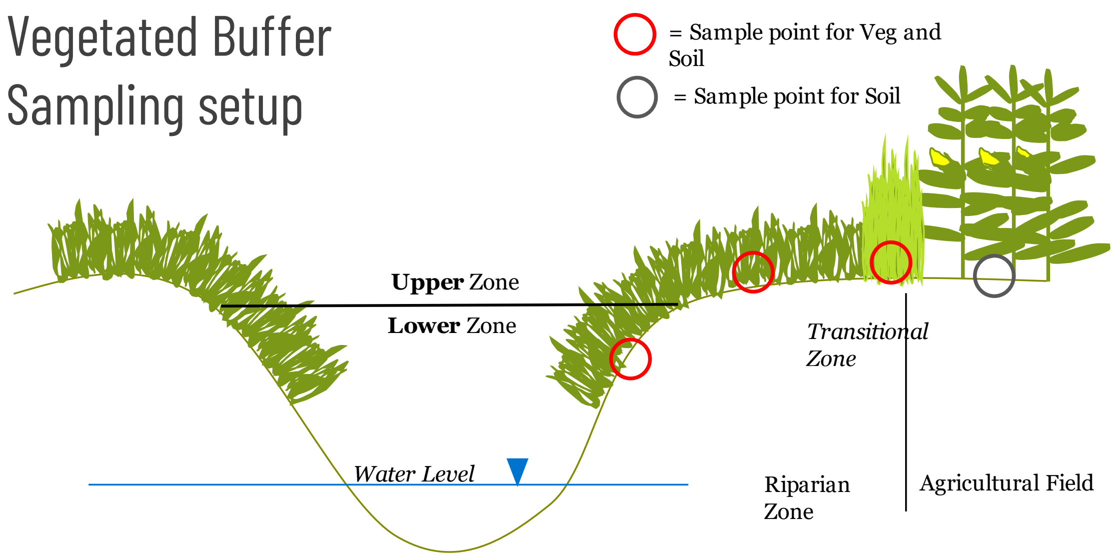


Figure 3-4: Sampling setup diagram of model vegetated buffer. Circles represent locations for sample acquisition (black for soil sample collection, red for both soil and vegetation sample collection)

Soil samples were obtained using a hand auger and a composite sample of the top 5 cm of soil was made from 10-15 soil samples per sampling zone (sampling zones roughly 3m x 0.5m transect parallel to watercourse). This was done in triplicate for each zone. Additional soil cores were taken for the determination of bulk density using standard techniques (*i.e.*, a cylinder of known volume was driven into the soil and then oven dried at 105^{0}C for 2+ days to obtain a dry weight per unit volume).

Vegetation samples were collected from 3 randomly selected sampling plots for each sampling zone. Vegetation was harvested with a serrated knife or electric clippers 5cm above ground surface in a 0.5m x 0.5m plot, giving a total area of $0.25m^2$. The total mass of the clipped vegetation gave a surface density of vegetation for each sampling plot (determined for both field moist and dry weights). Buffer vegetation was predominantly grass species in all zones. Where non-grass species were growing in relative abundance (>25% by visual estimate) those species were sampled in addition to the grass species by the same procedure outlined above. Non-grass species within the studied buffer sites consisted of goldenrod (*Solidago*, *Asteraceae*) in Ontario, a genus of tall flowering herbaceous perennial plants that typically grows in disturbed soil along field edges (MacKinnon et al., 2009). Individual species were not identified as the genus contains over 100 variate species. In Manitoba, the only non-grass species sampled were nettles (*Urticaceae, Urtica*), another herbaceous perennial plants (MacKinnon et al., 2009). While locations of nettle growth contained a variety of weeds, nettles were easily identified and numerous so taken as a representative species. However, this non-grass species sampling was simply meant to exemplify the variety in extractable P content and freezing susceptibility by plant type and are not included in later analysis unless explicitly mentioned.

Temperature sensors were installed on the soil surface of the upper and lower buffer zones (Figure 3-4) at each site to observe freezing temperatures experienced over the NGS for riparian vegetation (5TM Moisture/Temp sensors from Decagon Devices Inc. with EM-50 data logger from Onset Ltd., OR; HOBO TidbiT V2 Temperature sensor and logger from Onset Ltd.) The temperature probes were enclosed in radiation shields and put down between senesced vegetation on the soil surface. Water level loggers were placed in center of the stream flow path at all sites to measure fluctuating water levels over the non-growing season (HOBO U20-001-04 Water Level Logger from Onset Ltd.). The water level loggers were installed in perforated ABS pipes (Figure 3-4) and secured to stakes or rebar to ensure high flows and ice jams did not dislodge them. Water level logger readings were corrected for barometric fluctuations by a nearby barometric pressure logger. Both temperature loggers, barometric loggers, and water level loggers were downloaded every 2 months on average. Data was cleaned to omit obvious errors from logger malfunctioning or failure.

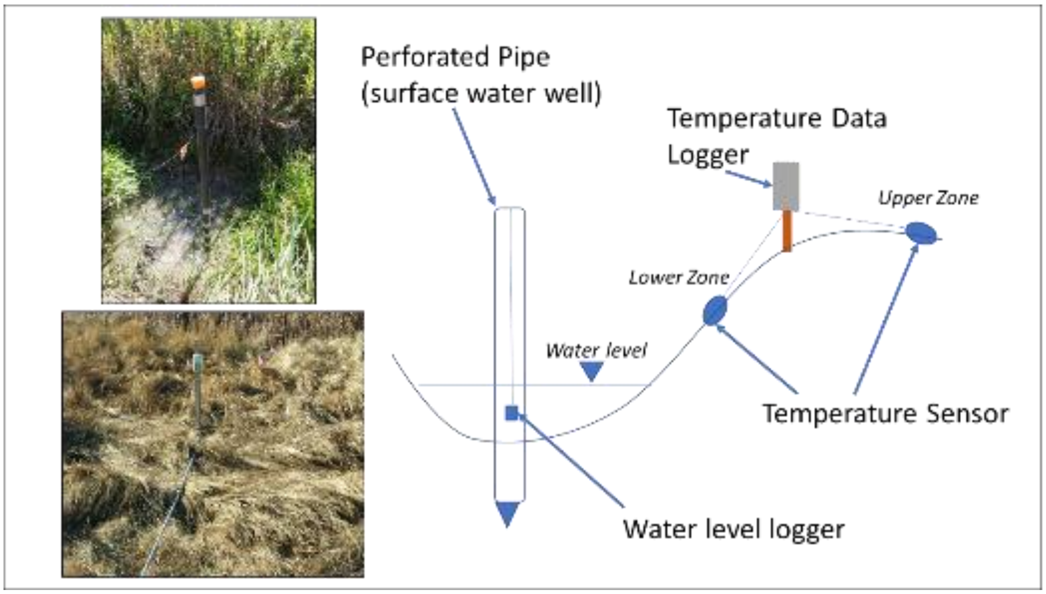


Figure 3-5: Pictures and Diagrams of Field Instrumentation to gather temperature and water level data at each site (EM50 temperature loggers depicted)

Experiment 2: Vegetation Management

Site MH1 was chosen for further analysis to uncover the effects of vegetation management on buffer functionality. This site was chosen as it was easily accessible to laboratory facilities and had a uniform topography over a large length of waterway, allowing more confidence in the samples being representative of field values. Sampling zones at the site were chosen so that only areas growing grass were sampled. Intact soil cores were obtained in order to gauge the effectiveness of vegetation management techniques through a laboratory experiment.

To obtain the soil columns, 10.2 cm (4”) diameter clear PVC cylinders were manually driven into the soil of either the Lower or Upper buffer zones. The cores were then dug out to minimize disturbance of the soil structure. Vegetation in the soil cores was subjected to one of the three management techniques (Figure 3-2); (1) – Intact (control): Vegetation was left uncut and unmanaged; (2) – Cut: Vegetation was cut 5cm above soil surface, then cut into 5 to 10cm lengths and placed back onto the soil column surface; (3) – Harvest: Vegetation was cut 5cm above soil surface and removed. From this we obtained 3 vegetation treatment columns from 2 sampling zones (upper and lower) with each combination of factors obtained in triplicate, resulting in 18 cores. Soils were manually extruded out of the base so that each cylinder had 5cm of soil to which the vegetation was rooted to.

3.2.4 Sample Processing and Experimental Treatments

<u>Topographic Experiment</u>

Soil and vegetation samples were stored in sealed polyethylene bags in ice-packed coolers and shipped to the University of Waterloo Biogeochemistry Lab for analysis. All samples were processed within 24 h of collection. Upon arrival, subsamples (3 g vegetation, 5 g soil) were oven dried at 65C to determine the gravimetric moisture content. These dried samples allowed calculations to be expressed in units of grams of dry mass, and dried samples were further utilized for TP (vegetation) and OlsenP (soil) analysis. For Olsen-P analysis, oven-dried samples were sieved (<2mm) prior to analysis. TP and OlsenP samples were not obtained for site ELM2. For determining frost susceptibility and release of P in buffer vegetation, field moist subsamples (3 g each) were subjected to one of two freezing conditions, either moderate (-5^{0}C) or severe (-25^{0}C) for 36 to 48 hours and subsequently extracted for the determination of WEP through the method described in the next section. Soil samples were not subjected to freezing but field moist samples were also extracted with water for the determination of WEP.

Vegetation Management Experiment

The soil/ vegetation columns from site MH1 were taken back to the lab and soil was extruded from the base and removed to ensure each core had only 5cm of soil. The cores were then capped on the top and bottom and subjected to a deep freeze treatment for 5 days (-18^{0}C). After the 5 days, cores were taken out of the freezer and the top cap was removed. The cores were then ‘flooded’ with 500mL of DI water and aerated periodically using a peristaltic pump to prevent stagnant and anoxic conditions, and to better simulate oxygen rich flood waters. The column flood water was syringe extracted after 1 day of flooding and the ‘simulated runoff’ was analyzed for TDP, SRP and TP. Vegetation samples were taken from intact and cut columns post freezing and flooding for additional WEP and TP analysis, following procedure outlined previously.

3.2.5 Analytical Methods

Water Extractable Phosphorus (WEP) was determined through the following procedure. Field moist samples (3g vegetation, 5g soils) were weighed out into 100 mL plastic cups. Milli-Q grade water was added, 90 mL for vegetation and 50 mL for soils resulting in weight:volume ratios of 1:30 and 1:10 for vegetation and soils, respectively. (Note: previous experiments showed the higher weight: volume ratio was needed to fully cover vegetation). Cups with sample and water were then capped and shaken at 250 RPM for 1 hour on a shaking table. Soil sample extractions were gravity filtered through a Whatman 42 filter into secondary plastic cups to ease the final filtering process, which was syringe filtered through a 0.45 μm cellulose acetate filter. Vegetation sample extractions were filtered only once through a 0.45 μm cellulose acetate filter.

TP content in plants was obtained through a digestion procedure involving concentrated sulfuric acid and a digest mixture (0.08% (m/m) Se powder, 2.76% (m/m) $Li_2SO_4*H_2O$, 30% H_2O_2 solvent) on approximately 0.2g of ground and sieved (1mm) dry plant material (Parkinson & Allen, 1975). 5mL of H_2SO_4 and 4mL of digestion mixture are added before the samples go through a heated (360^0C for 3 hours) digestion procedure. Digestions were vacuum filtered through a 0.45 µm cellulose acetate filter before the concentration of SRP in fully digested samples was obtained. The relative amount of P that is bioavailable for uptake in soils can typically be estimated by the extraction of P using sodium bicarbonate (Olsen et al., 1954). This OlsenP content of soil samples was also obtained for Fall soils after dried, sieved (2mm) soil samples of approximately 1g were extracted with 20mL of 0.5M $NaHCO_3$ (pH of 8.5) in 50mL Erlenmeyer flasks after 30 minutes of shaking @ 200RPM following the Amacher et al., (2003) protocol. OlsenP extractions were filtered with Whatman 42 filter paper before analysis for SRP.

Filtered WEP samples of soil and vegetation, as well as runoff samples from vegetation treatment columns, were run through two analysis lines to obtain results for SRP and TDP. TDP concentration analysis utilized a persulfate UV in-line digestion. The concentrations of P were determined calorimetrically using a molybdate/ascorbic acid method at the University of Waterloo Biogeochemistry Lab (Bran Luebbe AA3 system, Seal Analytical Ltd., Methods (SRP|TDP); G-103-93, detection limit 0.001 mg/L | G-092-95 Rev 1, detection limit 0.01 mg/L). All extractions (WEP, TP, OlsenP) were obtained in triplicate. Variability of extractions is encapsulated in the results. Analytical replicates (35 of 795 samples, ~5%) were within 5% of reported concentrations or within 1 unit of detection limit resolution. Blanks were below detection limit or within 1 unit of detection limit resolution.

Concentrations in extractions were obtained in weight per unit volume (mg [P]/L). These were converted to mg [P]/ kg of dry soil or vegetation based on moisture content subsampling results and known volumes of the extractions. Drying procedure for soils and vegetation consisted of air drying followed by a minimum of 3 days of oven drying @ 50^0C. For vegetation, P content on a by area basis were obtained from biomass densities. For soils, soil bulk densities multiplied by depth sampled (5cm) gave surface densities of the sampled topsoil. Soil bulk density values were obtained from past work conducted at the sites or collected during the Fall sampling campaign in which case 6cm diameter sampling cores were manually driven into the top 5cm of soil. These were then fully dried @ 105^0C for a minimum of 5 days. Change in P content over the NGS was calculated as:

$$\mathbf{1}. \quad \% = \frac{(\mu_{Spring} - \mu_{Fall})}{\mu_{Fall}} \qquad \qquad \mathbf{2}. \quad \Delta NGS = \mu_{Spring} - \mu_{Fall}$$

Where % is the percent change and ΔNGS is the total change over the NGS, and μ is the mean P content of the sample in either Fall or Spring. Therefore, a positive value for either equation indicates a net increase in P over the NGS, and negative value indicates a net decrease.

When concentrations of P species from one sample are compared to each other, for example to determine what percentage of TP in plant samples is recovered as WEP, the concentrations normalized to dry matter (in units of mg/kg) are used.

3.2.6 Statistical Methods

Statistical analysis was conducted using R (version 3.6.1) (R Core Team, 2022) and through R Studio (RStudio Team, 2022). Figure creation used the R package ‘ggplot2’ (Wickham, 2016). The assumptions of normality could not be met, nor achieved with data transformation. Thus, only non-parametric statistical tests were used throughout analyses to test for significance. Alpha values were set at $p < 0.05$. To test for topographic trends while controlling for site variability, the Friedman test was used on the mean of triplicate values for each site and zone combination. Significant results indicate differences in non-parametric rank of each topographic sampling zone, and visual observation indicates what trends exist (decreasing/increasing with higher topographic position). Analysis between moderate/severe treated vegetation samples was conducted through a Kruskal-Wallis H test.

3.3 Results

3.3.1 Spatial Differences in P Supply in Soil and Vegetation Collected Prior to the Non-Growing Season (Autumn)

There were significant differences in soil WEP between topographic position within each VBS, with greater (Friedman test, $p = 0.002$) mean WEP concentrations at higher topographic positions relative to lower positions in VBS and field soils across all sites (Figure 3-5). However, this spatial pattern was not significant for Olsen P concentrations (Friedman test, $p=0.368$). The percentage of WEP obtained as SRP was also significantly correlated to the topographic gradient (Friedman test, $p=0.008$). At the three sites that included a Transitional sampling zone at the field/VBS interface, the Transitional zone soil WEP concentrations were distinctly higher than soil WEP in the rest of the VBS, and occasionally higher than WEP in the adjacent field soils (Figure 3-5). Significant topographic differences were also observed between upper and lower zone grass WEP concentrations under moderate freeze (control) conditions (Friedman test, $p=0.034$), but not for severe freeze conditions (Friedman test, $p=0.48$) or for TP concentrations (Friedman test, $p=0.71$) (Figure 3-6).

The topographic trends for soils and vegetation across all sites (Figure 3-5 and Figure 3-6) did not change when the grass biomass and soil density of the top layer of soil were considered to analyze P concentrations on a by area basis in units of kg/ha. The relative WEP concentration in VBS soils and grass were approximately equal for Manitoba sites, whereas P concentrations for Ontario sites were greater in the grass compared to soils.

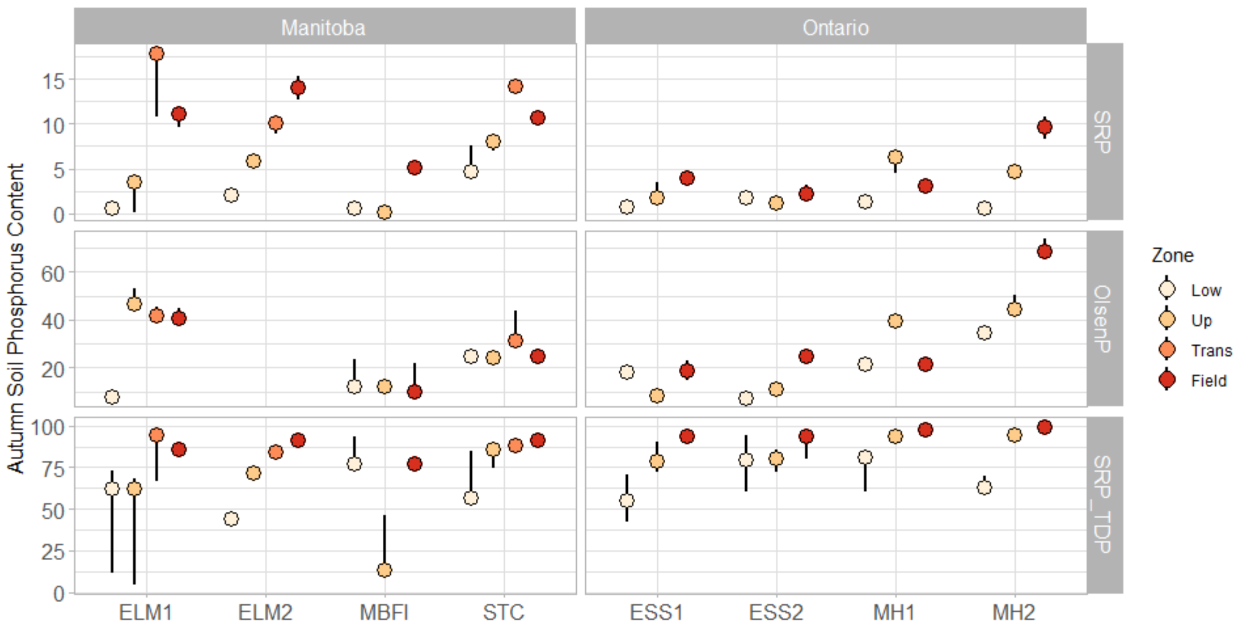


Figure 3-6: Water Extractable Phosphorus (top row) and Olsen P (middle row) concentrations in soils at each site. Percent of total WEP extracted as SRP (bottom row) expressed as a percentage. OlsenP values were not obtained for site ELM2. Zones are ordered by topographic position; Low, Up, Transitional, Field

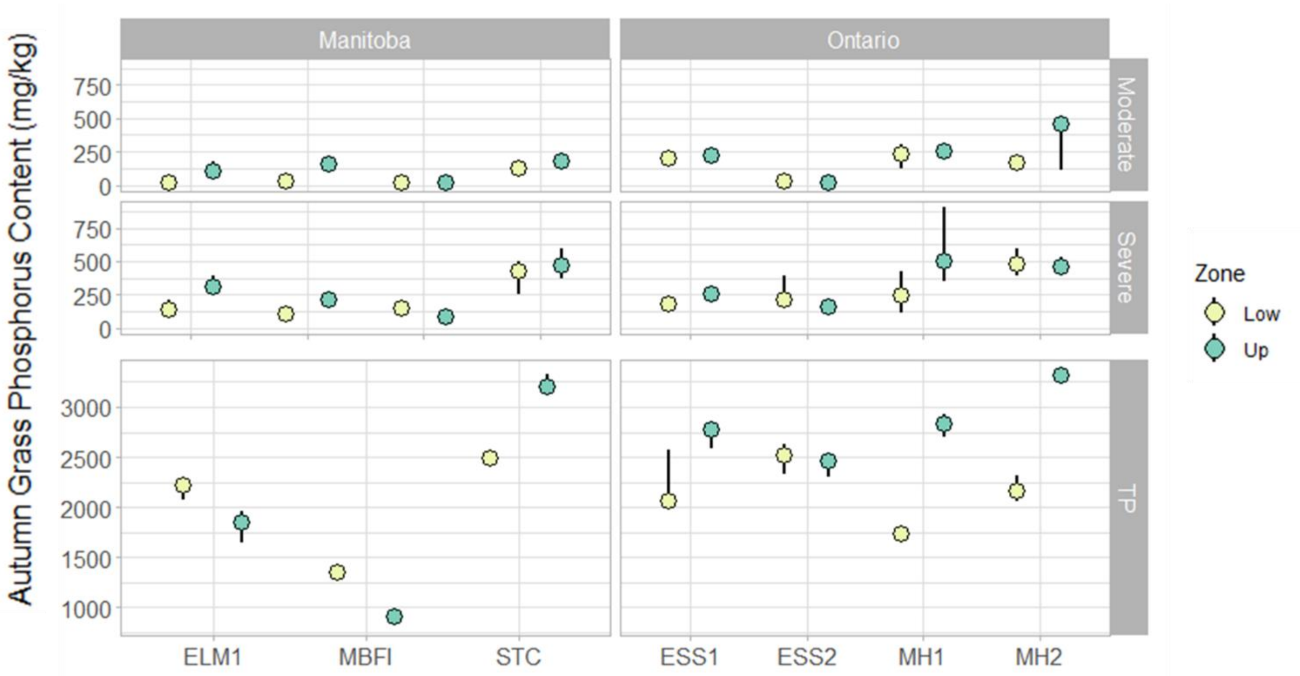


Figure 3-7: Phosphorus pools in buffer grasses. WEP results shown for samples after moderate (control) and severe freeze treatments. Total Phosphorus (TP) shown in bottom row. Site ELM2 was not sampled for TP. Error bars indicate range (n=3).

3.3.2 Importance of Freezing Severity in Winter P Loss from VBS Vegetation

The exposure of fall-collected grasses to both moderate (- 5^0C) and severe (-25^0C) freezing temperatures in a controlled laboratory experiment consistently led to greater WEP concentrations following severe freezing treatment relative to moderate freezing (Figure 3-7). This was apparent in both Low slope ($p=0.0002$) and Up slope ($p=0.002$) positions in the buffer. Grass samples from the laboratory severe freezing treatment released 14 ±5% of TP, while moderate freezing treatments released 6 ±4% of TP.

Other non-grass species sampled from VBS sites showed varying susceptibility to an increase in freezing severity (Appendix D). The significance of the effect was comparable to those measured in grass samples for nettles (p=0.004), but goldenrod samples had no significant difference between freezing treatments in released WEP (p=0.07). When subjected to a moderate freeze treatment, less than 1% of the TP in nettle is available as WEP, whereas in goldenrod samples anywhere from 16 ±9% of TP is available as WEP. After a severe freeze the water extractable pools increase marginally for goldenrod (20 ±8%), whereas the increase for nettle samples is more substantial (6 ±3%).

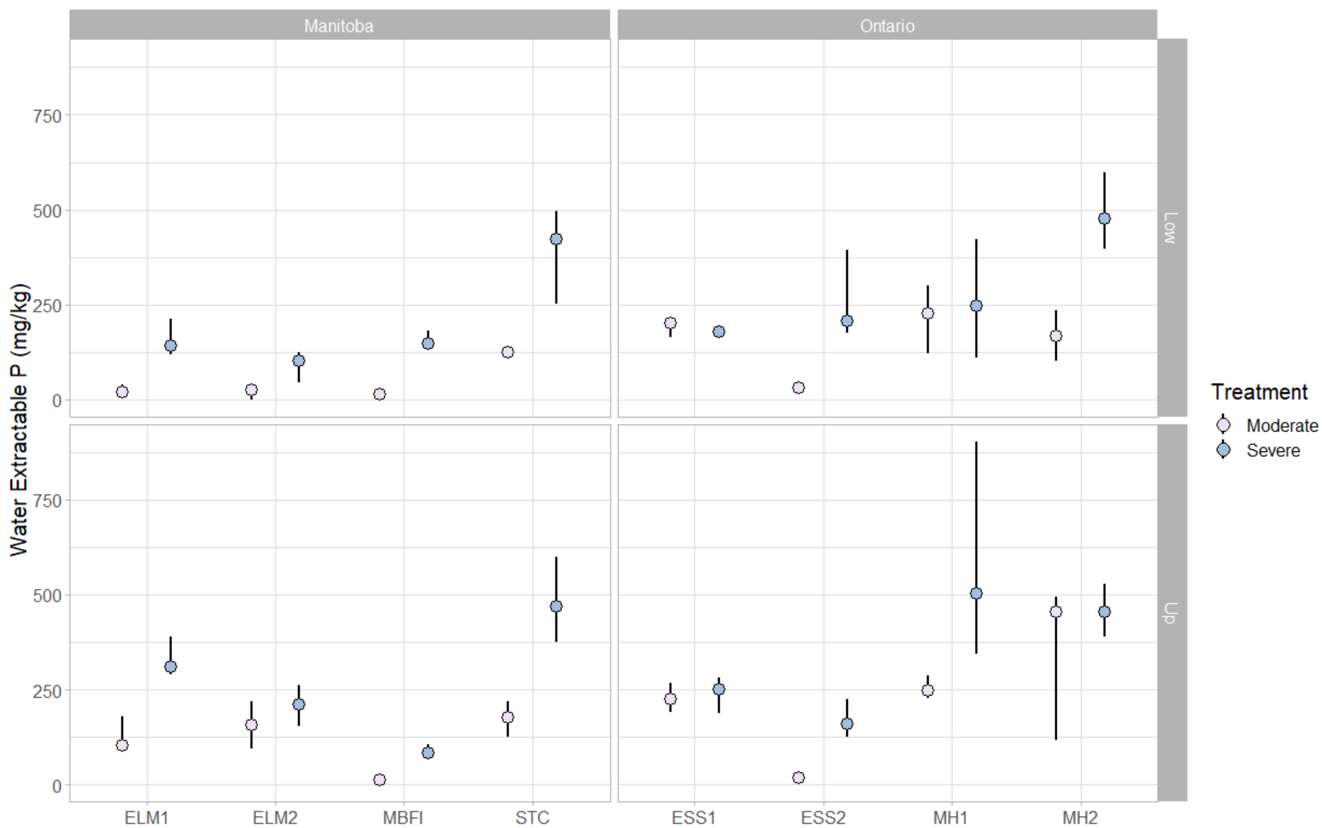
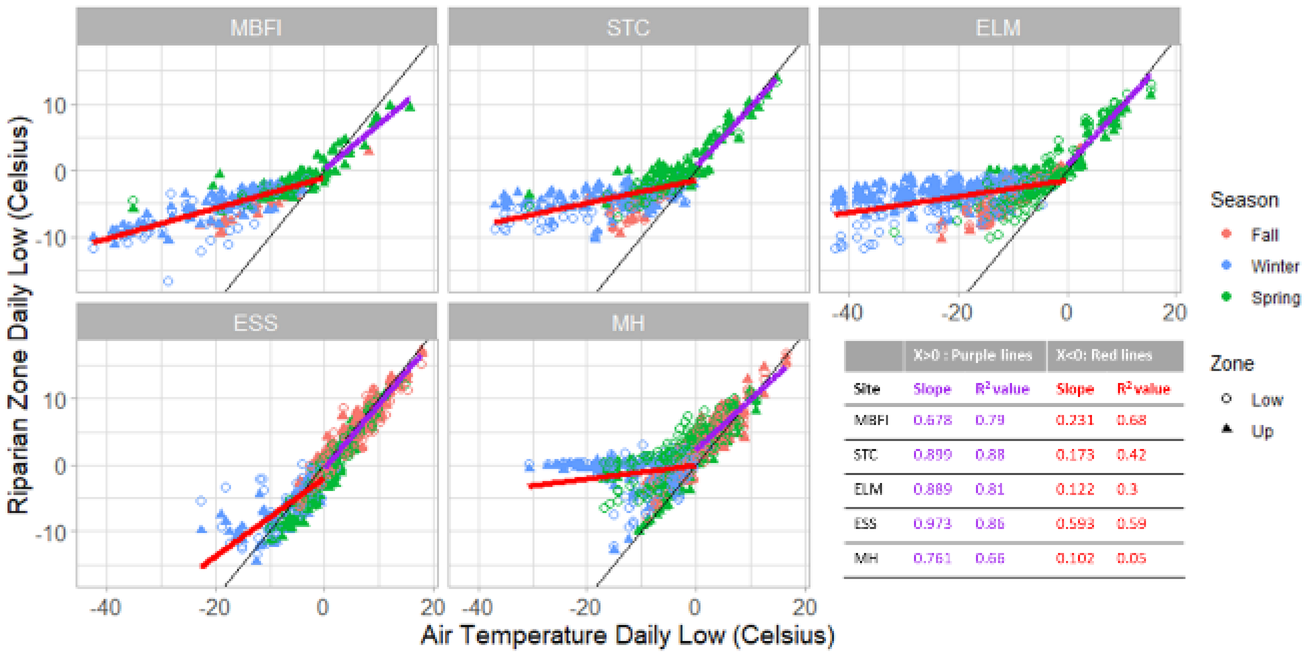


Figure 3-8: Freezing severity effect on WEP concentrations in VBS grasses in upper and lower zones. Freezing exposure treatments were performed on Fall sampled vegetation only.

Air temperatures were colder at the Manitoba sites relative to the Ontario sites over the NGS. However, both regions experienced cold winter conditions with air temperatures falling below -20^{0}C in Ontario and -40^{0}C in Manitoba (Figure 3-8). Observed daily minimum VBS ground surface temperatures at both upper and lower topographic zones within the eight study sites demonstrates that the severe minimum air temperatures experienced (as low as -40^{0}C) across the sites were seldom experienced beneath the snowpack at the soil surface in winter (Figure 3-8). Indeed, winter minima at the surface rarely fell below -10^{0}C, at both the Ontario and Manitoba sites.



	X>0 : Purple lines		X<0: Red lines	
Site	Slope	R^2 value	Slope	R^2 value
MBFI	0.678	0.79	0.231	0.68
STC	0.899	0.88	0.173	0.42
ELM	0.889	0.81	0.122	0.3
ESS	0.973	0.86	0.593	0.59
MH	0.761	0.66	0.102	0.05

Figure 3-9: Daily minimum air temperature (x-axis) and daily minimum VBS zone temperature (y-axis) experienced at each site for both upper and lower zones (symbols). Sites within the same climactic region are grouped together (MH, ESS, ELM). Linear regression slopes and R^2 values are included for when air temperatures are above (purple) and below (red) zero. Black line indicates a 1:1 relationship between air and VBS zone temperature. Seasons based on month (i.e. Fall → SON; Winter → DJF; Spring → MAM)

3.3.3 Observed Changes in Soil and Vegetation WEP Throughout the Non-Growing Season

The measured change in sample WEP concentrations over the NGS, from the Fall of 2020 to the Spring of 2021, indicate that WEP concentrations generally increased for soils and decreased for grasses over that period for both provinces (Figure 3-9). Ontario sites exhibited net losses of P from the VBS as decreases in grass WEP concentrations were typically greater than gains in soil WEP. In contrast, the greater changes in soil WEP and diminished changes in grass WEP results in calculated Net NGS P gains for most Manitoba sites.

Water levels recorded at each site over the NGS demonstrate differences in the exposure of vegetation and soil to inundation (**Appendix B).** A greater number of the Ontario sampling zones (n=5) experienced inundation by floodwaters (black circles in Figure 3-9) relative to the Manitoba sites (n=2). However, despite these differences in exposure to runoff, the observed changes in P concentrations in soils or grasses did not differ significantly among sampling sites that experienced flooding and those that did not (Figure 3-9). Therefore, conclusions cannot be drawn as to the effect that VBS inundation has on NGS P pools.

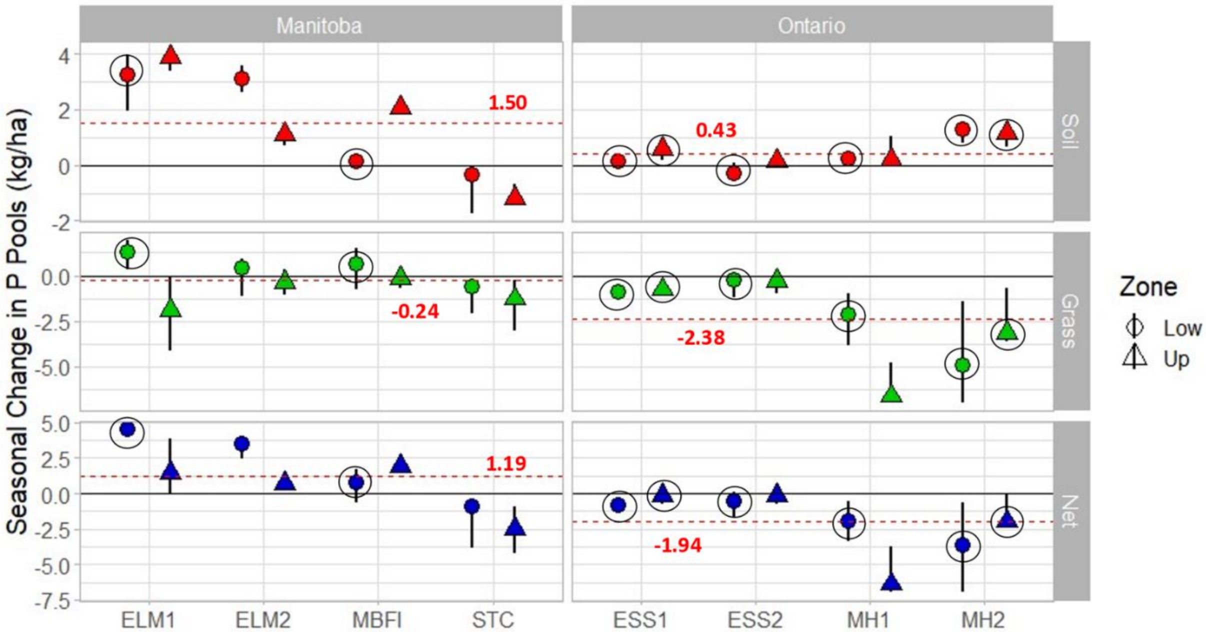


Figure 3-10: Seasonal changes in mean areal concentration of P at each site for soil WEP (top), grass WEP (middle), and net change (both soil and grass change). Positive values indicate a net increase in P concentrations over the NGS, negative values indicate a decrease. Black circles indicate zones that experienced NGS flooding between sampling dates. Values in red indicate the average of median values for that province and category of WEP pool (soil, grass, or net). Note: lower bound Net and Grass factor error bars for sites MH1 and MH2 are not included in the figure range to ease readability.

3.3.4 Simulated Phosphorus Runoff from Frozen VBS Soil and Vegetation Columns

Vegetation management strategies applied to mesocosms in a laboratory setting revealed dramatic differences in SRP losses from columns following freezing treatment. In general, all runoff and vegetation P concentrations were more pronounced for the upper zone compared to the lower presumably due to the elevated grass P content in upper versus lower zones (Figure 3-9). The removal of VBS grasses before freezing and flooding (Harvest treatment) decreased SRP and TP concentrations in floodwater compared to unmanaged grass (Intact treatment). In contrast, cutting the grass and leaving it on the soil surface (Cut treatment) increased relative SRP and TP concentrations in simulated floodwaters (Figure 3-9). The majority of P was in a dissolved form (TDP) (76± 11%), and of that dissolved portion 96± 1.5% was SRP for all treatment/zones except for the harvested treatment of the lower zone (70% SRP), indicating that the majority of P in simulated runoff was in a dissolved and reactive form. By extrapolating simulated runoff concentrations in mg/L to areal concentrations in kg/ha, vegetation management of harvesting versus cutting can be seen to decrease potential SRP loss by 3 kg/ha and 10 kg/ha for lower and upper zones, respectively.

Following the freezing and subsequent flooding treatment, the post treatment vegetation was analyzed for TP and WEP remaining in biomass. Vegetation that was unmanaged (intact) had significantly ($p<0.001$) smaller residual WEP and TP concentrations compared to columns that had the vegetation cut in both up and low zones (Figure 3-9**)**.

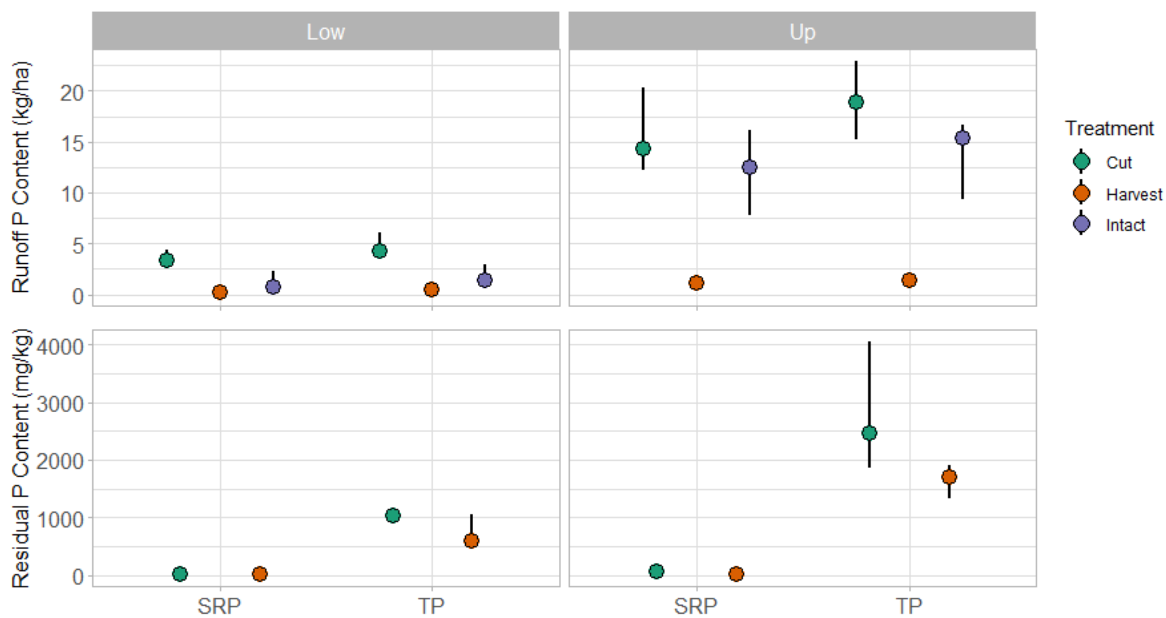


Figure 3-11: SRP and TP in; Top - simulated NGS runoff from buffer soil/ vegetation columns; Bottom – Residual P content in vegetation after column flooding and runoff collection. Phosphorus concentrations are shown in mg[P]/L for the Low zone (left) and Upper zone (right) columns.

3.4 Discussion

3.4.1 Phosphorus Content in the Critical Field Edge Zone

This research has provided evidence that the upper, field adjacent VBS zones have greater soil P pools compared to zones further from the field and adjacent to the watercourse, addressing one of the objectives of this thesis. The results from the eight VBS sites in this study and their wide range of site conditions indicate that elevated soil P concentrations in the upper VBS zone relative to the lower zone might be a typical attribute of these systems in Canadian landscapes (Figure 3-5). These increased soil P concentrations at the field/VBS interface are expected based on the understood functioning of buffers during the growing season, in which fine soil particles which easily bind P are transported by overland runoff and trapped by the initial section of VBS along the flow path. Indeed, the VBS soil P concentrations in this study are typical values as seen in other studies (Roberts et al., 2012; Stutter et al., 2009). These fine particles represent the majority of PP lost to runoff from agricultural fields and are usually deposited within the first 5m of the buffer (Syversen & Borch, 2005), resulting in elevated soil P levels (Uusi-Kämppä & Jauhiainen, 2010). VBS in Manitoba have shown this characteristic inflated soil P within concentrated flow paths through the VBS (Sheppard et al., 2006) and within the first 2m of the VBS edge (Habibiandehkordi, Lobb, & Owens, 2019) as a result of sediment entrapment. The results of this study confirm this trend for VBS in both provinces and outside of concentrated flow paths. Although these VBS soils typically possess further sorption capabilities and are not ‘P saturated’ (Habibiandehkordi, Lobb, & Owens, 2019), soils with increased soil P concentrations have been linked to increased TDP in runoff (Aye, Nguyen, Bolan, & Hedley, 2006; Satchithanantham, English, & Wilson, 2019). Therefore, due to the elevated soil P content, upper VBS soils closer to the field edge pose a greater risk to TDP losses in contrast to lower VBS soil.

One hypothesis of this study was that lower regions of VBS would have decreased soil and vegetation P concentrations because they are more susceptible to NGS flooding. The reasoning being that flooded soils typically release bound P once anoxic conditions are experienced (Amarawansha et al., 2016), and the release of P by senesced vegetation over the NGS is dictated by contact time with floodwaters (Lozier et al., 2017). While the lower zones of this study were inundated more often and for longer periods of time than upper zones (Appendix B), it appears that the flooding status had no observable effect on either soil or vegetation P concentrations, indicating that proximity to the watercourse and increased risk to flooding did not correspond to an increase in measurable P losses.

By comparing Fall and Spring soil samples, it is evident that soil P concentrations increase over the NGS in both Upper and Lower zones of the VBS. This result is comparable to what was observed by (Kieta et al., 2022) in an analysis of VBS in Manitoba, where soil Olsen P levels from the Fall to Spring increased by 24 to 44% in that time period. One explanation for this effect is given by the results from Nash et al (2021), who show that soil P mobilization occurs through two main processes during runoff events. They state that typical soil extraction tests like the WEP method used for this study replicate the initial quicker P mobilization process which involves the transport of nutrients in the upper mixing layer (upper soil/ detritus layer) from small to medium sized runoff events, while the second process is much slower and involves diffusion and dispersion of nutrients from subsurface soils, detritus, and soil aggregates into the upper mixing layer from longer periods of runoff generation (Nash et al., 2021). It is possible that the activation of the secondary rate-dependent process during the NGS, when soils are saturated and wet for extended periods of time, would mobilize deeper legacy P sources from the VBS soils. Once P is mobilized into the active mixing layer of the topsoil, it is at risk of surface transport and losses through the primary supply-dependent transport process. If that is the case, then the increase of extractable soil P from Fall to Spring observed in the results of this study only indicates more favorable conditions for TDP runoff during the Spring and does not indicate any net gains or losses of P by the buffer soils. An alternative process to explain the elevated Spring soil P levels could be the uptake of P by soils over the NGS and during the early spring. The source of this P could be from senesced vegetation, both in the VBS and from upland areas, as has been indicated as the reason for high P VBS soils in other studies (Räty et al., 2010). Through this process, the P derived from senesced vegetation 'charges' the VBS soils until it is accumulated into vegetation biomass or, more likely, lost through runoff. These results and uncertainty in the governing processes highlight that more clarity is needed on the causes of elevated soil P in VBS during the Spring. We recommend robust field scale VBS experiments over the NGS to provide answers in future studies.

3.4.2 Potential Contribution of Frozen VBS Vegetation to Dissolved P Losses

In contrast to the clear topographic trend of soil test P in VBS, this study has shown that concentrations of P in VBS grasses had no trend between upper and lower zones, except for a loose correlation in moderate freeze treatment samples. We hypothesized that there would be evidence of additional P uptake in upper zone vegetation compared to lower zones due to the difference in soil P levels but that was not clearly observed. The lack of evidence to support excess P uptake could be attributed to excess uptake by grass in both upper and lower zones, as evidenced by the high Olsen P values (>10 mg/kg) for nearly all buffer soils. Even for fast growing, high nutrient use cash crops like corn, Olsen P values above 12 mg/kg do not typically result in enhanced economic yields (OMAFRA, 2015). Therefore even the lowest Olsen P levels from the VBS of this study likely contain adequate available P to sustain the nutrient needs of grass. Alternatively, the uptake of excess P could be stunted by a limitation of other essential nutrients such as Nitrogen, as has been observed in other studies involving VBS vegetation (Räty et al., 2010). Whatever the mechanistic reasoning, these results support a lack of any topographic trend for VBS vegetation P content.

The relationship between increased freezing severity and increased available VBS grass P concentrations is a relationship that has also been observed in studies examining the freezing of cover crops and native terrestrial grasses (Cober et al., 2018; Lozier & Macrae, 2017; Øgaard, 2015). The deeper freezing results in more ice crystal formation, which damages the cell wall of plant cells and causes the release of intracellular nutrients upon lysis of the cell (Elliott, 2013). Cover crop species that were genetically chosen to be frost tolerant, and native perennial grasses which would have freezing adaptations for their winter environments, had a greater resistance to mild freezing temperatures but not severe freezing temperatures (Cober et al., 2018; Lozier & Macrae, 2017; Øgaard, 2015). Supporting the original hypothesis of this research, the VBS vegetation in this study also demonstrate a greater resistance to moderate freezing when compared to severe, as the greater severity of freezing results in an increase in released P. From these results, one can infer that VBS vegetation in colder regions that experience more severe freezing could be at risk of greater P losses. However, other factors may be of more importance, as results presented here have indicated the mix of species present in the VBS to be a non-trivial matter in determining total and extractable P concentrations. The relative susceptibility of vegetation to freezing temperatures depends on that species particular resistance to freezing, which is a result seen with the study of frost tolerance in cover crops as well (Cober, Macrae, & Van Eerd, 2019). The difference between species in freezing susceptibility and TP content has implications for the risk posed by leached vegetation P during the

NGS, as non-grass vegetation could represent larger potential sources of P compared to grass on an equivalent area basis.

To contextualize the potential NGS P release from VBS vegetation, WEP results of this study were compared with annual tributary SRP loads taken from other studies focused on these site catchments (Irvine, Macrae, Morison, & Petrone, 2019; J. Liu et al., 2021; Macrae, English, Schiff, & Stone, 2007b; Price et al., 2021). These preliminary calculations indicate that P release from all senesced VBS grasses throughout the catchment could account for up to 60% of total catchment SRP loads in Ontario and 30% in Manitoba, with even higher proportions for non-grass vegetation (Appendix C). This is an important comparison when considering VBS take up less than 1% of the total area of the catchment. However, these calculations make a few assumptions, such all of the released vegetation P would contribute to tributary P loads and some assumptions on average VBS width over the entire catchment. These estimates should help inform a worst case scenario as the actual effect of NGS conditions on VBS vegetation contributions to catchment P loads is still unclear.

3.4.3 Impact of NGS Conditions on VBS Vegetation P Dynamics

Despite low minimum air temperatures experienced at all sites (< -20^{0}C), the relatively warmer ground surface temperatures recorded for the VBS sites indicate that the vegetation would have been insulated from the harshest of colder air temperatures over the NGS. This could be attributed to insulation from the snowpack visually observed at all sites, and supports the idea that the unrealistic cold temperature exposure has been indicated as the reason for the overestimation of plant P release in many laboratory freezing experiments (Øgaard, 2015; Roberson et al., 2007). Lower topographic areas of the landscape such as riparian corridors and wetlands would collect additional snow due to re-distribution by wind and would retain their snowpack for longer than upland fields (Fang &

Pomeroy, 2009), which would increase this effect of snowpack insulation and reduce the number of Freeze-Thaw cycles (FTC) experienced. The most southerly sites in this study (ESS1 and ESS2) lacked much of the insulating effects on temperature seen at other sites, and consequently experienced some of the coldest temperatures. This is in contrast to one of the original hypotheses of this thesis, which assumed that vegetation in the coldest regions would experience the coldest temperatures. This area of Ontario does not have long lasting snow cover during the NGS compared to the other sites, and so has a greater potential for freezing temperatures on the ground (Macrae et al., 2021). Even so, the minimum temperatures recorded at all sites were significantly warmer than the severe freeze treatment temperatures grass samples were subjected to. There is also a discrepancy in the number of snow-covered days experienced between the two provinces of this study. The Waterloo region, where both sites MH1 and MH2 are, has an average of 95 days a year with a snow cover depth of at least 1cm, whereas the climate station nearby site MBFI in Manitoba indicates a yearly average of 133 days for the same snow cover depth (Environment and Climate Change Canada, 2022). The more persistent snowpack in Manitoba and its insulating affect could explain the greater number of cold ground surface observations in the Ontario sites near Waterloo compared to those in Manitoba.

Despite the insulating effect of snowpack that protected buffer vegetation from severe freezing temperatures, there was still a dramatic loss in P over the NGS. Seasonal losses of TP in grasses were on the order of 42 ±16% while only 14 ±6% of TP was shown to be released through laboratory severe freezing treatments. This indicates that the minimum temperature experienced is likely not the primary mobilizing factor on vegetation P, and instead is more likely to be attributed to the number of FTC and contact time with water. For cover crops, an increase in the number of FTCs that are experienced by vegetative tissue is linked to an increase in P release from the tissues (Bechmann, Kleinman, Sharpley, & Saporito, 2005; Lozier & Macrae, 2017; Whitfield et al., 2019).

After a single FTC cover crops released only 1% of plant TP as WEP, whereas after 8 FTC 100% of TP was available as WEP (Bechmann et al., 2005). In addition, senesced and frozen vegetation releases more nutrients when subjected to wet, ponded conditions compared to simulated rainfall or WEP extractions (Lozier & Macrae, 2017). The amount of P released from VBS vegetation is then going to be highly dependent on the particular NGS conditions of that year, as regular variability in snowpack and the onset of freezing temperatures from year to year has been shown to have a dramatic effect on actual TP losses from cover crops, even on the same field (Sturite et al., 2007). The extended period of fluctuations above and below freezing that is observed under the snowpack in the VBS likely extracted most TP through a combination of continuously alternating FTC and ponded/ saturated conditions. The future expectation for NGS conditions throughout the Canadian agricultural landscape is that we are likely to see a decrease in the snowpack and frozen conditions due to climate change (Contosta, Casson, Nelson, & Garlick, 2020; Henry, 2008). Where conventionally we might expect warmer average NGS temperatures to minimize nutrient losses from VBS vegetation due to freezing, our results indicate that the severity of the freeze is less important than the FTC and wet conditions experienced, which will be impacted by the decreased snowpack. Climate change is expected to increase the number of FTC experienced by VBS, and would thereby exacerbate P released through freezing processes.

Results that indicate a positive total net change in WEP pools for Manitoba sites over the NGS, and a negative total net change in WEP pools for Ontario sites, could be explained by the higher Fall concentrations in Manitoba site soils, and lower concentrations in Fall grasses. This in turn is likely attributed to the difference in sampling dates between the two provinces. For Ontario, sampling was conducted from Sept 14th – Sept 21st, and April 13th – April 15th, whereas for Manitoba the dates were Sept 28th – Oct 8th, and March 29th – April1st. The earlier fall sampling and later spring sampling for Ontario sites would have coincided with warmer temperatures in both cases, and the Ontario samples were exposed to field conditions for about 3 more weeks than the Manitoba samples. Additionally, the Manitoba climate is generally colder, with an earlier onset of the NGS (Table 1). Due to these factors, it is likely that Manitoba vegetation had already begun translocating nutrients into the surrounding soil upon initial Fall sampling. This is supported by the relatively higher soil P levels which could be a result of translocation into the root zone by vegetation (Kieta et al., 2022; Kröger et al., 2007). Historical data series from Environment and Climate Change Canada climate stations in proximity to the Manitoba sites indicate that minimum air temperatures below the freezing point (0^{0}C) were experienced on 2 or 3 days in the weeks before the sampling dates (Environment and Climate Change Canada, 2022). For Ontario sites, there were no minimums below 0^{0}C experienced before sampling (Environment and Climate Change Canada, 2022). These early freezing temperatures at Manitoba sites would decrease the vegetation P content dramatically and enhance the translocation of P pools into the root zone (Räty et al., 2010). Due to these differences in sample pre-conditions, it is difficult to draw compelling comparisons of the change in P pools over the NGS between Ontario and Manitoba sites with the current experimental setup. Further understanding of the movement of P pools in VBS during the NGS could be gained from studies with more temporally intensive sampling over the NGS of both vegetation and soils.

3.4.4 Implications of Vegetation Management in Canadian Buffers

Simulated flooding on soil/vegetation columns showed a dramatic effect on SRP released in runoff following different vegetation management treatments. When compared to the control treatment where vegetation was left intact, harvesting of the vegetation reduced TP and SRP in floodwater, while cutting and leaving (mowing) the vegetation increased TP and SRP in floodwater. This corroborates one of the original hypotheses of this work, which was that VBS vegetation harvesting effectively reduces P in NGS runoff. The high SRP:TP ratio is typical of NGS runoff through VBS in cold climates (Sheppard et al., 2006; Vanrobaeys et al., 2019) and has been attributed to the release of plant bound P (Uusi-Kämppä & Jauhiainen, 2010). The decrease in TP, predominantly due to SRP reductions, after harvesting in this study is further evidence of the importance of vegetation in TDP losses from VBS. Harvested columns with no vegetation exhibit dramatically lower concentrations of SRP in runoff, supporting the efficacy of vegetation management as a strategy for reducing the SRP loading from VBS. This also shows that removing the vegetation after cutting is important in the management of VBS, as the cut vegetation still acts as a source of P during simulated flooding and increases SRP in flood water. The higher SRP in runoff from harvested upper columns compared to harvested lower columns indicates that there is also a greater degree of phosphorus leaching from soils in the upper zone which typically have higher soil test P levels (Figure 3-5), but the differences were minimal (0.9 ±0.3 kg/ha) with the majority of the SRP losses originating from vegetation.

Despite having higher TP released in runoff water, the columns subjected to a cut and leave vegetation treatment showed still greater TP concentrations left in post-treatment vegetation than the intact columns. Therefore, the increase in TP from cutting and leaving the vegetation was not a short-term effect from the first extraction, and results indicate further TP release from cut versus intact vegetation is possible. Intact vegetation with reduced pools of P for extraction could be explained through the translocation of nutrients into the root zone once columns were subjected to freezing temperatures. This is a common nutrient storage technique over the NGS for trees (T Ericsson, 1994), and has been suggested as the reason for dramatic decreases in VBS vegetation nutrient concentrations upon initial autumn frosts (Kieta et al., 2022; Räty et al., 2010). This transfer of P elevates soil P concentrations making them more susceptible to P losses over the NGS (Kröger et al., 2007). Therefore, this translocation of nutrients by VBS vegetation to the root zone and soils is an important area for future studies.

The harvesting of VBS vegetation as a means of nutrient extraction, or vegetative mining, is commonly recommended by researchers as a primary method in improving buffer functionality in cold climates (Dosskey et al., 2010; Hénault-Ethier et al., 2019; Räty et al., 2010; Roberts et al., 2020; Stutter et al., 2009). Assuming TP concentrations in Fall VBS vegetation is the maximum removable pool of P from the VBS, then the harvesting of VBS grass at the sites of this study has the potential to remove anywhere from 5 – 35 kg[P]/ha (median 17.8), and the values for non-grass vegetation would be even higher (median 52 and 67 kg[P]/ha for nettle and goldenrod, respectively). These results are comparable to other studies that have quantified removable P by vegetative mining (Table 2).

Table 3-2: Rate of P removal by vegetation harvesting from other studies that explicitly measured the P content of harvested vegetation for the purposes of nutrient removal.

Study	**Vegetation Type**	**P removal annual kg/(ha*yr)**	***Notes***
(Kelly et al., 2007)	Mixed	25.25	*4 year study, 15m buffer*
	Grass	15.5	*4 year study*
(Marino & Berardo, 2005)	Alfalfa	15.25	*Not riparian, unfertilized*
(Koerselman, Bakker, & Blom, 1990)	Wetland*	3.9 – 5.6	*Harvest exceeded input loads*
(Hénault-Ethier et al., 2019)	Tree	7.67	*3 year study*
	Tree	18.33 - 28.67	*3 year study*
(Räty et al., 2010)	Grass	3.3 – 4.7	*Harvested in August*

(Kiedrzynska, Wagner, & Zalewski, 2008)	Wetland*	40	*Cited from (Idyz, 2013)*
	Tree	173	
(Izydorczyk et al., 2013)	Wetland*	3.3 - 13	*7 species*
(Hille et al., 2019)	Grass	5 – 24	*Ryegrass, 2 sites*

* - *Wetland vegetation type consists of a variety of herbaceous and macrophytic wetland vegetation species*

Due to the clear link between the removal of buffer vegetation and the decrease in SRP losses from soil columns, these results suggest a need for further study into the efficacy of VBS management through vegetation harvesting in Canadian landscapes as a means to alleviate NGS TDP loads. Further research should focus on the economic viability of buffer vegetation use as 'green manure' (Brown et al., 2019) or livestock feed (Räty et al., 2010) in Canadian settings, which could involve economic incentive programs as seen in other areas (Dal Ferro et al., 2019). Additionally, these landscapes are unsuited for heavy machinery that is typically used for farm operations, meaning there needs to be some investigation into practical harvesting methods. The prioritization of vegetative nutrient mining in the upper zones alone would decrease soil P levels from the highest saturated section of buffer, while permitting the lower zone to remain as additional filtering and streambank stabilization during the NGS and warrants further studies.

Multiple strategies will likely be needed to combat the issue of TDP loss from VBS in Canada. For example, it is unlikely that vegetation management alone will effectively reduce P loads if the loading rate of P in manure and fertilizer remain high or increases (Baulch et al., 2019). The reduction of soil P concentrations occurs slowly through harvesting, and research from Denmark predicts that it would take 50 – 300 years to reduce buffer soil P concentrations to environmentally safe levels through vegetative mining alone (Hille et al., 2019). For water bodies experiencing eutrophication problems today, those timelines are likely inadequate.

Although these results indicate strong reasoning to support the management of VBS through harvesting in Canada to mitigate diffuse phosphorus pollution, VBS are highly multifunctional landscape units that also stabilize riverbanks and provide a natural means of flood management (Cole, Stockan, & Helliwell, 2020). Other terrestrial benefits include increasing biodiversity, providing transport corridors for wildlife, natural pest control, sustaining pollinators, sequestering carbon, and providing cultural aesthetics of a naturally vegetated streambank (Cole et al., 2020; Haddaway et al., 2018). While VBS harvesting may impact these ecological services, there is also potential for VBS harvesting to have co-benefits related to enhancing biodiversity and controlling invasive species (Hille, Larsen, Rubaek, Kronvang, & Baattrup-Pedersen, 2018). Therefore, there is need for the studies of VBS as BMPs for nutrient retention to link with other disciplines and provide a more holistic view of the services provided by VBS, and what effects VBS harvesting will have on them.

3.5 Conclusion

The results from this work demonstrate the topographic and seasonal patterns of VBS P concentrations adjacent to agricultural fields in Canadian climates. There is a clear topographic gradient of increasing soil P levels in VBS for the upper slope (topographically elevated) sections. This does not appear to be caused by the greater chance of lower zones being subjected to longer periods of inundation, as the inundation of both upper and lower zones did not have an observable effect on NGS P losses of vegetation or soils. Instead, it is more likely upper zones are first to intercept TDP and PP from field runoff and so retain greater P concentrations in the soil. The increase in VBS soil P over the NGS could be explained by the conversion of fixed, subsurface P pools to mobile surface P pools caused by the wet and flooded NGS conditions in the study sites.

Through lab experiments, the susceptibility of buffer grasses and other vegetation to freezing temperatures was evaluated and determined that while more severe freezing released greater amounts of P from vegetation, the actual temperatures experienced by VBS vegetation in a field setting are milder than what samples were subjected to due to insulation from snowpack. In addition, the species of vegetation will likely have a greater impact on P losses during the NGS due to the observed variability in grass versus non-grass species. These results also highlight the potential efficacy of vegetation management in Canadian VBS to mitigate terrestrial P losses to waterways over the NGS. It was shown that harvesting of VBS vegetation reduces TP and SRP loads in simulated NGS runoff from soil/grass columns after flooding, while cutting and leaving the vegetation exacerbates P losses.

Information gained from this study can provide a more complete understanding of the risk and potential risk management of P losses over the NGS in Canadian VBS systems. As BMPs continue to be implemented throughout the landscape to combat freshwater eutrophication issues it is important to understand the practical limitations of each method, which leads to the need for a multiplicity of strategies to be employed. In addition, the benefits and drawbacks of these methods outside of the P and eutrophication lens needs to be taken into account for any decision making in the future, particularly for VBS which provide a host of other important functions in the landscape related to water quality, water quantity, biodiversity, and aesthetics (Cole, Stockan, & Helliwell, 2020; Haddaway et al., 2018). The results from this study can help direct future research into VBS management strategies with a focus on balancing some of these issues, such as temporal and/or spatial variation in harvesting strategies which may help preserve VBS benefits while reducing TDP losses.

Chapter 4
Potential Non-Growing Season Phosphorus Release from Vegetation Growing in Phosphorus Rich Soils

4.1 Introduction

Nutrient loads originating from agricultural activities are contributing to freshwater eutrophication in many areas of the world (Mateo-Sagasta et al., 2018; Schindler, 2012). Nutrients and manure applied to agricultural lands can lead to diffuse, non-point sources of nutrient contamination throughout the landscape. In addition, intensive agricultural areas related primarily to livestock operations, can lead to rural point sources of nutrient contamination in relatively small areas (Irvine et al., 2019; Withers et al., 2009). These highly concentrated nutrient loads from farmyards, bunker silos, and manure storage areas are critically important to mitigate, yet many of the common Best Management Practices (BMP) applied to non-point sources of agricultural nutrient contamination are not designed for point sources with high nutrient concentrations. Consequently, common BMPs such as vegetated buffer strips (VBS) can quickly lose their efficacy and become legacy phosphorus (P) stores and/or potential sources of P in the landscape (Pluer, Plach, Hassan, Price, & Macrae, 2022; Stutter et al., 2009). Given that P is a key driver of eutrophication (Schindler, 2012), the potential mobilization of P from legacy stores in the landscape is problematic and in need of investigation (Sharpley et al., 2013).

Phosphorus is typically retained in VBS physically through the trapping of particulate P (PP), and geochemically through the adsorption of total dissolved P (TDP) to soil particles (Dorioz et al., 2006). Phosphorus retained in these VBS can subsequently be taken up by vegetation and incorporated into biological pools (Dosskey et al., 2010). However, recent work suggests that plant senescence and the freezing conditions in winter can lead to the release of significant quantities of SRP to runoff (Kieta et al., 2018). Indeed, freezing temperatures can cause the lysis of plant cells, spilling the intracellular components, and resulting in greater extractability of nutrients from vegetation biomass (Elliott, 2013). This has been demonstrated in quasi-natural vegetation growing in VBS (Kieta et al., 2022) as well as cover crops on agricultural fields (Cober et al., 2018; Lozier et al., 2017). The release of P from cover crops following freezing has been shown to increase with frost magnitude (Cober et al., 2018). However, to date, no studies have focused on the winter release of P from vegetation grown in P-rich soils (*i.e.*, sites with high legacy P), particularly under different winter severities.

The issue of past land use management activities resulting in long lasting stores of P in the landscape is often referred to by the term 'Legacy P' (Sharpley et al., 2013). When such legacy sites are found in hydrologically connected areas, they often become *critical source areas* for P in runoff (Sharpley, Kleinman, Flaten, & Buda, 2011). To understand the potential mechanisms of nutrient transport from these zones, it is therefore important to explore relationships between soil and vegetation P, and P in runoff. It is unclear if the accumulation of legacy P in soil leads to greater P accumulation in vegetation. Previous studies have demonstrated the ability of plants to take up luxury P in elevated P settings, or have excess P take up during the Spring (Hill, 1979; Kröger et al., 2007); however, this has not been demonstrated in the quasi-natural vegetation typically found in VBS (*i.e.*, grasses). The greater accumulation of P in the biomass of plants grown in soils with high legacy P may be a particularly significant observation in cold agricultural regions where freezing readily occurs and such P may be released to runoff. The fact that soils are high in P with limited or no ability to retain additional P (Pluer et al., 2022; Price et al., 2021) increases the likelihood that P released from vegetation will pass to adjacent surface water bodies.

To begin to understand the environmental impacts of high legacy P soils on P dynamics in cold climates, a small pilot project was initiated to investigate the potential for winter P release from vegetation grown in soil with high legacy P. Soil and vegetation samples were collected from two heavily P-impacted sites receiving direct inputs of nutrient-rich effluent from nearby bunker silos on dairy farms in Ontario, Canada, and subjected to freeze-thaw cycles in a laboratory setting. These bunker silo sites provide ideal conditions to study the impact of nutrient rich soils, as the effluent from bunker silos is typically very high in nutrients but flows are relatively low, meaning the soils that first intercept this runoff will become highly saturated with P while other nearby soils will receive none or little of the direct silage runoff (Gebrehanna et al., 2014). Previous studies at these same sites have demonstrated spatial variability in the P content of soils, with the nearly complete P saturation of soil in locations receiving direct inputs of bunker silo effluent, and smaller soil P concentrations in nearby sections (Pluer et al., 2022; Price et al., 2021). The goal of the study was to collect preliminary information on P dynamics in high legacy P soils to help refine future research questions and to provide guidance on field sampling protocols. To achieve this goal the two objectives of this experimental study are to determine: (1) If quasi-natural vegetation (predominantly grasses) grown in soils with elevated P have greater P accumulation than vegetation grown in soils with smaller amounts of P; and (2) If increases in water extractable P concentrations following freezing treatments are greater in vegetation grown in P-rich soils. It was hypothesized that P concentrations in vegetation would be positively correlated with soil P concentrations as a result of increased P uptake in the presence of excess P pools, and that this would lead to increased water extractable P concentrations in vegetation following frost.

4.2 Site Description and Methods

4.2.1 Experimental Design

Soil (top 5 cm) and vegetation (above ground biomass) samples were collected from two sites receiving bunker silo effluent. Sampling zones were selected from sections within each site that had varying levels of soil P (classified as high, medium and low) and P saturation (Pluer et al., 2022; Price et al., 2021), permitting comparison of vegetation P concentrations across these zones. In the laboratory, vegetation residues were subjected to one of three freezing conditions (control 4^0C, moderate -5^0C frost or severe -25^0C frost) and subsequently analyzed for water extractable P (WEP) concentrations. Soil samples were analyzed for both WEP and plant available (Olsen) P for comparison to plants.

4.2.2 Study Site Selection

Two sites in Southwestern Ontario were selected for this study. Both sites were located on moderate sized dairy farms (~300 cows) equipped with bunker silos. Previous studies identified that the bunker silo effluent and farmyard runoff had led to significant accumulation of P within isolated sections of downstream treatment systems (Pluer et al., 2022), which led to greater P concentrations in shallow groundwater within these zones and contributed to significant P losses to downstream water bodies at one site (Irvine et al., 2019; Price et al., 2021). These previous studies permitted the delineation of these zones into subsections with contrasting soil P levels (highly elevated/nearly P saturated; intermediate/medium; and low soil P with a high P sorption capacity) (Figure 4-1). Soils within both sites had silt-loam textures. Additional details regarding the site characteristics can be found in Pluer et al. (2022) and Price et al. (2021).

Bunker silo runoff from the first site (INN) was directed into a settling forebay/vegetated swale complex that was installed in 2015. Runoff that collects in the forebay is directed through a slag filter, and then into a vegetated swale (Figure 4-1). The purpose of the slag filter material is to adsorb SRP in the bunker silo runoff, which results in reduced soil P values in the vegetated swale portion of the installation. The inflow of the forebay is also higher than portions of the forebay further along the flow path. Therefore, our high, medium, and low sampling zones were chosen as directly at the inflow point of the forebay, adjacent to the inflow pipe into the slag filter, and in the vegetated swale after the slag filter, respectively (Figure 4-1).

At the second site (STZ), bunker silo runoff was allowed to flow across a small farm lane directly into a 30m wide buffer before discharging directly into a stream (Figure 4-1). Vegetation closest to the bunker silo that can be managed with equipment is mowed seasonally. A concentrated flow path through the buffer provides a sampling point that has high soil P, while adjacent sections of the buffer that receive diffuse and indirect runoff have moderate soil P levels. Samples from the opposite bank of the stream provide a low soil P sampling zone (Figure 4-1).

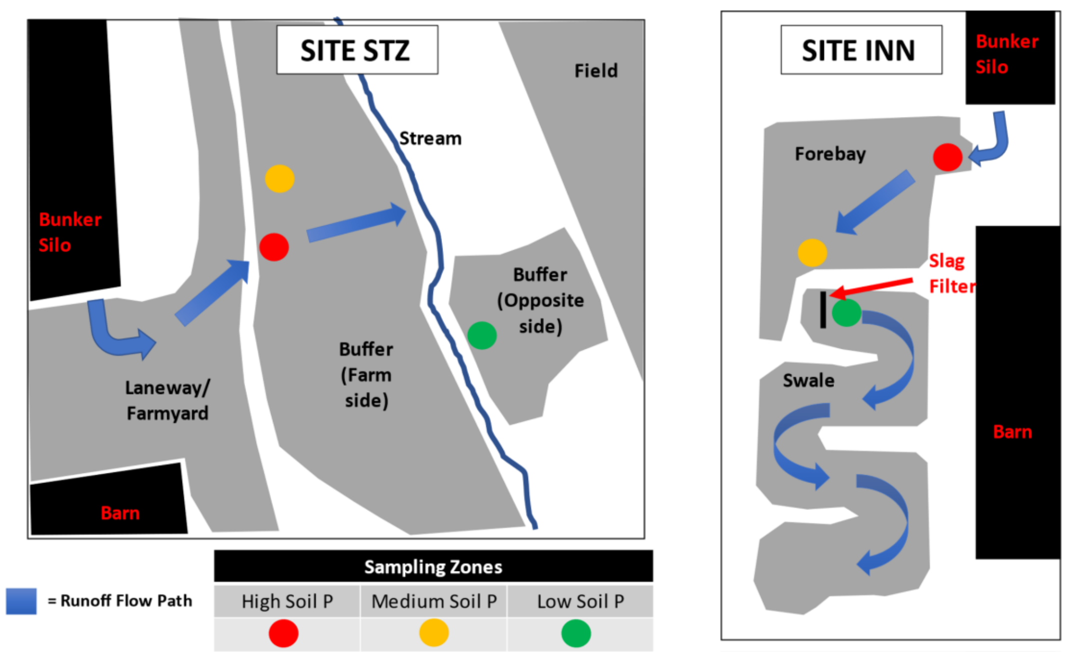


Figure 4-12: Site diagrams depicting locations of sampling zones relative to bunker silos and predominant bunker silo runoff pathways.

4.2.3 Sample Collection

Soil and vegetation material were collected from each of the three zones with contrasting soil P concentrations at each of the two study sites. Soil samples (10-15 samples composited) were collected from the top 5 cm of soil over a 1 m^2 section of each zone using a hand auger. The predominant grass species (>75% of biomass by visual inspection) was harvested 5cm above the ground surface in three 0.25m^2 areas. The three harvested sections resulted in 3 biomass weights for determination of areal surface density of grass P pools. Soil bulk densities were taken from previous research conducted at these sites and multiplied by the depth of soil sample (5cm) to give an areal surface density of soil P pools.

4.2.4 Sample Processing and Analytical Methods

All sample processing and analyses were conducted in the Biogeochemistry Lab at the University of Waterloo. Bulk soil and grass samples were transported to the laboratory in sealed polyethylene bags stored in coolers and processed within 24 hours of collection. Samples were first homogenized by hand. Representative subsamples (in triplicate) of vegetation (3g) and soil (5g) were oven dried at 65^{0}C for 48 hours to determine their moisture content gravimetrically, which allowed the expression of WEP concentrations in units of dry mass. The dried soil and grass samples were subsequently processed for the determination of Olsen P and total vegetation P, respectively.

In triplicate, field moist soil and grass subsamples were subjected to one of three freezing treatments: Control (+4^{0}C), Moderate (-5^{0}C), or Severe (-25^{0}C) before being extracted for WEP. The grass samples were kept in treatment conditions for 48 h in temperature-controlled chambers prior to extraction, whereas the soil samples were extracted within 24 hours of sample collection. In addition, 5 g field moist soil samples (in triplicate) from one site (INN) from the “High” and “Low” soil P sections were subjected to the same freezing treatments.

Soil and vegetation samples were extracted for the determination of water extractable P (WEP) using similar procedures. Field moist samples were weighed (5g soil, 3g grass) into 125 mL polyethylene containers. Deionized (Milli-Q) water was added to each container, 90 mL for vegetation and 50 mL for soils resulting in weight:volume ratios of 1g:30mL and 1g:10mL for vegetation and soils. The greater volume of water for vegetation was needed to ensure complete coverage of the material during the extraction. Containers were capped and shaken at 250 RPM for 1 hour on a shaking table. Soil sample extractions were first gravity filtered through a coarse filter (Whatman no. 42) and subsequently syringe filtered through a 0.45 μm cellulose acetate filter. The extractants from the vegetation samples were filtered only once through 0.45 μm cellulose acetate filters. Extractants were stored in plastic 20 mL scintillation vials prior to analysis.

For the determination of TP, vegetation samples (Control samples only, done in triplicate) were subject to a digestion procedure. Concentrated sulfuric acid (5 mL) and a digest mixture (4 mL of 0.08% (m/m) Se powder, 2.76% (m/m) $Li_2SO_4*H_2O$, H_2O_2 solvent) was added to 0.2g of ground and sieved (1mm) dry plant material and subsequently heated to 360^0C for 3 h (after Parkinson & Allen, 1975) using a BD28s/BD50s Block Digestion system (Seal Analytical, Seattle, USA). The digested material was cooled and subsequently vacuum filtered through a 0.45 μm cellulose acetate filter and stored in a glass 20 mL scintillation vial prior to analysis.

Dried soil samples (in triplicate) were analyzed for their plant-available P using sodium bicarbonate extractions (OlsenP) (after Olsen et al., 1954). Dried, sieved (2mm) soil samples (~ 1g) were extracted with 20 mL of 0.5M $NaHCO_3$ (pH of 8.5) in 50mL Erlenmeyer flasks after 30 minutes of shaking @ 200RPM following the Amacher et al., (2003) protocol. The extracted material was first gravity filtered (Whatman 42), subsequently passed through 0.45 µm cellulose acetate filter paper and then stored in glass 20 mL scintillation vials.

Filtered WEP samples of soils and vegetation analyzed colorimetrically (Bran Luebbe AA3, Seal Analytical, Seattle, USA). Samples were analyzed using the molybdenum blue method, done simultaneously for soluble reactive P (SRP) (G-103-93, detection limit 0.001 mg/L) and total dissolved P (TDP (G-092-95 Rev 1, detection limit 0.01 mg/L). The TDP analysis utilized a persulfate UV in-line digestion. As noted above, all extractions were obtained in triplicate. Analytical replicates (35 of 795 samples, ~5%) were found to be within 5% of reported concentrations or within 1 unit of detection limit resolution. Blanks were below detection limit or within 1 unit of detection limit resolution. The Non-reactive P (NRP) content of WEP extractions was calculated as the difference between TDP and SRP (TDP – SRP = NRP).

Concentrations of the various P forms are expressed in mg/kg (dry material) in this paper. For each extraction, the mass of P extracted (mg/mL * mL extractant added) was divided by the dry mass of material extracted (g). The proportion of the field moist material that was dry matter was determined gravimetrically (described above). Concentrations of P in soil and plant matter were expressed as pools (kg) per unit area (ha) by multiplying concentrations (mg/kg) by the density of the material (kg/ha biomass or kg/ha in the top 5cm of the soil profile).

4.2.5 Statistical Methods

Statistical analysis was conducted using R (version 3.6.1) (R Core Team, 2022) and through R Studio (RStudio Team, 2022). Figure creation used the R package ‘ggplot2’ (Wickham, 2016). The direct correlation between soil and vegetation P concentrations was explored through the use of simple linear models and the reporting of associated r^2 values which explain how much variation can be explained by the model. Linear model results were not explored when comparing P concentrations to the categorical parameters of soil P level and freeze treatment, and instead non-parametric Scheirer-Ray-Hare test was used. The assumptions of normality could not be met with parametric testing therefore only non-parametric statistical tests were used throughout analyses to test for significance. Statistical tests were performed on data from each site independently unless indicated. Alpha values were set at $p < 0.05$.

4.3 Results

4.3.1 Spatial Differences in Phosphorus Content of Non-Frozen Vegetation and Soil

Spatial differences in soil WEP and Olsen P content were found at both sites. Within each site, the three sections sampled had distinctly different concentrations of both WEP and Olsen P and these were classified as having High, Medium and Low soil test P for the purposes of this study. Both Soil WEP and Olsen P were greater at site INN compared to the same zones at site STZ with the exception of the Olsen P levels in the High sampling zone. Results from linear models representing each site independently show significant linear correlations between soil WEP and Olsen P concentrations (r^2 = 0.97 at INN; 0.99 at STZ). At site INN, grass WEP (r^2 = 0.74) was found to have a significant positive correlation with soil WEP levels, while grass TP (r^2 = 0.42) had a significant negative correlation (Figure 4-2). There was no correlation of grass WEP or TP to soil WEP levels at site STZ. When comparing the same grass WEP and TP pools to soil Olsen P rather than soil WEP, results did not differ in terms of significance or direction of trend for either site.

While both the non-reactive and reactive portions of WEP (NRP, SRP) were determined for all samples, the concentrations of NRP were negligible for soils (< 0.6 mg/kg) and grasses (< 8 mg/kg).

Soil WEP-SRP concentrations were 6 – 15% of Olsen P concentrations, with Medium and High soil P zones exhibiting a greater relative proportion of WEP to Olsen P. Vegetation WEP represented a very small percentage of vegetation TP (<5%) at both sites. Although the sites had similar soil WEP and Olsen P concentrations, vegetation TP was considerably greater at site STZ compared to site INN (Figure 4-2). In general, concentrations of WEP in grass was comparable to WEP concentrations in soil (0 – 50 mg/kg) with the exception of the High soil P zone vegetation at site INN (60-125 mg/kg).

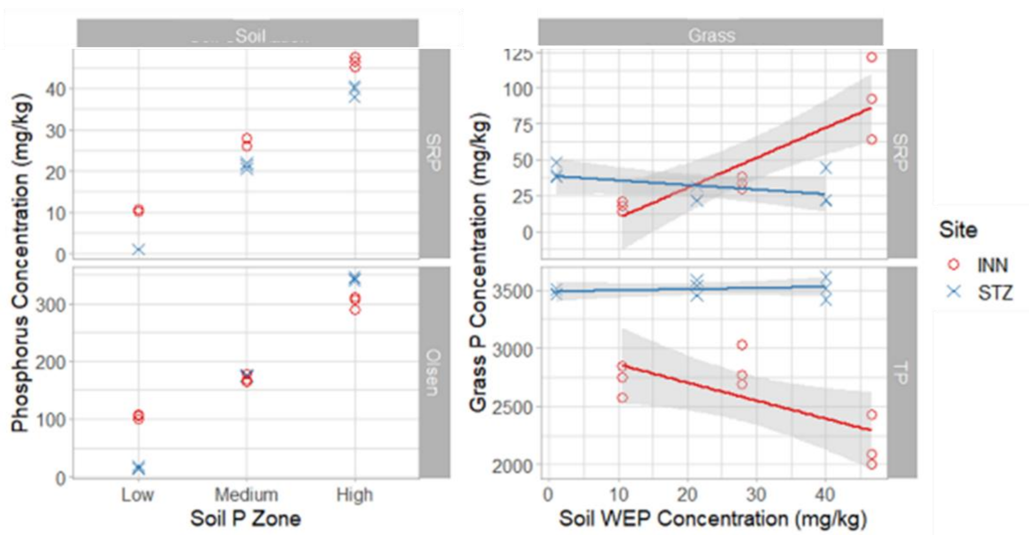


Figure 4-13: Phosphorus concentrations of: (Left) - Control treatment/ non-frozen soil samples compared to the corresponding soil P sampling zone; and (Right) - Control treatment grass samples compared to soil WEP concentrations from which they were obtained. Lines indicate a best fit linear model with standard error shaded.

4.3.2 Freezing Effect on Water Extractable Phosphorus in Vegetation Growing in Soils with Varying Soil P Contents

Without accounting for the soil P zone of the sample, WEP concentrations in grass samples were significantly greater ($p<0.001$ for both sites) in plants subjected to moderate and severe freezing (frozen) relative to the Control treatment (unfrozen) at both sites (Figure 4-3, boxplots). Between both freeze treatment levels, the severe freeze treatment had a statistically greater effect ($p=0.012$) than the moderate freeze at site INN only (p=0.1 at STZ). Vegetation biomass from site INN had 2%, 12%, and 22% of TP extractable as WEP from Control, Moderate, and Severe treatment vegetation, respectively. Similarly, site STZ had 1%, 17%, and 22% from Control, Moderate, and Severe treatment vegetation. There was no freeze treatment effect on site INN soils and site STZ soils were not subjected to freezing treatments.

When accounting for soil P level (High, Medium, Low) in addition to the freeze treatment effect, there was no difference in soil WEP concentrations attributable to freeze treatments from the low P zone (p>0.05, Figure 4-3) but in the high P soil, WEP concentrations were greater for the soil subjected to the severe frost treatment (p=0.019). There was no apparent effect of soil P status on the susceptibility of grass samples to freezing treatment for either site (Figure 4-3). Indeed, although grass WEP concentrations were greater in higher soil P zones at site INN for the Control and Moderate treatments, this pattern was not observed in samples subjected to severe freezing. At site STZ, High soil P level vegetation did not have greater WEP concentrations for any of the freeze treatment groups. Scheirer-Ray-Hare tests with soil P level and freeze treatments as factors did not find significant effects on vegetation or soil WEP concentrations, and no significant interaction between both factors.

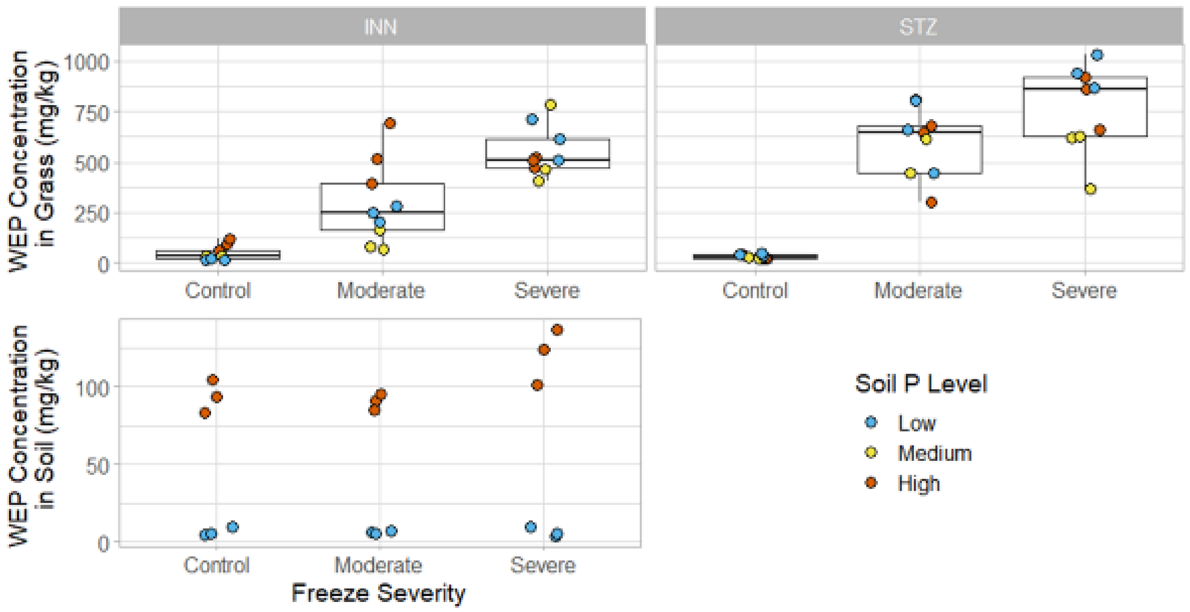


Figure 4-14: The effect of freezing severity on WEP concentrations in grass (top) and soil (bottom) samples from both study sites. Data point colour corresponds to soil P level zone of each sample. Box plots represent the median and range of data without accounting for the factor of soil P level. Susceptibility to freezing treatment was only assessed for soils from site INN, and only from Low and High soil P level zones.

Similar to what was observed in the soil samples, the majority of WEP in grass samples was recovered as SRP with minimal fractions of NRP. Although NRP concentrations increased alongside SRP concentrations when exposed to more severe freezing, NRP concentrations are significantly lower than SRP concentrations, particularly for samples exposed to freezing. For moderate and frozen samples, the fraction of NRP in WEP accounted for less than 6% of all WEP, whereas for control samples NRP accounted for as much as 29% of all WEP.

When viewing soil and vegetation sample WEP concentrations as areal concentrations in kg/ha, the topsoil (top 5 cm) was a greater pool of WEP than the Control treatment vegetation (Figure 4-4).

However, vegetation subjected to freezing has comparable potential WEP concentrations to soils, and even exceeded soil pools at some locations (Figure 4-4). Exceptions to this were found at the High soil P zones at both sites, where vegetation WEP pools were always greater than 50% of soil WEP pools.

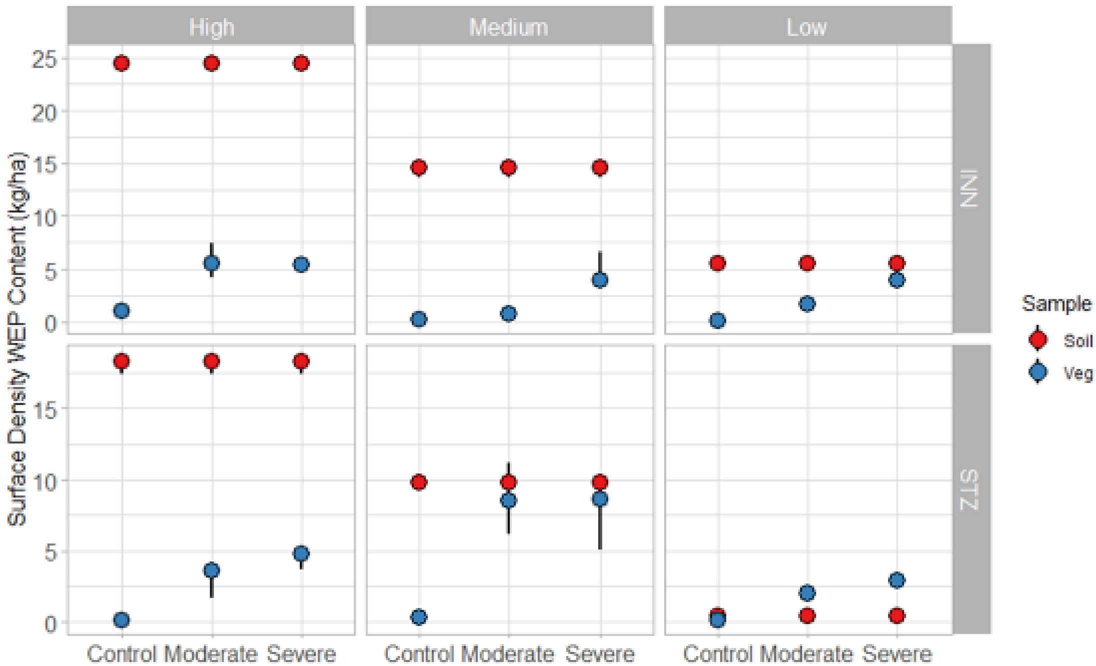


Figure 4-15: Areal concentration of soil WEP (red) compared to areal concentrations of control and frozen grass samples (blue). Points and error bars indicate median and minimum/maximum, respectively, of n=3 samples. Soil WEP values are for unfrozen soils.

4.4 Discussion

4.4.1 Correlation of Total Phosphorus in Vegetation to Soil Phosphorus Levels

Results showed a lack of correlation between vegetation TP and soil P concentrations at both sites (Figure 4-2), indicating a lack of evidence to support luxury P uptake by vegetation when exposed to bunker silo runoff. While luxury P uptake is not studied as extensively as luxury uptake of other nutrients, the original hypothesis of this study was that this correlation would exist as the uptake of excess P by vegetation has been documented through other studies (Kieta et al., 2022; Kröger et al., 2007; Penn et al., 2023).

The type of vegetation at these sites could explain the lack of correlation in these results. Due to obvious physiological differences, the type of vegetation (grass, herbaceous, shrub, wetland) will have a dramatic impact on the uptake rate and accumulation of P into biomass (Maucieri, Salvato, & Borin, 2020), and could account for the lack of soil to vegetation correlation at these sites. There is a lack of research surrounding the ability of terrestrial grass species adapted to cold climates to accumulate P, as previous studies that identify luxury P uptake have focused on vegetation in wetlands (Kröger et al., 2007) or from other climates (Marques et al., 2019). Additionally, there is variety at the grass species level in the nutrient uptake potential and strategies for harnessing limited or excess nutrients. In a study investigating the nutrient homeostasis of invasive and natural grass species, the researchers found that the invasive grass species exhibited increased growth in high nutrient conditions when compared to the growth of natural grass (Harvey & Leffler, 2020). The authors suggest that in eutrophic conditions invasive plants have an advantage over native plants due to the ratio of nutrients they incorporate into biomass. Other studies have shown that the tissue cycling rate and nutrient demand inherent to the physiology of each grass species affects the accumulation of P in high P fertilization settings, with the most resource conservative species increasing TP content by 21% and the most aggressive resource capturing species increasing TP by 140% (Marques et al., 2019). Invasive or more eutrophic friendly, high tissue cycling rate species could exhibit excess P uptake, while other species are less inclined to accumulate additional P resources. As this study did not explicitly identify the individual grass species or their physiological nutrient accumulation methods, it remains uncertain what affect speciation could have on the detection of luxury P uptake in grass but remains an area for future research. Another confounding factor that could mask the identification of luxury P uptake could be the translocation of excess nutrients from aboveground biomass to the root zone. This has been observed in VBS vegetation for both Phosphorus and Nitrogen, and typically occurs at the onset of the freezing temperatures in cold climates (Malhotra et al., 2018; Räty et al., 2010). As this mechanism is meant to store nutrients for future use, this translocation could result in excess P pools being stored in belowground tissues which were not sampled in this study.

Results from site STZ showing a lack of excess TP content in VBS vegetation growing in high soil test P zones was surprising, as a previous study measuring the relationship between soil Olsen P and plant TP in a VBS indicated a positive, significant relationship (Kieta et al., 2022). While both studies sampled similar types of vegetation, the VBS in that study was attenuating the nutrients from non-point source field runoff, and as such the Olsen P concentrations were more typical of buffers filtering diffuse agricultural runoff (<40 mg/kg Olsen P). In contrast, the soils at the sites in this study were heavily saturated with P due to the concentrated runoff from the bunker silos and had higher Olsen P values (> 100 mg/kg Olsen P for all but one zone). Due to the high soil test P levels at these sites, there is unlikely any limitation of P for the vegetation to achieve adequate growth requirements at every sampling zone. For popular cash crops grown in Ontario, Olsen P soil test levels above 12 mg/kg have not been found to increase economic yields, including nutrient hungry cultivated crops such as corn (OMAFRA, 2015). Therefore, even in the most P limited zone of this study (Olsen P ~ 15 mg/kg) there is no indication that vegetation growth would be limited by a lack of P, and instead growth may be inhibited by a lack of other soil requirements.

Although the presence of P is necessary for healthy plant growth, there are a variety of other nutrients and soil characteristics needed for biomass production. Soils that lack these components could inhibit plant growth and mask excess P uptake. For example, results from an incubation experiment comparing the growth of plants grown in buffer strip and arable field soils (Roberts et al., 2020) show that the soil organic Carbon levels, not the P levels, had a strong correlation to biomass production and total P content of vegetation. Therefore, while there is little evidence for luxury uptake of P by the vegetation at these sites, it could occur under different circumstances depending on the vegetative species or the soil type and nutrient status. Therefore, assessing the impact of Olsen P soil levels on TP in vegetation may need to be done on individual plant species and that aggregation of biomass may obscure the luxury P effect. Further studies should investigate the mechanisms and the factors that lead to luxury P uptake in a variety of common VBS plant species. These studies should also take into account other soil properties and nutrient levels that could impact P uptake, including the effect that high P runoff such as bunker silo effluent has on soil geochemistry. This information can be used to help evaluate and guide buffer area BMPs to reduce P loss to the environment.

4.4.2 Effect of Freezing on Extractable Phosphorus in Vegetation and Soils

The soil samples in this study were not susceptible to freezing, with WEP concentrations remaining similar for soils from the same sampling zones regardless of the temperature experienced (Figure 4-3). This corresponds with results from the literature, which typically show a lack of freezing effect on soil P extractability (Bechmann et al., 2005). The minor increase in WEP concentrations for high P soils after severe freezing could be attributed to a proportionally higher amount of trace organic plant detritus in the soil samples, as the high P sampling zone at this site was directly adjacent to the bunker silo. Alternatively, natural variation in soil P levels could explain this discrepancy, as only two soil P zones at a single site were tested for any soil susceptibility to freezing temperatures. The effects of freezing on soils were found to be negligible in a preliminary investigation of the sites, and so extensive testing was not performed as a part of this pilot study.

The correlation of WEP concentrations from unfrozen vegetation to soil P status in only one of the sites (STZ) and not the other (INN) does not allow us to draw any significant conclusions about the P extractability of unfrozen vegetation in BMPs with high soil P (Figure 4-2). However, after being subjected to freezing temperatures there was no identifiable trend in WEP concentrations for either site (Figure 4-3), and so the cause of the correlation between unfrozen vegetation and soil WEP at STZ is masked by the release of additional extractable pools after freezing. This is the inverse observation of another study, in which the vegetation WEP concentrations only had significant correlations to soil P concentrations when the vegetation was frozen or dried, and no correlation when unfrozen (Roberson et al., 2007). The authors of that paper suggest that the relationship between soil test P and vegetation WEP is influenced by the proportion of vegetation TP that is extracted, and that with greater percentage of the TP extracted the correlation improves. As vegetation TP concentrations in this study were not found to correlate to soil P levels (Figure 4-2), it is expected that as proportionally more of the total vegetation P is made extractable (i.e. WEP) through freezing, any trends that do exist for unfrozen vegetation will disappear.

The relative amounts of vegetation P that are extractable increased as the freezing severity increased for vegetation grown in all soil P conditions (Figure 4-3). These results are corroborated by the relative TP that was extractable as WEP from vegetation in another similar study, in which frozen and frozen/thawed alfalfa released an average of 8% and 14% of TP as WEP, with the freezing treatment set at -5^{0}C for 24 hours (Roberson et al., 2007). That is comparable in result and method to the Moderate treatment in this study after which 12% and 17% (INN and STZ) of TP was released as

WEP. Unfrozen samples in that study only released an average of 1% of TP, which is similar to the control sample results in our study (2% and 1%).

Soil and vegetation WEP results visualized as areal concentrations indicates that high P soils typically pose the greater potential P loss risk than vegetation regardless of freeze severity (Figure 4-4). However, in lower soil P areas, frozen vegetation can contribute similar amounts or more WEP as compared to unfrozen soil. Despite these results there are a few important methodological factors to consider from this study. As discussed previously, WEP concentrations from frozen vegetation in this study would likely be greater under actual NGS field extraction conditions compared to the laboratory conditions applied in the lab. Therefore, areal concentrations of vegetation WEP could actually be similar or even greater than impacted soils. Conversely, while a single FTC may underestimate what is truly at risk for P losses from vegetation, it is important to keep in mind that only the top five centimetres of soil was analyzed, and areal calculations are for only those top five centimetres. Soil P concentrations from deeper in the soil column can still be significant (Price et al., 2021) and can be mobilized during periods of inundation or snowmelt (Nash et al., 2021). The subsoil properties and level of P saturation can also affect the risk of P leaching from topsoil, leading some to question the efficacy of only measuring the soil test P for the topsoil in P leachate studies (Andersson, Bergström, Djodjic, Ulén, & Kirchmann, 2013). The subsoils typically have greater P sorption capabilities and are able to attenuate P losses by binding mobilized P from top soils (Andersson et al., 2013; Aye et al., 2006). Therefore, both NGS soil and vegetation available WEP from this study are likely underestimations, or lower bounds. This is an important caveat as when those results are compared to typical areal watershed P loads, the potential P contribution of these impacted BMP is very high. To illustrate, the range of values calculated in this study for soil and vegetation P concentrations (5 – 25 kg/ha) are more than an order of magnitude higher than the values obtained for the STZ site watershed annual P loads (0.15 kg/ha), as shown by results from another study (Irvine et al., 2019). To summarize, the experimental approach taken in this pilot study likely represents a lower bound estimate of potential contributable WEP concentrations from nutrient rich BMP surrounding bunker silos, which still represent concerningly large potential contributions to watershed P losses.

4.4.3 Limitations and Areas for Future Research

While the results of this study allow us to draw some interesting conclusions, those conclusions are not very strong as a major limitation of a pilot study such as this is the limited number of data points. There are 2 sites in this study, and at each of these sites, 3 sampling zones corresponding to soil P levels were sampled. Though sampling was done in triplicate, effectively there are only 6 aggregate samples of vegetation and soils for this study. All vegetation was subjected to one of 3 freezing treatments, meaning a total of 18 vegetation samples out of those 6 aggregate samples. If a greater number of sites were added to a similar study one might uncover certain confounding factors that would explain, for example, the two sites of this study having conflicting trends for the WEP content of unfrozen vegetation. This would also present an opportunity to investigate similar sites in other geographic areas outside of Ontario or Canada and on different farm types, providing a more fulsome analysis of these systems.

The bunker silo effluent at these sites was used as a pseudo-natural method of loading soils with P to ensure a range of soil P levels were sampled. This experimental setup could have some drawbacks, as bunker silo effluent is also quite acidic as evidenced by the ability for it to dissolve steel and concrete structures over time (Gebrehanna et al., 2014). Since the pH of soils can have a strong effect on the mobility of bound P (Hinsinger, 2001), there should be further study on the other effects bunker silo effluent has on soil characteristics and P pools. By investigating highly impacted sites in different settings, such as filtering manure runoff or legacy P sites filtering diffuse edge-of-field runoff, any unaccounted effects bunker silo effluent has on soil P mobility can be accounted for.

The work in this thesis is predicated on the idea that terrestrial grass species are able to take up luxury P, thereby increasing the relative proportion of P in the biomass. While some past studies have been referenced that discuss luxury P in this context (Tom Ericsson, 1994; Heckman et al., 2003; Kröger et al., 2007; Penn et al., 2023; Solovchenko et al., 2019), it is not very prevalent in the soil/plant biogeochemistry literature. One potential methodological error is the presence of fine particulate 'dirt' on vegetation samples that could have skewed vegetation WEP results and masked any correlation between vegetation and soil P concentrations. As such, future studies may benefit from a 'wash' cycle before analysis of vegetation P content to remove such debris, although caution is advised with this approach as this could unintentionally release some vegetation P. In addition, further work is needed to identify the factors that result in luxury P uptake in plants, including the species dependency on luxury nutrient uptake mechanisms, to ensure luxury P uptake is realistically expected in these settings. Vegetation sampling undertaken for future studies should include species identification and separation of species before processing and analysis.

Another drawback in this research is the assumption of in-lab freezing representing typical NGS conditions. For this study, the freeze treatment was applied for a single block of time, resulting in a single Freeze-Thaw Cycle (FTC). It is typical in this field of study to analyze the affect of multiple FTC, as that is seen as more representative of conditions in the field where temperatures would fall below and rise above the freezing point multiple times throughout the NGS. Enhanced P release due to multiple FTC compared to a single FTC has been observed for macrophytic riparian vegetation

(Whitfield et al., 2019) as well as typical grass and cover crop species (Øgaard, 2015). A threshold of five FTC has been observed in frozen vegetation biomass extraction experiments for maximum nutrient release under severe freezing conditions (Bechmann et al., 2005; Costa, Liu, Roste, & Elliott, 2019), after which additional WEP release from further FTC diminishes. In addition, freezing plant biomass in water as an extraction method is seen as more representative of actual NGS conditions, and resulted in similar nutrient extraction concentrations as five FTC (Costa et al., 2019). For experiments investigating vegetation P leaching under actual field (non-laboratory) conditions, results from (Øgaard, 2015) showed that biomass leachate P after seven FTC is still less than what is leached from vegetation under field conditions over the NGS. They concluded that the minimum temperatures experienced, in addition to the NGS conditions (multiple FTC and wet) experienced by the vegetation, were both important factors affecting NGS P leaching from plants (Øgaard, 2015). The importance of experienced NGS conditions is also highlighted in the variability of results from a study examining field scale nutrient losses in cover crops, in which annual vegetation P losses ranged over the four years from 11% to 60% due to variability in NGS conditions (Sturite et al., 2007), further highlighting the impact that NGS conditions can have on P losses. Therefore, the WEP concentrations from vegetation in this study are likely not representative of actual field scale losses because; 1) vegetation was subjected to only a single FTC; and 2) field scale conditions extract more nutrients than multiple severe FTC administered in a laboratory setting. Future studies conducted in the lab should try to replicate both typical and 'ponded' extraction methods, as well as the number of FTC expected to be experienced by vegetation. Alternatively, field-based studies taking samples throughout the NGS could provide this insight.

4.5 Conclusion

Overall, this pilot project resulted in valuable insights into the question of how high legacy P soils influence P dynamics in cold climates. Although the plant bioavailable P fractions of the soil (Olsen P) were elevated, there was no consistent increase in plant bound TP pools compared to the areas with less heavily P saturated soils in both VBS and constructed wetland sites. WEP in non-frozen vegetation was correlated to the soil P level at one site (INN), but not the other (STZ). Once subjected to either freezing treatment, there was no identifiable trend between WEP in vegetation and soils. This is inconsistent with the hypothesis of this thesis, which predicted some correlation of grass P content to the soil P content in these heavily impacted systems. This is important for the management of critically P saturated bunker silo sites, as one cannot expect higher P zones to have a greater productivity of P uptake by vegetation based on this study.

The amount of WEP from vegetation in these systems increased with increasing freezing severity, with Control treatment samples (+4^{0}C) resulting in the least amount of WEP and Severe Freezing treatment samples (-24^{0}C) resulting in the most. Additionally, the soils receiving direct bunker silo effluent are highly saturated with P, likely representing a critical area for P losses during runoff generation events and inhibiting the geochemical ability for soil adsorption from released vegetation P after freezing. Therefore, a P management strategy for bunker silo sites should be implemented that focus on saturated zone vegetation and soils in addition to the bunker silo facilities themselves in order to ensure these areas do not contribute to watershed scale P loads. The results of this project also identified some key areas for further research to better understand the nature of these systems and outlined several recommendations for experimental design. Ultimately continuation of research in these parts of the agricultural landscape is an important component of our overall aim to reduce nutrient loading and improve water quality.

Chapter 5
Major Conclusions of Thesis

The efficacy of VBS as a long-term P mitigation strategy in cold climates has been questioned due to VBS typically exhibiting net SRP losses over the NGS (Kieta et al., 2018). As unmanaged landscape units, there is speculation that they have a limited effective lifetime, and that human intervention through management of these systems might be required to sustain functionality (Stutter et al., 2019). These issues have been documented across various jurisdictions, indicating a mechanistic reason for the observed P release from cold climate VBS (Aye et al., 2006; Satchithanantham et al., 2019; Uusi-Kämppä & Jauhiainen, 2010). The aim of this thesis was to investigate these mechanisms, in part by measuring any related topographic gradient in soil or vegetation P concentrations over the NGS. Chapter 3 of this thesis demonstrates that the preferential saturation of upper VBS sections adjacent to fields was common across Ontario and Manitoba, despite differences in soil type and NGS conditions. Chapter 4 demonstrates that vegetation in high soil P sites do not have a correlated elevation in biomass P, meaning vegetation P is expected to be consistent across VBS zones with a wide range in soil P concentrations.

VBS sites are primed for P mobilization from soils at the end of the NGS as evidenced by the elevated extractable soil P concentrations in the Spring (Chapter 3). These elevated Spring soil P levels in VBS soils could be partially attributed to the uptake of vegetation P released upon lysis of the plant cells (Jones, 1992), as vegetation P was lost over the NGS. For these zones with high P saturation there is a decreased ability to adsorb additional P, and so they would be at a greater risk of TDP losses due to: 1) greater mobilized soil P pools and 2) decreased ability of the soil to adsorb P in runoff. This thesis has also directly validated the effects of vegetation management in VBS to alleviate TDP losses. The harvesting of vegetation effectively reduced P loads from small scale benchtop soil column extractions, while cutting and leaving the vegetation exacerbated the problem as compared to the control treatment of leaving the vegetation intact. As there appears to be no topographic or soil P related correlation to the P concentration in vegetation, the preferential harvesting of certain sections of the VBS may prove an efficient method of removing P from the VBS system while maintaining some of the ecological and nutrient buffering benefits (Baulch et al., 2019; Vidon et al., 2019). VBS zones with high P soils would be best to target, such as the topographically higher sections adjacent to upland agricultural operations, and those intercepting bunker silo runoff. This vegetation is most effective to remove as it is typically easier accessed than the lower zones, and most important to remove as the soil no longer has the adsorption capabilities to mediate any of the released P, meaning there is a greater likelihood of P from that vegetation resulting in surface water transport to rivers and lakes. Additionally, there is evidence that over time this management strategy could decrease the soil P levels to less critical concentrations (Hille et al., 2019), especially if combined with other P mitigation strategies on the landscape. The use of more nutrient hungry vegetation could enhance the nutrient remediation and nutrient reuse of the VBS but could impact other aspects of the VBS and should be an area of future study.

This thesis has highlighted the NGS conditions important to nutrient release from VBS vegetation, which can influence the methods employed in future VBS studies. While severe freezing temperatures are experienced in cold climate zones, it may not be advisable to subject vegetation to extreme freezing to test the potential nutrient extractability as the snowpack insulates vegetation at the ground surface from experiencing those extremes. It is more important to recreate the repeated freezing and thawing and wet saturated conditions experienced over the NGS rather than the actual extreme cold temperatures, as that has a greater impact on P pool fluxes (Øgaard, 2015). Therefore, future studies should employ field scale experiments of P release from VBS vegetation to better capture actual NGS conditions or align laboratory methods with expected NGS conditions. More temporally intensive sampling throughout the NGS could also help further understand the flux of P occurring in VBS soils and vegetation, including the translocation of P by the plants into the soil which could be masking excess P uptake.

The results of this thesis indicate that WEP from VBS vegetation and soil is predominantly in a soluble and reactive form (SRP), with negligible amounts bound up in non-reactive forms (NRP). This is important to highlight as soluble P is more readily used by plants and algae and is recognized as the predominant species of P causing current eutrophication in surface water bodies (Jarvie et al., 2017). As such, VBS should be further targeted for remediation and management to retain or reuse the SRP that is abundantly present in these systems. While retaining particulate P will remain the predominant VBS function during the growing season, the management of these systems through vegetation harvesting could alleviate the measurable loss of SRP from the landscape during the NGS and Spring wet up.

To conclude, this thesis has demonstrated the viability of vegetation management as a means to effectively reduce the P loads originating from VBS over the NGS. However, there is a need for additional field scale studies on this topic to determine the positive and negative impacts that could result from vegetation harvesting as a P management strategy for agricultural nutrient BMP in the NGS. Areas for future VBS research have been identified to further help inform the P transport pathways, including the luxury P uptake ability of typical VBS species, and the translocation of P into the root zone during the Fall. This deeper understanding could inform subwatershed models (Jiang et al., 2020) or pilot scale stewardship programs to measure the effect of widescale VBS vegetation management on surface water P loads. Ultimately, the projects supported by this enhanced understanding can help to alleviate the eutrophication issues experienced in lakes and rivers, ensuring the protection of our surface water resources for this and future generations.

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Appendix A

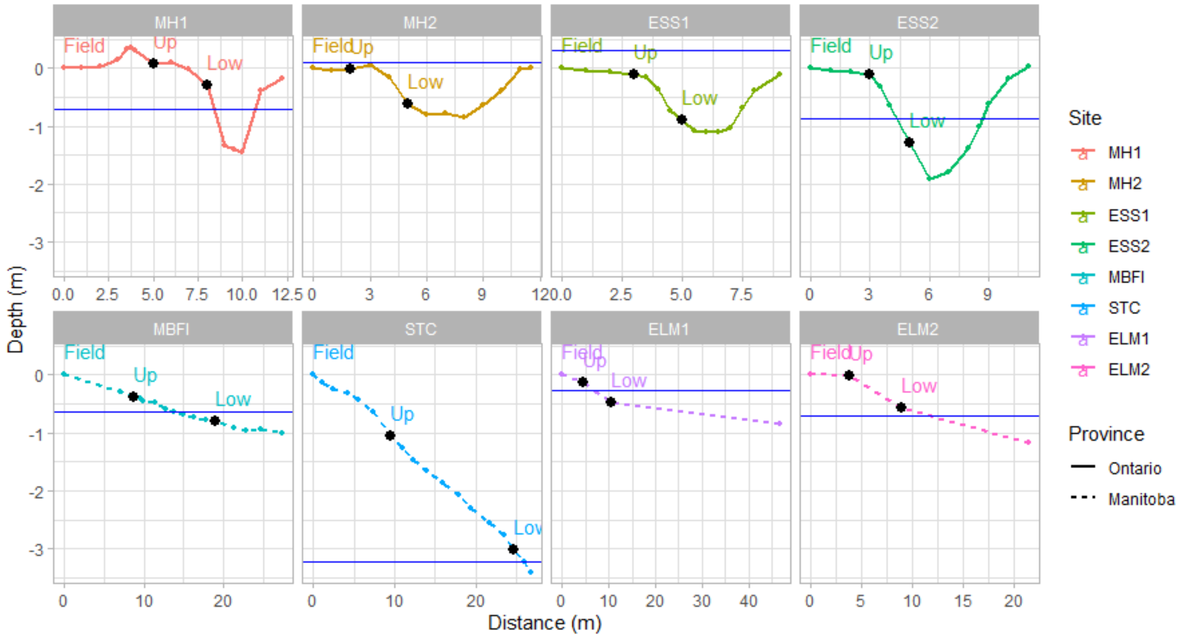

Figure A - Bathymetry of each site. The max water level experienced during the 2020-2021 NGS is indicated by the horizontal blue line. Field, Up, and Low sampling zones for each site are indicated and labelled.

Appendix B

Table B - Time that each zone was inundated during the growing season. The wide range in recorded timeframes is due to corrected data, logger malfunction, and different installation dates.

Province	Ontario				Manitoba			
Site	**MH1**	**MH2**	**ESS1**	**ESS2**	**MBFI**	**STC**	**ELM1**	**ELM2**
Total Recorded Time (days)	164	211	206	155	148	118	153	153
Lower Zone Flooded (days)	0	129.9	33.8	5.5	11.7	0	5.7	0
Upper Zone Flooded (days)	0	1.0	1.2	0	0	0	0	0

Appendix C

Previous studies have calculated annual tributary P loads from the watersheds of sites MH1 and MH2 (Irvine, Macrae, Morison, & Petrone, 2019; M. L. Macrae et al., 2007a; Price, Plach, Jarvie, & Macrae, 2021). By calculating total VBS area in the watersheds and extrapolating areal SRP values in kg/ha, we can compare loads from those studies with the potential P released from the vegetation in this study both in units of kg of SRP. By using the cumulative watercourse length for each watershed published in previous studies (Irvine et al., 2019) and assuming a theoretical VBS width of six metres throughout the subwatershed (three metres on each side of all watercourses in the catchment), the total theoretical contribution of VBS grass to annual SRP loads ranges from 9 - 27% and 21 – 62% for sites MH1 and MH2, respectively (table 3).

Table C - Comparison of potential SRP contribution of VBS vegetation over the NGS season with known annual sub-watershed SRP loads from previous studies. Values with a superscript are taken from the associated reference.
Reference: a – (Irvine et al., 2019), b – (Macrae et al., 2007a), c – (Price et al., 2021)
** - assuming 6m VBS (3m on each side of the watercourse)*

Site	**MH1**		**MH2**	
Watershed Area (ha)	270 [a]		1477 [a]	
Drainage density (m/ha)	10.42 [a]		12.88 [a]	
Length of watercourse (m)	2813		19,024	
Area of VBS in catchment (ha) *	1.69		11.4	
VBS in watershed (%)	**0.63**		**0.77**	
Annual catchment SRP loads (kg)	16 [b] / 27 [a] / 32 [b]		222 [a] / 340 [c] / 384 [c]	
Potential SRP loads from all grass VBS vegetation in catchment (kg)	Moderate	Severe	Moderate	Severe
	6.73	9.92	34.31	58.94
Watershed SRP loads potentially attributable to VBS vegetation (%)	**21 – 45**	**31 – 62**	**9 – 15**	**15 – 27**

An analysis of mean annual P concentrations in runoff from 10 fields in the STC watershed of Manitoba indicate edge of field DRP loads typically range from 0.5 to 11 kg/y (median 2 kg/y). With the assumption that VBS take up a similar percentage of the catchment area compared to sites MH1 and MH2 (~0.75%), the vegetation at site STC could account for 0.4-9% (moderate freeze) and 1.4-30% (severe freeze) of annual DRP loads through nutrient release after freezing.

Appendix D

Mean P content (+/- standard deviation) in VBS vegetation species for each Province. WEP values for Moderate (WEP-M) or Severe (WEP-S) treatments. Units are in mg [P] per kg of dry vegetation, and kg [P] per hectare (kg/ha). Percentage of TP that is extracted as WEP calculated using mean values and propagating sd as error

Province		**Ontario**		**Manitoba**	
Type		**Grass**	**Goldenrod**	**Grass**	**Nettle**
WEP-M	**mg/kg**	183 (129)	546 (234)	96.2 (78.6)	32.5 (9.89)
	kg/ ha	1.99 (1.86)	9.66 (6.75)	0.91 (0.741)	0.321 (0.093)
	% of TP	**7.39 (5.39)**	**15.84 (8.65)**	**4.83 (4.39)**	**0.760 (0.233)**
WEP-S	**mg/kg**	335 (186)	679 (130)	262 (157)	253 (142)
	kg/ ha	3.97 (4.77)	10.6 (4.96)	2.59 (1.31)	2.74 (1.77)
	% of TP	**13.52 (7.94)**	**19.7 (7.65)**	**13.17 (9.46)**	**5.92 (3.33)**
TP	**mg/kg**	2478 (474)	3446 (1164)	1990 (788)	4277 (143)
	kg [P] / ha	23.8 (17.7)	67.4 (37.0)	19.4 (7.57)	52.9 (1.77)